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TEMPORAL EVOLUTION OF ORGANOCHLORINE AND ORGANOPHOSPHATE PESTICIDE RESIDUES IN WELLS IN THE AKKAR REGION (LEBANON)

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Abstract

The Akkar plain is the second largest agricultural area in Lebanon. This region produces huge amount of regular crops such as maize, fruits and vegetables. In order to protect the crops, farmers use large quantities of many pesticides (including authorised and prohibited molecules) without respecting the recommended doses. In this work, we wanted to study the evolution of OCPs and OPPs residues at three-year intervals in water wells in the Akkar region. 20 OCPs and 8 OPPs were monitored in eight wells in different villages in the plain and mountains of Akkar. Solid phase extraction (SPE) method was used for pesticide extraction, followed by gas chromatography-mass spectrometry (GC-MS) analysis. The results revealed an increasing concentration of OCPs and OPPs in groundwater over the last three years (between 2017 and 2019-2020). This increase in contamination is due to the uncontrolled and still unregulated (by the authorities) use of pesticides, and also to the introduction of new crops. The concentrations found in groundwater confirm that some banned pesticides are still widely used. The calculation of the theoretical pesticide intake suggests that pesticide concentrations in Akkar represent a greater health risk for the population consuming well water during the rainy season.

Keywords: Akkar, Pesticides, Groundwater, OCPs, OPPs, Pollution.

1. Introduction

Most of Lebanon's agricultural production is located in the Bekaa, Baalbek, El Hermel and Akkar regions (FAO, 2010). Water consumption for agriculture represents about 60-70% of the total water consumption in Lebanon (MoE/LEDO/ECODIT, 2001; Geara-Matta et al., 2010). Many private wells have been drilled for crop irrigation (Youssef et al., 2015) but also for domestic consumption (over 33,000) (ACS, 2007). Lebanon is a large producer of potatoes (572,109 tons in 2019), oranges, apples, and grapes (Fruit: 54,244 tons in 2019) (Tilasto, 2020), and imports around 6,641 tons/year of pesticides (Abou Zeid et al., 2020). Soil runoff and leaching have led to the infiltration of pesticides from application areas into aquifers (Huber et al., 2000; Blanchouda et al., 2007). The excessive and uncontrolled use of pesticides has led to severe contamination of groundwater in these areas (Chbib et al., 2017; Chbib et al., 2018). Several studies have highlighted the presence of a wide diversity of pesticides in the waters of northern or southern Lebanon (El-Osmani et al., 2014; Youssef et al., 2015, Chbib et al., 2017; Helou et al., 2019; Chbib et al., 2020). In particular, these studies have pointed to the significant presence of organochlorine pesticides (OCPs) and organophosphate pesticides (OPPs), known as persistent organic pollutants (POPs). The reported high concentrations in Lebanese groundwater have been related to the hydrogeological characteristics of the unsaturated zone that enhance the percolation/infiltration factors (Hancock et al., 2008). Infiltration of pesticides is influenced soil type and rock lithologies, adsorption properties of compounds, and the time interval between application and the first rainfall (Brown and Van Beinum, 2009).

The presence of pesticides poses health problems since groundwater is also used as a source of drinking water for a large part (i.e., 28%) of the population (6 million people) (MEW, 2010; WHO and UNICEF, 2019). Under some circumstances, human exposure to pesticides (and other POPs), even at low levels, can result in increased cancer risk, reproductive disorders, endocrine disruption, alterations of the immune system, genotoxicity, neurotoxicity, and birth defects (WHO, 2020). In particular, people in agricultural areas may directly consume water from wells - due to the lack of water treatment systems and/or the absence of a supply network and old infrastructure. This situation affects many countries around the world (Hu et al., 2011; Zhao and Pei, 2012).

Since 2010, Akkar Region, the second-largest agricultural plain in Lebanon, has been the object of monitoring campaigns for the presence of pesticides. Thus, El-Osmani et al. (2014) highlighted the presence of several organochlorine pesticides (OCPs) in the groundwater of the region. Similarly, Chbib et al. (2017) highlighted the pollution risks caused by OPPs and ONPs

(organophosphate and organonitrogen pesticides). Their works also highlighted a recent illegal use of OCPs that exceeded the limit established by the European Union Drinking Water Directive (DCE, 1998). Halwani et al. (1999) and Baroudi et al. (2012) reported that groundwater in Akkar is also significantly contaminated by nitrates and nitrites due to the use of agricultural fertilizers.

In 1982, the Lebanese government created a scientific group to control the shipment, sale, and use of pesticides (Lebanese government, 1982). Then, Lebanon signed the Montreal Protocol in 1993 (MULTILATERAL Montreal Protocol on Substances that Deplete the Ozone Layer) and the Stockholm Convention in 2001 against the application of pesticides. The World Health Organization (WHO) and Food and Agriculture Organization (FAO) 2011 and the United States Environmental Protection Agency set 48 and 21 pesticides and related compounds; respectively in the drinking water quality guidelines and national drinking water regulations (WHO and FAO, 2011; USEPA, 2009a). Lebanon has also adopted a concentration of 0.1 µg/L for a single pesticide and 0.5 µg/L for the sum of pesticides as acceptable values for drinking water (i.e., based on the European Union Drinking Water Directive WFD, 1998). However, agricultural activities are considered the main economic sector in poor regions of developing countries, such as the Akkar Region in Lebanon. Farmers' concerns are not really related to health issues and even less to environmental issues. The absence of governmental control encourages anarchic (use of prohibited molecules) and intensive (without respecting recommended doses) pesticide use.

The risk of serious pollution has prompted scientists to set up monitoring studies of pesticide residues in groundwater and drinking water to protect the health of the region's inhabitants. The objectives of this work are to carry out new campaigns (3 years after the first one) to monitor OCPs and OPPs contamination of groundwater in the Akkar Region and to assess the current potential health risk.

2. Materials and methods

1. Wells description and sampling.

The Akkar plain is used to grow regular crops such as potatoes, wheat, corn, fruit trees (nectarines and apples), strawberries, olives and vegetables. Several of these crops are on the "dirty dozen" list, which represents fruits and vegetables containing huge amounts of pesticides. In order to protect crops (and have abundant harvests), farmers in Akkar use many pesticides (including insecticides, fungicides, and others). Pesticides (authorised or prohibited molecules) are used intensively without respecting the recommended doses and in an anarchic way (each farmer treats when he wants). A list of banned active chemicals in Lebanon is detailed in supporting information Table SI 1. Many of these compounds are still used by farmers.

Water samples were taken from eight private wells in different areas with different crop types. Six of the selected wells were the same as those studied by Chbib et al. (2017). Chbib et al. (2017) have studied the contamination of Akkar groundwater by OCPs and OPPs. More details on the studied wells are presented in the Supporting Information (Figure SI 1 and Table SI 2). Two sampling campaigns were organized in June 2019 (dry season) and October 2020 (wet season). Water sampling was performed using pre-cleaned 2.5 L amber glass bottles and samples were immediately stored at 4°C for no more than 24h. Selected sampling sites differ in their crop type; and therefore, in the type of used pesticides. Indeed, sites n°1 and 2 are close to the coastal zone where dense population describes this portion of the plain. Moreover, greenhouses and intensive agricultural activities exist such as olive crops. Near sites n°3 to 6, annual crops, vineyards, citrus, and olives crops are commonly cultivated. Sites n°7 and 8 are in the Akkar high mountains and the main agricultural activity is fruit trees cultures and more recently vegetable crops.

In Lebanon, groundwater tends to flow through well-developed karst conduits that make storage capacity difficult (MoEW and UNDP, 2014). They are characterised by a relatively high flow rate. The geological map of Lebanon is presented in the supplementary information (Figure SI 2).

2. Micropollutants analysis

2.1. Pesticides

Based on the information provided by the inhabitants of the Akkar Region and the previous analyses performed in 2012 and 2015 (El-Osmani et al., 2014; Chbib et al., 2017), it was selected to monitor 20 OCPs and 8 OPPs for two standard solutions of organochlorine (20 compounds) and organophosphate (8 compounds) pesticides purchased from Restek. Pesticide concentrations in these solutions were 200 mg/L for each OCP (organochlorine pesticides AB n°1, Restek n°32291) and 2000 mg/L for each OPP (organophosphorus EPA 8270, Restek n°32419). These standard solutions were used to prepare an external calibration ranging from 10 ng/mL to 250 ng/mL for each compound in Dichloromethane (DCM). For the presentation of results, OCPs were divided into three groups: DDT and its metabolites, HCH and its isomers, and cyclodiene insecticides. The main properties (CAS number, molecular weight (MW), and the octanol/water partition coefficient (log Kow)) of the selected OCPs and OPPs are given in the Supporting information (Table SI 3)

2.2. Extraction procedure

For each site, a 500 mL water sample was extracted by solid-phase extraction (SPE) on an Autotrace 150 (Thermo Scientific Inc., Waltham, USA) according to Laurent (2013) and Zind (2020). Briefly, Oasis HLB cartridges (6cc), purchased from Waters Corporation (MA, USA), were conditioned with 5 mL MeOH followed by 5 mL UPW. The water sample (500 mL) was loaded at a constant flow rate of 10 mL/min. Then the cartridges were washed with 5 mL of UPW, dried under a nitrogen flow for 5 min at 10 mL/min, and stored at -80°C until analysis.

Organochlorine and organophosphorus pesticides were eluted with 8 mL of DCM. The elute was evaporated to approximately 1 mL under a gentle stream of nitrogen at 30 °C using a TurboVap® LV system (Biotage AB, Uppsala, Sweden), afterward, it was collected in a glass vial for analysis.

2.3. GC/MS analysis

The target pesticide residues were analyzed by gas chromatography (GC) tandem-mass spectrometry (MS) (GC-MS: 7890A GC system, 5975C, Agilent®). Separation of the compounds was carried out on a DB-35MS UI column (30 m length, 0.25 mm diameter, 0.25 µm film thickness). The carrier gas was Helium at a constant flow rate of 1mL/min. The temperature of GC was programmed as follows: the initial temperature of 90 °C (hold 1.3 min), increased to 125°C at 15°C/min, 165°C at 5 °C/min, 195°C at 2.5°C/min and finally, it was increased to 280°C at 20°C/min (hold for 4 min).

Pesticides were analysed by gas chromatography coupled to a mass spectrometer in Selected Ion Monitoring (SIM) mode. The analytical parameters, the retention time (RT), and mass-to-charge-ratio (m/z) were presented in the supporting information (Table SI 4 and 5; respectively).

Further details regarding pesticides method validation (i.e., linearity, limits of detection and quantification, repeatability, and reproducibility) were presented in the Supporting Information (SI 6, Tables SI 7, and SI 8).

2.4. AHC (Agglomerative Hierarchical Clustering)

Agglomerative hierarchical clustering is an iterative classification method that works from the dissimilarities between the grouped objects. Two objects, when clustered together, minimize a given agglomeration criterion, thus creating a class comprising of the two objects. The dissimilarity between this class and the $N-2$ other objects is then calculated using the agglomeration criterion. The two objects or the classes of objects, which clustered together minimize the agglomeration criterion, are then clustered together. This process continues until all the objects have been clustered. This clustering was applied to determine whether the classes could be identified based on the pharmaceutical compound concentrations or the pesticide concentrations. The AHC was realized when using the similarity matrix (Pearson's coefficient of correlation) and the Simple linkage agglomeration method (XLStat-Basic add-in for Microsoft Excel™).

2.5. Physico-chemical analyses of groundwater

On-site measurements of pH and conductivity were performed during the two sampling campaigns. Heavy metals (i.e., Fe, Zn, Pb, Cu, Mn, and Cd) and mineral composition (Total Hardness - TH, calcium hardness, chloride, nitrate, nitrite, sodium, potassium, and sulfate) were also analyzed. Data were not discussed but they are given in supporting information (Tables SI 9, 10, and 11).

3. Results and discussion

3.1. Organochlorine pesticides (OCPs)

OCPs are usually divided into four groups: Dichlorodiphenyltrichloroethane DDT and its analogs, benzene hexachloride HCH and its isomers, cyclodiene insecticides, and other OCPs (Smith et al., 1991). However, they have long been widely applied in developing countries,

because of their low cost and high efficacy on a wide range of pests (Lallas, 2001; Gupta, 2004; FAO, 2005; Jayaraj et al., 2016). They have also been widely criticized for their carcinogenic, mutagenic, or reprotoxic effects on wildlife and humans (Rauschenberger et al., 2009). As a result, they have been banned from use in several countries around the world, but also in Lebanon (Fenster et al., 2006; Abou Zeid et al., 2020;).

3.1.1. DDT and its metabolites

DDTs are listed as part of the most toxic pollutants by the USEPA (USEPA, 2009b). After application to plants, they can be evaporated and transported into the atmosphere away from areas of application, or they bind to soil particles and then leach out and gradually infiltrate into groundwater during heavy rainfall (Malaguerra et al., 2012). DDTs are regularly cited among the most abundant group of OCPs due to their high stability in the environment. Nevertheless, they undergo - under aerobic or anaerobic conditions - a biodegradation process that transforms them into DDDs (dichlorodiphenyldichloroethane) and DDEs (dichlorodiphenyldichloroethylene) (Leterme et al., 2006). These degraded products are more toxic than their parent compound and are also widely monitored. DDT was «officially» banned in 1998. However, this compound was still one of the most used pesticides in Lebanon during our sampling campaign (2019-2020). One of the reasons is the absence of governmental control. Moreover, the product can be easily purchased. This was confirmed by a farmer in Akkar who showed us labels on bottles of plant protection products.

In 2015, 4,4'-DDD ranged from <LoD to 0.25 µg/L and was detected only at site n°5 (Table 1), whereas in 2019, it ranged from <LoD to 0.23 µg/L (nb. in common sites with the 2015 campaign – sites 1 to 6) and was detected at 4 different sites (sites n°1-2-3 and 4). In 2020, 4,4'-DDD was detected in all sites and the mean value was equal to 0.71 µg/L. The average concentration of 4,4'-DDT was 0.31 µg/L in 2015 and then it increased in 2019 (2.82 µg/L) and decreased in 2020 (average value of 0.70 µg/L). The average value of 4,4'-DDE found in 2019 seems to have increased 12 times since 2015 and then increased again 4 times in 2020. Thus, our results show that DDTs are still present in the Akkar Region due to the reported high values that exceed the limit (0.1 µg/L) set by the European Union Drinking Water Directive (DCE, 1998).

Table 1 DDT concentrations ($\mu\text{g/L}$) in Akkar water wells.

Site :	1	2	3	4	5	6	7	8
2015^a								
4,4'-DDE	0.02	0.02	0.03	0.02	0.07	0.01	n.a.	n.a.
4,4'-DDT	0.27	0.27	0.28	0.28	0.39	0.37	n.a.	n.a.
4,4'-DDD	<LoD	<LoD	<LoD	<LoD	0.25	<LoD	n.a.	n.a.
$\Sigma\text{DDTs} - 2015$	0.29	0.29	0.31	0.30	0.71	0.38	-	-
<i>ratio (DDE+DDD)/DDT</i>	<i>0.07</i>	<i>0.07</i>	<i>0.11</i>	<i>0.07</i>	<i>0.82</i>	<i>0.03</i>	-	-
<i>ratio 4,4'-DDE/4,4'-DDT</i>	<i>0.07</i>	<i>0.07</i>	<i>0.10</i>	<i>0.07</i>	<i>0.18</i>	<i>0.02</i>	-	-
2019^b								
4,4'-DDE	0.20	0.64	0.22	0.23	0.46	0.43	3.85	0.59
4,4'-DDT	<LoD	<LoD	4.16	<LoD	2.73	1.58	1.89	1.74
4,4'-DDD	0.11	0.23	0.10	0.04	<LoD	<LoD	<LoD	<LoD
$\Sigma\text{DDTs} - 2019$	0.31	0.87	4.48	0.27	3.19	2.01	5.73	2.33
<i>ratio (DDE+DDD)/DDT</i>	-	-	<i>0.08</i>	-	<i>0.17</i>	<i>0.27</i>	<i>2.04</i>	<i>0.34</i>
<i>ratio 4,4'-DDE/4,4'-DDT</i>	-	-	<i>0.05</i>	-	<i>0.17</i>	<i>0.27</i>	<i>2.04</i>	<i>0.34</i>
2020^b								
4,4'-DDE	2.72	1.24	<LoD	<LoD	1.96	0.71	1.84	2.85
4,4'-DDT	0.70	0.70	0.69	0.70	0.70	0.70	0.70	0.70
4,4'-DDD	0.72	0.71	0.71	0.71	0.71	0.72	0.72	0.72
$\Sigma\text{DDTs} - 2020$	4.14	2.65	1.40	1.41	3.37	2.12	3.26	4.27
<i>ratio (DDE+DDD)/DDT</i>	<i>4.89</i>	<i>2.79</i>	<i>1.02</i>	<i>1.02</i>	<i>1.02</i>	<i>2.04</i>	<i>3.65</i>	<i>5.11</i>
<i>ratio 4,4'-DDE/4,4'-DDT</i>	<i>3.87</i>	<i>1.77</i>	-	-	<i>2.82</i>	<i>1.01</i>	<i>2.63</i>	<i>4.07</i>

222 a: Chbib et al., 2017; b: this study; n.a.: not analyzed

223 Dai et al. (2011) proposed to use the 4,4'-DDE/4,4'-DDT ratio to better understand the
 224 behavior of DDTs. This ratio indicates the atmospheric transport of DDT compounds, due to
 225 the more efficient transport of 4,4'-DDE. For the Akkar Region (sites n° 1 to 6), results in Table
 226 1 show that the average value of this ratio increased from 0.085 in 2015, to 0.16 in 2019 and
 227 2.37 in 2020, suggesting an increasing source of DDTs coming from atmospheric deposition.
 228 These measurements suggest a decreasing presence of the parent compound in Akkar
 229 groundwater. Another ratio (DDE+DDD)/DDT can provide information on the biodegradation
 230 of DDT (parent compound) into DDE and DDD: a ratio below 0.5 may indicate recent inputs
 231 of DDT while a ratio higher than 0.5 indicates long-term biotransformation of DDT. Results in
 232 Table 1 show that in 2015 and 2019 (sites n° 1 to 6), the ratio is below 0.5 suggesting that DDT
 233 was still used in the Akkar Region, while in 2020, the ratio was higher than 0.5 (i.e. average
 234 value of 3.4) rather suggests the biodegradation of the DDT. Thus, the results of both ratios
 235 tend to suggest that the source of DDTs in the Akkar groundwater aquifer changed with time.
 236 The current presence of DDT seems to come mainly from atmospheric deposition or the
 237 biodegradation of former DDT use. It is important to note that these molecules have been
 238 banned since 1998 (Abou Zeid et al., 2020) but they can be unintentionally supplied with other
 239 pesticides as impurities (Zhao et al., 2009).

3.1.2. HCH and its isomers

HCH has seven isomers (α , β , γ , δ , ϵ , η , ι) including γ -HCH which has a strong effect on insects; and specifically on the American cockroach (Tanaka, 2019). HCHs are among the most stable POPs (Persistent Organic Pollutants) and the β -HCH isomer is notably very stable in the environment (JMPR, 1973).

The results shown in Table 2 also show that all isomers of HCHs (α , β , γ , δ) were detected in 2019 and 2020. In 2019, the highest average concentration was observed for δ -HCH at 0.48 $\mu\text{g/L}$. While in 2020, γ -HCH was the most concentrated isomer of HCHs with an average concentration equal to 12.4 $\mu\text{g/L}$. In 2019, ΣHCHs concentrations ranged from 0.83 $\mu\text{g/L}$ (site n°1) to 3.05 $\mu\text{g/L}$ (site n°5) with an average value equal to 1.60 $\mu\text{g/L}$ whereas, in 2020, these values increased between 4.28 $\mu\text{g/L}$ (site n°3) and 34.69 $\mu\text{g/L}$ (site n°7), with a mean value equal to 14.79 $\mu\text{g/L}$.

Table 2 HCH concentrations ($\mu\text{g/L}$) in Akkar water wells.

Site:	1	2	3	4	5	6	7	8
2015^a								
α -HCH	2.16	1.62	0.04	1.46	1.30	3.28	n.a.	n.a.
β -HCH	0.18	0.22	0.36	0.15	0.16	0.04	n.a.	n.a.
γ -HCH	1.91	2.27	1.63	1.14	1.91	0.56	n.a.	n.a.
δ -HCH	0.02	0.03	0.01	0.01	0.07	<LoD	n.a.	n.a.
$\Sigma\text{HCHs} - 2015$	4.27	4.14	2.04	2.76	3.44	3.88	-	-
<i>ratio α/γ</i>	<i>1.13</i>	<i>0.71</i>	<i>0.02</i>	<i>1.28</i>	<i>0.68</i>	<i>5.86</i>	-	-
2019^b								
α -HCH	0.13	0.15	0.31	0.20	0.73	0.34	0.42	0.38
β -HCH	0.25	0.38	0.84	0.31	0.63	0.35	0.35	0.36
γ -HCH	0.11	0.26	0.34	0.14	0.81	0.36	0.41	0.37
δ -HCH	0.34	0.42	0.46	0.26	0.87	0.50	0.54	0.49
$\Sigma\text{HCHs} - 2019$	0.83	1.21	1.95	0.91	3.05	1.56	1.71	1.60
<i>ratio α/γ</i>	<i>1.11</i>	<i>0.59</i>	<i>0.91</i>	<i>1.49</i>	<i>0.90</i>	<i>0.95</i>	<i>1.03</i>	<i>1.02</i>
2020^b								
α -HCH	1.14	0.84	0.08	0.50	0.29	0.58	5.96	2.17
β -HCH	0.39	0.40	0.03	0.22	0.12	0.18	0.69	1.04
γ -HCH	10.11	14.20	3.97	10.15	4.01	8.21	25.18	20.72
δ -HCH	0.12	0.29	0.20	0.89	0.53	0.30	2.85	1.96
$\Sigma\text{HCHs} - 2019$	11.76	15.73	4.28	11.76	4.95	9.28	34.69	25.89
<i>ratio α/γ</i>	<i>0.11</i>	<i>0.06</i>	<i>0.02</i>	<i>0.05</i>	<i>0.07</i>	<i>0.07</i>	<i>0.24</i>	<i>0.10</i>

a: Chbib et al., 2017; b: this study; n.a.: not analyzed

HCH may result from the utilization of lindane (i.e., 99 % γ -HCH) or from commercial mixtures that contain several HCH isomers: α -HCH (~65%), β -HCH (~8.5%), γ -HCH (~12.5%), and δ -HCH (~ 8%). Thus, the α -HCH/ γ -HCH ratio is an indicator of HCH origin as a ratio between 4 and 7 might be related to the use of commercial mixtures, while a ratio near 0 is related to lindane usage (Zhao et al., 2009; Dai et al., 2011). The ratio (see Table 2) varies from 0.59 to 1.49 in 2019, while it varied from 0.02 to 0.24 in 2020, which suggests that HCHs have been supplied by lindane usage. This decrease in the ratio follows the high concentrations

of γ -HCH observed in 2020 (nb. compared to the other isomers). The reported half-life of HCH is maximum of 20 weeks. Though it's banned in the region since 1998, it is still detected in the water over the years 2019 and 2020 which might be indicating the continued use of this pesticide.

3.1.3. Cyclodiene insecticides

Cyclodiene insecticides correspond to several OCPs such as endosulfans, heptachlors, aldrin, dieldrin, endrin isomers, and chlordane isomers. They have been widely used in Lebanon to protect crop yield since 1939 (Brooks, 1977). Cyclodiene insecticides pollutants are also well-known to be transported in the atmosphere over a long distance (Prado et al., 2009).

Endosulfan is an insecticide composed of α -endosulfan (70%) and β -endosulfan (30%) (Jiang et al., 2009). According to the literature, the proportion of its two forms reflects its degradation state. In Akkar Region, the average value of the α -endosulfan/ β -endosulfan ratio was 1.32 in 2019 (Table 3). This value (below 2.33) suggests that the presence of endosulfan was related to old applications. However, recent measurements in 2020 show that the current ratio is 6 revealing a recent intake/use of this compound (Zhang et al., 2011; Qu et al., 2015). A by-product of endosulfan has also been monitored in Akkar groundwaters. Endosulfan sulfate is a metabolite produced by biodegradation in soil (Jia et al., 2010). This by-product is more toxic and can persist in soil for a long time (Fujii et al., 2012). The average concentration of endosulfan sulfate found in Akkar (for common sites between the different monitoring campaigns) was 1.03 $\mu\text{g/L}$ in 2013 (El-Osmani et al., 2014), then this value decreased in 2015 (0.82 $\mu\text{g/L}$) as well as in 2019 (0.28 $\mu\text{g/L}$), and it is currently increased slightly in 2020 to 0.56 $\mu\text{g/L}$.

Table 3 Cyclodiene insecticides concentrations (µg/L) in Akkar water wells.

Site :	1	2	3	4	5	6	7	8
2015^a								
Endosulfan	0.07	0.06	0.03	0.08	0.07	0.03	n.a.	n.a.
Endosulfan sulfate	0.81	0.71	0.47	0.72	0.56	1.65	n.a.	n.a.
Aldrin	3.79	1.96	1.00	2.06	9.33	1.43	n.a.	n.a.
Dieldrin+Endrin	4.84	2.72	0.24	3.38	0.74	2.02	n.a.	n.a.
Endrin Aldehyde	<LoD	<LoD	0.02	0.02	0.05	0.02	n.a.	n.a.
Endrin Ketone	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	n.a.	n.a.
Metoxychlor	<LoD	<LoD	<LoD	<LoD	0.11	<LoD	n.a.	n.a.
Heptachlor (H)	4.84	3.87	<LoD	4.28	6.13	3.63	n.a.	n.a.
Heptachlor Epoxide (HE)	4.01	2.50	2.96	6.66	7.04	15.50	n.a.	n.a.
ratio H/HE	1.21	1.54	<LoD	0.64	0.87	0.23	-	-
Cis-Chlordane	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Trans-Chlordane	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
ΣCyclodienes - 2015	18.36	11.82	4.72	17.20	24.03	24.28	-	-
2019^b								
Endosulfan α	0.37	0.34	0.43	0.16	0.63	0.33	0.37	0.33
Endosulfan β	0.26	0.21	0.17	0.16	0.44	0.41	0.41	0.41
ratio α/ β	1.44	1.62	2.57	0.98	1.45	0.81	0.90	0.80
ΣEndosulfan (α + β)	0.62	0.55	0.60	0.33	1.07	0.74	0.78	0.74
Endosulfan sulfate	0.32	0.15	0.22	0.04	0.46	0.35	0.36	0.35
Aldrin	0.21	0.27	0.17	0.13	0.65	0.33	0.37	0.34
Dieldrin + Endrin	9.51	14.00	2.98	<LoD	2.95	0.28	<LoD	0.53
Endrin Aldehyde	0.31	0.31	0.25	0.26	<LoD	<LoD	<LoD	<LoD
Endrin Ketone	0.34	2.80	0.23	0.11	0.95	0.40	0.50	0.36
Methoxychlor	0.40	0.64	0.28	0.24	0.68	0.54	0.70	0.54
Heptachlor (H)	0.21	0.22	0.34	0.18	1.09	0.57	0.52	0.48
Heptachlor Epoxide (HE)	0.24	0.32	0.16	0.13	0.40	0.35	0.37	0.39
ratio H/HE	0.89	0.69	2.21	1.36	2.77	1.62	1.40	1.23
Cis-Chlordane	0.24	0.20	0.99	0.57	1.75	0.89	1.16	1.03
Trans-Chlordane	0.23	0.16	0.14	0.11	0.42	0.35	0.37	0.36
ΣCyclodienes - 2019	12.64	19.61	6.34	2.09	10.42	4.81	5.13	5.11
2020^b								
Endosulfan α	3.54	3.18	0.54	1.23	1.64	3.87	5.95	10.96
Endosulfan β	0.65	0.64	0.64	0.64	0.64	0.64	0.65	0.65
ratio α/ β	5.48	4.96	0.84	1.92	2.56	6.00	9.21	16.84
ΣEndosulfan (α + β)	4.19	3.82	1.18	1.87	2.28	4.51	6.59	11.61
Endosulfan sulfate	0.33	1.21	0.34	0.29	0.29	0.53	1.22	0.30
Aldrin	0.94	1.04	0.22	1.14	0.37	1.32	5.82	3.16
Dieldrin + Endrin	0.38	1.22	<LoD	2.22	0.24	1.54	5.89	2.07
Endrin Aldehyde	8.82	5.31	<LoD	6.18	6.12	5.39	9.00	<LoD
Endrin Ketone	11.46	6.90	<LoD	8.03	7.95	7.00	11.70	<LoD
Methoxychlor	0.28	0.18	0.18	4.29	0.23	8.62	0.73	3.57
Heptachlor (H)	0.41	0.35	0.04	1.89	0.21	0.32	2.66	1.09
Heptachlor Epoxide (HE)	3.31	4.67	0.37	5.36	<LoD	1.55	6.98	7.66
ratio H/HE	0.12	0.07	0.11	0.35	-	0.21	0.38	0.14
Cis-Chlordane	33.22	31.27	<LoD	5.60	26.20	7.51	22.34	56.98
Trans-Chlordane	3.54	3.18	0.54	1.23	1.64	3.87	5.95	10.96
ΣCyclodienes - 2020	66.87	59.17	2.87	38.10	45.54	42.17	78.87	97.40

a: Chbib et al., 2017; b: this study; n.a.: not analyzed

Endrin and dieldrin are also chlorinated pesticides of the cyclodiene family which are widely used as insecticides. Dieldrin is the epoxide of aldrin, another chlorinated pesticide. The values presented in this work (Table 3) correspond to the sum of dieldrin + endrin since it was not possible to differentiate them by GC-MS.

In 2019, the concentration of dieldrin + endrin ranged from <LoD (sites n°4 and 7) to 14.00 µg/L (site n°2), while in 2020, the values ranged from <LoD (site n°3) to 5.89 µg/L (site n°7). Analyses also revealed the presence of some of their degradation products in Akkar waters: endrin aldehyde and endrin ketone, generated by photolytic degradation of endrin (Kuranchie-Mensah et al., 2012). Endrin ketone was not detected in 2015 but began to be detected in 2019 at low levels (average concentration of 0.71 µg/L). In 2020, results show that endrin ketone values are even higher, reaching 11.7 µg/L for site n°7. Similarly, endrin aldehyde was detected in 2015 at low concentrations (0.05 µg/L for site n°5) and then at 0.28 µg/L on average in 2019. In 2020, the average value is 24 times higher (8.84 µg/L), but it is worth mentioning that some sites (sites n°3 and 8) remained residue-free.

Heptachlor is another non-systemic organochlorine insecticide used in Akkar primarily against soil insects. This compound is present in the 2020 samples (Table 3), but it was also found during previous groundwater monitoring campaigns (Chbib et al., 2017). Higher values were detected in 2015 (average of 4.55 µg/L) than in 2019 (average of 0.45 µg/L) and in 2020 (average of 0.87 µg/L). Moreover, the results highlight that heptachlor is found at lower concentrations than its main by-product, heptachlor epoxide (i.e., on average, in 2015 and 2020). Heptachlor epoxide was detected in all samples (except for site n° 5) in the 2020 sampling. The average heptachlor epoxide concentration in 2015 was 6.45 µg/L and ranged from 2.50 µg/L to 15.50 µg/L. In 2020, the average heptachlor epoxide concentration was 4.27 µg/L. According to the performed literature review, the ratio of heptachlor/heptachlor epoxide is used to determine whether the presence of heptachlor is related to a recent or historical intake of this pesticide (Salem et al., 2014). In Akkar Region, the ratio (shown in Table 3) was greater than 1 for the 2015 (sites n° 1 and 2) and 2019 campaigns (except for sites n° 1 and 2), while it is less than 1 in 2020 - for all sites. This value indicates that the current presence of heptachlor (2020) originates from previous applications of this compound.

Methoxychlor is a synthetic organochlorine insecticide that was developed to replace DDT. Due to its toxicity to humans and the environment (EPA, 2016), it has also been banned in many countries. In the Akkar Region, methoxychlor was detected in 2015 only at site n°5 (0.11

µg/L) (Table 3). In 2019, the concentration of methoxychlor ranged from 0.24 (site n°4) to 0.70 µg/L (site n°7) with an average value of 0.50 µg/L. In 2020, concentrations seem to have increased: the mean value is greater at 2.26 µg/L - with variations from 0.18 µg/L (sites n°2 and 3) to 8.62 µg/L (site n°6).

Trans-chlordane (nb. the main isomer of chlordane) has been found in Akkar water wells. It is known to be carcinogenic and the most bioaccumulative of the chlordane family (Luzardo et al., 2014). Trans-chlordane was detected at all sites in 2019 and 2020 (Table 3), with an average concentration of 0.27 µg/L and 3.86 µg/L (i.e.14 times higher), respectively. The other chlordane isomer, cis-chlordane, also shows a similar trend between 2019 and 2020 with an increase from 0.85 µg/L to 26.16 µg/L (average values), respectively.

All these results for cyclodiene insecticides show that this family is widely present in the Akkar groundwater. Thus, total cyclodiene concentrations (Σ cyclodienes) (Table 3) ranged from 4.72 µg/L (site n°3) to 24.28 µg/L (sites n°6) in 2015 to between 3.27 µg/L (site n°4) to 21.69 µg/L (site n°2) in 2019. In 2020, concentrations range from 2.33 µg/L (site n°3) to 30.80 µg/L (site n°6) with a high value for site n°7 (50.59 µg/L).

Table 4 Total OCPs concentrations (µg/L) in Akkar water wells.

Site :	1	2	3	4	5	6	7	8
2015^a								
Σ HCHs	4.27	4.14	2.04	2.76	3.44	3.88	n.a.	n.a.
Σ DDTs	0.29	0.29	0.31	0.30	0.71	0.38	n.a.	n.a.
Σ Cyclodienes	18.36	11.82	4.72	17.20	24.03	24.28	n.a.	n.a.
ΣOCPs - 2015	37.69	29.22	7.40	37.38	44.85	43.88	n.a.	n.a.
2019^b								
Σ HCHs	0.83	1.21	1.95	0.91	3.05	1.56	1.71	1.60
Σ DDTs	0.31	0.87	4.48	0.27	3.19	2.01	5.73	2.33
Σ Cyclodienes	12.17	19.25	5.21	1.42	8.24	3.57	3.60	3.71
ΣOCPs - 2019	13.77	21.69	12.77	3.27	16.66	8.37	12.58	9.04
2020^b								
Σ HCHs	11.76	15.73	4.28	11.76	4.95	9.28	34.69	25.89
Σ DDTs	4.14	2.65	1.40	1.41	3.37	2.12	3.26	4.27
Σ Cyclodienes	30.11	24.71	2.33	31.28	17.69	30.80	50.59	29.46
ΣOCPs - 2020	82.77	77.55	8.55	51.27	53.86	53.57	116.82	127.57

a: Chbib et al., 2017; b: this study; n.a.: not analyzed

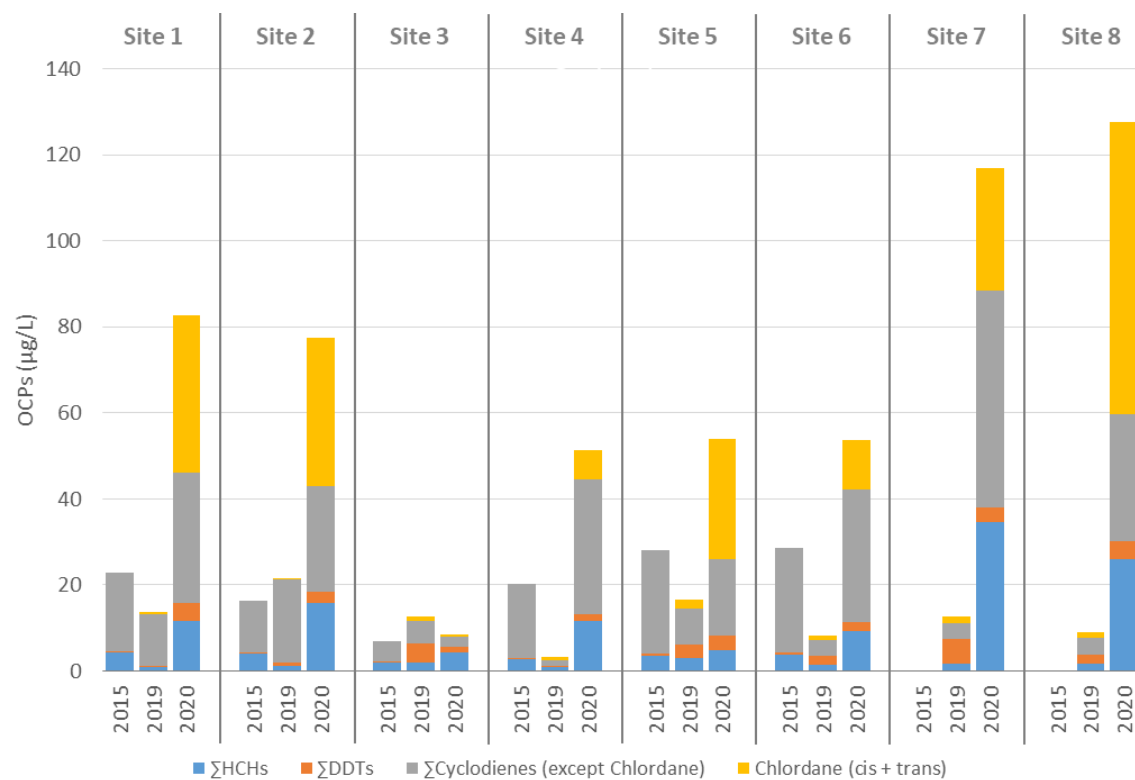


Fig 1 Organochlorine pesticides (OCPs) distribution (µg/L) in Akkar water wells.

Total OCPs concentrations (shown in Table 4 and Figure 1) ranged from 7.40 µg/L (site n°3) to 44.85 µg/L (site n°5) in 2015, from 3.27 µg/L (site n°4) to 21.69 µg/L (site n°2) in 2019, and from 8.55 µg/L (site n°3) to 127.57 µg/L (site n°8) in 2020. The Cyclodiene family is always the most abundant among OCPs. Note that in 2020, among the cyclodiene, chlordane (Figure 1) was present in very high concentrations as compared to 2019 (these compounds were not measured in 2015). The most contaminated was site n°5 in 2015, regarding Σ OCPs as well as the number of pesticides with the highest concentration (8/18). In 2019, regarding the maximum OCP concentrations, the most contaminated was site n°2, but the site with the highest number of maximum concentrations for several pesticides was also site n°5 (11/19). In 2020, sites n°7 and 8 were the most contaminated (i.e., maximum concentrations and number of pesticides with the highest concentrations).

3.2. Organophosphate pesticides (OPPs)

Due to their high stability in the environment and their high toxicity, especially in the nervous system of humans and animals (Viswanathan et al., 2009), OCPs have been gradually replaced by OPPs and ONPs by farmers. OPPs are characterized by the low cost and high efficiency on a wide range of pests and insects. In addition, 50% of insecticides belong to the OPP class (Rodrigues et al., 2011). They are also easily available commercially (Li et al., 2007). Furthermore, OPPs are widely known to degrade rapidly depending on multiple conditions such as application method, formulation, climate, and plant life cycle (Sankararamakrishnan et al., 2005).

In 2019, OPPs (Σ OPPs) concentrations (Table 5) ranged from 1.15 µg/L to 7.76 µg/L. In 2020, concentrations increased substantially up to 50.99 µg/L (site n°5) and 702.10 µg/L (site n°7). In 2015, average value (ie. 43.63 µg/L) were relatively higher than in 2019 but much lower than in 2020.

Table 5 Organophosphate pesticides (OPPs) concentrations ($\mu\text{g/L}$) in Akkar water wells.

Site :	1	2	3	4	5	6	7	8
2015^a								
O,O,O-Triethylphosphate	0.08	0.70	0.27	0.20	0.12	0.18	n.a.	n.a.
Thionazin	1.91	3.29	2.82	1.77	2.14	1.52	n.a.	n.a.
Sulfotep	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	n.a.	n.a.
Dimethoate	3.63	2.90	3.18	3.57	4.32	3.90	n.a.	n.a.
Disulfoton	1.05	2.01	1.88	1.39	3.93	2.12	n.a.	n.a.
Methyl parathion	40.36	25.76	22.18	39.25	26.80	25.63	n.a.	n.a.
Parathion	2.12	1.48	1.25	2.78	3.75	1.57	n.a.	n.a.
Famphur	0.96	0.66	1.48	1.12	1.30	14.46	n.a.	n.a.
$\Sigma\text{OPPs} - 2015$	50.11	36.80	33.06	50.08	42.36	49.38	-	-
2019^b								
O, O, O-Triethylphosphate	5.58	0.18	0.23	2.43	3.13	0.91	0.26	0.40
Thionazin	0.28	0.26	0.11	0.39	0.48	0.29	0.23	0.22
Sulfotep	0.23	0.20	0.10	0.24	0.26	0.15	0.19	0.19
Dimethoate	0.39	0.12	0.14	0.49	0.77	0.35	0.42	0.41
Disulfoton	0.24	0.10	0.09	0.42	0.55	0.16	0.18	0.19
Methyl parathion	0.30	1.19	0.26	0.99	1.44	0.59	0.13	0.13
Parathion	0.23	0.09	0.08	0.10	0.10	1.57	0.44	0.38
Famphur	0.39	0.57	0.16	0.70	1.03	1.02	0.97	0.82
$\Sigma\text{OPPs} - 2019$	7.64	2.72	1.15	5.77	7.76	5.03	2.81	2.76
2020^b								
O, O, O-Triethylphosphate	7.69	7.44	3.94	6.07	1.98	4.62	413.49	9.21
Thionazin	37.70	48.93	56.56	42.05	17.56	35.52	94.52	87.19
Sulfotep	0.26	0.41	0.51	0.41	0.12	1.85	0.89	1.56
Dimethoate	6.28	7.91	9.45	6.34	2.51	4.55	13.62	14.60
Disulfoton	62.09	76.33	89.08	60.83	21.83	43.91	136.74	147.70
Methyl parathion	19.14	22.93	26.42	16.87	5.86	8.18	39.73	53.04
Parathion	7.17	1.92	7.69	1.54	1.05	7.04	2.06	25.28
Famphur	0.31	0.38	0.38	0.45	0.09	1.54	1.05	2.50
$\Sigma\text{OPPs} - 2020$	140.64	166.25	194.02	134.55	50.99	107.21	702.10	341.09

a: Chbib et al., 2017; b: this study; n.a.: not analyzed

Some OPPs seem to have been discontinued or used less between 2015 and 2019-2020. For example, the average concentrations of famphur and methyl parathion were 3.33 $\mu\text{g/L}$ and 30.00 $\mu\text{g/L}$, respectively, in 2015 while they are 0.52 $\mu\text{g/L}$ and 16.57 $\mu\text{g/L}$, respectively, in 2020 (sites #1-6). The concentrations of these two compounds are very high for site 8 in 2020 (2.50 and 53.04 $\mu\text{g/L}$ respectively). On the contrary, sulfotep (Table 5) was not detected in 2015 but was quantified in 2019 and 2020 with a mean value equal to 0.19 $\mu\text{g/L}$ and 0.75 $\mu\text{g/L}$, respectively. These observations suggest that farmers in Akkar probably started using this insecticide after 2015. Concentrations of many other OPPs have increased between 2019 and 2020. Thus, in 2019 the highest concentrations were 5.58 $\mu\text{g/L}$ for O, O, O-triethyl phosphate, 0.48 $\mu\text{g/L}$ for thionazin, 0.77 $\mu\text{g/L}$ for dimethoate, 0.55 $\mu\text{g/L}$ for disulfoton, and 1.57 $\mu\text{g/L}$ for parathion. In 2020, the highest concentrations were 413.49 $\mu\text{g/L}$ for O, O, O-triethylphosphate, 94.52 $\mu\text{g/L}$ for thionazin, 14.60 $\mu\text{g/L}$ for dimethoate, 147.70 $\mu\text{g/L}$ for disulfoton, and 25.28 $\mu\text{g/L}$ for parathion.

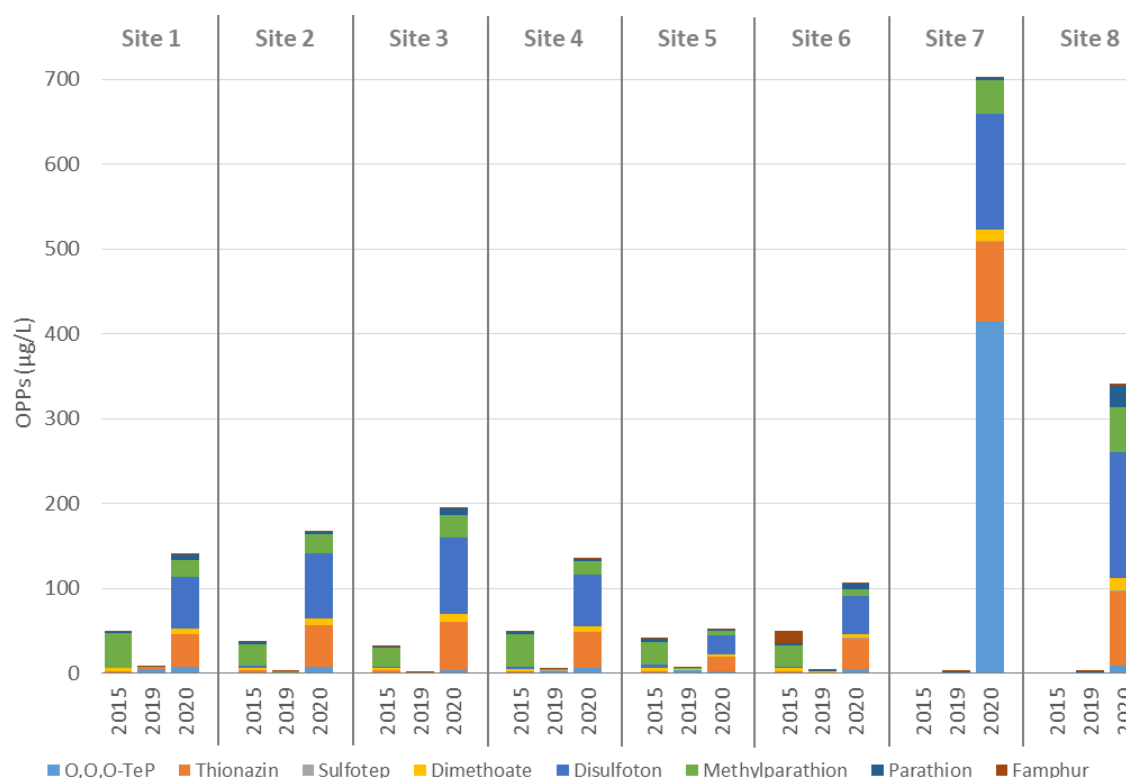


Fig 2 Organophosphate pesticides (OPPs) distribution (µg/L) in Akkar water wells.

The most contaminated site was site n°5 in 2015, regarding the number of pesticides with the highest concentration (3/8), while the highest \sum OPPs were for site n°1 (Table 5 and Figure 2). In 2019, the most contaminated site was also n°5, regarding \sum OPPs as well as the number of pesticides with the highest concentration (6/8). In 2020, sites n°7 and 8 were the most contaminated (i.e., maximum concentrations and number of pesticides with the highest concentrations).

3.3. Vulnerability factors of Akkar groundwater

In Akkar, pollution is mainly due to agricultural activities with the presence of many small and medium-sized farms. Olives and vegetables (28%), cereals (24%), food crops (21%), and pomegranates (11%) are the dominant crops (MoA, 2015). Annual crops (cereals and vegetables) are located in the north, polyculture and fruit growing in the southeast, and olive growing and greenhouse activities in the west (Figure 3). Agricultural discharges are responsible for diffuse pollution (eg. fertilization and use of phytosanitary products), and point-source pollution (eg. discharges from livestock buildings, leaks during the use of phytosanitary products). Discharges related to urbanized areas and human activities contribute - to a lesser extent - to the pollution of this region.

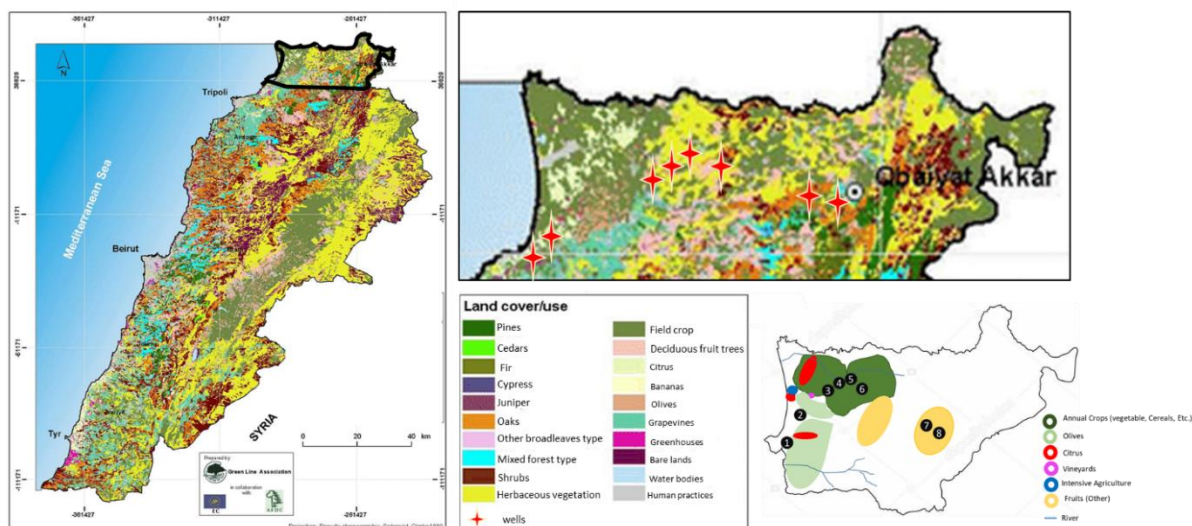


Fig 3 Agricultural map of Akkar for the different crops (LNCSSR-LMOA, 2002).

3.3.1. Evolution of phytosanitary practices on Akkar Plain

The monitoring results highlight a significant change in pollution (ie. the composition and concentrations of pesticides and/or their metabolites or derivatives) of groundwater between 2015 and 2019-2020. Thus, in 2015 and 2019 well n°5 was the most polluted in pesticides, while in 2020 wells n°7 and 8 are the most polluted. This observation suggests a change in cultivated plants and/or phytosanitary practices of certain farmers. In 2019, the farmers started growing spinach in greenhouses, which requires large quantities of water and pesticides. The greenhouses were built close to the wells (n°7 and 8) to facilitate access to water. Thus, the increase in the concentrations of several pesticides such as 4,4'-DDD, methoxychlor and many OPPs between 2015, 2019 and 2020 could be the result of this change of agricultural activities. Our results suggest also that the gradual replacement of OCPs by OPPs led to higher concentrations of OPPs in Akkar groundwater: 413.49 $\mu\text{g/L}$ for O, O, O-triethylphosphate (well n°7), vs. 56.98 $\mu\text{g/L}$ for cis-chlordane (well n°8). Some other compounds also seemed to have been progressively abandoned by farmers, such as methyl parathion, or heptachlor (cf. heptachlor/heptachlor epoxide ratio). In Lebanon, the number of registered active ingredients of chemical pesticides was 106 in December 2019, while the number of formulations totaled 128. The number of biorational formulations registered was about 26, 19 of which are pheromones, while only 3 were belonging to the microbial category biopesticides.

During the sampling campaign in 2019, farmers confirmed using pesticides without following manufacturers' recommendations. Thus, the survey indicated that farmers use oxychloride every 15 days, while the recommendation is to use it every 30-35 days. Similarly, the metalaxyl

+ mancozeb preparation recommends a dosage of 0.5 L in 200 L of water (AGRITECH, 2012), while farmers in Akkar apply it at 1 L in 4 L of water. They are therefore using 100 times more pesticides than the recommended use. This “anachic” behavior of farmers is also consistent with the use of banned pesticides as suggested by monitoring results.

3.3.2. Influence of land use

The effect of land use on groundwater quality was studied by agglomerative hierarchical clustering (AHC). The AHC managed to classify the sites into 4 distinct groups (Figure 4) based on the dataset of OCP and OPP concentrations in the wells in 2020. The results confirm the impact of land use on contamination patterns.

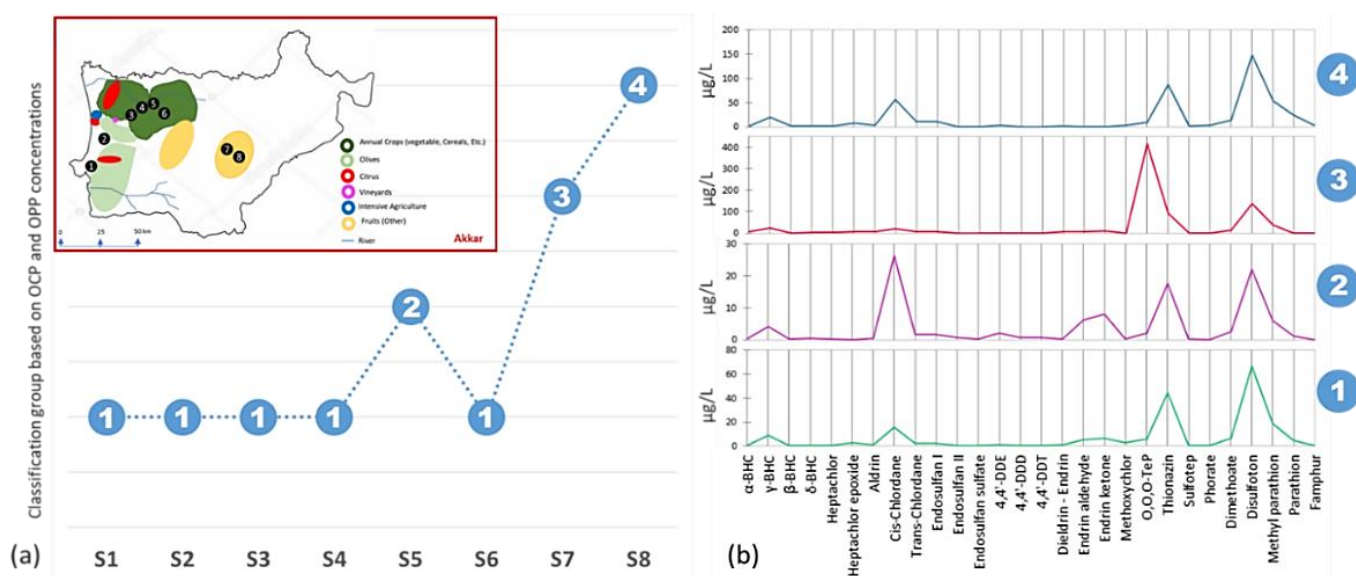


Fig 4 Overview of the pesticide pollution in Akkar’s wells. (a) is the assignment of each sampled site to one of the classes defined by the AHC (1 to 4) for pesticides. (b) are the concentration profiles of the classes defined by the AHC (each curve represents the barycenter of its class) for pesticides. The AHC was done with 4 levels with a 95% cutoff.

The results show that sites n°5, 7 and 8 differ from the others by their pattern and levels of pesticide contamination. Thus, the well no. 8 (group #4) is distinguished by significant concentrations of cis-chlordane, endosulfan- α , 4,4'-DDE, thionazin, and disulfoton. Their presence in high concentrations is consistent with the establishment of spinach crops (nb. plant vulnerable to insects and nematodes). The well n°7 (group #3) is distinguished by very high concentrations of α -HCH, γ -HCH, aldrin, dieldrin, endrin isomers, O, O, O-triethylphosphate,

thionazine and disulfoton. This site is used for the production of vegetable crops (including spinach) and fruit.

Sites n°1 to 4 and site n°6 (group #1) are characterized by high concentrations of thionazin and disulfoton. Sites n°1 and 2 are known for their intensive agricultural activities (i.e., olives and annual crops). Thionazine and disulfoton are known to be applied between April and May (and the application is repeated in July) for the treatment of olives against insects. For the protection of annual crops, insecticide and fungicide applications are also made in late April and early May. With the spring rains, these pesticides are leached and then infiltrate the soils to the underground water reservoirs. Thionazin and chlordane are banned in Lebanon since 1998 (decision 94/1, Abou Zeid et al., 2020), but it seems that they are still used because of the high levels detected. Disulfoton, an organophosphate acetylcholinesterase inhibitor used as an insecticide (banned by US government in 2009; EPA, 2009); is still used for olives trees and fruit trees in Akkar Region.

The well n°5 (group #2) is distinguished by the presence of numerous compounds at low concentrations (without preponderant compounds). This observation is consistent since this site is not characterized by intensive agricultural activities.

3.3.4. Delay factor between application periods - infiltration time - sampling periods

Several studies highlighted the impact of rainfalls on the transport of pesticides to surface and groundwater. Bloomfield (1996) showed that pesticides sprayed during the dry season persist in cracked soil until the rainy season and then infiltrate to a considerable depth (i.e. tens of meters). This “seasonal” process could also explain the increase in pesticide concentrations that were observed during the 2020 campaign. Indeed, the first campaign in 2019 was conducted in the dry season, while the second was conducted in the wet season, which may promote the transport of pesticides applied and then reached groundwater.

The highly fissured carbonate aquifers in the Akkar Region are characterized by high porosity and permeability that facilitate the transport of water and pollutants (DAR-IAURIF, 2004). The transport of pesticides from the surface to into rocks depends also on many factors including the structure and size of the cracks (Bloomfield, 1996). Baran et al. (2008) were able to explain the variations in atrazine concentration in the “Trois Fontaine” source (France) by a rapid transport within the hydrogeological scheme.

Furthermore, the distribution of pesticides in the aquifer can also be influenced by several other factors: water table, variation in groundwater levels (due to anthropogenic activities such as over-pumping), and hydrogeological properties (Hakoun et al., 2017). The physico-chemical characteristics of the compounds are also very important. Thus, OCPs and OPPs tend to adhere to the solid surface of aquifers (Moore and Ramamoorthy, 1984) because they have low water solubility and high octanol-water partition coefficients. Organochlorine pesticides move more slowly than the average groundwater flow rate. During their transport in an aquifer, they are distributed between the aqueous and aqueous-solid phases. Thus, their mobility depends on the time spent in each phase. The delay factor depends on the affinity of the compound with the mobile and immobile phases. Chilton et al. (2005) pointed out that it largely affects the transport of some pesticides. Thus, the delay factor could explain the current presence of old pesticides (i.e., heptachlor).

3.3.5. Natural degradation/transformation of pesticides

The presence of pesticides in groundwater is also strongly linked to biodegradation processes. Some soil microorganisms (e.g., bacteria or fungi) can feed and grow on pesticides as an energy source or can degrade by co-metabolism (Rashid et al., 2016). Thus, the highlight of huge concentrations of heptachlor epoxide in Akkar water wells suggests an important role of biodegradation by soil microorganisms, at least for heptachlor. In addition, the increased concentrations of endrin aldehyde and endrin ketone strongly suggest degradation of endrin - presumably by solar photolysis (Hassaan and El Nemr, 2020). As well, chemical reactions such as photolysis (at the soil surface) and hydrolysis also contribute to the transformation of some pesticides. However, it is important to note that the degradation processes are specific to each compound. For example, 2,4-D (1-chloro-2-[2,2-dichloro-1-(4-chlorophenyl) ethyl] benzene) is known to be generally degraded in a short time (i.e., almost less than 14 days) in soil, while 2,4,5-T (2-(2,4,5-trichlorophenoxy) acetic acid) takes a long time to be degraded (Hassaan and El Nemr, 2020). Similarly, chlordane and heptachlor are persistent pesticides, with half-times measured in decades, i.e., 10 years and 2 years; respectively, (Jayaraj et al. 2016).

3.4. Health risk assessment related to pesticide contamination in Akkar Region

The presence of many pesticides at significant - even high - concentrations raises the question of the health risk and the existing diseases for the locals (nb. consuming groundwater in the Akkar Region). To evaluate this risk, a health risk assessment study was therefore carried out using the methodology described by Chbib et al. (2020). For this purpose, the OCP and OPP

508 concentrations measured in 2019 and 2020 in the different wells were transposed into an
509 equivalent ingested dose. The theoretical average daily dose (ADD in mg/kg-day) of pesticides
510 via ingestion pathway (defined by the US EPA Exposure Factors handbook) was calculated
511 using different parameters of human exposure like magnitude, frequency, and duration of
512 exposure to each type of pesticide:

513
$$ADD = (C * IR * EF * ED) / (BW * AT)$$

514 Where C is the concentration of pesticides in Akkar groundwater (mg/l),
515 IR is the intake rate = 3L/day (corresponding to water intake from drinking and cooking)
516 EF is the exposure frequency (day/year)
517 ED is the exposure duration (year)
518 BW is the body weight = estimated at 70 kg for adults
519 AT is the average time (days)

520 ADD was calculated for daily exposure to pesticides, $EF * ED / AT = 1$.

521
522 The hazard quotient (HQ) (i.e., representing the non-carcinogenic risk) was calculated as
523 follows (Goumenou and Tsatsakis, 2019):

524 $HQ = ADD / RfD$; with RfD, the specific reference dose for each pesticide (in mg/kg-day).

525 RfD values are presented in the Supporting Information (Table SI 12).

526

Table 6 The hazard quotient of several pesticides founds in the water wells of the Akkar Region.

2020									
Site :	1	2	3	4	5	6	7	8	Average HQ
OCPs									
α-BHC	0.10	0.07	0.01	0.04	0.02	0.05	0.51	0.19	0.12
□-BHC	0.02	0.04	0.03	0.13	0.08	0.04	0.41	0.28	0.13
γ-BHC	1.44	2.03	0.57	1.45	0.57	1.17	3.60	2.96	1.72
4,4'-DDT	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
4,4'-DDD	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Endosulfan	0.01	0.01	0.00	0.01	0.01	0.02	0.02	0.04	0.02
Aldrin	1.34	1.49	0.31	1.63	0.53	1.89	8.31	4.51	2.50
Methoxychlor	0.00	0.00	0.00	0.04	0.00	0.07	0.01	0.03	0.02
Heptachlor	0.04	0.03	0.00	0.16	0.02	0.03	0.23	0.09	0.07
Heptachlor epoxide	10.91	15.40	1.22	17.67	0.00	5.11	23.01	25.25	12.32
Cis-Chlordane	2.85	2.68	0.00	0.48	2.25	0.64	1.91	4.88	1.96
Trans-Chlordane	0.30	0.27	0.05	0.11	0.14	0.33	0.51	0.94	0.33
OPPs									
Sulfotep	0.02	0.04	0.04	0.04	0.01	0.16	0.08	0.13	0.06
Dimethoate	1.35	1.70	2.03	1.36	0.54	0.98	2.92	3.13	1.75
Disulfoton	67.39	81.78	95.44	65.18	23.39	47.05	146.51	158.25	85.62
Methyl parathion	3.28	3.93	4.53	2.89	1.00	1.40	6.81	9.09	4.12
Parathion	1.54	0.41	1.65	0.33	0.23	1.51	0.44	5.42	1.44
2019									
Site :	1	2	3	4	5	6	7	8	Average HQ
OCPs									
α-BHC	0.01	0.01	0.03	0.02	0.06	0.03	0.04	0.03	0.03
□-BHC	0.18	0.27	0.60	0.22	0.45	0.25	0.25	0.26	0.31
γ-BHC	0.02	0.04	0.05	0.02	0.12	0.05	0.06	0.05	0.05
4,4'-DDT	0.00	0.00	0.36	0.00	0.23	0.14	0.16	0.15	0.13
4,4'-DDD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Endosulfan	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aldrin	0.30	0.39	0.24	0.19	0.93	0.47	0.53	0.49	0.44
Methoxychlor	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00
Heptachlor	0.02	0.02	0.03	0.02	0.09	0.05	0.04	0.04	0.04
Heptachlor epoxide	0.79	1.05	0.53	0.43	1.32	1.15	1.22	1.29	0.97
Cis-Chlordane	0.02	0.02	0.08	0.05	0.15	0.08	0.10	0.09	0.07
Trans-Chlordane	0.02	0.01	0.01	0.01	0.04	0.03	0.03	0.03	0.02
OPPs									
Sulfotep	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.02
Dimethoate	0.08	0.03	0.03	0.11	0.17	0.08	0.09	0.09	0.08
Disulfoton	0.26	0.11	0.10	0.45	0.59	0.17	0.19	0.20	0.26
Methyl parathion	0.05	0.20	0.04	0.17	0.25	0.10	0.02	0.02	0.11
Parathion	0.05	0.02	0.02	0.02	0.02	0.34	0.09	0.08	0.08

528 The obtained HQ values (in Table 6) show that the pesticide concentrations in Akkar Region
529 represent an unacceptable health risk for the population consuming water from wells. This work
530 shows that the risk is increasing between the dry season and the wet season. In the 2019 samples,
531 only one compound exceeded the threshold of 1 (heptachlor epoxide), whereas, in 2020, 8
532 compounds exceed this threshold. If the value of HQ exceeds 1, there is an unacceptable risk
533 of adverse non-carcinogenic effects on human health, while if the HQ is less than 1, it is at an
534 acceptable level (USEPA, 2001 c).

535 The most threatening compound is disulfoton, which has values 100 times above the threshold
536 (HQ = 23.39 - 158.25; it was found only in 2020). The other compounds with the highest health

537 risk are γ -BHC, aldrin, cis-chlordane, dimethoate, methyl parathion, parathion, and heptachlor
538 epoxide. Among them, the HQs of heptachlor epoxide - a degradation product of heptachlor -
539 show that the degradation/dissipation of former pollutants also represents a significant health
540 risk. Chbib et al. (2020) also highlighted significant average HQ for some pesticides in samples
541 collected from July 2015 to November 2017. Thus, there is an HQ of 29.7, 4.75, and 2.51 for
542 heptachlor epoxide, methyl parathion, and disulfoton, respectively. For the other pesticides in
543 common with this study, the values found by Chbib et al. (2020) were less than 1 (e.g., for
544 BHC, heptachlor, dimethoate, parathion) or 0.01 (e.g., for 4,4'-DDT, endosulfan,
545 methoxychlor). The risk is probably even higher when considering the mixture of all these
546 compounds and their degradation products. For the risk assessment of a mixture of chemicals,
547 the individual HQ are combined to form the hazard index (HI): if $HI < 1$ the risk level is
548 acceptable whereas if $HI > 1$ the risk level is unacceptable. This requires access to specific
549 correction factors (CF) which correspond to the ratio of the permitted contribution to exposure
550 of water to overall dietary exposure. Unfortunately, CF were not available for all the pesticides
551 found in Akkar (Goumenou and Tsatsakis, 2019).

552 Results highlight the urgent need to carry out in-depth epidemiological studies among the Akkar
553 population to assess the consequences of exposure to pesticides (via water, food, and air). Many
554 studies suggested a biological impregnation of the resident population. Thus, several OCPs
555 were detected in blood serum samples taken in the cross-sectoral study from 2013 to 2014;
556 however, values remained at concentration excluding a health risk (Harmouche-Karaki et al.,
557 2018). Smadi and Darra (2019) performed a study on 120 samples of breast milk in a Syrian
558 refugee camp in North Lebanon. They detected pesticide residues like chlorpyrifos (until 2.32
559 $\mu\text{g/L}$ in one sample), methamidophos, and lufenuron. Over the past few years, Lebanese
560 populations were cautious to consume strawberries and vegetable crops, because a shocking
561 study showed the higher concentrations of pesticide residues that may be present in field crops
562 (Kfoury et al., 2002; Hattam, 2009).

563 In Lebanon, farm workers exposed to pesticides have a 4-time higher risk of having life-
564 threatening acute intoxications than other workers (Salameh and Abi Saleh, 2004). Many
565 Lebanese farmers suffered from subacute intoxications and other different symptoms without
566 being hospitalized (Salameh and Abi Saleh, 2004). Salameh et al. (2006) showed that asthma
567 in adult patients was highly correlated with professional and non-professional exposures to
568 pesticides. Youssef et al. (2015) called for the establishment and enforcement of regulations to

reduce the impact of pesticides on the environment and human health due to the contamination of ground and surface water sources in South Lebanon.

4. Conclusions

Groundwater monitoring in the Akkar region shows that groundwater quality is degraded by the uncontrolled use of pesticides on crops and fruit trees. The calculation of the theoretical dose of pesticides by ingestion suggests that pesticide concentrations represent a health risk for the population consuming groundwater from wells, especially during the rainy season. All the OCPs and OPPs studied were detected - with values exceeding the level limits set by the European Union and taken up by Lebanon - in the groundwater. Pesticide concentrations have changed over the years (2015- 2019/2020), due to changes in practices (use of banned products or abandonment of certain substances, new mixtures) and crops (e.g. spinach), biogeochemical processes, hydrogeological characteristics of rocks and retarding factors. However, monitoring data suggest a change in the compounds used rather than a decrease in the use of pesticides. Therefore, the authorities should increase measures to limit exposure and risks to the population and to set up a monitoring programme for water quality and population health.

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