Distribution of organochlorine pesticides in suspended particulate matter and sediment from the Bizerte Lagoon, Tunisia

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Abstract: *The contamination of the marine environment by organic pollutants is of great concern. The Bizerte Lagoon is the second largest lagoon in Tunisia, and is known for different industrial and fishing activities. Due to their social and economic impact, a comprehensive assessment of the spatial distribution and partitioning of seven OCPs between suspended particulate matter (SPM) and surface sediments is essential. Total organic carbon (TOC) contents in sediment ranges from 0.05% found in station S3 to 5.22% found in station S5. The OCPs were investigated in SPM and sediment from fourteen sampling stations in the Bizerte Lagoon. The levels of OCPs in SPM varied between 0.91 ng g^{-1} and 15.15 ng g^{-1}. The concentrations of OCPs in sediments are in the range of 0.09-18.29 ng g^{-1}. The Hexachlorobenzene (HCB) and ∑DDT are the most dominant compounds in different studied matrices. Distribution of HCB, ∑DDT and other OCPs are different indicating different sources of contaminations. The concentrations of OCPs in different matrices are generally similar to the background levels from the Mediterranean Sea and pose no threat to human and aquatic living species.*
Keywords: *OCPs; SPM; sediments; distribution; Bizerte lagoon.*

I.   Introduction

The natural environment continuously receives foreign chemicals due to urban and industrial activities. Pesticides present a vast class of compounds that have been used all over the world for many decades because of their advantages and benefits. The application and release to the aquatic ecosystems of these organic compounds has become a matter of concern (Pinto et al. 2016). In the last century, thousands of organochlorine pesticides (OCPs) have been produced and released into the environment which constitute one of the most important persistent organic pollutants (POPs) (Zhou et al. 2006). Many of these pesticides belong to endocrine-disrupting chemicals and due to their persistence, high lipid solubility, and carcinogenic properties, OCPs threatened the ecosystem, human health and wild animals (Yan et al. 2014) (Tang et al. 2008). These compounds and their metabolites were the main cause of birth defects, immune system dysfunction, endocrine disruptions, and cancer (Montuori et al. 2016). Millions of people are poisoned and hundred are dying each year around the world from pesticide poisoning, and a great number of them live in the developing countries (Sarkar et al. 2008). Their intensive use throughout the agricultural world for crop protection in the past has caused their persistence in the environment. Many research shows that OCPs are still detected in various matrices including: Mud (Ju et al. 2009), SPM (Liu et al. 2013), surface sediment (Liu et al. 2013), drinking water (Eissa et al. 2013), surface water (Schreiber et al. 2013), ground water (Raposo Junior et al, 2007), seal (Shaw et al. 2005), mineral water (Salinas et al. 2010), air (Castro-Jiménez et al. 2008), mold (Castro-Jiménez et al. 2008) and water milfoil (Schreiber et al. 2013) even after their use has been banned for the past several decades. The principal ways that OCPs enter water systems include water runoff, agricultural storm-water discharges. It picks up and carries away pesticides, finally depositing them into surface water lagoons, rivers, coastal waters, and ground waters (Campo et al. 2013). Due to their hydrophobicity and lipophilicity properties, OCPs are insoluble in water. They are removed from the water column and adsorbed on the SPM due to their high affinity for organic matter, and finally accumulated in the bottom of aquatic systems by sedimentation (Li et al. 2016). Sediments represent a source from which OCPs can reenter the water by desorption and resuspension and therefore contribute to measurable concentration in the water and biota of many surface water systems and cause secondary pollution (Kuranchie-Mensah et al. 2012). The roles of SPM are fundamental in monitoring the reactivity, transport and biological effects of substances in marine environments. Release of organic contaminants can happen at any time via re-suspension by natural or human activities and therefore, their absence in water may not indicate their

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real bioavailability (Pinto et al. 2016). The SPM provides a crucial connection for chemical constituents between the water, sediment and food chain (Turner et al. 2002).

The OCPs were never produced in Tunisia, the importation and use of dieldrin and heptaclor was banned in 1980 and of DDT, aldrin and endrin in 1984. Despite the restriction on the use of OCPs in Tunisia, such composed existed in the various matrices of the marine environment: sediment (Derouiche et al. 2004), biota (Ameur et al. 2013), water (Necibi et al. 2015), sediment cores (Necibi et al. 2019), milk (Hassine et al. 2012), and even in breast milk (Ennaceur et al. 2008). In May 2001, the Stockholm Convention was adopted to protect human health and the environment from POPs, Tunisia became a party to this convention in 17 June 2004 (Ju et al. 2009).

The Bizerte Lagoon is the second largest lagoon and the most economically important areas in Tunisia. This lagoon is also known a fishery and aquaculture park related to the presence of three mytiliculture sectors. It is subject to many anthropic pressures including, industrial activities and urbanization (Ameur et al. 2013).

The OCPs levels have been widely recorded around the world. However, very little information exists on their environmental levels in different compartments (sediment, and SPM) in the Bizerte Lagoon and there are no previous studies on the distribution of OCPs between different matrices. The goal of the present study was to investigate the partitioning and the spatial distribution of OCPs between SPM and sediments in the Bizerte Lagoon from Tunisia and to provide useful information for the ecological remediation in this lagoon.

II. Materials and methods

Study area
The Bizerte Lagoon is situated in the northern most part of Tunisia, between latitude and longitude; 37°08' and 37°14'N; 9°48' and 9°56'E. The surface area is 128 km^2 and the sea depth is between 3 and 12 m. The lagoon is connected to the Mediterranean Sea and to the Lake Ichkeul by straight channels; they assured the exchanges of water between the Mediterranean and the lake. The salinity of the lagoon ranged between 32.5 psu and 38.5 psu. The water temperature ranged between 10°C during winter and 29°C during summer. There are four main zones of anthropogenic influence (figure 1):
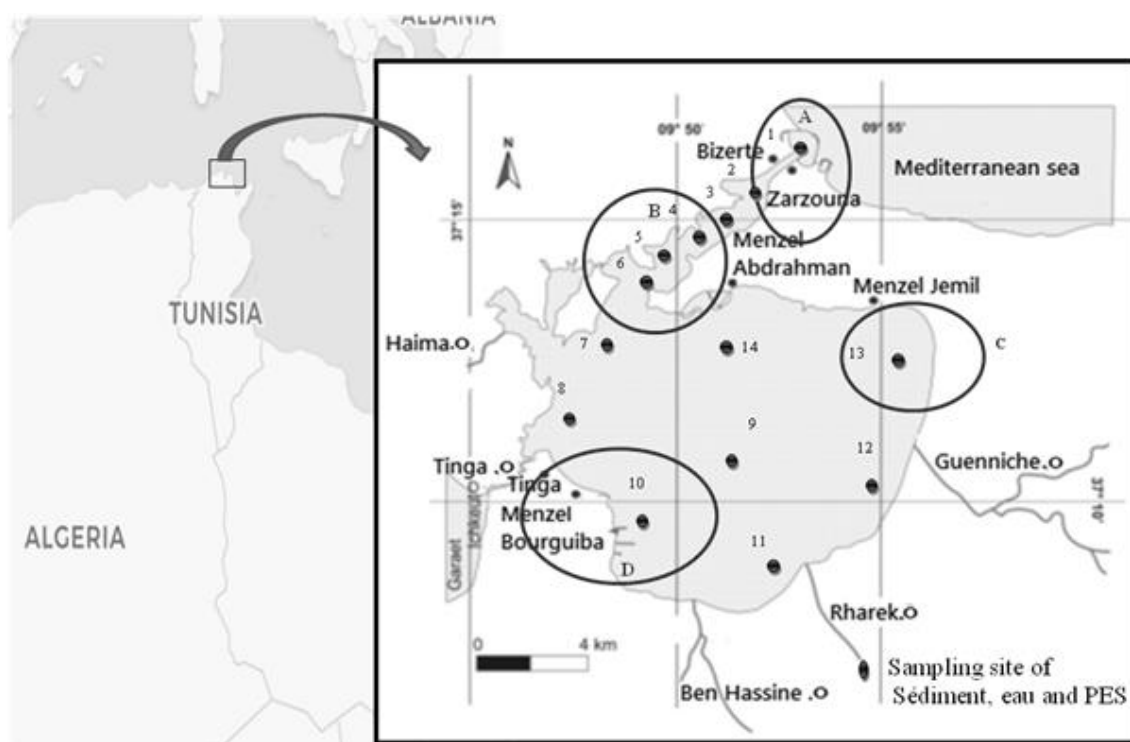

Figure 1. Study areas with sampling station and different types of industrial areas (A, B, C and D) in the Bizerte Lagoon.

Zone A: oil refineries, food and ceramic industries.
Zone B: Factories of cement productions, treatment of metals (copper craft, asbestos) and sprinkling beverages.
Zone C: ceramics and metallurgy activities.
Zone D: metallurgical activities (Fe, Zn, Cd, Sn, Hg), naval constructions and tire productions.

Sample collection

Surface sediment samples were taken from fourteen stations in July 2016 with the aid of global positioning system (GPS). The same first layer of the surface sediment (1–2 cm depth) was collected (about 1–2 kg) at all stations using the Van Veen grab. The surface water was collected from each sampling station in precleaned 2 L amber glass bottles washed twice with water samples. Two litters of water were filtered through 0.45 mm glass fibre filters to obtain SPM. Sampling of water and sediment was realized with three replicates at each sampling site. Each sample was homogenized to form a composite sample for each sampling site, and then transported to the laboratory. Sediment and SPM samples were freeze-dried and stored at -20°C until analysis. Total Organic Carbon (TOC) of sediment samples was analyzed with a TOC Analyzer (SHIMADZUH544051).

Table 1: Description of samples collected from the Bizerte Lagoon

Sites	Latitude (N)	Longitude (E)	Water depth (m)
S1	37°17°10	09°54°03	23
S2	37°16°33	09°53°00	9
S3	37°15°52	09°52°05	12
S4	37°15°17	09°51°24	11
S5	37°15°11	09°51°00	4
S6	37°13°37	09°48°56	11
S7	37°11°01	09°48°01	5
S8	37°11°41	09°49°01	7
S9	37°10°52	09°51°00	10
S10	37°09°06	09°49°37	6,5
S11	37°10°10	09°53°05	6
S12	37°11°10	09°54°00	5
S13	37°13°09	09°54°46	5
S14	37°13°04	09°52°00	5

Quality assurance and quality control

The sample extractions were performed according to the procedure proposed by the UNEP/ IAEA-EL/MELS (IAEA et al, 2012) with some improvement. Appropriate blanks were analysed with each set of analyses, internal standards and in addition a sediment reference material (IAEA, 417) with certified concentrations of OCPs was analysed for quality control purposes. Recoveries ranged from 70% and 89% for the IAEA 417. The reported results were corrected with recoveries of surrogate internal standards. Recoveries for surface water varied between72% to 93% and for SPM and sediment ranged between 91% and 98%. The method detection limits (MDL) obtained for SPM and sediment were 0.018 ng g^{-1} for PCB 29; 0.014 ng g^{-1} for PCB 198; 0.021 ng g^{-1} for εHCH and 0.002 ng g^{-1} for Endosulfane Id4. The average recoveries and relative standard deviations (RSDs) of OCPs were first obtained to evaluate the method performance by multiple analyses of three replicates spiked samples of SPM, sediment and water with 1 mL of internal standard solution. The standard deviation (RSD %) was below 1.2% for OCPs in SPM and sediment which reveals a good repeatability of the method (Table 2).

Table 2: Analytical Performance of OCPs Extraction in Sediments by the Soxhlet Extractor.

Compounds	certified values of IAEA 417 (ng g-1)	Founded values (ng g-1)	Recovery %	RSD % (n=5)	Confidence Interval 95%
HCB	1.2	1.10	97.7	0.69	0.9 – 1.5
Lindane	0.54	0.64	91	0.48	0.39 – 0.69
heptachlor	2.0	2.3	97.7	0.69	1.1 – 2.9
Aldrin	1.6	1.62	97.7	0.69	1.0 – 2.2
Dieldrin	2.3	2.49	98	1.22	1.2 – 3.4
Endrin	7.1	7.4	98	1.22	4.3 – 9.9
pp' DDT	19.0	16.09	91	0.48	15.8 – 22.2
pp' DDE	14.0	14.7	91	0.48	12.1 – 15.9
pp' DDD	21.0	20.96	91	0.48	18.1 – 23.9

Reagents and standards

All chemicals, reagents were of analytical grade and the highest purity possible. Hexane and dichloromethane, used for the extraction of OCPs, were provided from SIGMA-ALDRICH (France), Florisil used in the cleaning were purchased from MERCK (Germany). The mixture of internal standards (IS) (PCB29, PCB198, εHCH and Endosulfane Id4) and two external standard mixtures, the first containing (heptachlor, aldrin, dieldrin, endrin) and the second standards mixture containing (HCB, lindane, pp' DDT, pp' DDE, pp' DDD) were supplied by the International Atomic Energy Agency (IAEA) for chromatography analysis.

Analytical procedure
Extraction
Extraction of sediment and SPM was performed by a Soxhlet extractor for 8 hours. A mixture of hexane and dichloromethane (50/50, v/v) was used and 1mL of IS were added to sediment samples before Soxhlet extraction to determine the recoveries during the analytical procedure.
Concentration and purification
Extracts were concentrated with a rotavapor. Activated copper was used for sediment to remove sulfur compounds. All of the extracts were evaporated under a gentle flow of nitrogen gas.

Column chromatography
        The final extracts were purified following a cleanup procedure on a glass column packed with florisil (pre-filled at 130°C for 8 h) with the bottom and plugged with clean glass wool. The extract was added to the top of the column and adequate solvent was selected to obtain three fractions. The fraction one (F1) including HCB, heptachlor, pp' DDT and aldrin was eluted with hexane. This was then further the fraction two (F2) including lindane and DDTs was eluted with a mixture of hexane and dichloromethane (70/10, v/v) followed by the fraction three (F3) including dieldrin and endrin eluted by 100% dichloromethane.

Gas chromatography
        Analysis of OCPs was performed using Varian 4000 gas chromatograph equipped with a ^{63}Ni electron capture detector (ECD), CP-8400 auto sampler and CP-8410 auto-injector and a HP5 fused silica capillary column (30 m x 0,32 mm x 0,25 μm). The injector and detector were maintained at 280 °C and 300 °C respectively. The column temperature was initially held at 50 °C increased to 140 °C at a rate of 20 °C min^{-1} then increased to 260 °C at the rate of 3 °C min^{-1}. Injection volumes were 1 μL in the splitless mode. The make-up gas used was nitrogen at a flow rate of 25 mL min^{-1} and the carrier gas was helium at flow rate of 1 mL min^{-1}.

Statistical analysis
        The statistical analysis was made by the well-known techniques of Principal Component Analysis (PCA). Correlation analysis was conducted to reveal the relationships between OCPs and TOC. All statistical analyses were performed using Statistica 6 software package.

III.   Results And Discussions
Residual levels of OCPs in SPM and sediment
Residual levels of OCPs in SPM
        The concentrations of OCPs compounds in SPM samples are summarized in table 3. Levels of total OCPs ranged from 0.91 to 15.15 ng g^{-1} in SPM. The less contaminated stations of SPM were S1, S3 and S5 with ∑OCPs concentration 0.91, 3.65 and 3.30 ng g^{-1} respectively. The most polluted stations of SPM were S9, S10 and S13 with ∑OCPs concentrations 13.74, 15.15 and 12.94 ng g^{-1}, respectively. The highest concentration of OCPs in the SPM samples was 15.15 ng g^{-1} recorded for station S14, while the lowest one was 0.91 ng g^{-1} observed at station S1. It could be explained for station S1 by the exchange of water between the lagoon and the Mediterranean Sea, which reduced the concentration of such type of organic contaminants. Station S14 was near the city of Menzel Abderrahman which receives direct inputs of untreated urban and industrial sewage. The ∑DDT represented the sum of pp' DDD, pp' DDE and pp' DDT. The ∑DDT were detected in five sampling stations from the Bizerte Lagoon SPM samples. The highest level of ∑DDT was observed in S5 (5.05 ng g^{-1}) near the mouth of Tinja River which represent a dumping site for agricultural inputs. The lindane and ∑DDTs were the predominant compounds in SPM, they represent 20.9 % and 43.9 % respectively of the total of OCPs measured in the Bizerte Lagoon. Dieldrin and heptaclor present the lowest percentage 0.23 % and 6.10% respectively of the total of OCPs found in SPM. The concentrations of pp' DDT and its metabolites in SPM varied in the order pp' DDE> pp' DDD> pp' DDT, they account 43.90%; 40.16% and 15.94% respectively of the total of DDTs obtained in SPM.

Residual levels of OCPs in sediment
        Fourteen samples of superficial sediments were analyzed. The results of the OCPs analysis are summarized in table 3. HCB and pp' DDE were detected in thirteen sampling station. The highest concentration of ΣOCPs was registered in station S5 (16.29 ng g^{-1}) while the lowest concentration was recorded at station S3 (0.09 ng g^{-1}). Relatively high concentrations of ΣOCPs (15.96 ng g^{-1}) were also found in station S10 located in Zone D which is characterized by significant industrial and agricultural activities. The levels of pp' DDT and its metabolites in this study, varied in the order of pp' DDT> pp' DDE> pp' DDD. The levels of ΣDDT obtained varies between 0.03 and 13.49 ng g^{-1}, between ND and 8.89 ng g^{-1} for pp' DDD and between ND and 3.66 ng g^{-1}

for pp' DDE. The highest concentration of pp' DDT (8.79 ng g^{-1}) was recorded in station S5. This station is close to zone B characterized by industrial activities (cement and metallurgy). The TOC% in sediment ranges from 0.05% recorded in station S3 to 5.22% recorded in station S5. The TOC% found in the different stations are presented in table 3. The lowest percentages of TOC% are founded at stations S12 (0.43%), and S13 (0.47%), these two stations are therefore considered the least rich in organic matter. The TOC % of the rest of the sediment samples are also considered relatively low (<2%). In the sediment the ΣDDT represents 78.04% of the ΣOCP and it was considered dominant in comparison with the others composes of OCPs. The concentrations of pp' DDT and its metabolites in surface sediment varied in the order pp' DDD> pp' DDE> pp' DDT, they present 35.26 %; 17.03 % and 11.83 % respectively of the total of OCPs in surface sediment.

Table 3. Concentrations of OCPs in SPM and sediment (ng g^{-1}) collected from the Bizerte Lagoon.

	matrice	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
HCB	sediment	0.07±0.14	0.12±0.04	0.05±0.71	0.36±0.2	1.97±0.44	0.72±0.18	2.89±0.03	0.4±0.01	0.28±0.03	3.96±0.43	ND	2.58±0.23	1.06±0.08	1.71±0.05
	SPM	0.25±0.14	1.92±0.14	1.56±0.15	0.89±0.03	0.35±0.15	1.06±0.33	0.81±0.01	0.09±0.01	5.92±0.19	1.17±0.71	0.37±0.01	0.77±0.05	0.68±0.33	4.96±0.65
Heptaclor	sediment	ND	ND	ND	0.06±0.01	0.16±0.03	1.22±0.55	0.25±0.03	ND	0.65±0.5	1.4±0.07	0.04±0.01	0.69±0.09	0.05±0.04	ND
	SPM	ND	ND	2.09±0.12	ND	ND	ND	ND	ND	ND	ND	3.11±0.17	1.12±0.01	ND	ND
Aldrin	sediment	ND	0.04±0.01	ND	0.03±0.01	0.58±0.02	2.3±0.09	0.23±0.04	ND	0.01±0.01	0.84±0.09	ND	ND	0.22±0.01	ND
	SPM	0.66±0.09	3.22±0.03	ND	ND	ND	ND	ND	ND	6.75±0.05	2.76±0.03	2.03±0.01	ND	1.92±0.04	1.25±0.09
Dieldrin	sediment	0.56±0.18	ND	0.03±0.01	ND	0.05±0.01	ND	0.01±0.02	0.01±0.02	ND	0.02±0.01	ND	0.01±0.01	ND	ND
	SPM	ND	ND	ND	ND	0.24±0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin	sediment	0.26±0.03	ND	0.01±0.01	ND	0.04±0.01	ND	ND	ND	ND	ND	ND	ND	ND	ND
	SPM	ND	ND	ND	1.19±0.02	0.91±0.01	2.05±0.15	ND	0.85±0.03	1.07±0.11	6.09±0.19	ND	3.97±0.48	2.25±0.10	1.13±0.15
Lindane	sediment	ND	ND	ND	0.19±0.01	ND	ND	0.55±0..3	ND	ND	ND	ND	ND	ND	ND
	SPM	ND	ND	ND	4.03±0.13	1.80±0.09	ND	ND	ND	ND	ND	2.83±0.15	1.54±0.91	8.09±0.03	2.54±0.09
pp' DDD	sediment	5.93±0.34	ND	ND	ND	3.04±0.18	ND	5.23±0.78	2.84±0.27	ND	8.89±0.13	ND	0.13±0.01	0.13±0.01	ND
	SPM	ND	ND	ND	ND	ND	1.50±0.05	1.52±0.09	ND	ND	3.96±0.13	ND	ND	ND	ND
pp' DDT	sediment	ND	ND	ND	ND	8.79±0.73	ND	ND	ND	ND	ND	ND	ND	ND	ND
	SPM	ND	ND	ND	ND	ND	ND	1.60±0.08	ND	ND	1.17±0.41	ND	ND	ND	ND
pp' DDE	sediment	1.55±0.31	0.63±0.09	ND	0.04±0.01	3.66±0.24	0.88±0.36	0.87±0.16	0.34±0.04	0.45±0.05	0.85±0.02	2.3±0.13	1.02±0.02	0.03±0.01	0.03±0.01
	SPM	ND	1.48±0.04	ND	ND	ND	1.10±0.01	ND	5.05±0.61	ND	ND	ND	ND	ND	ND
ΣDDT	sediment	7.48±0.22	0.63±0.03	ND	0.04±0.01	15.49±3.07	0.88±0.12	6.10±0.31	3.18±0.10	0.45±0.02	9.74±0.05	2.30±0.04	ND	0.16±0.01	0.03±0.01
	SPM	ND	1.48±0.01	ND	ND	ND	2.60±0.02	3.12±0.06	5.05±0.20	ND	5.13±0.18	ND	ND	ND	ND
ΣOCP	sediment	8.37±0.08	0.79±0.01	0.09±0.03	0.65±0.03	18.29±0.51	5.12±0.13	10.03±0.10	3.59±0.02	1.39±0.08	15.96±0.09	2.34±0.01	4.43±0.05	1.49±0.02	1.74±0.01
	SPM	0.91±0.03	6.62±0.03	3.65±0.04	6.11±0.03	3.30±0.04	5.71±0.07	3.93±0.01	5.99±0.03	13.74±0.05	15.15±0.16	8.34±0.05	7.40±0.21	12.94±0.07	9.88±0.14
TOC %	sediment	1.99	2.28	0.05	0.66	5.22	4.06	1.73	1.44	1.26	2.02	1.18	0.43	0.47	1.19

The OCPs distribution and partitioning between SPM and sediment

The distributions of OCPs residues between SPM, and sediment are summarized in table 3. In the SPM, the highest content of OCPs was recorded at station S10 followed by those at station S13. However, the contents of OCPs in the sediment at station S2, S3 and S4 were lower, while those at station S5, S7 and S10 were higher. Table 3 shows that the HCB and DDTs were the most compounds detected in SPM and sediment samples collected from the Bizerte Lagoon. The large amount of the urban and industrial wastewater from the industrial zone of Manzel Bourguiba, zone D might be the cause for the higher OCPs contents in the SPM in station S10. While the effects of zone B might produce higher OCPs contents in the sediment in station S5. Unlike the water

and SPM that are affected by the source of OCPs at short term, the sediments are affected by the deposition of SPM at long term (Wu et al. 2013). The spatial distributions of OCPs in sediment would be mainly attributed to the sources of OCPs, the particle size and its organic carbon content, as well as the hydrodynamic conditions in the deposition environment (Li et al. 2012). The fine particulate matter with a large specific surface area and high organic carbon content has strong ability for OCPs adsorption (Turner et al. 2002). The OCPs contents in the agricultural runoff-deduced particles may be higher than those in the waste water containing particles, but the contributions of the agricultural runoff-deduced particles to the sediments are not continuous, which are controlled by the rainfall in the lagoon catchments.
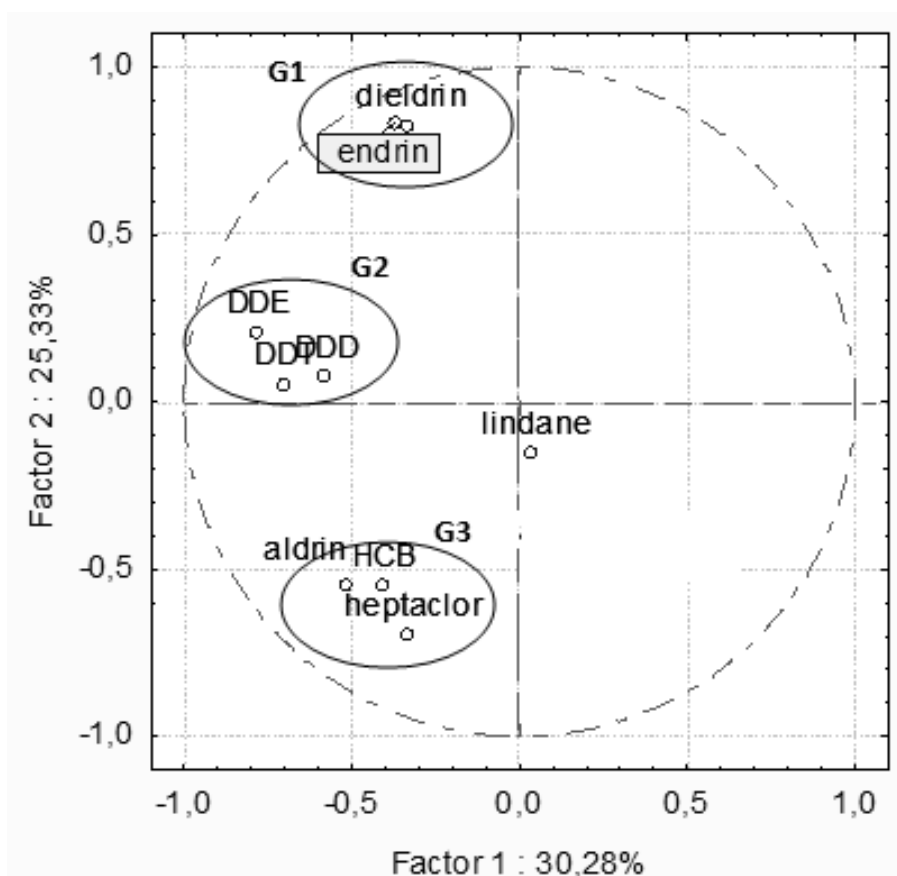

Figure 2. Principal component analysis for individual OCPs in sediment collected from the Bizerte Lagoon.

Correlation and Principal component analysis

The spatial distribution of OCPs in sediments and SPM can be influenced by the hydrological and sedimentological characteristics of the Bizerte Lagoon such as water flow, water currents and TOC content. Hydrophobic residues that enter the aquatic environment are largely adsorbed by sediments. Absorption depends on both the characteristics of the sediment, its organic matter content, the particle size and the chemical concerned (Wang et al. 2013). Correlation matrices of OCPs for sediment and SPM are listed in Table 4 and 5 respectively. These results showed that there was a significant positive correlation between TOC contents and levels of DDE ($p< 0.001$) and DDT ($p<0.01$). This suggests that the distribution of DDTs may be controlled mainly by the distribution of organic matter in the sediments. To estimate the possible sources of OCPs in the catchment, the contamination pattern was further studied. There was a significant positive correlation between pp' DDE and pp' DDT ($p<0.01$) probably reflecting a common origin of the DDT for sediment (see Table 4). Similarly, the correlation between pp' DDT and pp' DDD ($p<0.05$) suggests that these contaminants may have a common source for SPM (Table 5). In this study, the significant correlation between pp' DDT and pp' DDD ($p< 0.01$), indicated that pp′ DDD are originated mainly from the degradation of pp′ DDT. Significant correlation between endrin and dieldrin ($p< 0.01$) was founded in sediment indicated that endrin originated mainly from the degradation of dieldrin (Table 4).

Table 4: Correlation matrix of OCPs levels in sediments of the Bizerte lagoon.

	TOC	HCB	heptaclor	aldrin	dieldrin	endrin	lindane	DDD	DDT	DDE
TOC	1,000	0,160	0,225	0,638**	0,100	0,153	-0,068	0,261	0,711**	0,689**
HCB		1,000	0,543*	0,206	-0,213	-0,228	0,320	0,588*	0,184	0,133
heptaclor			1,000	0,707**	-0,219	-0,243	-0,122	0,284	-0,118	-0,052
Aldrin				1,000	-0,134	-0,125	-0,074	0,106	0,126	0,149
dieldrin					1,000	0,996***	-0,106	0,437*	0,001	0,237
Endrin						1,000	-0,120	0,414*	0,074	0,292
lindane							1,000	0,260	-0,100	-0,090
DDD								1,000	0,120	0,253
DDT									1,000	0,774**
DDE										1,000

$*p < 0.05$; $**p < 0.01$; $***p < 0.001$

PCA was carried out to further identify the possible sources of OCPs, and the component matrixes were presented in figure 2 and 3. In the case of sediment, PC1 and PC2 represent 30.28% and 23.87 % of the total variance. The dieldrin and endrin formed group G1, pp' DDD, pp' DDT and pp' DDE constituted group G2, Aldrin, HCB and heptachlor formed group 3. For the SPM, PC'1 and PC'2 represents 39.72 % and 26.29 % of the total variance. The OCPs in SPM were divided into three groups the first group G'1 includes aldrin and HCB, second group G'2 include endrin, DDD and DDT third group includes lindane, heptachlor, DDE and dieldrin (Figure 3). The contamination by OCPs in all groups can be attributed mainly to agricultural activities and atmospheric deposition while common sources for OCPs can be produced by activities from areas A and B for groups G1 and G2. Industrial sources of the area C and D can appear in groups G'1 and G'2.
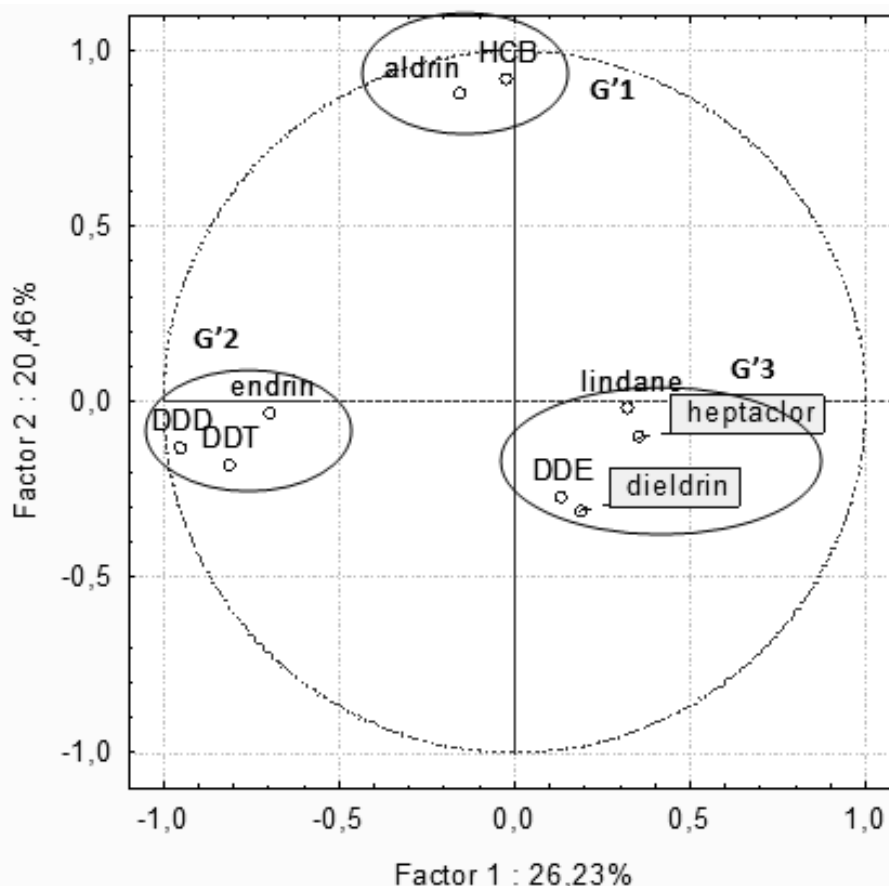

Figure 3. Principal component analysis for individual OCPs in SPM collected from the Bizerte Lagoon.

Table 5: Correlation matrix of OCPs levels in SPM of the Bizerte lagoon.

	HCB	heptaclor	aldrin	Dieldrin	endrin	lindane	DDD	DDT	DDE
HCB	1,000	-0,186	0,682**	-0,186	-0,042	-0,120	-0,112	-0,124	-0,218
heptaclor		1,000	-0,089	-0,134	-0,182	0,038	-0,220	-0,195	-0,198
aldrin			1,000	-0,198	0,087	-0,055	0,058	-0,035	-0,155
dieldrin				1,000	-0,079	0,039	-0,126	-0,112	-0,114
endrin					1,000	0,086	0,672**	0,280	-0,129
lindane						1,000	-0,302	-0,266	-0,271
DDD							1,000	0,755**	-0,106
DDT								1,000	-0,165
DDE									1,000

*p < 0.05; **p < 0.01; ***p < 0.001

Comparison with study from the words

The Comparisons of OCPs contents in SPM, and sediments from Bizerte Lagoon with those from other regions worldwide are investigated. The levels of OCPs in SPM taken from the Bizerte Lagoon varied between 0.91-15.15 ngg^{-1}. It is lower than that found in the SPM taken from Yangtze river (china) (Jiang et al. 2000) with concentrations varying between 11.3-21.87 ng g^{-1}. The concentrations of OCPs obtained in sediment samples in this study are higher than those found in the Masan Bay (korea) (Hong et al. 2003) with concentrations (Σ10OCP) ranging between 0.02 and 89.2 ng g^{-1} and those recorded in Lake Chaohu (China) with concentrations (Σ24OCP) ranging from 0.9 ng g^{-1} to 36.9 ng g^{-1} (Liu et al., 2013). The concentrations of OCPs obtained in the Bizerte Lagoon are higher than those found in the same region in 2001 with ΣOCP concentrations ranging from 0.18 ng g^{-1} to 3.78 ng g^{-1} and lower that those obtained in 2011 with ΣOCP concentrations ranging from 0.8 ng g^{-1} to 14.6 ng g^{-1} (Barhoumi et al. 2013) (Trabelsi et al. 2012). The results show that the concentration of ΣOCP found in this work is lower than found in the Lake Manyas (Turkey) with concentrations (Σ15OCP) ranging between 17.05-39.14 ng g^{-1} (Erkmen et al. 2013).

Table 6: Concentration limits of OCPs in SPM and sediment matrices (ng g^{-1}).

	TEC (ng g^{-1})	PEC (ng g^{-1})	ER-L (ng g^{-1})	ER-M (ng g^{-1})	LOD (ngg^{-1})	Range in sediment (ng g^{-1})	Range in SPM (ng g^{-1})
HCB	-	-	_	_	0.018	ND-1.97	0.09-5.92
Heptaclor	2.47	16.0	_	_	0.018	ND-1.22	ND-3.11
Aldrin	-	-	_	_	0.018	ND-0.84	ND-6.75
Dieldrin	6.67	910	0.02	8	0.002	ND-0.56	ND-0.24
Endrin	62.41	1300	0.02	45	0.002	ND-0.26	ND-6.09
Lindane	2.37	499	_	_	0.021	ND-0.55	ND-8.02
pp' DDD	4.88	28	2	20	0.021	ND-3.04	ND-3.96
pp' DDT	4.16	63.9	1	7	0.021	ND-8.79	ND-1.60
pp' DDE	3.16	31.3	2	15	0.021	ND-3.66	ND-5.05

Risk and health effects of OCPs

In the present study, the consensus-based sediment quality guidelines (CB-SQGs) suggested by MacDonald in 2000 (MacDonald et al. 2000) were used to evaluate the potential ecological risk of OCPs in the SPM and sediment from the Bizerte Lagoon. The TEC means the concentration of the pollutant lower than it was predicted to be nontoxic, while PEC means the concentration of the pollutant greater than its corresponding was predicted to be toxic. If the concentration of pollutants was between its TEC and PEC it was predicted to be neither toxic nor nontoxic (MacDonald et al. 2000). The TEC and PEC obtained for this study was presented in table 6. The residual levels of OCPs in sediment and SPM from the Bizerte Lagoon were lower than their corresponding TECs, suggesting that they would have no adverse effects on aquatic organisms (table 6).

IV. Conclusion

In this study, levels of concentration by OCPs in SPM and the sediment has been assessed in the Bizerte Lagoon, which is known for many decades as a fishing and industrial area. Results show that OCPs concentrations in sediment were higher than the levels in SPM. The predominant compounds are HCB and ΣDDT in different matrices. An efficient control must take into account of urban and industrial discharges. Results show that levels of OCPs obtained in SPM and sediment in this study pose no threat to human and aquatic living species

Acknowledgments

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