Chapter

# Persistent Organic Pollutants in the Bizerte Lagoon Ecosystem: Occurrence, Distribution, and Ecotoxicological Assessment Using Marine Organism

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## Abstract

Marine ecosystem represents an ecologically and economically important water bodies for human and animal living. Their increasing pollution by persistent organic pollutants has represented a major environmental alarm during the last years. In the current study, we examined the occurrence, local distribution and ecotoxicological menace of organic pollutants, comprising brominated flame retardants (BFR), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and organochlorine pesticides (OCPs) in different matrices from the Northern Tunisian Coastal Ecosystem (Bizerte lagoon). The pollutant existence in this biome is related with a negative impact on the biocenosis health. Many approach including (i) chemical analyses; (ii) taxonomic structure and ecological indices analyses; (iii) and biochemical experimental studies, were investigated to determine the ecosystem quality and the contaminant effects. Our chapter introduces the baseline information on the organic contaminations extent and toxicological impact, as well as, it contribute to evaluate the ecological quality of this marine coastal ecosystem.

**Keywords:** Persistent Organic Pollutants (POPs), Mediterranean coastal lagoon, Occurrence, Distribution, Ecotoxicological evaluation

## 1. Introduction

The expansion of the anthropoid industrial activities has led to the pollution of many ecosystems. The daily release of agricultural, industrial and commercial chemicals into the aquatic ecosystem has induced various toxic effects on marine organisms [1]. Among Mediterranean coastal environments, many lagoons are exposed to human-induced pressures. The Bizerte lagoon is one of them, located near an industrial and agricultural area of Northern Tunisia, known as a receptor of numerous industrial wastes, chemical fertilizers and pesticides via runoff and soil erosion, conducting to a lessening in fish and bivalves' production [2].

These organisms accumulate chemicals directly from contaminated water and indirectly via the food chain. In addition, these are used as sentinels' species because they have the capacity to bio-concentrate toxic compounds. Their main advantage is the rapid response to low concentrations of aquatic contaminant [3].

Biomonitoring of the aquatic environment has based both on the quantification of pollutant concentrations in bioindicator organisms and on the biological analyses (ecological indices and biomarkers). The chemical analyses were performed after pollutants extraction from different matrices (water, sediment, and marine organism), using instruments by Gas chromatography separation connected or not to a mass spectrometer (GC–MS) [4–15]. Nevertheless, the biological analyses were performed both firstly; by nematodes taxonomic structure and ecological indices determination to assess the chemicals toxicity, secondly, by biomarkers assessment who are known as tools for contamination impacts evaluation in the marine environment. Some of these have been incorporated in ecological monitoring programs [16].

The biomarkers have been classified in different types, such as biomarkers exposure and response, or as general and specific biomarkers [17]. Antioxidant enzymes such as catalase (CAT), reduced glutathione (GSH) and Glutathione-S-transferase (GST) have been used as biomarkers reflecting the exposure and toxicity of contaminants [18]. The Acetylcholinesterase (AChE) activity has been used as a biomarker of exposure to several pesticides (organophosphate and carbamate insecticides) in aquatic environments [19]. The high concentrations of Malondialdehyde (MDA) have been reflected the lipid peroxidation expression that indicates cell damage [20].

This aim of the present chapter was to describe the previous studies focused on the determination of pollutant concentrations in bio-indicator organisms and to discuss the results of biological assessment of their toxicities in order to provide clearer and more informative data concerning the Bizerte lagoon coastal ecosystem state.

## 2. Persistent organic pollutants (POP)

### 2.1 Definition

Persistent organic pollutants (POPs) are organic chemical compounds having physical and chemical properties that result in their widespread dissemination, persistence and accumulation. They are known by their characteristics: persistence, bioaccumulation, transport, and toxicity effects. POPs have a lifespan that can reach many years, because of their resistance to chemical and biological degradation. They are lipophilic and tend to disperse widely across ecosystems; they accumulate to high concentrations in the wildlife tissues biomagnifying up the food chain. They are semi-volatile, allowing for long-range transport in air or absorbed to particulate matter in environmental matrices such as air or water.

These chemicals are organic substances of natural or anthropogenic origin, once released into the environment; they remain intact for exceptionally long periods of time [21]. The major intentional man-made sources of POPs are industrial sources like incinerating plants, power stations, agricultural sprays, heating stations and evaporation from water surfaces, soil, or from the landfills.

## 3. Sampling location

### 3.1 Bizerte lagoon

The Bizerte Lagoon is located in the Tunisia northern littoral (Mediterranean Sea) (latitude, 37°80′–37°14′ N; longitude, 9°46′–9°56′ E). It spread 128 $km^2$ of

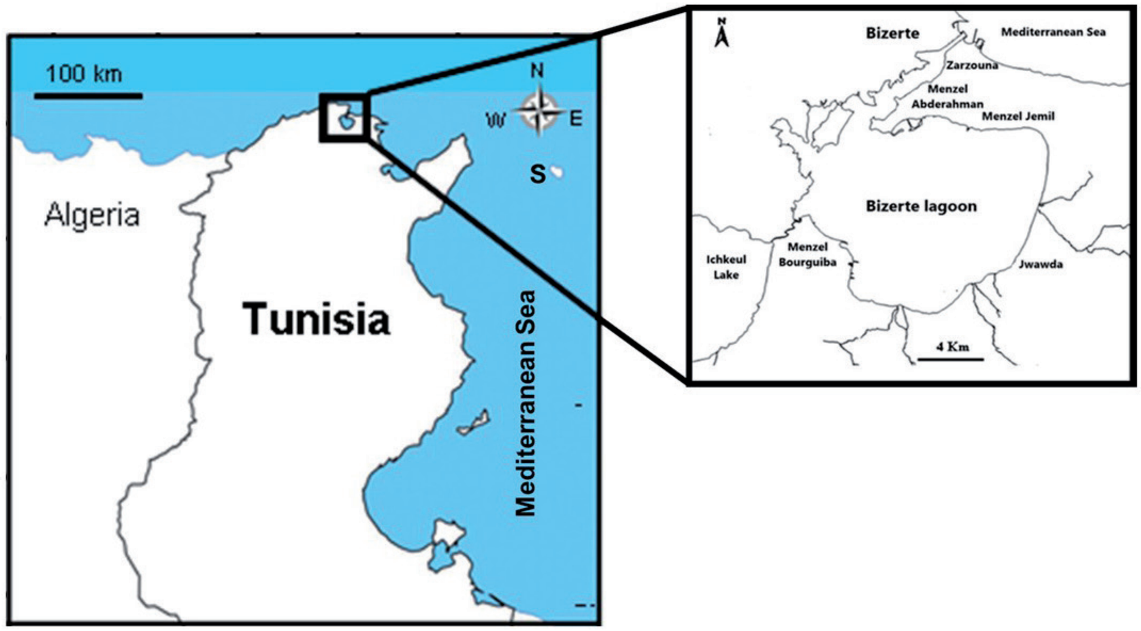


**Figure 1.**
*Location of the Bizerte lagoon (northern Tunisia).*

area and 7 m of mean depth. In the north it communicates by a 7-km-long canal with the Mediterranean Sea, nonetheless, in the South with the Ichkeul Lake by the River of Tinja. This lagoon is under tributaries of many rivers such as Gueniche, Ben Hassine, Mrezig, Garek, and Tinja has a high importance in terms of seafood products exports; it show an economically significant body of water due to a variety of peach and aquaculture activities (oysters and mussels farming).

Due the population growth and technological development around the lagoon, this ecosystem is compelling to the influence of divers' physical factors that highly fluctuate during the year. It is severely affected by human activities on its shores, including the four harbors presence, urban development (bounded by the cities of Bizerte, Zarzouna, Menzel Jemil, Menzel Abderrahmane, Menzel Bourguiba and Tinja), and receives urban effluents, agricultural inputs and industrial discharges from many industrial units related to various fields of activity such as cement, steel plant, a metal factory, and a refinery (**Figure 1**) [22].

In the lagoon of Bizerte, the water column is under the influence of the winter contributions of rains and fresh water in provenance of the wadis, particularly that of Ichkeul [23]. On the other hand, the water column is under the influence of the winter contributions of rains and fresh water in provenance of the wadis, particularly that of Ichkeul [23]. On the other hand, the water exchange between the Mediterranean and the Ichkeul make the temperature and salinity of the lagoon vary between (10–29°C) and (32.5–38.5‰), respectively.

## 4. POPs in the Bizerte lagoon

Due to their persistent nature and ability to undergo long-range transport, POPs are ubiquitous in the environment. They are found in soil, lake and river sediment, benthos, water columns and the atmosphere. They enter and accumulate in the food chain through various pathways, such as deposition onto crops, soil ingestion by grazing animals, and bioaccumulation up through trophic levels. At concentrations typically found in food, the adverse health effects caused by POPs are almost entirely chronic (including cancer), disruption of the endocrine system, neurotoxicity, and development damage.

The occurrence of POPs is reported major in the aquatic environment pollution of which released into water bodies from a large variety of anthropogenic sources such as agricultural and municipal waste effluents, industrial coastal activities, atmospheric deposition, maritime transport and accidental spill [24, 25]. Many studies have been carried out for monitoring the organic pollutants and their impact on different aquatic ecosystems around the Bizerte lagoon. The most identified POP chemicals in Bizerte lagoon ecosystems are belonging the families of brominated (and chlorinated) aromatics, including brominated flame retardants (BFR) such as polybrominated diphenyl ethers (PBDEs) and their methoxylated analogues (MeO-PBDEs) [4–9]; polychlorinated biphenyls (PCBs) [10–12]; polycyclic aromatic hydrocarbons PAHs [13, 14]; and organochlorine pesticides (OCPs) [11, 12, 15].

### 4.1 Brominated flame retardants (BFRs)

Brominated flame retardants (BFRs) are brominated organic compounds used as additive flame retardants in plastics, paints, textiles, electronics, and vehicles. PBDEs and analogs (such as the methoxylated PBDEs (MeO-PBDEs)), have been found in many environmental matrices such as, aquatic organism, water, sludge, and sediment [26], and in fish and marine mammals [27], respectively. Contamination by BFRs is of environmental concern due to their persistence, potential for endocrine disruption and bioaccumulation, and long-range transport. It has been reported their adverse effect, such as morphological, immunological, and behavioral modifications, and enzyme induction [28, 29].

The levels of the BFRs in two species like in sea bass (*Dicentrarchus labrax*) and mullet (*Mugil cephalus*) collected from the Bizerte Lagoon were examined. The PBDE mean concentrations in fish were 45.3 and 96.2 ng/g lw respectively in mullet and sea bass. MeO PBDE concentrations in mullet and sea bass were 6.46–286 ng/g lw and 49.4–798 ng/g lw, respectively [4]. In other study, polybrominated diphenyl-ethers (PBDEs) and methoxylated polybrominated diphenyl ethers (MeO-PBDEs) were determined in *solea solea* muscle. Mean levels of these compounds were 279 ng/g lw in sole [5]. In addition, sediment and urchins were used for the levels analysis of halogenated flame retardants (HFRs) and the methoxylated-PBDEs. The sediment concentrations were found between nd – 51.8 ng/g dry weight (dw) for the HFRs, and not detected for rest compounds. However, the levels of polybrominated diphenyl ethers (PBDEs), halogenated norbornenes (HN) and methoxylated PBDEs (MeO-PBDEs) were 3.67 to 56.9 ng/g lipid weight (lw), 4.52 to 116 ng/g lw and nd - 364 ng/g lw, respectively, in sea urchins [8].

Ameur et al. determined the concentrations of HFRs and MeO-PBDEs in *Hexaplex trunculus* collected in the same ecosystem and found that the mean tissue levels vary between 187 and 264 ng/g lw [6]. Recently, Mekni et al. measured the presence of the Brominated flame-retardants in sediment and fish eel (*Anguilla Anguilla*) samples [9]. Sediment HFR (halogenated flame-retardants) levels were 3.30–28.5 ng/g dry weight (dw), while OPFR (organophosphate flame retardants) levels were 9.77–164 ng/g dw [9]. However, the levels were 4.72–151 ng/g lipid weight (lw) and 19.7–2154 ng/g lw were estimated in fish, respectively.

### 4.2 Polychlorinated biphenyls (PCBs)

PCBs are produced and used in a wide range of industrial applications, such as inks, coatings, electrical transformers, and paints. Despite their prohibitions, they can also be found in various compartments such as sediments [4, 10, 30], in biota [31, 32], in human blood, breast milk and serum [33, 34].

Concentrations of polychlorinated biphenyls (PCBs) were determined in sediments at range between 0.89 and 6.63 ng/g dw [10], and in fish species collected from Bizerte Lagoon were found 164 to 336 ng/g lw and from 282 to 642 ng/g lw, respectively in mullet (*Mugil cephalus*) and sea bass (*Dicentrarchus labrax*). PCB-118, PCB-138, PCB-153 and PCB-180 were dominant contaminants in the studied fish species, accounting respectively for 9.00%, 14.0%, 28.5% and 23.6% of total PCBs [11]. Polychlorinated biphenyls (PCBs) were measured in fish (*solea solea*) muscle and the mean levels were 1417 and 315 ng/g lipid weight (lw) [5]. Recently, the concentration of polychlorinated biphenyls (PCBs) identified in water samples were ranged between 3 and 10.4 ng $L^{-1}$. PCB-28 (0.2–1.4 ng $L^{-1}$) and PCB-52 (0.8–3.5 ng $L^{-1}$) were the predominant PCB congeners [35].

### 4.3 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are an important class of persistent organic pollutants derived from anthropogenic or natural sources. They are formed as a consequence of incomplete combustion of organic matter; they are also found in the crude oil components and derived products. Natural sources of PAHs include forest-fires and post-depositional transformation of biogenic precursors [36]. PAHs reach the marine environment via such sources as effluent discharges, urban run-off, atmospheric transport, and agricultural runoff. Because of their low water solubility and their hydrophobicity, PAHs in the aquatic environment rapidly become associated with inorganic and organic suspended particles [37, 38] and subsequent deposition in sediment. PAHs accumulate in aquatic sediments after adsorption to particles due to their high hydrophobicity and low solubility [38, 39].

Total PAHs identified in sediments from 10 stations around the Bizerte lagoon (Menzel Abderahmen, Menzel Jemil, Oued Guenniche, Oued Garek, Oued Ben Hasssin, Mnzel Bourguiba...) were ranged between 83.3–447 (ng/g dry wt) [13] with a mean value of 218 ng/g dry wt. Only anthracene, acenaphthene, and phenanthrene are found in all stations. Recently, Barhoumi et al. have been showed that form many station (n = 18), the total concentration varied between 16.9 to 394.1 (ng/g dry wt) with a mean concentration of 85.5 ng/g dry wt [14]. The maximum levels of PAHs were found along the channel and were ranged between 160.2–394.1 (ng/g dw), followed by station at the nearness of the mouth of the Tinja River which is affected by agricultural inputs (102.8 ng/g dw). The same researchers have showed the presence of PAHs levels in two different species, mussels (*Mytilus galloprovincialis*) (107.4 to 430.7 ng/g dw) and fish (*Anguilla anguilla*) (114.5–133.7 ng/g dw). In addition, Naphthalene was the most important hydrocarbon identified in mussels (31.5–272.6 ng/g dw) and fish (57.9–68.6 ng/g dw) [40]. More recently, 16 PAHs were measured in 40 surface sediment samples from the Bizerte lagoon and the high concentrations of total PAHs were 122–19600 ng/g [15].

### 4.4 Organochlorine pesticides (OCPs)

The organochlorine pesticides (OCPs) represent one of the most known persistent organic pollutants (POPs), which have caused great concern all over the world as a result of their persistence for many years, high lipophilicity, long range transportation, chronic and acute toxicities and bioaccumulation [41]. The OCPs have been produced and used for agricultural and industrial purposes for a long time and on a large scale. Organochlorine pesticides had been used throughout the world thanks to exceptional insecticidal and fungicidal properties [42].

The OCPs concentrations were measured in fish such as *Mugil cephalus* and *Dicentrarchus labrax* and the mean levels were found from 52.9 to 157 ng/g lw and from 158 to 265 ng/g lw, respectively [11]. In other study, Barhoumi et al. have found that the total sediments concentrations of OCPs from 1.1 to 14.0 ng/g dw (average value, 3.3 ng/g dw) [12]. Among the OCPs, the concentrations range of DDTs (dichlorodiphenyltrichloroethane) in addition with its metabolites and HCB (hexachlorobenzene) were 0.3–11.5 ng/g dw (1.9 ng/g dw) and 0.6–2.5 ng/g dw (1.4 ng/g dw), respectively. Lately, sediment has examined for study the vertical distribution of organochlorine pesticides (OCPs). The OCPs concentrations ranged from 26.98 ± 0.04 ng/g found at 3 cm depth and 10.23 ± 0.02 ng/g at 6 cm depth in site SC1 (located in the mouth of the channel connecting the lagoon to the Mediterranean Sea). However, in station SC2 (located in the metallurgy of Menzel bourguiba), the concentrations are of the order of 11.77 ± 0.11 ng/g (9 cm deep) and 1.47 ± 0.02 ng/g (20 cm deep) [43].

## 5. POPs impact on marine organism

The occurrence of chemicals compounds in aquatic environment has led researchers to examine biological effects on aquatic organisms. Persistent organic pollutants (POPs) are toxic chemicals that adversely affect organism health and the environment. Many effects are associated to POPs exposure such as immune alteration, reproductive disorder, endocrine disruption, and neurological disorders. In the Bizerte lagoon, the use of marine organisms as bio-indicators of contaminant loads (and as models of laboratory toxicity studies), has enabled the gathering of information on the state of the ecosystem under consideration.

Laboratory research has documented many effects of POPs in a wide range of aquatic organism. Toxicity of these compounds are associated to various biochemical and population effect in benthic nematodes, marine phytoplankton, and bivalves. Among these studies, Louati et al. studied the response of microbial communities following sediment enrichment in anthracene as well as the monitoring of their biomass, activity and composition following the bioremediation [44]. A significant reduction of bacterial abundance, a strongly oxygen consumption inhibition, as well as, a microbial structure modification in comparison with the control were registered. In other study, marine nematodes communities were subjected to a 100 ppm polycyclic aromatic hydrocarbons mixture of phenanthrene, fluoranthene, and pyrene during 30 days. Abundance, diversity, and taxonomic structure were changed. *Spirinia parasitifera* became the resistant species to PAHs contamination while *Oncholaimus campylocercoides* and *Neochromadora peocilosoma* were strongly inhibited [45].

Othman et al. studied the toxicity of PAHs mixtures on natural phytoplankton communities [46]. Results show that PAHs decreased the photosynthetic potential with a dramatic change in phytoplankton community composition (size classes and chlorophyll a) were strongly affected. The diatom *Entomoneis paludosa* appeared favored under PAH exposure as evidenced by increase in cell density, whereas autotrophic flagellates and dinophytes were strongly reduced. In other study, the anthracene toxicity was studied on the benthic bivalves *Ruditapes decussatus.* A change of the siphon movement and decreasing filtration rate were recorded. In addition, the oxidative stress status of the gills was affected with the modification of proteins [47]. Exposure of the pelagic organism (*Mytilus galloprovincialis*) to anthracene induced the enzymatic activities such as, acetylcholinesterase (AChE), glutathione (GSH), and malondialdehyde (MDA) in digestive gland. A reduction of the filtration rates and an increase in lipid peroxidation in digestive gland were registered. Finally, the GSH content as well as AChE activity have been reduced in digestive gland [48]. Study examined the Benzo[a] Pyrene (B[a]P) toxicity in

*Mytilus galloprovincialis* and *Ruditapes decussatus* showed an increase of the total oxyradical scavenging capacity (TOSC) in the digestive gland after exposure to 100 and 300 μg/L concentrations of B[a]P. The superoxide dismutase (SOD), glutathione S-transferase (GST), and catalase (CAT) activities in gills and digestive gland were significantly induced. A significant increase of the GST activity and a decrease of AChE activity in digestive glands and gills were recorded in the two species. Interestingly, an increase of MDA level in the gills and digestive gland only in *Ruditapes decussatus* species [49].

Recently, Nasri et al. investigated the meiobenthic response to the polybrominated diphenyl ether (BDE-47) exposure in laboratory during one month [50]. BDE-47 caused a decrease in the bacterial abundance, and the nematodes taxonomic diversity as well as a change of all functional traits abundance, especially, the feeding group, amphid shape, and adult length were the most affected. In other study, Nasri et al. determined the taxonomic and trophic response of marine nematodes with the same concentrations of BDE-47 [51]. Species abundance and all univariate indices were significantly affected. BDE-47 treatment caused the microvores group represented by two species of *Terschellingia* to be replaced by the more resistant trophic groups such as epigrowth feeders (*Paracomesoma dubium*) and facultative predators (*Metoncholaimus pristiurus*).

## 6. Conclusions

The uses of chemical and biological analyses are promising tools for determining the quality of the Bizerte lagoon ecosystem and to survey the effects of the contaminants from anthropological activities. As a result, several studies have shown the effectiveness of the use in addition of sediments, associated organisms, such as marine bivalves, to monitor pollution [52]. They are specific indicators of different matrices in the ecosystem in relation to their position, and they show different rates of biotransformation and bioaccumulation compared to xenobiotics [53].

## Conflict of interest

The authors declare no conflict of interest.

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