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

4
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Abstract

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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.

40 **1. Introduction**

41 Most of Lebanon's agricultural production is located in the Bekaa, Baalbek, El Hermel and
42 Akkar regions (FAO, 2010). Water consumption for agriculture represents about 60-70% of
43 the total water consumption in Lebanon (MoE/LEDO/ECODIT, 2001; Geara-Matta et al.,
44 2010). Many private wells have been drilled for crop irrigation (Youssef et al., 2015) but also
45 for domestic consumption (over 33,000) (ACS, 2007). Lebanon is a large producer of potatoes
46 (572,109 tons in 2019), oranges, apples, and grapes (Fruit: 54,244 tons in 2019) (Tilasto, 2020),
47 and imports around 6,641 tons/year of pesticides (Abou Zeid et al., 2020). Soil runoff and
48 leaching have led to the infiltration of pesticides from application areas into aquifers (Huber et
49 al., 2000; Blanchouda et al., 2007). The excessive and uncontrolled use of pesticides has led to
50 severe contamination of groundwater in these areas (Chbib et al., 2017; Chbib et al., 2018).
51 Several studies have highlighted the presence of a wide diversity of pesticides in the waters of
52 northern or southern Lebanon (El-Osmani et al., 2014; Youssef et al., 2015, Chbib et al., 2017;
53 Helou et al., 2019; Chbib et al., 2020). In particular, these studies have pointed to the significant
54 presence of organochlorine pesticides (OCPs) and organophosphate pesticides (OPPs), known
55 as persistent organic pollutants (POPs). The reported high concentrations in Lebanese
56 groundwater have been related to the hydrogeological characteristics of the unsaturated zone
57 that enhance the percolation/infiltration factors (Hancock et al., 2008). Infiltration of pesticides
58 is influenced soil type and rock lithologies, adsorption properties of compounds, and the time
59 interval between application and the first rainfall (Brown and Van Beinum, 2009).

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

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

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

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

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

98

99 **2. Materials and methods**

100 **1. Wells description and sampling.**

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

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

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

127 **2. Micropollutants analysis**

128 **2.1. Pesticides**

129 Based on the information provided by the inhabitants of the Akkar Region and the previous
130 analyses performed in 2012 and 2015 (El-Osmani et al., 2014; Chbib et al., 2017), it was
131 selected to monitor 20 OCPs and 8 OPPs for two standard solutions of organochlorine (20
132 compounds) and organophosphate (8 compounds) pesticides purchased from Restek. Pesticide
133 concentrations in these solutions were 200 mg/L for each OCP (organochlorine pesticides AB
134 n°1, Restek n°32291) and 2000 mg/L for each OPP (organophosphorus EPA 8270, Restek
135 n°32419). These standard solutions were used to prepare an external calibration ranging from
136 10 ng/mL to 250 ng/mL for each compound in Dichloromethane (DCM). For the presentation
137 of results, OCPs were divided into three groups: DDT and its metabolites, HCH and its isomers,
138 and cyclodiene insecticides. The main properties (CAS number, molecular weight (MW), and
139 the octanol/water partition coefficient (log Kow)) of the selected OCPs and OPPs are given in
140 the Supporting information (Table SI 3)

141 **2.2. Extraction procedure**

142 For each site, a 500 mL water sample was extracted by solid-phase extraction (SPE) on an
143 Autotrace 150 (Thermo Scientific Inc., Waltham, USA) according to Laurent (2013) and Zind
144 (2020) Briefly, Oasis HLB cartridges (6cc), purchased from Waters Corporation (MA, USA),
145 were conditioned with 5 mL MeOH followed by 5 mL UPW. The water sample (500 mL) was
146 loaded at a constant flow rate of 10 mL/min. Then the cartridges were washed with 5 mL of
147 UPW, dried under a nitrogen flow for 5 min at 10 mL/min, and stored at -80°C until analysis.

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

152 **2.3. GC/MS analysis**

153 The target pesticide residues were analyzed by gas chromatography (GC) tandem-mass
154 spectrometry (MS) (GC-MS: 7890A GC system, 5975C, Agilent©). Separation of the
155 compounds was carried out on a DB-35MS UI column (30 m length, 0.25 mm diameter, 0.25
156 µm film thickness). The carrier gas was Helium at a constant flow rate of 1mL/min. The
157 temperature of GC was programmed as follows: the initial temperature of 90 °C (hold 1.3 min),
158 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
159 increased to 280°C at 20°C/min (hold for 4 min).

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

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

167 **2.4. AHC (Agglomerative Hierarchical Clustering)**

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

179 **2.5. Physico-chemical analyses of groundwater**

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

185

186 **3. Results and discussion**

187 **3.1. Organochlorine pesticides (OCPs)**

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

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

196 **3.1.1. DDT and its metabolites**

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

210 In 2015, 4,4'-DDD ranged from <LoD to 0.25 µg/L and was detected only at site n°5 (Table
211 1), whereas in 2019, it ranged from <LoD to 0.23 µg/L (nb. in common sites with the 2015
212 campaign – sites 1 to 6) and was detected at 4 different sites (sites n°1-2-3 and 4). In 2020,
213 4,4'-DDD was detected in all sites and the mean value was equal to 0.71 µg/L. The average
214 concentration of 4,4'-DDT was 0.31 µg/L in 2015 and then it increased in 2019 (2.82 µg/L)
215 and decreased in 2020 (average value of 0.70 µg/L). The average value of 4,4'-DDE found in
216 2019 seems to have increased 12 times since 2015 and then increased again 4 times in 2020.
217 Thus, our results show that DDTs are still present in the Akkar Region due to the reported high
218 values that exceed the limit (0.1 µg/L) set by the European Union Drinking Water Directive
219 (DCE, 1998).

220

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.
ΣDDTs - 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
ΣDDTs - 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
ΣDDTs - 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).

242 **3.1.2. HCH and its isomers**

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

247 The results shown in Table 2 also show that all isomers of HCHs (α , β , γ , δ) were detected in
 248 2019 and 2020. In 2019, the highest average concentration was observed for δ -HCH at 0.48
 249 $\mu\text{g/L}$. While in 2020, γ -HCH was the most concentrated isomer of HCHs with an average
 250 concentration equal to 12.4 $\mu\text{g/L}$. In 2019, ΣHCHs concentrations ranged from 0.83 $\mu\text{g/L}$ (site
 251 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
 252 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
 253 equal to 14.79 $\mu\text{g/L}$.

254 **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>

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

256 HCH may result from the utilization of lindane (i.e., 99 % γ -HCH) or from commercial
 257 mixtures that contain several HCH isomers: α -HCH (~65%), β -HCH (~8.5%), γ -HCH
 258 (~12.5%), and δ -HCH (~8%). Thus, the α -HCH/ γ -HCH ratio is an indicator of HCH origin as
 259 a ratio between 4 and 7 might be related to the use of commercial mixtures, while a ratio near
 260 0 is related to lindane usage (Zhao et al., 2009; Dai et al., 2011). The ratio (see Table 2) varies
 261 from 0.59 to 1.49 in 2019, while it varied from 0.02 to 0.24 in 2020, which suggests that HCHs
 262 have been supplied by lindane usage. This decrease in the ratio follows the high concentrations

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

267 **3.1.3. Cyclodiene insecticides**

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

272 Endosulfan is an insecticide composed of α -endosulfan (70%) and β -endosulfan (30%) (Jiang
273 et al., 2009). According to the literature, the proportion of its two forms reflects its degradation
274 state. In Akkar Region, the average value of the α -endosulfan/ β -endosulfan ratio was 1.32 in
275 2019 (Table 3). This value (below 2.33) suggests that the presence of endosulfan was related
276 to old applications. However, recent measurements in 2020 show that the current ratio is 6
277 revealing a recent intake/use of this compound (Zhang et al., 2011; Qu et al., 2015). A by-
278 product of endosulfan has also been monitored in Akkar groundwaters. Endosulfan sulfate is a
279 metabolite produced by biodegradation in soil (Jia et al., 2010). This by-product is more toxic
280 and can persist in soil for a long time (Fujii et al., 2012). The average concentration of
281 endosulfan sulfate found in Akkar (for common sites between the different monitoring
282 campaigns) was 1.03 $\mu\text{g/L}$ in 2013 (El-Osmani et al., 2014), then this value decreased in 2015
283 (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
284 $\mu\text{g/L}$.

Table 3 Cyclodiene insecticides concentrations ($\mu\text{g/L}$) 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.
Methoxychlor	<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.
<i>ratio H/HE</i>	<i>1.21</i>	<i>1.54</i>	<i><LoD</i>	<i>0.64</i>	<i>0.87</i>	<i>0.23</i>	-	-
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
<i>ratio α/β</i>	<i>1.44</i>	<i>1.62</i>	<i>2.57</i>	<i>0.98</i>	<i>1.45</i>	<i>0.81</i>	<i>0.90</i>	<i>0.80</i>
Σ Endosulfan ($\alpha + \beta$)	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
<i>ratio H/HE</i>	<i>0.89</i>	<i>0.69</i>	<i>2.21</i>	<i>1.36</i>	<i>2.77</i>	<i>1.62</i>	<i>1.40</i>	<i>1.23</i>
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
<i>ratio α/β</i>	<i>5.48</i>	<i>4.96</i>	<i>0.84</i>	<i>1.92</i>	<i>2.56</i>	<i>6.00</i>	<i>9.21</i>	<i>16.84</i>
Σ Endosulfan ($\alpha + \beta$)	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
<i>ratio H/HE</i>	<i>0.12</i>	<i>0.07</i>	<i>0.11</i>	<i>0.35</i>	-	<i>0.21</i>	<i>0.38</i>	<i>0.14</i>
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

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

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289

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

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

304 Heptachlor is another non-systemic organochlorine insecticide used in Akkar primarily against
305 soil insects. This compound is present in the 2020 samples (Table 3), but it was also found
306 during previous groundwater monitoring campaigns (Chbib et al., 2017). Higher values were
307 detected in 2015 (average of 4.55 µg/L) than in 2019 (average of 0.45 µg/L) and in 2020
308 (average of 0.87 µg/L). Moreover, the results highlight that heptachlor is found at lower
309 concentrations than its main by-product, heptachlor epoxide (i.e., on average, in 2015 and
310 2020). Heptachlor epoxide was detected in all samples (except for site n° 5) in the 2020
311 sampling. The average heptachlor epoxide concentration in 2015 was 6.45 µg/L and ranged
312 from 2.50 µg/L to 15.50 µg/L. In 2020, the average heptachlor epoxide concentration was 4.27
313 µg/L. According to the performed literature review, the ratio of heptachlor/heptachlor epoxide
314 is used to determine whether the presence of heptachlor is related to a recent or historical intake
315 of this pesticide (Salem et al., 2014). In Akkar Region, the ratio (shown in Table 3) was greater
316 than 1 for the 2015 (sites n° 1 and 2) and 2019 campaigns (except for sites n° 1 and 2), while it
317 is less than 1 in 2020 - for all sites. This value indicates that the current presence of heptachlor
318 (2020) originates from previous applications of this compound.

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

322 $\mu\text{g/L}$) (Table 3). In 2019, the concentration of methoxychlor ranged from 0.24 (site n°4) to 0.70
 323 $\mu\text{g/L}$ (site n°7) with an average value of 0.50 $\mu\text{g/L}$. In 2020, concentrations seem to have
 324 increased: the mean value is greater at 2.26 $\mu\text{g/L}$ - with variations from 0.18 $\mu\text{g/L}$ (sites n°2
 325 and 3) to 8.62 $\mu\text{g/L}$ (site n°6).

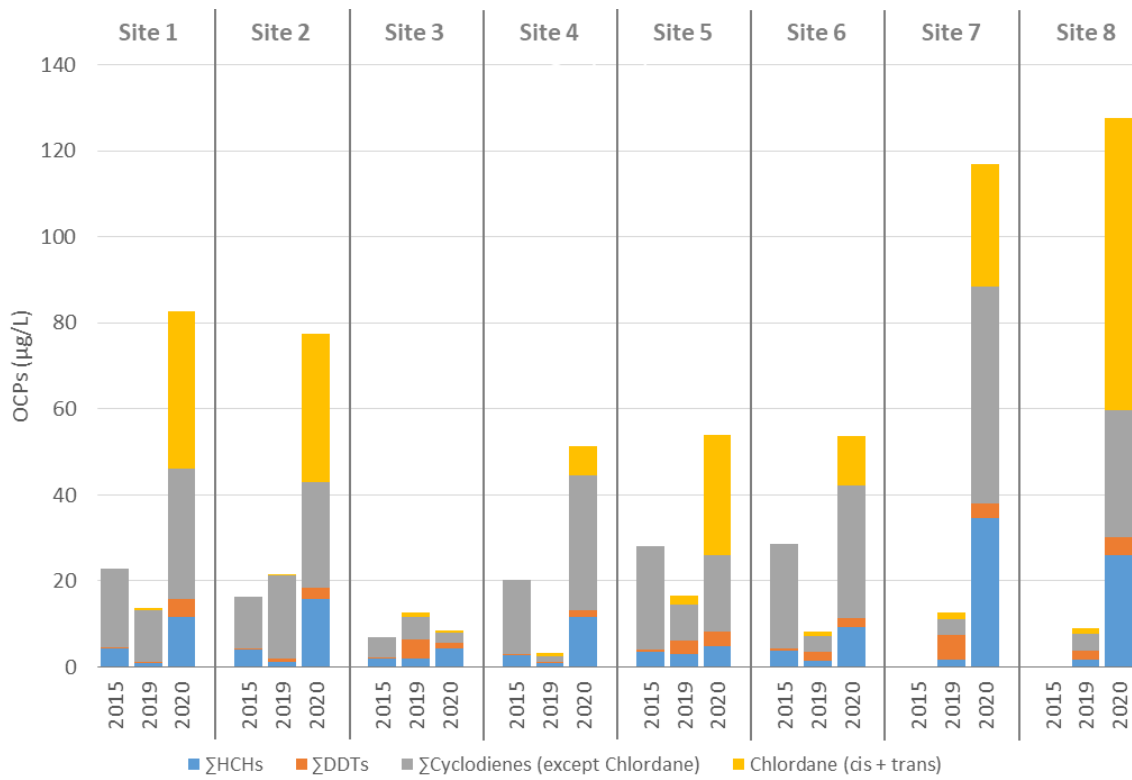
326 Trans-chlordane (nb. the main isomer of chlordane) has been found in Akkar water wells. It is
 327 known to be carcinogenic and the most bioaccumulative of the chlordane family (Luzardo et
 328 al., 2014). Trans-chlordane was detected at all sites in 2019 and 2020 (Table 3), with an average
 329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

332 All these results for cyclodiene insecticides show that this family is widely present in the Akkar
 333 groundwater. Thus, total cyclodiene concentrations ($\Sigma\text{cyclodienes}$) (Table 3) ranged from 4.72
 334 $\mu\text{g/L}$ (site n°3) to 24.28 $\mu\text{g/L}$ (sites n°6) in 2015 to between 3.27 $\mu\text{g/L}$ (site n°4) to 21.69 $\mu\text{g/L}$
 335 (site n°2) in 2019. In 2020, concentrations range from 2.33 $\mu\text{g/L}$ (site n°3) to 30.80 $\mu\text{g/L}$ (site
 336 n°6) with a high value for site n°7 (50.59 $\mu\text{g/L}$).

337 **Table 4** Total OCPs concentrations ($\mu\text{g/L}$) in Akkar water wells.

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

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



339

340

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

341 Total OCPs concentrations (shown in Table 4 and Figure 1) ranged from 7.40 µg/L (site n°3)
342 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
343 from 8.55 µg/L (site n°3) to 127.57 µg/L (site n°8) in 2020. The Cyclodiene family is always
344 the most abundant among OCPs. Note that in 2020, among the cyclodiene, chlordane (Figure
345 1) was present in very high concentrations as compared to 2019 (these compounds were not
346 measured in 2015). The most contaminated was site n°5 in 2015, regarding Σ OCPs as well as
347 the number of pesticides with the highest concentration (8/18). In 2019, regarding the maximum
348 OCP concentrations, the most contaminated was site n°2, but the site with the highest number
349 of maximum concentrations for several pesticides was also site n°5 (11/19). In 2020, sites n°7
350 and 8 were the most contaminated (i.e., maximum concentrations and number of pesticides with
351 the highest concentrations).

352 **3.2. Organophosphate pesticides (OPPs)**

353 Due to their high stability in the environment and their high toxicity, especially in the nervous
354 system of humans and animals (Viswanathan et al., 2009), OCPs have been gradually replaced
355 by OPPs and ONPs by farmers. OPPs are characterized by the low cost and high efficiency on
356 a wide range of pests and insects. In addition, 50% of insecticides belong to the OPP class
357 (Rodrigues et al., 2011). They are also easily available commercially (Li et al., 2007).
358 Furthermore, OPPs are widely known to degrade rapidly depending on multiple conditions such
359 as application method, formulation, climate, and plant life cycle (Sankararamakrishnan et al.,
360 2005).

361 In 2019, OPPs (Σ OPPs) concentrations (Table 5) ranged from 1.15 µg/L to 7.76 µg/L. In 2020,
362 concentrations increased substantially up to 50.99 µg/L (site n°5) and 702.10 µg/L (site n°7). In
363 2015, average value (ie. 43.63 µg/L) were relatively higher than in 2019 but much lower than
364 in 2020.

365

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.
ΣOPPs - 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
ΣOPPs - 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
ΣOPPs - 2020	140.64	166.25	194.02	134.55	50.99	107.21	702.10	341.09

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

368 Some OPPs seem to have been discontinued or used less between 2015 and 2019-2020. For
 369 example, the average concentrations of famphur and methyl parathion were 3.33 $\mu\text{g/L}$ and 30.00
 370 $\mu\text{g/L}$, respectively, in 2015 while they are 0.52 $\mu\text{g/L}$ and 16.57 $\mu\text{g/L}$, respectively, in 2020 (sites
 371 #1-6). The concentrations of these two compounds are very high for site 8 in 2020 (2.50 and
 372 53.04 $\mu\text{g/L}$ respectively. On the contrary, sulfotep (Table 5) was not detected in 2015 but was
 373 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.
 374 These observations suggest that farmers in Akkar probably started using this insecticide after
 375 2015. Concentrations of many other OPPs have increased between 2019 and 2020. Thus, in
 376 2019 the highest concentrations were 5.58 $\mu\text{g/L}$ for O, O, O-triethyl phosphate, 0.48 $\mu\text{g/L}$ for
 377 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
 378 2020, the highest concentrations were 413.49 $\mu\text{g/L}$ for O, O, O-triethylphosphate, 94.52 $\mu\text{g/L}$
 379 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
 380 parathion.

381

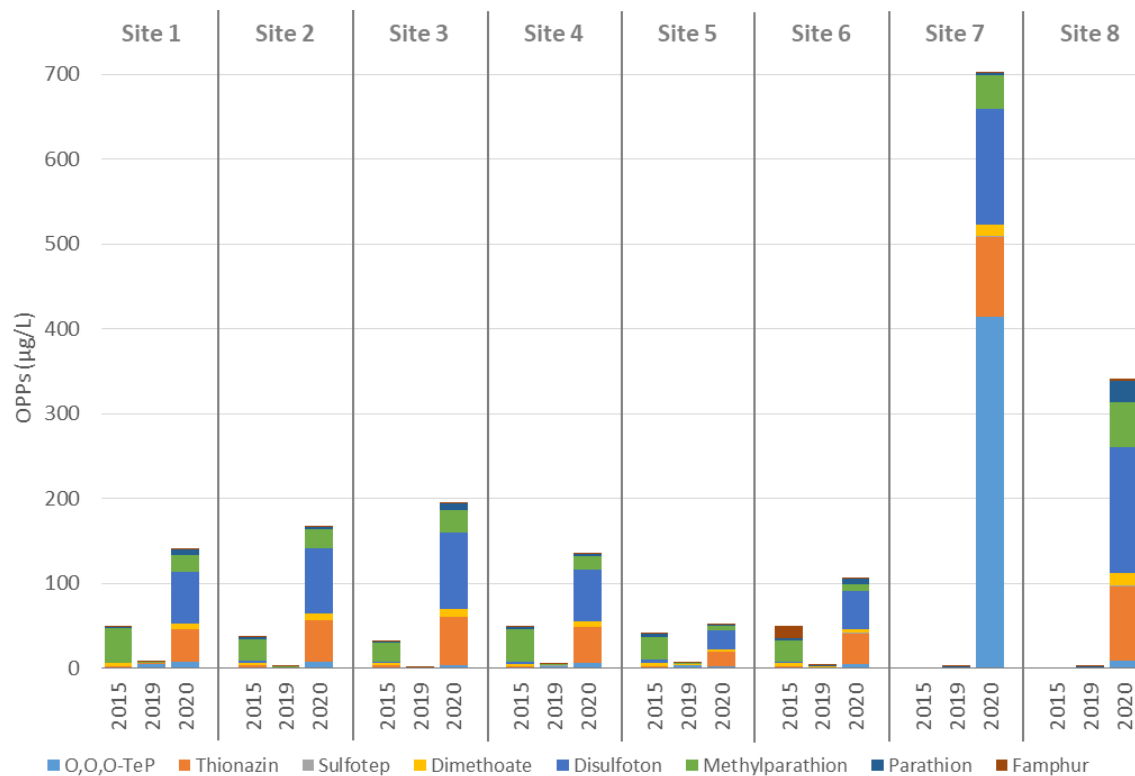


Fig 2 Organophosphate pesticides (OPPs) distribution ($\mu\text{g/L}$) in Akkar water wells.

382

383

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

390 3.3. Vulnerability factors of Akkar groundwater

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

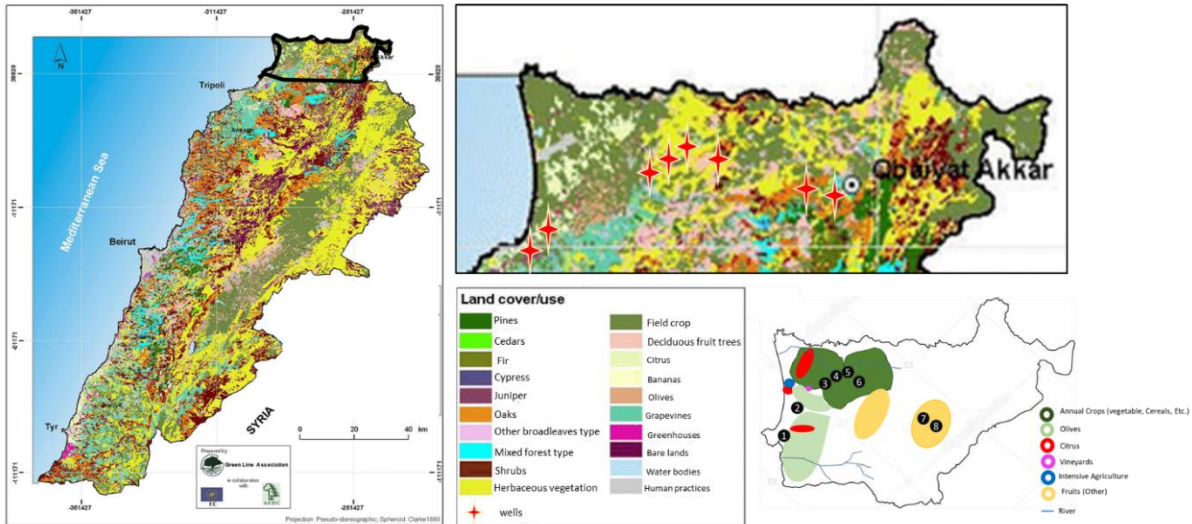


Fig 3 Agricultural map of Akkar for the different crops (LNCSSR-LMOA, 2002).

400
401

402

403 3.3.1. Evolution of phytosanitary practices on Akkar Plain

404 The monitoring results highlight a significant change in pollution (ie. the composition and
 405 concentrations of pesticides and/or their metabolites or derivatives) of groundwater between
 406 2015 and 2019-2020. Thus, in 2015 and 2019 well n°5 was the most polluted in pesticides,
 407 while in 2020 wells n°7 and 8 are the most polluted. This observation suggests a change in
 408 cultivated plants and/or phytosanitary practices of certain farmers. In 2019, the farmers started
 409 growing spinach in greenhouses, which requires large quantities of water and pesticides. The
 410 greenhouses were built close to the wells (n°7 and 8) to facilitate access to water. Thus, the
 411 increase in the concentrations of several pesticides such as 4,4'-DDD, methoxychlor and many
 412 OPPs between 2015, 2019 and 2020 could be the result of this change of agricultural activities.
 413 Our results suggest also that the gradual replacement of OCPs by OPPs led to higher
 414 concentrations of OPPs in Akkar groundwater: 413.49 µg/L for O, O, O-triethylphosphate (well
 415 n°7), vs. 56.98 µg/L for cis-chlordane (well n°8). Some other compounds also seemed to have
 416 been progressively abandoned by farmers, such as methyl parathion, or heptachlor (cf.
 417 heptachlor/heptachlor epoxide ratio). In Lebanon, the number of registered active ingredients
 418 of chemical pesticides was 106 in December 2019, while the number of formulations totaled
 419 128. The number of biorational formulations registered was about 26, 19 of which are
 420 pheromones, while only 3 were belonging to the microbial category biopesticides.

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

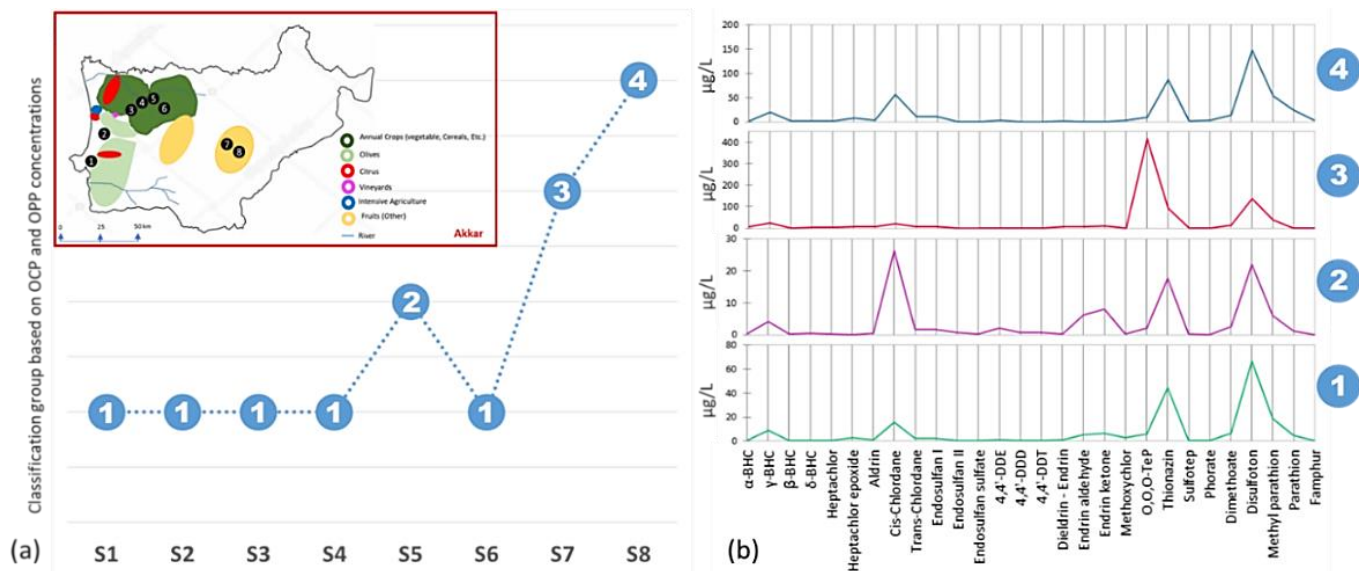
424 + mancozeb preparation recommends a dosage of 0.5 L in 200 L of water (AGRITECH, 2012),
 425 while farmers in Akkar apply it at 1 L in 4 L of water. They are therefore using 100 times more
 426 pesticides than the recommended use. This “anachic” behavior of farmers is also consistent
 427 with the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

428

429 3.3.2. Influence of land use

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

434



435

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

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

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

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

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

462 **3.3.4. Delay factor between application periods - infiltration time - sampling periods**

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

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

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

488 **3.3.5. Natural degradation/transformation of pesticides**

489 The presence of pesticides in groundwater is also strongly linked to biodegradation processes.
490 Some soil microorganisms (e.g., bacteria or fungi) can feed and grow on pesticides as an energy
491 source or can degrade by co-metabolism (Rashid et al., 2016). Thus, the highlight of huge
492 concentrations of heptachlor epoxide in Akkar water wells suggests an important role of
493 biodegradation by soil microorganisms, at least for heptachlor. In addition, the increased
494 concentrations of endrin aldehyde and endrin ketone strongly suggest degradation of endrin -
495 presumably by solar photolysis (Hassaan and El Nemr, 2020). As well, chemical reactions such
496 as photolysis (at the soil surface) and hydrolysis also contribute to the transformation of some
497 pesticides. However, it is important to note that the degradation processes are specific to each
498 compound. For example, 2,4-D (1-chloro-2-[2,2-dichloro-1-(4-chlorophenyl) ethyl] benzene)
499 is known to be generally degraded in a short time (i.e., almost less than 14 days) in soil, while
500 2,4,5-T (2-(2,4,5-trichlorophenoxy) acetic acid) takes a long time to be degraded (Hassaan and
501 El Nemr, 2020). Similarly, chlordane and heptachlor are persistent pesticides, with half-times
502 measured in decades, i.e., 10 years and 2 years; respectively, (Jayaraj et al. 2016).

503 **3.4. Health risk assessment related to pesticide contamination in Akkar Region**

504 The presence of many pesticides at significant - even high - concentrations raises the question
505 of the health risk and the existing diseases for the locals (nb. consuming groundwater in the
506 Akkar Region). To evaluate this risk, a health risk assessment study was therefore carried out
507 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:

$$513 \quad \text{ADD} = (C * \text{IR} * \text{EF} * \text{ED}) / (\text{BW} * \text{AT})$$

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, $\text{EF} * \text{ED} / \text{AT} = 1$.

521

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

524 $\text{HQ} = \text{ADD} / \text{RfD}$; 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 found 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

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

571

572 **4. Conclusions**

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

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596 5. References

- 597 Abou Zeid, M.I., Jammoul, A.M., Melki, K.C., Jawdah, Y.A., & Awad, M.K. (2020). Suggested policy and
598 legislation reforms to reduce the deleterious effect of pesticides in Lebanon. *Heliyon*, 6(12), e05524.
599 <https://doi.org/10.1016/j.heliyon.2020.e05524>
- 600 ACS (Central Administration of Statistics). (2007). Compendium Statistique National sur les Statistiques de
601 l'Environnement Au Liban 2007, République Libanaise Présidence de Conseil des Ministres, Beyrouth, Liban.
- 602 AGRITECH. (2012). "Major use of pesticides". Retrieved June 18, 2021, available at:
603 https://agritech.tnau.ac.in/crop_protection/pdf/6_Major_use_fungicides.pdf
- 604 Baran, N., Lepiller, M., & Mouvet, C. (2008). Agricultural diffuse pollution in a chalk aquifer (Trois Fontaines,
605 France): Influence of pesticide properties and hydrodynamic constraints. *Journal of Hydrology*, 358(1-2), 56-
606 69. <https://doi.org/10.1016/j.jhydrol.2008.05.031>
- 607 Baroudi, M., Bakkour, H., Halwani, J., Taha, S., El-Osmani, R., & Mouneimne, A.H. (2012). Determination of
608 pesticide, nitrates, and nitrites level in groundwater of Akkar plain in north Lebanon. *Journal of Applied Sciences*
609 *Research*, 8, 4663-4667.
- 610 Blanchouda, H., Moreau-Guigona, E., Farrugiab, F., Chevreuila, M., & Mouchelb, J.M. (2007). Contribution by
611 urban and agricultural pesticide uses to water contamination at the scale of the Marne watershed. *Science of Total*
612 *Environment*, 375, 168-179. <https://doi.org/10.1016/j.scitotenv.2006.12.009>
- 613 Bloomfield, J. (1996). Characterization of hydrogeological significant fracture distributions in the chalk: an
614 example from the upper chalk of southern England. *Journal of Hydrology*, 184(3-4), 355-379.
615 [https://doi.org/10.1016/0022-1694\(95\)02954-0](https://doi.org/10.1016/0022-1694(95)02954-0)
- 616 Brooks, G.T. (1977). Chlorinated Insecticides: Retrospect and Prospect.
- 617 Brown, C.D., & van Beinum, W. (2009). Pesticide transport via subsurface drains in Europe. *Environmental*
618 *Pollution*, 157, 3314-3324. <https://doi.org/10.1016/j.envpol.2009.06.029>
- 619 Chbib, C., Net, S., Hamzeh, M., Dumoulin, D., Ouddane, B., & Baroudi, M. (2017). Assessment of pesticide
620 contamination in Akkar groundwater, northern Lebanon. *Environmental Science and Pollution Research*, 25,
621 14302-14312. <https://doi.org/10.1007/s11356-017-8568-6>
- 622 Chbib, C., Sahmarani, R., Net, S., Baroudi, M., Ouddane, B. (2018). Distribution of Organochlorine Pesticides
623 and Heavy Metals in Lebanese Agricultural Soil: Case Study—Plain of Akkar. *International Journal for*
624 *Environmental Research*, 12, 631-649.
- 625 Chbib, C., Ziade, F., Baroudi, M., Net, S., Ouddane, B. (2020). Pesticides contamination and nervous disorders in
626 an agricultural area in Akkar, Lebanon. A cross-sectional study. *Annals Epidemiology*, 3(1), 1012.
- 627 Chilton, P., Stuart, M., Goody, D., Williams, R., & Johnson, A. (2005). Pesticide fate and behaviour in the UK
628 chalk aquifer, and implications for groundwater quality. *Quarterly Journal of Engineering Geology and*
629 *Hydrogeology*, 38(1), 65-81. <https://doi.org/10.1144/1470-9236/04-014>
- 630 Dai, G., Liu, X., Liang, G., Han, X., Shi, L., Cheng, D., & Gong, W. (2011). Distribution of organochlorine
631 pesticides (OCPs) and poly chlorinated biphenyls (PCBs) in surface water and sediments from Baiyangdian Lake
632 in North China. *Journal of Environmental Sciences*, 23, 1640-1649. [https://doi.org/10.1016/S1001-0742\(10\)60633-X](https://doi.org/10.1016/S1001-0742(10)60633-X)
- 634 DAR-IAURIF. (2004). Schéma d'Aménagement du Territoire Libanais, Rapport Final, L0215-RPT-10 REVA 11
635 de 233). Retrieved June 18, 2021, available at: https://www.localiban.org/IMG/pdf/fr_intro.pdf
- 636 DCE (Directive Cadre sur l'eau). (1998). On the quality of water intended for human consumption. Brussels,
637 Belgium: Council Directive, 83.
- 638 El-Osmani, R., Net, S., Dumoulin, D., Baroudi, M., Bakkour, H., & Ouddane, B. (2014). Solid Phase Extraction
639 of Organochlorine Pesticides Residues in Groundwater (Akkar Plain, North Lebanon). *International Journal of*
640 *Environmental Research*, 8(4), 903-912. <https://doi.org/10.22059/IJER.2014.783>
- 641 EPA (Environmental Protection Agency). (2016). Methoxychlor. Retrieved June 18, 2021, available at:
642 <https://www.epa.gov/sites/default/files/2016-09/documents/methoxychlor.pdf>

- 643 FAO (Food Agricultural Organization). (2005). Proceedings of the Asia Regional Workshop. Bangkok: Regional
644 Office for Asia and the Pacific.
- 645 FAO. (2010). Agriculture in Lebanon: Facts and Figures, The Core Module of the Census of Agriculture 2010.
- 646 Fenster, L., Eskenazi, B., Anderson, M., Bradman, A., Harley, K., Hernandez, H., Hubbard, A., & Barr, B. (2006).
647 Association of in utero organochlorine pesticide exposure and fetal growth and length of gestation in an
648 agricultural population. *Environmental Health Perspectives*, 114 (4), 597-602. <https://doi.org/10.1289/ehp.8423>
- 649 Fujii, Y., Ito, Y., Harada, K.H., Hitomi, T., Koizumi, A., & Haraguchi, K. (2012). Comparative survey of levels
650 of chlorinated cyclodiene pesticides in breast milk from some cities of China, Korea and Japan. *Chemosphere*, 89,
651 452-457.
- 652 Geara-Matta, D., Moilleron, R., El Samrani, A., Lorgeoux, C., & Chebbo, G. (2010). State of Art about water uses
653 and wastewater management in Lebanon. *World Wide Workshop for Young Environmental Scientists*, 1-12.
- 654 Goumenou, M., & Tsatsakis, A. (2019). Proposing new approaches for the risk characterisation of single chemicals
655 and chemical mixtures: The Source Related Hazard Quotient (HQS) and Hazard Index (HIS) and the Adversity
656 Specific Hazard Index (HIA). *Toxicology Reports*, 6, 632-636. <https://doi.org/10.1016/j.toxrep.2019.06.010>
- 657 Gupta, P.K. (2004). Pesticide exposure-Indian scene. *Toxicology*, 198, 83-90.
658 <https://doi.org/10.1016/j.tox.2004.01.021>
- 659 Hakoun, V., Orban, P., Dassargues, A., & Brouyere, S. (2017). Factors controlling spatial and temporal patterns
660 of multiple pesticide compounds in groundwater (Hesbaye chalk aquifer, Belgium). *Environmental Pollution*, 223,
661 185-199. <https://doi.org/10.1016/j.envpol.2017.01.012>
- 662 Halwani, J., Ouddane, B., Baroudi, M., & Wartel, M. (1999). Contamination par les nitrates des eaux souterraines
663 de la plaine d'Akkar au Liban du Nord. *Cahiers d'études et de recherches francophones/Santé*, 9(4), 219-223.
- 664 Hancock, P.J., Boulton, A. J., & Humphreys, W.F. (2008). Aquifers and hyporheic zones: Towards an ecological
665 understanding of groundwater. *Hydrogeology Journal*, 13(1), 98-111. <https://doi.org/10.1007/s10040-004-0421-6>
- 666 Harmouche-Karaki, M., Matta, J., Helou, K., Mahfouz, Y., Fakhoury-Sayegh, N., & Narbonne, J.F. (2018). Serum
667 concentrations of selected organochlorine pesticides in a Lebanese population and their associations to
668 sociodemographic, anthropometric and dietary factors: ENASB study. *Environmental Science and Pollution
669 Research*, 25, 14350-14360. <https://doi.org/10.1007/s11356-017-9427-1>
- 670 Hassaan, M., & El Nemr, A. (2020). Pesticides pollution: Classifications, human health impact, extraction and
671 treatment techniques. *Egyptian Journal of Aquatic Research*, 46, 207-220.
672 <https://doi.org/10.1016/j.ejar.2020.08.007>
- 673 Helou, K., Harmouche-Karaki, M., Karake, S., Narbonne, JF. (2019) A review of organochlorine pesticides and
674 polychlorinated biphenyls in Lebanon: Environmental and human contaminants. *Chemosphere*, 231, 357-368.
675 <https://doi.org/10.1016/j.chemosphere.2019.05.109>
- 676 Hu, Y., Qi, S., Zhang, J., Tan, Zhang, J., Wang, Y., & Yuan, D. (2011). Assessment of organochlorine pesticides
677 contamination in underground rivers in Chongqing, Southwest China. *Journal of Geochemical Exploration*, 111,
678 47-55. <https://doi.org/10.1016/j.gexplo.2011.07.006>
- 679 Huber, A., Bach, M., & Frede, H.G. (2000). Pollution of surface waters with pesticides in Germany: modeling
680 non-point source inputs. *Agriculture, Ecosystems & Environment*, 80(3), 191-204. [https://doi.org/10.1016/S0167-8809\(00\)00145-6](https://doi.org/10.1016/S0167-8809(00)00145-6)
- 682 Hattam, J. et al. (2009). Pesticide scare drives organic purchases in Lebanon. Retrieved June 18, 2021, available
683 at: <https://www.treehugger.com/green-food/pesticide-scare-drives-organic-purchases-in-lebanon.html>
- 684 Jayaraj, R., Megha, P., & Sreedev, P. (2016). Organochlorine pesticides, their toxic effects on living organisms
685 and their fate in the environment. *Interdisciplinary Toxicology*, 9(3-4), 90-100. <https://doi.org/10.1515/intox-2016-0012>
- 687 Jia, H., Liu, L., Sun, Y., Sun, B., Wang, D., Su, Y., Kannan, K., & Li, Y.F. (2010). Monitoring and modeling
688 Endosulfan in Chinese surface soil. *Environmental Science & Technology*, 44, 9279-9284.
689 <https://doi.org/10.1021/es102791n>

690 Jiang, Y. F., Wang, X. T., Jia, Y., Wang, F., Wu, M. H., Sheng, G. Y. & Fu, J. M. (2009). Occurrence, distribution
691 and possible sources of organochlorine pesticides in agricultural soil of Shanghai, China. *Journal of Hazardous*
692 *Materials*, 170(2-3), 989-997. <https://doi.org/10.1016/j.jhazmat.2009.05.082>.

693 JMPR (Join Meeting on Pesticides Residues). (1973). BHC (Technical). Retrieved June 18, 2021, available at:
694 <http://www.inchem.org/documents/jmpr/jmpmono/v073pr05.htm>

695 Kuranchie-Mensah, H., Atiemo, S.M., Palm, L.M., Blankson-Arthur, S., Tutu, A.O., & Fosu P. (2012).
696 Determination of organochlorine pesticide residue in sediment and water from the Densu river basin, Ghana.
697 *Chemosphere*, 86, 286-92. <https://doi.org/10.1016/j.chemosphere.2011.10.031>

698 Kfoury, L., Hilan, C., & El-Amil, R. (2002). Residue analysis OF pesticides commonly used BY LEBANESE
699 farmers ON strawberries. *Lebanese Science Journal*.

700 Lallas P. (2001). Reproductive Effects in Birds Exposed to Pesticides and Industrial Chemicals. The Stockholm
701 Convention on persistent organic pollutants. *American Journal of International Law*, 95, 692-708.
702 <https://doi.org/10.1289/ehp.95103s7165>

703 Laurent, E. (2013). Évaluation de l'état de contamination des bassins versants par les résidus de médicaments :
704 Utilisation des biofilms épilithiques comme marqueur d'imprégnation du milieu. Thesis from University of
705 Poitiers.

706 Lebanese Government. (1982). Conditions for the authorization of pesticide' importation, selling, preparation, and
707 use in Lebanon. Decree 5029, Beirut.

708 Leterme, B., Vanclooster, M., Rounsevell, M., & Bogaert, P. (2006). Discriminating between point and non-point
709 sources of atrazine contamination of a sandy aquifer. *Science of the Total Environment*, 362, 124-142.
710 <https://doi.org/10.1016/j.scitotenv.2005.06.010>

711 Li, L., Liu, F., Qian, C., Jiang, S., Zhou, Z., & Pan, C. (2007). Determination of organophosphorus pesticides in
712 *Lycium barbarum* by gas chromatography with flame photometric detection. *Journal of AOAC International*, 90,
713 271-276.

714 LNCSR-LMOA (Lebanese National Council for Scientific Research/National Council for Scientific Research-
715 Lebanese Ministry of Agriculture). (2002). Land cover/use maps of Lebanon at 1.20.000 scale.

716 Luzardo, O.P., Ruiz-Suarez, N., Henriquez-hernandez, L.A., Valeron, P.F., Camacho, M., Zumbado, M., & Boada,
717 L. D. (2014). Assessment of the exposure to organochlorine pesticides, PCBs and PAHs in six species of predatory
718 birds of the Canary Islands, Spain. *Science of the total environment*, 472, 146-153.
719 <https://doi.org/10.1016/j.scitotenv.2013.11.021>

720 Malaguerra, F., Albrechtsen, H.J., Thorling, L., & Binning, P.H. (2012). Pesticides in water supply wells in
721 Zealand, Denmark: a statistical analysis. *Science of the Total Environment*, 414, 433-444.
722 <https://doi.org/10.1016/j.scitotenv.2011.09.071>

723 MoEW (Ministry of Energy and Water) & UNDP (United Nation Development Program). (2014). Assessment of
724 the Groundwater Resources of Lebanon.

725 MEW (Ministry of Energy and Water). (2010). Strategy estimates.

726 MoA. (2015). Akkar permanent and temporary cultivated land per produce.

727 MoE/LEDO/ECODIT. (2001). "Lebanon state of the environment report". Prepared by ECODIT, 246 pages +
728 Appendixes.

729 Moore, J.M. & Ramamoorthy, S. (1984). Organic chemicals in natural waters: New York, Springer- Verlag. 1984,
730 289.

731 Prado, B., Duwig, C., & Hidalgo, C. (2009). Transport, sorption and degradation of atrazine in two clay soils from
732 Mexico: Andosol and Vertisol. *Geoderma*, 232-234, 628-639. <https://doi.org/10.1016/j.geoderma.2014.06.011>

733 Qu, C., Qi, S., Yang, D., Huang, H., Zhang, J., Chen, W., Yohannes, H.K., Sandy, E.H., Yang, J., & Xing, X.
734 (2015). Risk assessment and influence factors of organochlorine pesticides (OCPs) in agricultural soils of the hill
735 region: A case study from Ningde, southeast China. *Journal of Geochemical Exploration*, 149, 43-51.
736 <https://doi.org/10.1007/s11356-016-7834-3>

- 737 Rashid, M. I., Mujawar, L. H., Shahzad, T., Almeelbi, T., Ismail, I. M. I., & Oves, M. (2016). Bacteria and fungi
738 can contribute to nutrients bioavailability and aggregate formation in degraded soils. *Microbiological Research*,
739 *183*, 26-41. <https://doi.org/10.1016/j.micres.2015.11.007>
- 740 Rauschenberger, R.H., Sepúlveda, M.S., Wiebe, J.J., Wiebe, J.E., Honeyfield, D.C., & Gross, T.S. (2009). Nutrient
741 and organochlorine pesticide concentrations in American alligator eggs and their associations with clutch viability.
742 *Journal of Aquatic Animal Health*, *21*(4), 249-61. <https://doi.org/10.1577/H07051.1>
- 743 Rodrigues, F. M., Mesquita, P., Oliveira, L. S., Oliveira, F. S., Filho, A. M., Pereira, P. A., & Andrade, B. J. (2011).
744 Development of a headspace solid-phase microextraction/gas chromatography–mass spectrometry method for
745 determination of organophosphorus pesticide residues in cow milk. *Microchemical Journal*, *98*, 56-61.
746 <https://doi.org/10.1016/j.microc.2010.11.002>
- 747 Salameh, P., Waked, M., Baldi, I., Brochard, P., & Saleh BA. (2006). Respiratory diseases and pesticide
748 exposure: a case-control study in Lebanon. *Journal of Epidemiology and Community Health*, *60*(3), 256-61.
749 <https://doi.org/10.1136/jech.2005.039677>
- 750 Sankararamkrishnan, N., Sharma, A. K., & Sanghi, R. (2004). Organochlorine and organophosphorus pesticide
751 residues in groundwater and surface waters of Kanpur, Uttar Pradesh, India. *Environment International*, *31*(1),
752 113-120. <https://doi.org/10.1016/j.envint.2004.08.001>
- 753 Smadi, N., Jammoul, A., & El Darra, N. (2019).
754 Assessment of Antibiotic and Pesticides Residues in Breast Milk of Syrian Refugee Lactating Mothers. *Toxics*,
7(3), 39. <https://doi.org/10.3390/toxics7030039>
- 755 Smith, A.G., Hayes, Jr W.J., & Laws, J.E. (1991). Handbook of pesticide toxicology: classes of pesticides.
756 Handbook of pesticide toxicology: classes of pesticides, vol.2. Academic Press, INC New York, 731-915, Chapter
757 15.
- 758 [Salameh, P.R., & Abi Saleh, B. \(2004\). Symptoms and acute pesticide intoxication among agricultural workers
759 in Lebanon. *Lebanese Journal Medical*, *52*\(2\), 64-70.](#)
- 760 Tanaka, K. (2019). Studies on the metabolism, mode of action, and development of insecticides acting on the
761 GABA receptor. *Journal of Pesticide Science*, *1*(4), 71-86. <https://doi.org/10.1584/jpestics.J18-04>
- 762 Tilasto. (2020). Lebanon statistics and data. Retrieved June 18, 2021, available at:
763 <https://www.tilasto.com/en/country/lebanon/>
- 764 USEPA. (2009) a. National primary drinking water regulations. Retrieved June 18, 2021, available at:
765 <https://water.epa.gov/drink/contaminants/index.cfm>
- 766 USEPA. (2009) b. Persistent Organic Pollutants: A Global Issue, A Global Response. Retrieved June 18, 2021,
767 available at: [https://www.epa.gov/international-cooperation/persistent-organic-pollutants-global-issue-global-
768 response](https://www.epa.gov/international-cooperation/persistent-organic-pollutants-global-issue-global-response)
- 769 USEPA. (2001) c. Baseline human health risk assessment Vasquez Boulevard and I-70 superfund site, Denver CO.
- 770 Viswanathan, S., Radecka, H., & Radecki, J. (2009). Electrochemical biosensor for pesticides based on
771 acetylcholinesterase immobilized on polyaniline deposited on vertically assembled carbon nanotubes wrapped
772 with ssDNA. *Biosensors and Bioelectronics*, *24*(9), 2772-2777. <https://doi.org/10.1016/j.bios.2009.01.044>
- 773 WHO (World Human Organization) & FAO (Food Agricultural Organization). (2011). International code of
774 conduct on the distribution and use of pesticides: guidelines for quality control of pesticides. World Health
775 Organization. Retrieved June 18, 2021, available at: <https://apps.who.int/iris/handle/10665/70574>
- 776 WHO (World Human Organization), & UNICEF (United Nations Children's Fund). (2019). Joint Monitoring
777 Program (JMP).
- 778 WHO (World Health Organization) (2020). Persistent Organic Pollutants (POPs). Retrieved June 18, 2021,
779 available at: http://www.who.int/foodsafety/areas_work/chemical-risks/pops/en/
- 780 Youssef, L., Younes, G., Kouzayha, A., & Jaber, F. (2015). Occurrence and levels of pesticides in South Lebanon
781 water. *Chemical Speciation & Bioavailability*, *27*(2), 62-70. <https://doi.org/10.1080/09542299.2015.1023092>
- 782 Zhang, J., Qi, S., Xing, X., Tan, L., Gong, X., Zhang, Y., & Zhang, J. (2011). Organochlorine pesticides (OCPs)
783 in soils and sediments, southeast China: a case study in Xinghua Bay. *Marine pollution bulletin*, *62*(6), 1270-1275.
784 <https://doi.org/10.1016/j.marpolbul.2011.03.010>

- 785 Zhao, Y.Y., & Pei, Y.S. (2012). Risk evaluation of groundwater pollution by pesticides in China: a short review.
786 *Procedia Environmental Sciences*, 13, 1739-47. <https://doi.org/10.1016/j.proenv.2012.01.167>
- 787 Zhao, Z., Zhang, L., Wu, J., & Fan C. (2009). Distribution and bioaccumulation of organochlorine pesticides in
788 surface sediments and benthic organisms from Taihu Lake, China. *Chemosphere*, 77(9), 1191-8.
789 <https://doi.org/10.1016/j.chemosphere.2009.09.022>.
- 790 Zind, H. (2020). Etat d'imprégnation de différents compartiments du milieu aquatique par des résidus de
791 médicaments et leurs produits de dégradation. Thesis from University of Poitiers.