Organchlorine Insecticides and Polychlorinated Biphenyls Residues in Soil and Water Samples Collected From El-Gabal El-Akhdar, Libya

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ABSTRACT

Organochlorine insecticides (OCIs) such as HCH (α, β and γ Hexachlorocyclohexane), DDT (dichloro-diphenyl-trichloroethane) and its metabolites, aldrin, dieldrin and endrin were determined in soil and groundwater samples collected from different locations at El-Gabal (AlJabal) El-Akhdar, Libya during summer (August 2014) and winter (January 2015) seasons. In addition, the residues of PCBs (polychlorinated biphenyls) species were inspected and determined. Generally, the calculated Σ DDT of the detected residues of DDT family members that have been detected in summer were higher (with a maximum of 10.110 µg/l) than those detected in soil samples of winter season (a maximum of 4.547 µg/l). The results demonstrated the absence of endrin in the majority of the study sites. The results indicated the presence of about seven species of PCBs in the soil samples at different sites (PCB28, PCB52, PCB101, PCB118, PCB135, PCB138 and PCB180). It was observed that OCI residues were detected in ground water samples during summer season at few sampling sites but they were almost absent during winter season. Water samples analysis in winter showed that there were only four sites that have been found to contain members of DDT isomers.. The residues of endrin were found in high levels in both water samples of summer (2.09 µg/l) and winter (1.25 µg/l) as compared with OCIs. Meanwhile, *o,p* DDE (0.9155 µg/l) and αHCH (1.3230 µg/l) were detected at high concentrations during winter season in water samples. In winter, the results indicated that the highest concentration of PCB species was detected in water samples collected in summer and was found in Qandula location (PCB 101= 7.239 µg/l), while the lowest mean of concentration was presented in the location of Al-Abraq where PCB 28 reached a concentration of 0.062 µg/l

Keywords: Organochlorine insecticides (OCIs), Polychlorinated biphenyls (PCBs), Residue analysis, El-Gabal El-Akhdar, Libya, irrigation underground water, soil

INTRODUCTION

In Libya, chlorinated hydrocarbons and other pesticides are being used for controlling pests of an agriculture and public health importance since there were no regulations or recommendations of pesticides application. The organochlorine compounds are broad spectrum insecticides, and were the most widely used in many countries for agricultural purposes and control of mosquitoes (Bouman, 2004; Blaso *et al*., 2005). Organochlorine insecticides are very stable compounds and it has been cited that the degradation of dichloro-diphenyl-trichloroethane (DDT) in soil ranges from 4 to 30 years, while other chlorinated are stable for many years after application, due to a high resistance to chemical and biological degradations (Afful *et al.*, 2010). Organochlorine insecticides (OCIs) have been dispersed ubiquitously in the environment (Yi-Fan *et al*., 1996). When applied on a field, they can meet a variety of fates: some may be lost to the atmosphere through volatilization and transported long distances from their sites of application; others are carried away by surface runoff or photo-degraded by sunlight. When entering into the soil, pesticides may be taken up by plants or degraded; but they may also be transported through the unsaturated zone to ground-waters or via drains, reach surface water bodies. Consequently, considerable levels of OCIs have been detected in different components of human environment such as air, water, soil, plants and animals (Patton *et al.*, 1991). Calamari and Naeve (1994) concluded that the concentrations of pesticides found in various aquatic compartments, with few exceptions are lower than in other parts of the world, in particular in developed countries which have a longer history of high pesticide consumption and intense use.

OCIs are now less widely used than previously because of a number of disadvantages including environmental persistence, bioaccumulation and their toxic action upon the nervous systems (Hellwell, 1988). Also their entry into an ecosystem adversely affects many non-target organisms including fish and birds (Ayas *et al*., 1997). Their effects may be acute, resulting in mass mortality or chronic, involving changes in survival growth and reproduction (Kocan and Landolt, 1989). They and their degradation products are more toxic for animals (Barlas, 1997) and play important role in the population declines of water birds (Fox *et al.*, 1991). Contamination of water bodies by pesticide residues has been an issue of serious concerns due to the health risks associated with them (Golfinopoulos *et al*., 2003). It is well known that DDT was listed by the Stockholm Convention as 1 of 12 persistent organic pollutants (POPs) in 2004 (Zhu *et al.*, 2005). Organochlorines such as chlorinated insecticides and

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polychlorinated biphenyls (PCBs) represent important groups of POPs (persistent organic pollutants), which have caused worldwide concern as toxic environmental contaminants (Covacia *et al*., 2005).

The term polychlorinated biphenyls, or PCBs, refers to a class of synthetic organic chemicals that are, to a large degree, chemically inert. PCBs have been widely used as additives to oils in electrical equipment, hydraulic machinery, and other applications where chemical stability has been required for safety, operation, or durability. Although the chemical stability of many PCBs has been a benefit from the standpoint of commercial use, it has created an environmental problem because it translates into extreme persistence when the PCBs are eventually released into the environment. In fact, PCBs are among the most widespread environmental pollutants, having been detected in virtually all environmental media (indoor and outdoor air, surface and ground water, soil, and food) in almost every corner of the globe. Not only are PCBs often persistent, but many PCB-mixtures are also toxic. Exposure to low levels of PCBs is thought to cause various acute and chronic health effects (UNEP Chemicals, 1999).

Usage of OCIs has been prohibited in most of countries, but 70% of banned pesticides are still used in some parts of the world because of their low cost. The present work was carried out to determine some organochlorine insecticides (OCIs) and PCBs residues in soil and groundwater that used for irrigation at El-Gabal El-Akhdar, Libya.

MATERIALS AND METHODS

Samples collection

Table 1 and Fig.1 are showing the locations of soil and irrigation water (wells) samples collection from El-Gabal El-Akhdar in Libya.

Table 1. Locations of soil and water samples collected from different sites at El-Gabal El-Akhdar area in Libya

Site No.	Location	Site No.	Location	Site No.	Location
1	Qandula	6	Qasr-Libya	11	Masah
2	Qandula	7	Al-Haniyah	12	Masah
3	Marawah	8	Al-Haniyah	13	Al-Abraq
4	Marawah	9	Al-Wasita	14	Al Abraq
5	Qasr-Libya	10	Al-Wasita		

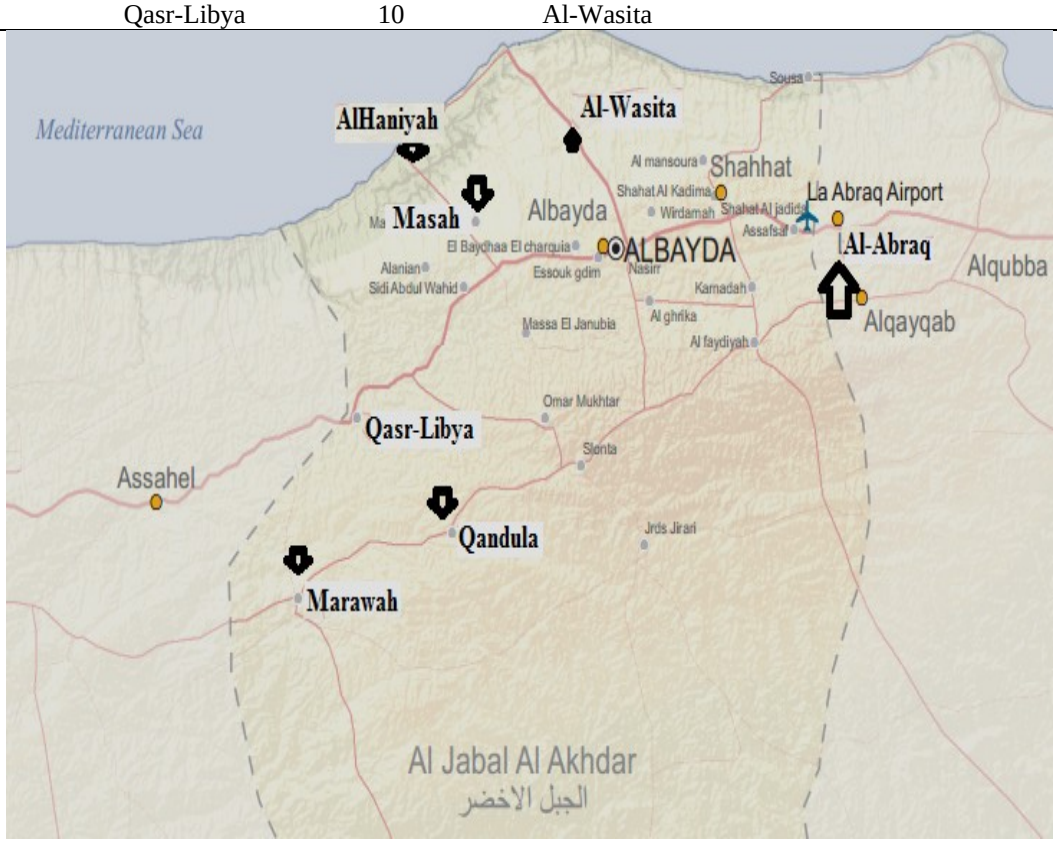

Figure 1. Different locations of study at El-Gabal El-Akhdar, Libya

A-Water samples

Water samples (3 liters/site) were collected from groundwater wells that are being used for irrigation at fourteen sites (Table1), stored at 4 ?C and transported to the laboratory for the analysis procedures (OCIs and PCBs residue determination).

B- Soil samples

Soil samples (2kg/site) were collected from the different selected locations of study using a stainless-steel grab sampler. Samples were taken from each location from the top 3 cm area, and then they were scooped into pre-cleaned wide-mouth glass bottles, placed in ice box, transported to the laboratory and stored at −20? C until analysis. OCIs and PCBs were determined within the collected soil samples.

Residues determination

A-Residues extraction

For water samples, liquid–liquid extraction (1000 ml of water sample+ 100 ml dichloromethane) was followed by gas chromatographic analysis (USEPA, 1980) to determine OCIs and PCBs residue. Extraction from soil was done and modified from that method described by USEPA (1996). Each sample (30g) was then thoroughly mixed with 90g of anhydrous sodium sulfate. The soil sample was then extracted with 250 ml (1:1) of n-hexane:dichloromethane for 8 hrs in a Soxhlet apparatus cycling 5–6 times/ h (Sporring *et al*., 2005). The extracts were then combined and desulfurized through activated copper powder and then concentrated to a few milliliters.

B-Identification and quantification of OCIs and PCBs residues

Identification and quantification of pesticide residues were done by using Gas Chromatograph-Mass Spectrometer, GCMS (Thermo Scientific Company - Trace DSQ II MS) on fused-silica capillary column (Thermo TR-35 MS [3.0m* 0.25mm] filled with 35% phenyl polyphenylene-siloxane (stationary phase). Organochlorine insecticides were quantified from individually resolved peak areas with the corresponding peak areas of the standards. Helium was used as carrier gas at flow rate of 2 ml/min. The temperature was programmed from 90–140° C with a rate of 5° C/min, then holed at 140 °C for1min, and from 140-250° C with a rate of 3° C/min and was holed at 250 °C for 1min, and from 250-300° C with a rate of 20° C/min and was holed at 300° C for 1min. The injector, ion source, and detector temperatures were set at 280° C, 250° C and 310° C, respectively. Three microliters (3µl) of each sample was injected in the split less mode and the purge time was 1 min. Retention time and peak areas were compared with the standards. The analysis process of the collected samples of irrigation water (ground water) and soil was carried out at the Central Lab. Unit of the National Institute of Oceanography and Fisheries, Alexandria, Egypt.

Statistical analysis

Data of the present investigation were subjected to the analysis of variance (ANOVA) using ″F Test″ following the randomized complete block design (RCBD), with three replicates for each treatment. The least significant differences (L.S.D) at the $0.05 \leq$ level were determined according to computer program (COSTAT software, 1988).

RESULTS AND DISCUSSION

A-Residues of OCIs and PCBsin soil samples

Although certain persistent pesticides have been banned for years, the results of the conducted study indicates the presence of chlorinated insecticide residues in some selected sites at different levels depending on the type of insecticide, the nature of region in addition to the season and date of sampling. However, OCIs residues were not detected and they were totally absent in some soil samples (sites 8, 10 and 11). Tables 2 and 3 show the analytical determination of the residues of DDT family representing DDT and its metabolites (products) (DDE and DDD), as well as the residues of α, β, γ isomers of HCH in addition to the residues of three other insecticides (aldrin, dieldrin and endrin) inspected in irrigation water and soil samples at El-Gabal El-Akhdar area, Libya. The differences in the concentrations of these insecticide residues in the soil samples may be due to the substantial inter-farm variation, the intensive use of pesticide and the rate of application as well as the differences in their degradation rate (Owusu-Boateng and Amuzu, 2013).

Results showed significant increase ($p \leq 0.01$) in site 6 (α-HCH), sites1, 3, 4, 5, 6, 9, 13 and14 (*p,p* DDE), sites 6, 9 and14 (*p,p* DDD) and site 9 (endrin) during summer season. During winter season, there were also significant increases in site 2 (*p,p* DDE), site 13 (*o,p* DDE), site 14, (dieldrin) and site 5 & 9 (endrin) .Concentrations of Σ HCH and Σ DDT were calculated by summing the three HCH isomers (α, β and γ) and six DDT members (metabolites), in respect.

1. HCH isomers

The concentrations of HCH isomers that have been found in the soil samples during summer season showed variations from one region to another, where the highest concentrations were found in Qaser-Libya location (site 6) (β HCH 1.537 µg/l) followed by the region of Marawah (site 3) (β HCH 0.405 µg/l) and then the

location of Al-Wasita (site 9) (β HCH 0.345 μg/l) (Table 2). The results of soil samples analysis in winter showed that the highest concentrations of HCH isomers were found in the Al-Haniyaha location (site 7) (β HCH= 4.610 μg/ l) followed by Al-Abraq (site 14) (β HCH 0.626 μg/l) and Al-Wasita (site 9) (α HCH 0.251μg/l) (Table 3).

It was noticed that HCHs concentrations were less and lower than those of DDTs'. This might be due to the different physicochemical and biological properties of these compounds (Tang *et al*., 2007).Therefore, HCHs concentrations were found to be low under the different seasons and locations conditions and this might be also due to less recent input of lindane (Gammexane®) (HCH). This could be also explained by the large amount of historical use of DDT in such specific farms (sites).

2. DDT family (metabolites)

Generally, the calculated Σ DDT of the detected residues of DDT family members that have been detected in summer were higher (with a maximum of 10.110 μg/l) than those detected in soil samples of winter season (a maximum of 4.547 μg/l). It was found that the locations of Qasr-Libya (site 6) (10.11 μg/l) and Al-Wasita (site 9) (8.67 μg/l) and Al-Abraq (sites 13 and14) (10.01 and 9.28 μg/l) contained the highest residues of DDT family members. In those soil samples of summer season, it was found that both isomers of *p,p* DDT and *o,p* DDT were recorded as very low concentrations in the all detected sites and sometimes they were totally absent. The *p,p* DDE isomer was found as a high concentration as 6.738 μg/ l (μg/l) (site 9), while the *o,p* DDE isomer was high in site 13 (4.537 μg/ l). Meanwhile, the *p,p* DDD isomer was higher in both sites 6 and 14 (6.121 and 6.642 ppb, respectively)(Table 2).

The soil samples analyzed in winter season showed that the highest concentration of DDT isomers was found in the location of Al-Abraq (site 13) where *p,p* DDE and *o,p* DDE were as high as 2.098 and 2.184 μg/ l, in respect (Table 3).

Σ DDT residues were lower in those samples of winter as compared with summer samples. Σ DDT was the highest (4.55 μg /l) in Al-Abraq (site 13) as determined in winter soil samples (Table 3). The presence of the DDT analogs (metabolites) indicated deterioration of DDT compound in the environment due to the decay of the solar radiation or metabolism by living organisms (Hooper *et al*., 1997 and Salem *et al*., 2014). The presented results also indicated that such chlorinated insecticides (OCIs), especially DDT, were used during past years in these selected location in El-Gabal El-Akhdar, Libya for study and therefore OCIs still detected with their metabolites (isomers). This can be related due to their low solubility and these results are in agreement with those reported by Dubus *et al.* (2000).

3. Aldrin, dieldrin and endrin residues

Residues of the insecticide aldrin were found in soil samples collected in the summer season where the highest mean concentration was detected in Al Wasita location (site 9) (0.582 μg /l), followed by that determined at the Al- Haniyah location (site 7) (0.288 μg /l). The results of the soil samples collected in the winter season revealed that aldrin residues were found in sites No. 3, 7, 9 and 14 and the highest mean concentration (0.781 μg /l) was detected in the location of Al-Wasita (site 9), while the lowest mean concentration of 0.121 μg /l was found in Marawah location (site 3).

Some areas of study where the soil samples were collected from them during the summer season were found to contain residues of dieldrin where the highest mean concentration of residues was found in Al Al-Abraq location (site 13) (0.523 μg /l) and the lowest mean concentration of residues of that compound was found in Qasr-Libya location (site 6) (0.045 μg /l) (Table 2).

In winter, the results of the soil samples analysis indicated that Al-Abraq location (site 14) contained the highest mean concentration of dieldrin (1.193 μg /l), while the lowest mean concentration was found in Marawah location (site 4) (0.039 μg /l).The results demonstrated the absence of endrin in the majority of the study sites which has been proved through the analysis of these soil samples collected in summer and endrin was found only in sites 5, 6 and 9 sites. At Al-Wasita location (site 9), the results demonstrated the highest mean concentration (3.130 μg /l) of endrin, while the lowest mean concentration of its residues (0.249 μg /l) was detected in Qasr-Libya location (site 5) during summer. Some soil samples that were collected in winter contained endrin and the highest mean concentration was detected in Qasr-Libya location (site 5) (2.881μg/l), while the lowest mean concentration was found in Al-Abraq location (site 13) (0.043 μg /l).

The accumulation of aldrin in soil samples analyzed during the present study was probably originated from its historical use where different formulations of organochlorine insecticides were extensively used in the past (Mawussi, 2008). Dieldrin was detected at some sites and this might be due to the little agricultural

Table 2. Mean concentration of OCIs residues in soil samples collected during summer season (µg/l) (ppb)

Insecticide	Qandula		Marawah		Qasr-Libya		Al -Haniya		Al Wasita		Masah		Al-Abraq		
	Sites														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Minimum Maximum
α-HCH	0.33± 0.021*	0.00	0.033± 0.002	0.00	0.028± 0.003	1.537 ± 0.118**	0.00	0.00	0.188± 0.017*	0.00	0.00	0.00	0.00	0.034 ± 0.003*	0.028 1.537
β –HCH	0.00	0.00	0.405 ± 0.036*	0.00	0.161± 0.015*	0.454 ± 0.025*	0.073± 0.007*	0.00	0.345± 0.031	0.00	0.00	0.00	0.00	0.283± 0.026	0.073 0.454
γ-HCH	0.00	0.00	0.00	0.00	0.213± 0.019*	0.093 ± 0.001*	0.00	0.00	0.083± 0.008*	0.00	0.00	0.00	0.00	0.074± 0.007*	0.074 0.213
Σ HCH	0.33	0.00	0.438	0.00	0.402	2.084	0.073	0.00	0.616	0.00	0.00	0.00	0.00	0.391	0.073 2.084
P,P DDT	0.00	0.00	0.00	0.00	0.00	0.121 ± 0.0013*	0.00	0.00	0.064± 0.006*	0.00	0.00	0.3681± 0.033*	0.109 ± 0.010*	0.129 ± 0.012*	0.064 0.368
O,P DDT	0.00	0.015± 0.001	0.00	0.00	0.00	0.027 ±0.002	0.00	0.00	0.044 ± 0.004*	0.00	0.00	0.00	0.0809± 0.007*	0.144 ± 0.013*	0.015 0.144
P,P DDE	3.388± 0.28**	0.0	2.384 ± 0.013**	2.994 ± 0.210**	5.678 ± 0.516**	2.728 ± 0.165**	0.00	0.00	6.738 ± 0.613**	0.00	0.00	0.00	4.6619 ± 0.424**	2.092 ± 0.190**	2.092 6.738
O,P DDE	0.00	0.00	0.223 ± 0.012	0.122 ± 0.013	0.332 ± 0.030	1.088 ± 0.098	1.046 0.095	0.00	1.505± 0.137	0.00	0.00	0.038 ± 0.003	4.5379± 0.413	0.161± 0.015	0.038 4.537
P,P DDD	0.00	0.00	0.0	0.00	0.024± 0.002	6.121 ± 0.52**	0.0	0.00	0.242 ± 0.022**	0.00	0.00	0.198± 0.018*	0.259± 0.024*	6.642 ± 0.604**	0.024 6.642
O,P DDD	0.00	0.00	0.031 ± 0.002	0.00	0.023± 0.002	0.023 ± 0.002	0.0	0.00	0.074± 0.007*	0.00	0.00	0.00	0.362 ± 0.033*	0.111± 0.010*	0.023 0.362
Σ DDT	3.39	0.02	2.64	3.11	6.06	10.110	1.05	0.00	8.67	0.00	0.00	0.60	10.01	9.28	0.020 10.110
Aldrin	0.00	0.00	0.118 ± 0.001*	0.087 ± 0.008*	0.0	0.147 ± 0.013*	0.288 0.026*	0.00	0.582± 0.053*	0.00	0.00	0.00	0.203± 0.018*	0.092± 0.008*	0.087 0.582
Dieldrin	0.00	0.00	0.221± 0.002*	0.067± 0.006*	0.0	0.045± 0.003*	0.064± 0.006*	0.00	0.139± 0.013*	0.00	0.00	0.00	0.523± 0.048*	0.083± 0.008*	0.045 0.523
Endrin	0.00	0.00	0.00	0.00	0.249± 0.023*	0.694± 0.063*	0.00	0.00	3.130 ± 0.285**	0.00	0.00	0.00	0.00	0.00	0.249 3.130

* Significant difference at level of 0.05, ** Significant difference at level of 0.01 and 0.00= not detected (ND).

Table 3. Mean concentration of OCIs residues in soil samples collected during winter season (µg/l) (ppb)

	Qandula		Marawah		Qasr-Libya		Al-Haniyaha		Al-Wasita		Masah		Al-Abraq		
	Sites														
Insecticide	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Minimum / Maximum
α-HCH	0.00	0.00	0.211± 0.019*	0.00	0.00	0.00	0.00	0.00	0.097± 0.009*	0.00	0.00	0.00	0.00	0.115± 0.010*	0.097 / 0.211
β –HCH	0.00	0.00	0.134± 0.012*	0.00	0.00	0.00	4.610 ± 0.419**	0.00	0.251± 0.023*	0.00	0.00	0.00	0.00	0.626 0.057*	0.134 / 4.610
γ-HCH	0.00	0.00	0.152± 0.014*	0.00	0.00	0.00	0.00	0.00	0.072 ± 0.007*	0.00	0.00	0.00	0.00	0.300± 0.027*	0.072 / 0.300
Σ HCH	0.00	0.00	0.497	0.00	0.00	0.00	4.610	0.00	0.420	0.00	0.00	0.00	0.00	1.041	0.420 / 1.041
P,P DDT	0.00	0.00	0.00	0.015 ±0.001	0.0	0.032± 0.003*	0.00	0.00	0.363± 0.033*	0.00	0.00	0.342± 0.031*	0.004± 0.000	0.107± 0.010*	0.004 / 0.363
O,P DDT	0.00	0.00	0.025± 0.002*	0.00	0.051± 0.005*	0.0	0.026± 0.002*	0.0	0.056± 0.005*	0.00	0.00	0.00	0.073± 0.007*	0.617± 0.056*	0.025 / 0.617
P,P DDE	0.00	1.459 ± 0.133**	0.00	0.00	0.00	0.015± 0.001	0.00	0.00	1.274± 0.116*	0.00	0.00	0.00	2.098± 0.191*	0.952± 0.087*	0.015 / 1.459
O,P DDE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.105± 0.010	0.00	0.00	0.014 ±0.001	2.184± 0.199**	0.091± 0.008*	0.091 / 2.184
P,P DDD	0.00	0.00	0.338± 0.031*	0.00	0.00	0.00	0.00	0.00	0.263 ± 0.024*	0.00	0.00	0.016± 0.001*	0.044± 0.004*	0.508± 0.046*	0.016 / 0.508
O,P DDD	0.00	0.00	0.029± 0.003*	0.00	0.00	0.00	0.00	0.00	0.097± 0.009*	0.00	0.00	0.00	0.144 ± 0.013*	0.011± 0.001*	0.011 / 0.144
Σ DDT	0.00	1.459	0.392	0.015	0.051	0.047	0.026	0.00	4.525	0.00	0.00	0.372	4.547	2.276	0.015 / 4.547
Aldrin	0.00	0.00	0.121± 0.011*	0.00	0.00	0.00	0.362± 0.033*	0.00	0.781± 0.071*	0.00	0.00	0.00	0.00	0.453± 0.041*	0.121 / 0.781
Dieldrin	0.00	0.00	0.00	0.039*± 0.004*	0.00	0.00	0.00	0.00	0.127± 0.012*	0.00	0.00	0.00	0.451± 0.041*	1.193 ± 0.108**	0.039 / 1.193
Endrin	0.00	0.00	0.628± 0.057*	0.0	2.881± 0.262**	0.00	0.00	0.00	2.115 ± 0.192**	0.00	0.00	0.00	0.043± 0.004*	0.674± 0.061*	0.043 / 2.881

* Significant difference at level of 0.05, ** Significant difference at level of 0.01 and 0.00= not detected (ND).

cultivation that has been practiced in the past or possibly due to little use of dieldrin at these sites in past. The highest concentrations of aldrin, dieldrin and dieldrin were found at the sampling site No.14 (Al-Abraq) during both seasons and this can be attributed to the intensive production of crops and the application of such chlorinated insecticides in this location. Concentrations and patterns of OCIs distribution could be influenced by the chemical and the physical properties of such OCIs that have been applied under certain environmental conditions (Montenegro *et al*., 1998).

The obtained results showed that soil samples contained DDT, DDD, DDE, HCH isomers, aldrin, dieldrin and endrin. The concentrations of the compounds were mostly found in the surface of soil samples. The results of this study showed that there is a variation in the levels of chlorinated insecticides residue from season to another and from one location to another. Kanatharana *et al.* (1994), El-Bouraie *et al.* (2011) and Mahugija *et al.* (2014) found that the concentration of the detected compounds varied according to the location and the samples collection period.

4. PCBs residues

Tables (4 and 5) demonstrated the results of analysis of the soil samples that have been collected in the summer (August/2014) and winter (January/2015) seasons. The PCBs species were detected in these samples collected from different sites of El-Gabal El-Akhdar area, Libya. The PCBs detection is a very important process for the assessment of a contaminant or pollution problem. Podlesakova *et al*. (1997) reported that PCBs monitoring was conducted in the United Kingdom, USA, Canada, Japan, and Sweden and it had a valuable environmental benefits.

The detection of PCB28 at site 13 (1.733 µg /l), PCB52 at sites 3, 4, 5, 6, 7and 9 (with a maximum of 15.089 µg /l), PCB118 at sites 7 and14 (with a maximum of 10.000 µg /l) and PCB 138 at site 14 (4.610 µg /l) showed a high significant increase during summer season as compared with the those samples of winter.

It was found that the sites 6 and 9 contained many PCB species (PCB28, PCB52, PCB101, PCB11, PCB135, PCB138 and PCB180).The highest mean concentration of PCB 52 (15.089 µg /l) was detected at Al-Wasita area (site 9), while Masah area showed the lowest concentration at site 12 (PCB135= 0.037 µg /l) as shown in Table 4. In winter soil samples, it was found that Qasr - Libya location (site 6) contained 7 PCB species (PCB28, PCB52, PCB101, PCB118, PCB135, PCB138and PCB180) and the highest mean concentration was that detected in Qasr -Libya location (site 6) (PCB118= 8.966 µg /l), while the lowest mean concentration was that detected in Al-Wasita location (site 9) (PCB135= 0.017 µg /l) as shown in Table 5.

The results of laboratory analysis indicated the presence of about seven species of PCBs in the soil samples at different sites (PCB28, PCB52, PCB101, PCB118, PCB135, PCB138 and PCB180). The results of this study are consistent with the results of previous studies, which monitored PCB species and detected the existence of about seven of the PCB in all parts of the world, particularly in samples such as soil (Covaci *et al*., 2002; Pawlak and Laamanen, 2010; Duc and Viet, 2013; Hassan *et al*., 2013).

The results also showed that PCB residues existed in the samples collected in summer more than those samples collected in winter, either in species number or concentration. The present results are in agreement with those reported by Tasdemir (2012) who found that the sampling date (spring or/and summer) had an effect on the PCB content in the soil, which may be increase in high soil temperature.

B- Residues of OCIs and PCBs in water samples

The mean concentrations of OCIs residues that have been detected in ground water samples in summer and winter seasons are demonstrated in Tables 6 and 7. It was observed that organochlorine insecticides residues were detected during summer season at few sampling sites but they were almost absent during winter season, although these insecticides might be used in agricultural purposes (insect control). This could be attributed to the process by which soil character during dry season promote adsorption of insecticides to soil particles (Leong *et al*., 2007; Shivani *et al*., 2012; Solomon, 2016) and therefore, water samples collected for the present study appeared to be free of OCIs. This can be attributed also to the fast rate of degradation that was accelerated through the variation of climatic conditions during summer in the area of study and these results are in agreement with those of El- Bouraie *et al*. (2011).

1. HCH isomers

The analysis of water samples collected during summer season (Table 6) showed that αHCH was detected only at Qandula location (site 1) (1.32 µg/l) and Qasr-Libya (0.12 µg/l). βHCH was totally absent where it was not detected in the all detected water samples collected from the selected different locations of El-Gabal El-Akhdar, Libya. Meanwhile, γHCH was only detected in Al-Abraq location (site 13) at a low concentration of 0.76 µg/l. Therefore, ΣHCH was present in Qandula location (site 1), (1.323 µg/l),

Table 4. Mean concentration of PCBs residues in soil samples in summer season (µg/l)

PCB Species	Locations at El-Gabal El-Akhdar														
	Qandula		Marawah		Qasr-Libya		Al-Haniya		Al-Wasita		Masah		Al -Abraq		
	Sites														Minimum
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Maximum
PCB28	0.00***	0.00	0.073±	0.0	0.075±	0.055±	0.073±	0.00	0.515±	0.00	0.00	0.00	1.733 ±	0.207	0.055
7012-37-5[$]			0.007*		0.007*	0.005*	0.007		0.047*				0.158**	±0.019*	1.733
PCB52	0.00	0.00	2.757 ±	14.362±	2.413±	14.497±	7.055±	0.00	15.089±	0.00	0.00	0.00	0.896±	1.648±	0.896
35693-99-3			0.251**	1.306**	0.219**	1.318**	0.641**		1.372**				0.081*	0.150*	15.089
PCB101	0.00	0.00	0.00	0.130±	0.062±	0.066±	1.7812±	0.00	1.244±	0.00	0.00	0.00	0.00	0.079±	0.066
37680-73-2				0.012*	0.006*	0.006*	0.162**		0.113*					0.007*	1.781
PCB118	0.00	0.00	0.00	0.00	0.182±	0.111±	10.000±	0.00	0.617±	0.00	0.00	0.00	0.00	0.146±	0.111
31508-00-6					0.017*	0.010*	0.909**		0.056*					0.013**	10.000
PCB135	0.00	0.00	0.00	0.00	0.00	0.188±	0.00	0.00	0.077±	0.00	0.00	0.037±	0.453±	0.0	0.037
52744-13-5						0.017*			0.007*			0.003*	0.041*		0.453
PCB138	0.00	0.00	0.00	0.00	0.00	1.459±	0.00	0.00	1.617±	0.00	0.00	0.00	1.193±	4.610±	1.193
35065-28-2						0.133*			0.147*				0.108	0.419**	4.610
PCB180	0.00	0.00	0.00	0.00	0.00	0.030±	0.00	0.00	0.107 ±	0.00	0.00	0.0943±	0.674±	0.00	0.030
35065-29-3						0.003*			0.010*			0.009*	0.061*		0.674

* Significant difference at level of 0.05, ** significant difference at level of 0.01 and *** 0.00: not detected (ND).
$ = CAS No. (Chemical Abstracts Service [CAS] Registry Number).

Table 5. Mean concentration of PCBs residues in soil samples in winter season (µg/l)

PCB Species	Locations at El-Gabal El-Akhdar														
	Qandula		Marawah		Qasr-Libya		Al-Haniyaha		Al-Wasita			Masah		Al-Abraq	
	Sites														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Minimum / Maximum
PCB28 7012-37-5[$]	0.00	0.00	0.00	0.00	0.052± 0.005*	0.157± 0.014*	0.00	0.00	0.432± 0.039*	0.00	0.00	0.00	0.683± 0.062*	0.203± 0.018*	0.052 0.683
PCB52 35693-99-3	0.00	0.00	0.863± 0.078*	0.00	0.00	0.983± 0.089*	0.00	0.00	2.042± 0.186**	0.00	0.00	0.00	0.221± 0.020*	0.00	0.221 2.042
PCB101 37680-73-2	0.00	0.00	0.00	0.00	0.00	0.844± 0.077*	0.00	0.00	1.017± 0.092**	0.00	0.155± 0.014*	0.00	0.00	0.00	0.155 1.017
PCB118 31508-00-6	0.00	0.00	0.161 ± 0.015*	0.00	0.00	8.966± 0.815**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.161 8.966
PCB135 52744-13-5	0.00	0.00	0.444 0.040*	0.00	5.194± 0.472**	0.497± 0.045*	0.00	0.00	0.017± 0.002	0.00	0.00	0.165± 0.015*	0.00	0.00	0.017 5.194
PCB138 35065-28-2	0.050± 0.004*	0.080 ± 0.003*	7.664 ± 0.682**	0.00	6.241± 0.567**	0.157 ± 0.014*	0.00	0.00	0.498± 0.045*	0.00	0.00	0.0	0.00	1.031 ± 0.094**	0.050 7.664
PCB180 35065-29-3	0.00	0.038± 0.002*	0.058± 0.003*	0.00	0.597± 0.054*	0.983± 0.089*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.038 0.983

* Significant difference at level of 0.05, ** significant difference at level of 0.01 and *** 0.00: not detected (ND).
$ = CAS No. (Chemical Abstracts Service [CAS] Registry Number).

Table 6. Mean concentration of OCIs residues in water samples collected in summer season (µg/l)

Insecticide	Qandula		Marawah		Qasr-Libya		Al-Haniyaha		Al-Wasita		Masah		Al-Abraq		Minimum / Maximum
	Sites														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
α-HCH	1.32± 0.12**	0.00***	0.00	0.00	0.00	0.12± 0.01*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12 1.32
β -HCH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.00
g-HCH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.76± 0.01	0.00	0.00 0.76
Σ HCH	1.32	0.00	0.00	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.76	0.00	0.12 1.32
p,p DDT	0.00	0.00	0.00	0.00	0.00	0.43± 0.02*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.43
o,p DDT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11± 0.01*	0.20*± 0.01	0.00	0.00	0.00	0.00	0.00	0.11 0.20
p,p DDE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.00
o,p DDE	0.00	0.00	0.18 ± 0.01*	0.0	0.0	0.32± 0.016*	0.00	0.00	0.00	0.00	0.00	0.00	0.91± 0.02	0.00	0.18 0.91
p,p DDD	0.00	0.38± 0.01*	0.00	0.00	0.00	0.00	0.00	0.18± 0.01*	0.00	0.00	0.00	0.00	0.00	0.00	0.18 0.38
o,p DDD	0.00	0.02± 0.002	0.00	0.00	0.00	0.21± 0.01*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02 0.21
Σ DDT	0.00	0.40	0.18	0.00	0.00	0.96	0.00	0.28	0.20	0.00	0.00	0.00	0.92	0.00	0.20 0.96
Aldrin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04 ± 0.01	0.00	0.00 0.04
Dieldrin	0.00	0.00	0.00	0.00	0.00	0.14± 0.01*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.14
Endrin	0.00	0.00	0.00	0.00	0.00	2.09± 0.12**	0.00	0.00	0.00	0.00	0.00	0.00	0.93 ± 0.07	0.00	0.93 2.09

* Significant difference at level of 0.05, ** significant difference at level of 0.01 and ***0.0= not detected (ND).

Table 7. Mean concentration of OCIs residues in water samples collected in winter season (µg/l)

Insecticide	Qandula	Marawah			Qasr-Libya		Al-Haniyaha		Al-Wasita		Masah		Al-Abraq		Minimum / Maximum
	Sites														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
α-HCH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.00
β –HCH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.00
δ-HCH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.00
Σ HCH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.00
p,p DDT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.464± 0.031*	0.00	0.00	0.00	0.00 0.464
o,p DDT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.00
p,p DDE	0.011 ± 0.002	0.00	0.00	0.00	0.00	0.00	0.915± 0.061*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.011 0.915
o,p DDE	0.00	0.00	0.00	0.00	0.00	0.663 ± 0.052*	0.00	0.00	0.00	0.00	0.658± 0.057*	0.0	0.0	0.0	0.658 0.663
p,p DDD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.00
o,p DDD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.00
Σ DDT	0.011	0.00	0.00	0.00	0.00	0.663	0.915	0.00	0.00	0.00	1.122	0.00	0.00	0.00	0.011 1.122
Aldrin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.00
Dieldrin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 0.00
Endrin	0.00	0.00	0.00	0.00	0.00	1.248 ± 0.011**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00 1.248

* Significant difference at level of 0.05, ** significant difference at level of 0.01 and ***0.0= not detected (ND).

Table 8. Mean concentration of PCB residues in water samples collected in summer season (µg/l)

PCB Species	Qandula		Marawah		Qasr-Libya		Al-Haniyah		Al-Wasita		Masah		Al-Abraq		Minimum Maximum
	Sites														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
PCB28 7012-37-5[$]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0621 ± 0.005	0.00	0.000 0.062
PCB52 35693-99-3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.3913± 0.09**	0.00	0.000 2.391
PCB101 37680-73-2	0.00	7.239 ± 0.682**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.1594 ± 0.011*	0.00	0.159 7.239
PCB118 31508-00-6	0.120± 0.010*	0.00	0.00	0.00	0.00	0.703± 0.053*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.120 0.703
PCB135 52744-13-5	0.00	0.00	0.00	0.00	0.00	0.00	1.700 ± 0.103**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000 1. 700
PCB138 35065-28-2	7.023± 0.399**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000 7.023
PCB180 35065-29-3	0.00	0.00	0.00	0.00	0.00	0.162± 0.017*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000 0.162

* Significant difference at level of 0.05, ** significant difference at level of 0.01 and ***0.00= not detected (ND).

$ = CAS No. (Chemical Abstracts Service [CAS] Registry Number).

Table 9. Mean concentration of PCB residues in water samples collected in winter season (µg/l)

PCB Species	Qandula		Marawah		Qasr-Libya		Al-Haniyah		Al-Wasita		Masah		Al-Abraq		Minimum / Maximum
	Sites														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
PCB28 7012-37-5[$]	0.00***	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000 / 0.000
PCB52 35693-99-3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000 / 0.000
PCB101 37680-73-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000 / 0.000
PCB118 31508-00-6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000 / 0.000
PCB135 52744-13-5	0.00	0.00	0.00	0.00	0.0	0.032 ± 0.001	0.00	0.00	0.00	0.00	0.00	0.00	15.194 ± 1.21**	0.00	0.032 / 15.194
PCB138 35065-28-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	16.241 ± 1.820**	0.00	0.000 / 16.241
PCB180 35065-29-3	0.050± 0.002*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.169± 0.015*	0.0	0.0	0.0	0.897± 0.060*	0.00	0.050 / 0.897

* Significant difference at level of 0.05, ** significant difference at level of 0.01 and ***0.00= not detected (ND).
$= CAS No. (Chemical Abstracts Service [CAS] Registry Number).

Al-Abraq (site 13) (0.76 μg/l) and Qasr-Libya (site 6) (0.12 μg/l) in summer. HCH isomers were found in very few locations at low concentrations and that might be due to their differences in physicochemical and biological properties, where they having higher vapor pressure (Tang *et al*., 2007). In winter, the collected water samples appeared to have no residue of the all detected OCIs.

2. DDT family (metabolites)

The results showed the existence of a small numbers of DDT isomers (metabolites) in water samples collected in summer (Table 6). The higher total (sum) concentration of DDT isomers and family (Σ DDT) (0.96 and 0.92 μg/l) were detected in Qasr-Libya (site 6) and Al-Abraq (site 13), respectively (Table 6). The products of DDT or its metabolites were found in few locations. Water samples analysis in winter showed that there were only four sites that have been found to contain members of DDT isomers (site 1, 6, 7 and 11) (Table 7).

The present investigation showed that both isomers of DDE (*p,p* and *o,p*) were the most common residues among the other isomers of DDT which could be an indication of less tendency of recent exposure to new sources of DDT and the lower accumulation of residues was probably accumulated through indirect sources such as long range transport or historical application (Hong *et al*., 1999; Zhang *et al*., 2003). This also might be an evidence of the usage of DDT in El-Gabal El-Akhdar area, long time ago because DDT metabolites (especially DDE) were detected at lower concentrations at certain sites that water samples have been collected from. The other reason might be that DDE has transported better in the atmosphere than other forms (Poolpak *et al*., 2008; Zhou, 2008).

3. Aldrin, dieldrin and endrin

The results indicated the presence of a low concentration of aldrin in water samples that have been collected in summer in the location of Al-Abraq (site 13 only) (0.0373 μg/l) (Table 6). Also, one site only was found to contain dieldrin (site 6) in Qasr-Libya location with a concentration of 0.140 μg/l. Moreover, endrin was the only compound among these three detected compounds **(**aldrin, dieldrin and endrin**)** detected in quantifiable amount (2.09 μg/l) in water samples collected from Qasr-Libya (site 6) during summer season.

For those samples collected during winter season, the residue level of endrin (1.248 μg/l) was the only detected one among the rest of the inspected residues (Table 7). It could be concluded that water samples collected during summer season contained high levels of OCIs than those collected in winter season. The residues of endrin were found in high levels in both samples of summer (2.09 μg/l) and winter (1.25 μg/l) as compared with the other all OCIs inspected at El-Gabal El-Akhdar, Libya. Meanwhile, *o,p* DDE (0.9155 μg/l) and αHCH (1.3230 μg/l) were detected at high concentrations during winter season in water samples.

The present study showed that the residues of aldrin, dieldrin and endrin are rarely present in irrigation groundwater but a little residues leaching from soils might be occurred.

4. PCBs species

The results of the detected residues of PCBs of summer and winter samples are presented in the Tables 8 and 9, in respect. There were significant variations in PCB compounds for both seasons of summer and winter. PCB52 was detected in site 13, PCB101 (site2), PCB135 (site7) and PCB138 (site 1) which showed a highly significant increase ($p \leq 0.01$) in water samples collected in summer. Meanwhile, results showed significant increase ($p \leq 0.01$) in PCB135 and PCB138 as they were detected in site 13.

In winter, the results indicated that the highest concentration of PCB species was detected in water samples collected in summer and was found in Qandula location (site 2) (PCB 101= 7.239 μg/l), while the lowest mean of concentration was presented in the location of Al-Abraq (site 13) where PCB 28 reached a concentration of 0.062 μg/l (Table 8).

The results of the laboratory analysis of water samples collected in winter showed that Al-Abraq location contains the highest number of PCB species (PCB 135, PCB 138, PCB 180) at site 13 and the highest mean concentration was found in the same area (PCB 138= 16.241 μg/l) as shown in Table 9. The presented results showed that concentration of PCBs in water were low and these results are similar to those obtained by Yu *et al*. (2014).

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الملخص العربي

متبقيات المبيدات الحشرية العضوية الكلورينية والمركبات ثنائية الفينيل عديدة الكلور في عينات الماء والتربة المجمعة من الجبل الأخضر – ليبيا

عبدالفتاح سيد عبدالكريم سعد ، السيد حسن محمد تايب ، ليلى عبدالفتاح محمد ، صلاح محمد إدريس حسن

تم تقدير متبقيات المبيدات الحشرية العضوية الكلورينية مثل سادس كلور الهكسان (ألفا ، بيتا ، جاما) والـ د. د. ت ونواتج تحلله و الألدرين والديلدرين والإندرين في عينات التربة ومياه الري الجوفية التي تم تجميعها من مواقع مختلفة بمنطقة الجبل الأخضر– ليبيا وذلك خلال صيف ٢٠١٤ (أغسطس) وشتاء ٢٠١٥ (يناير)، وبالإضافة إلي ذلك تم تقدير أنواع مختلفة من مركبات ثنائي الفينيل عديد الكلور في هذه العينات. وعامة في عينات التربة فإن إجمالي تركيزات الـ د.د.ت ونواتج تحلله التي تم تقديرها في الصيف كانت أعلي (حد أقصي وصل إلى ١٠,١١٠ميكروجرام/لتر) من تلك التي تم تقديرها في الشتاء (حد أقصي وصل إلى ٤,٥٤٧ميكروجرام/لتر). وقد أظهرت النتائج تغيب مبيد الإندرين في معظم مواقع الدراسة الحالية. كما بينت النتائج أيضاً وجود ٧ أنواع من مركبات ثنائي الفينيل عديد الكلور PCB28, PCB52, PCB101 PCB118, PCB135, PCB138 , PCB180 في مختلف المواقع.

وقد تم تقدير متبقيات المبيدات الحشرية العضوية الكلورينية في الماء الجوفية التي تستعمل في الري في مواقع قليلة ولم تتواجد هذه المركبات في العينات التي تم جمعها خلال الشتاء حيث تبين أن هناك فقط ٤ مواقع احتوت علي نواتج تحليل الـ د.د.ت هي مواقع جندولة ، قصر ليبيا ، الحنية ، مسة. وقد وُجد الإندرين بتركيزات عالية في كلاً من عينات الصيف (٢,٠٩ميكروجرام/لتر) وكذلك عينات الشتاء (١,٢٥ميكروجرام/لتر) بالمقارنة بالمركبات الأخري المقدرة في منطقة الجبل الأخضر. وفي نفس الوقت تم تقدير والكشف عن تواجد مركبات o,p DDE و αHCH بتركيزات عالية في عينات مياه الشتاء. وأظهرت النتائج وجود مركبات ثنائي الفينيل عديد الكلور بتركيزات عالية في المياه الخاصة بفصل الصيف وكان أعلي تركيز منها وُجد في منطقة قندولة (الموقع ٢) (PCB101 =٧,٢٣٩ ميكروجرام/لتر) بينما كان أقل تركيز في منطقة الأبرق (موقع ١٣) حيث كان تركيز PCB 28 =٠,٠٦٢ ميكروجرام/لتر.