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Solid Phase Extraction of Organochlorine Pesticides Residues in Groundwater (Akkar Plain, North Lebanon)

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ABSTRACT: Due to the uncensored use of pesticides in the agricultural regions of Lebanon, the contamination risks of drinking water by organic residues increase periodically in planting seasons. No previous work have been considered in North Lebanon plain concerning pesticide pollution though it is the second agricultural zone in Lebanon with an excessive activity. In this context, the aim of this study was to evaluate the contamination and to map the pollution level of groundwater by organochlorine pesticides in Northern Lebanon. Solid-phase extraction (SPE) cartridge embedded with Hydrophilic-lipophilic-balanced (HLB) copolymer were used for the isolation and trace enrichment of pesticide from water samples followed by gas chromatography coupled with mass spectrometry (GC/MS) to quantify pesticide concentrations. The levels of organochlorine pesticide recorded in groundwater of Akkar district exceeded the limits set by the Stockholm Convention on persistent organic pollutants with total amounts that can reach 14.2 µg/L. Contamination was also found to be more important inland with the frequent presence of banned pesticide such HCH isomers, 4,4'-DDT, aldrin and endrin. Appropriate remedial measures and systematic investigation of Organochlorine residues in water resources of the AKKAR district are necessary to check further aggravation of the situation.

Key words: SPE, HLB, GC-MS, organochlorine, Groundwater, Lebanon

INTRODUCTION

Pesticides are commonly used in agriculture not only to protect crops from being harmed but also to increase crop production. Their usage often constitutes an essential part of massive crop production. Organochlorine pesticides cover a large group of compounds that have the tendency for long range transport and trans-boundary dispersion and may lead to contamination of surface and ground waters. In Lebanon, the groundwater constitutes an important source of freshwater, although it is highly used for agriculture purpose (61% of groundwater in Lebanon is used for irrigation include 26.66% in North Lebanon) (Ministry of energy and water 2010) in water and soil. Contamination by these compounds has spread all over the world and continues to be detected although it usage is prohibited in European countries (Laws, 2000). In general, intensive agriculture combined with factors enhancing leaching and hydrogeogical characteristics of the unsaturated zone may lead to increased levels of nutrients and pesticide in groundwater (Hancok *et al.*, 2008). The effect of topography on the variation of pesticide concentration in groundwater due to focused recharge has also been examined (Dellin and Landon, 2002).

Organochlorine pesticides (OCPs) are chlorinated hydrocarbons that were extensively used from the 1940s through the 1970s for agricultural purposes and mosquito control. Representative compounds in this group include dichlorodiphenyltrichloroethane (DDT), aldrin, endrin and some isomers of hexachlorocyclohexane (HCH) such lindane. Due to their high persistence in the environment, low biodegradability and toxicological effects on human beings (Tanable *et al.*, 1994, Barceló and Hennion 1997, Wania and Mackay 1999, Huen *et al.*, 2012). Many Organochlorine pesticides were banned in developed countries (Fenster *et al.*, 2006). However, even though the use of pesticide has been drastically reduced with settings of more rigorous regulations and innovative application methods. OCPs continue to be detected in natural waters (Mattice *et al.*, 2010, Kaushik *et al.*,

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2010, Navarro *et al.,* 2010, IMO, S.T. *et al.,* 2007). In the European Union, water intended for human consumption must meet minimum specified requirements, including a maximum level of 0.1 μg/L for individual pesticide and a maximum of 0.5 μg/L for the sum of all pesticide, with an exception for aldrin, dieldrin, heptachlor and heptachlor epoxide, for which the limits have been set at are 0.03 μg/L (EU, 1997). While most of the developed countries have already forbidden, the reality is that some developing countries continue to produce and to use OCPs for agricultural activities (Monorith *et al.,* 2003). Remobilization of stock pesticide in soil, unsaturated zones as well as the time needed to renew the water of saturated zones have been identified as determinant factors explaining pesticide persistence in contaminated groundwater several years after the last application (Gutierrez and Baran, 2009). The water's apparent age (residence time) determined through tritium concentrations has been used to explain the spatial and temporal distribution of contaminants in groundwater (Tesoriero *et al.,* 2007, Gourcy *et al.,* 2009). In 2001, the Stockholm convention on persistent organic pollutants (POPs) underlined the necessity to control the global contamination produced by toxic chemicals including OCPs.

The Government of Lebanon signed the Stockholm Convention on May 2001, and ratified it in 2003 in favor of a global Non-Governmental organization (NGO) project called the International POPs Elimination Project (IPEP) in partnership with the United Nations Industrial Development Organization (UNIDO) and the United Nations Environment Program (UNEP) (Abu Jawdeh, 2006). The aim of this study was to obtain information about the occurrence of organochlorine pesticide in groundwater in Akkar to understand one of the most pressing public health issues.

Facing rural areas in North Lebanon, especially where there are no available data concerning this site of study even though it's the second agricultural zone in Lebanon and that is known to be highly susceptible for water pollution (Halwani *et al.,* 1999).

MATERIALS & METHODS

The study was focused on Northern Lebanon near Syrian borders (34.5506° N, 36.0781° E). Akkar district is an area of intensive agricultural uses that cover 788 km^2 characterized by the presence of a relatively large coastal plain, with high mountains to the east. As the second agricultural zone of Lebanon, the most widespread crops are cereals (wheat and corn), potatoes, grapes, fruit trees, olives and vegetables. Organochlorine pesticides are used in this zone without any control particularly at the Syrian borders where farmers are tempted to favor low cost and high efficiency on the back of ecological impacts. It has indeed been recently reported that underground water in this region is strongly contaminated by nitrates, nitrites and pesticide residues (Baroudi *et al*., 2012). For this study, the sampling network was limited to ten most vulnerable sites in term of frequency of usage according to an inquiry made with the agricultural in North Lebanon 2010. Samples were collected from wells in September 2012 (Table1). Geographical locations of the sampling sites according to the Middle East region and Lebanon are presented on Fig. 1.

Triplicate samples were collected from every single site using 1.5 L clean amber glass bottles. Prior

Table 1. Sampling sites details and coordinates

Sampling sites	Site names	Depth (m)	pH	GPS coordinates
1	Al Arida	65	6.5	34°37'60" N 35°58'60" E
2	Semmakieh	60	7.2	34°37'60" N 36°0'0" E
3	Al Knayseh	60	6.8	34°37'0" N 36°1'0" E
4	Massoudieh	60	6.5	34°60'55" N 36°04'90" E
5	Marlyat Hawara	65	6.4	34°56'06" N 36°02'39" E
6	Tall Mayan	70	6.8	34°59'80" N 36°03'78" E
7	Tall Abbas El Gharbi	70	6.5	34°34'60" N 36°4'0" E
8	Haret Al Jedideh	65	7.1	34°31'60" N 36°4'0" E
9	Qaabrine	65	6.9	34°57'28"N 36°02'95" E
10	Kobbet Al Chamra	60	7	34°53'90" N 35°99'41" E

Fig. 1. View of Middle East region, Lebanon and AKKAR district with the sampling locations

collection, groundwater was pumped for 10 minutes using the drilling pump installed for each well. Glass bottles were rinsed three times with the well's water before collection. Samples were immediately stored at 4°C in ice boxes for transport and were stored under refrigeration until analyzed (within 48 hours from sampling).

All solvents and chemicals were supplied from Dislab (France) and were HPLC or reagent-grade. No significant amount of analytes was showed in procedural blanks. Ultrapure water (Milli-Q) was produced by a Millipore apparatus with 18.2 M&!/cm resistivity. Whatman GF/A circles filter (ø 110 mm, 0.7µm) were purchased from Whatman (England). Supel-Select HLB SPE cartridges (200 mg / 6 mL) were purchased from Sigma-Aldrich (Saint-Louis, USA). 1-bromo-2-nitrobenzene was purchased from Restek (Bellefonte, USA) and was used as internal standard. Organochlorine pesticide standards (Organochlorine Pesticide Mix AB #3 and Method 525.2 Revised Chlorinated Pesticide Mix #2) were also supplied by Restek (Bellefonte, USA). Detected pesticides and their general structures are detailed in table 2. Eight calibration solutions ranging from 5 µg/L to 5 mg/L were prepared from stock solutions using hexane as solvent and were stored at 4°C. Glassware was washed with detergent (Decon, King of Prussia, USA), rinsed with ultrapure water and acetone and was dried at 120°C prior to use.

Pesticides residues were analyzed by gas chromatography (Varian 3900) equipped with a deactivated fused-silica guard column (5 m x 0.53 mm i.d.) and a RTX-5 SIL MS fused-silica capillary column (60 m x 0.25 mm i.d. x 0.25 µm film thickness), and coupled with a Varian Ion Trap Saturn 2000 Mass Spectrometer (MS) operating either in selected ion storage (SIS) or in full scan (FS) mode. Helium was used as carrier gas at a constant flow rate of 1 mL/min. Injection was performed in the splitless mode at 280°C and the injector was purged with helium after 1 min. The temperature of the GC was programmed as follows: initial temperature 80˚C (1 min), 10˚C/min ramp to 170˚C then 4˚C/min ramp to 230˚C and finally 3˚C/min to 280˚C and held for 2 min. The transfer line was help at 260°c. The ion trap mass spectrometer was held at 220°C with a scan time of 1 second/scan and emission current was at 10 uamps. Pesticide identification was completed on the basis of the retention time and the mass spectrum in full scan mode. Quantification was performed in the SIS mode using the most abundant ions; concentrations were determined relative to 1-bromo-2-nitrobenzene used as internal standard.

Water samples were filtered through a 0.7 µm particle retention glass filters, 750 mL of the filtered aqueous solutions were spiked with 25 µL of a 100 µg.Lsolution of 1-bromo-nitrobenzene and were adjusted to pH 6 using hydrochloric acid (37%) and was extracted by solid phase extraction

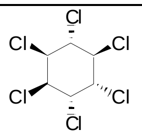
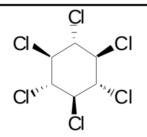
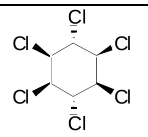
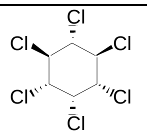
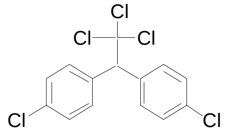
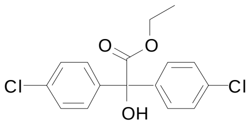
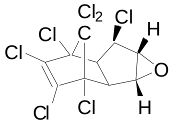
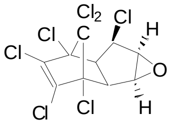
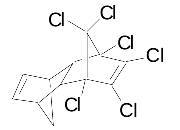
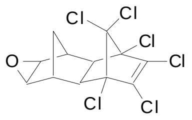
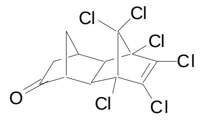
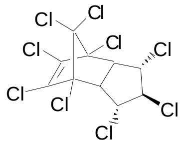
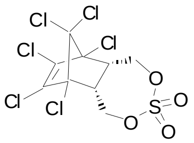
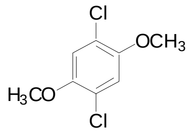
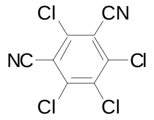
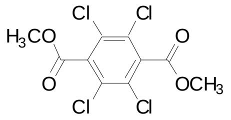
 α-HCH	 β-HCH	 γ-HCH (Lindane)	 δ-HCH
 4,4'-DDT	 Chlorobenzilate	 Heptachlor epoxide (isomer A)	 Heptachlor epoxide (isomer B)
 Aldrin	 Endrin	 Endrin ketone	 Transnonachlor
 Endosulfan sulfate	 Chloroneb	 Chlorothalonil	 DCPA methyl ester

Table 2. General structures of OCPs detected

(SPE). Hydrophilic-lipophilic-balanced (HLB) copolymer cartridges were chosen because of their ability to extract a broad range of compound. Each cartridge was firstly conditioned with 5 mL of a MeOH/AcOEt (1/1 v/v) mixture followed by 5 mL of methanol and 10 mL of ultra pure water. Filtered sample was then passed through the cartridge at a flow-rate of (2-5 mL/min) by mean of a vacuum SPE manifold. Once the retention step had been completed, the cartridge was washed with 5 mL of ultra-pure water followed by 5 mL H_2O/MeOH (95/5 v/v), and then dried in a nitrogen current for 5 min. The SPE cartridges were wrapped in aluminum foils in order to protect them from contamination and were kept frozen until they were sent to France for analysis. Retained components were then eluted with 2 x 5 mL of a MeOH/AcOEt (1/1 v/v) mixture. The organic phase obtained was concentrated under reduced pressure at 45°C followed by a slight stream of nitrogen to fix the final volume to 500 µL before analysis. Prior application onto real water samples, this extraction protocol was validated using pesticide-spiked ultra-pure water. Recoveries of organochlorine pesticide (OCPs) were found to range from 53 to 132% with a mean value of 98 %.

The peaks observed for the standards are showed in Fig. 2.

RESULTS & DISCUSSION

From a total of 28 OCPs (2 fungicides, 25 insecticides, 1 herbicide), 12 of them were not detected in any sample: *cis*- and *trans*-chlordane, 4,4'-DDD and 4,4'-DDE, heptachlor, dieldrin, endrin aldehyde, endosulfan I and II, methoxychlor, *cis*- and *trans*-permethrin. Our results showed the high levels of some organochlorine pesticides in the ten groundwater samples of the Akkar region. Recorded levels were found to be important with the sum exceeding the European Commission legislation in every sampling site (Fig.3). The most frequent pesticide residues were the isomer forms of hexachlorocyclohexane (HCH), chlorobenzilate, aldrin and heptachlor epoxide. The less abundant were DCPA methyl ester and chlorothalonil. Most contaminated sites were found inland (sites 4, 6, 9) whereas groundwater sampled near of the coast showed significant lower concentrations of OCPs (sites 1 and 10). Detailed occurrence of pesticide concentrations for each site is summarized in table 3. The concentrations obtained in this work are compared to other sites in the world (Table 4).

From the ten drilled wells that were subject to sampling, only one site (Al Arida, site 1) did not contain any isomers of HCH. Highest concentrations were found in samples of Tall Mayan (site 6), Qaabrine (site 9) and Har*et al* Jedideh (site 8) with sums of HCH concentrations respectively equal to 7.86, 7.11 and 3.66 µg/L. γ-HCH (lindane) and δ-HCH were the most common isomers with 80% of occurrence in the sampled sites and with concentrations respectively ranging from 0.17 to 0.77 µg/Land from 0.23 to 1.35 µg/L. The α- and β- isomer forms were less frequently detected (in respectively 3 and 2 sites) but with high concentrations in the range of respectively 2.85-6.42 µg/L and 0.45-0.57 µg/L. The above levels of HCH isomers are lower than those that have been recorded in 2005 in Syrian groundwater samples with concentrations ranging from 20.2 to 53.7 µg/L and from 10.6 to 136 µg/L for γ-HCH and δ-HCH respectively (Hajjar and Mouna, 2011). However, such levels of HCHs are cause of concern since these compounds are not only persistent in the environment, but are also highly toxic and can bioaccumulate in food chain (ATSDR, 2005).

4,4'-DDT residues were detected in all sampling site excepting at Al Arida (site 1) and Massoudieh (site 4). Other samples showed concentrations in the range from 0.19 to 0.69 µg/L, all exceeding the European

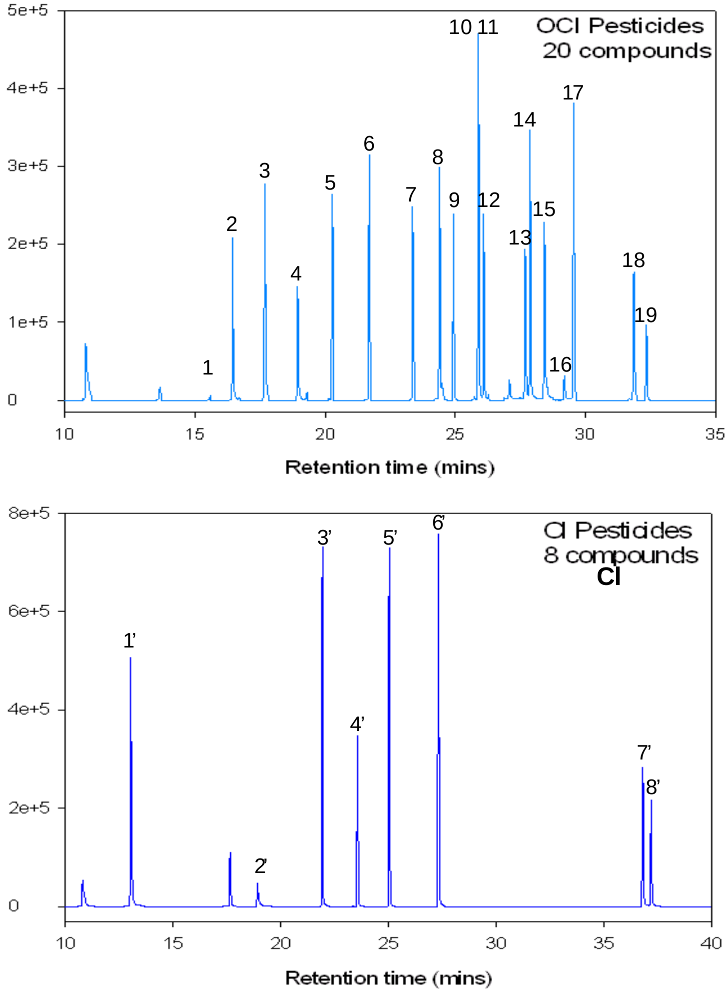


Fig. 2. Chromatograms standard solution of OCPs in SIS mode. A/ 1- alpha- lindane, 2- Beta BHC, 3- Gamma BHC, 4- Delta BHC, 5- Heptachlor, 6- Aldrin, 7- Heptachlor epoxide, 8- Cis-chlordane, 9- Trans-chlordane, 10- DDE, 11- Dieldrin, 12- Endrin, 13- Endosulfan I, 13- DDD, 14- Endrin aldehyde, 15- Endosulfan sulfate, 16- DDT, 17- Endrine ketone, 18- Metoxychlor.) and B/ 1'- Chloroneb, 2'- Chlorothalonil, 3'- DCPA, 4'- Heptachlor-epoxide, 5'- Trans-nonachlor, 6'- Chlorobenzilate, 7'- Cis-permethrin,8'- Trans-permethrin

Table 3. Concentration of Organochlorine pesticide detected in groundwater samples of the Akkar district. (N.D.: Not detected)

Compounds	**Abundant ions**	**LOD [µg/L]**	**site 1 [µg/L]**	**site 2 [µg/L]**	**site 3 [µg/L]**	**site 4 [µg/L]**	**site 5 [µg/L]**	**site 6 [µg/L]**	**site 7 [µg/L]**	**site 8 [µg/L]**	**site 9 [µg/L]**	**site 10 [µg/L]**
α-HCH	**181;219**	**0,06**	N.D.	N.D.	N.D.	N.D.	N.D.	6,42	N.D.	2,85	5,33	N.D.
β-HCH	**181;219**	**0,005**	N.D.	N.D.	N.D.	N.D.	N.D.	0,57	N.D.	N.D.	0,45	N.D.
γ-HCH (Lindane)	**181;219**	**0,06**	N.D.	0,21	0,69	0,18	0,77	0,41	0,17	0,54	0,72	N.D.
δ-HCH	**181;219**	**0,06**	N.D.	1,17	0,25	N.D.	1,35	0,46	0,23	0,27	0,61	0,23
4,4'-DDT	**165;235**	**0,06**	N.D.	0,26	0,19	N.D.	0,69	0,23	0,25	0,21	0,35	0,31
Chlorobenzilate	**409;411**	**0,005**	0,18	0,38	0,14	6,09	1,14	0,61	0,17	0,31	1,05	1,04
Heptachlor (isomer A)	**237;272**	**0,005**	0,11	0,05	0,08	0,07	0,09	0,07	N.D.	0,12	0,05	N.D.
Heptachlor (isomer B)	**237;272**	**0,005**	0,87	0,76	0,13	0,93	1,33	0,88	1,61	0,15	0,13	N.D.
Aldrin	**220;263;293**	**0,005**	0,42	0,34	0,15	0,16	0,72	0,28	0,19	0,29	0,29	N.D.
Endrin	**263; 281**	**0,06**	1,11	N.D.	2,46	2,47	1,44	1,37	1,73	2,28	N.D.	N.D.
Endrin ketone	**281;317**	**0,06**	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2,15	N.D.	N.D.
Transnonachlor	**289;291**	**0,005**	N.D.	0,04	N.D.	N.D.	0,13	N.D.	N.D.	N.D.	0,15	N.D.
Endosulfan sulfate	**229,272**	**0,06**	1,23	0,61	0,39	1,57	1,51	1,33	1,03	N.D.	0,24	N.D.
Chloroneb	**191;209**	**0,06**	N.D.	0,13	0,11	2,75	0,55	0,17	0,13	0,14	2,63	0,28
Chlorothalonil	**266**	**0,06**	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0,33	N.D.	N.D.	0,33
DCPA methyl ester	**302;335**	**0,005**	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0,03	0,04	0,04	N.D.

Table 4. Comparison of 9 OCPs pesticide concentrations in groundwater of Lebanon with others sites (concentrations in µg L^{-1})

	Chloroneb	4.4-DDT	Heptachlor (isomer A)	Endrin	α HCHc	β HCH	γ HCH	δ HCH	Aldrin	Heptachlor (isomer B)	References
Syria					10.6 – 13.6		20.2 – 53.7				Hajjar and Mouna (2011)
Gaza		0.3 - 1	0.4	0.1							Shomar *et al.* (2006)
Saudi Arabia	114										El-Saeid *et al.* (2011)
Thailand			1.369								Hudak and Thapinta (2005)
China		0.0049			0.0052	0,0025	0.0057	0.0006			Yang *et al.* (2013)
Guam Island	0.02-3.4		0.01-0.02	0.01-0.30					0.01	0.01-0.05	Denton and Sian-Denton (2010)
Norway		0.05									Haarstad and Ludvigsen (2007)
India			0.0124	0.0046	0.383	0.744	0.247	2.813	1.35	0.291	Singh *et al.* (2005)
Lebanon (Akkar)	0.06-2.75	0.06-0.69	0.005-0.12	0.06-2.47	0.06-6.42	0.005-0.57	0.06-0.77	0.06-1.35	0.005-0.720	0.005-1.330	This work

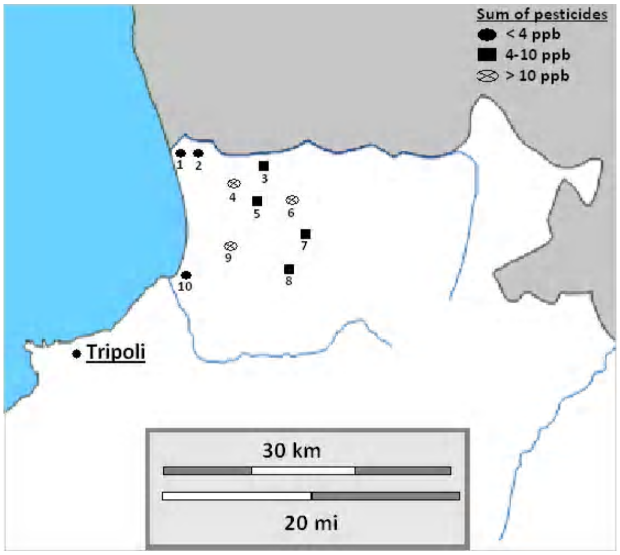


Fig. 3. Pollution level in the sampled sites in AKKAR region (sampling of September 2012)

Commission limit set at 0.1 µg/L. No significant traces of degradation products (4,4'-DDE and 4,4'-DDD) was found in studied samples. These levels of contamination are comparable with those recorded in groundwater samples of the Gaza Strip that varied from 0.3 to 1 µg/L (Shomar *et al.,* 2006) and in Norway groundwater 0.5 µg/L (Haarstad and Ludvigsen, 2007).

Chlorobenzilate was found to be present in all wells with levels ranging from 0.14 µg/L at Al Knayseh (site 3) to 6.09 µg/L at Massoudieh (site 4). Although structurally similar to DDT, chlorobenzilate is much more subject to biodegradation (Neilson, 1995). Recorded levels of groundwater contamination by chlorobenzilate tend to show that this compound is still used in the Akkar plain.

Heptachlor epoxide, which exists in two isomeric forms endo-heptachlor epoxide (isomer A) and exo-heptachlor epoxide (isomer B), is a transformation product of heptachlor used as insecticide. Heptachlor epoxide has been reported to be of greater toxicological significance because it is more stable and persists longer in the environment, especially isomer (ATSDR, 1993). This three compounds are listed in the Stockholm Convention are classified as possible human carcinogens (SC, 2004). Herein, no detectable amount of heptachlor was found, but heptachlor epoxide isomers were present in almost all samples except Kobb*et al* Chamra (site 10). Concentrations of isomer B (0.13 - 1.61 µg/L) were higher than those of isomer A (0.05 - 0.12 µg/L). Such levels largely exceed the limits set at 0.03 µg/L and are comparable to polluted ground waters in Thailand where concentrations reach 1.369 µg/L (Hudak and Thapinta, 2005).

Only well of Kobb*et al* Chamra (site 10) did not show detectable traces of aldrin. For the other sites, concentration was found to range from 0.15 to 0.72 µg/L. These high residues levels of aldrin are comparable to those recorded in alluvial groundwater aquifers of Gangetic plains in India, where like in Akkar, potato is one of the major crops grown in the area (Singh *et al.,* 2005).

Endrin is known to have a high potential to leach to groundwater (Montgomery 2010). High levels of endrin were indeed recorded for 70% of sampled wells with concentrations ranging from 1.11 to 2.47 µg/L. By contrast, endrin ketone was only once detected at a concentration of 2.15 µg/L in Har*et al* Jedideh (site 8). The high concentrations in aldrin and endrin ketone suggest that these compounds are still used in the Akkar district. Kobb*et al* Chamra (site 10) is the only area where no significant trace of such compounds could be detected.

Trans-nonachlor is not only one of the major constituents of the insecticide chlordane, but it is also the most bioaccumulative of this family of compounds and is also considered as potent carcinogen (Luzardo *et al.,* 2014). *trans*-nonachlor residues were detected in three sites (Semmakieh, Marlyat Hawara and Qaabrine) with concentrations respectively equal to 0.04, 0.13 and 0.15 µg/L. Groundwater samples were found to be more contaminated by endosulfan sulfate, which was detected in 70 % of wells at levels in the range 0.24 - 1.57 µg/L. No detectable amounts of parent endosulfan could be found that may suggest that recorded level of endosulfan sulfate is the result of former use of endosulfan in the Akkar plain.

Chloroneb and chlorothalonil are two fongicides still used since they are more recent and less toxic than the above-mentioned organochlorine pesticide. Al Arida (site 1) is the only site where no residue of such compounds has been detected. Chloroneb was indeed found to be present in 90 % of the sampled sites with concentrations ranging from 0.11 to 2.75 µg/L. This contamination is lower than the one reported recently in Saudi Arabia groundwater where concentrations can reach 114 µg/L (El-Saeid *et al.*, 2011) Chlorothalonil was only detected in Tall Abbas El Gharbi (site 7) and Kobb*et al* Chamra (site 10) with both levels of 0.33 µg/L.

DCPA methyl ester is an herbicide active ingredient mostly used to control crab grasses and a number of fruit and vegetable crops. This compound was found in sites 7, 8 and 9 (Tall Abbas El Gharbi, Har*et al* Jedideh, Qaabrine) at more acceptable levels in the range 0.03 – 0.04 µg/L.

CONCLUSION

The present study demonstrates that agricultural practices in the Akkar district have degraded the water quality and significant pesticide pollution was found in groundwater. Sixteen residues of pesticide have frequently been detected in the groundwater with values exceeding the level limits for drinking water according to the European Union. Coastal groundwater samples (from Al Arida, site 1 and Kobb*et al* Chamra, site 10) were found to be less contaminated than groundwater sampled inland where pollution can reach certain scary levels especially in sites Massoudieh, Tall Mayan and Qaabrine. Since the sampling was conducted in September 2012, we highly assume that pesticide found in groundwater were not only brought by irrigation but also by rain and rivers of other close areas. Moreover, the frequent high levels recorded for HCH isomers, 4,4’-DDT, aldrin and eldrin may suggest that such compounds are still in use despite the implication of Lebanon in the International POPs Elimination Project (IPEP). However the ignorance of farmers about the safe use of pesticide is generated from literacy and poverty; in another hand, factors such as soil characteristics, intensive application and the occurrence of point source contamination in the studied area reflects its relative frequent detection in this study.

Finally it must be pointed out that our research was constrained to only few sampling locations in Akkar. More detailed monitoring studies have to be carried out on different seasons to get a clear reference data for the entire location. Besides this work could be the database for future work that must be taken into account regarding this zone especially with the lack of information regarding Akkar plain.

We recommend continuous monitoring in shallow groundwater and wells near agricultural fields on yearly basis that would provide to prevent contamination of groundwater in general and a better understanding of each individual pesticide variability and persistence in groundwater as well as some of the important metabolites. Research is needed to investigate the type, quantity and concentration of pesticide used by farmers in order to increase awareness.

Epidemiological studies investigating the health effects of pesticide should be undertaken. Furthermore, policies aimed to reduce the potential contaminations of water by pesticide need to be developed and implemented. The pesticide most frequently occurring should be given a second opinion by the authorities whether they should stay sell.

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