

Polychlorinated Biphenyls in Sediments from Ghar El Melh lagoon, Tunisia

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Abstract The concentrations of 20 Polychlorinated biphenyls (PCBs) were determined in 12 superficial sediments collected from The Ghar El Melh lagoon. Sediment samples were extracted by Soxhlet and analyzed by Gas chromatography with electron capture detector. The concentrations of PCBs, as sum of the 20 congeners, ranged from not detected to 3.987 ng/g on a dry weight basis, with a predominance of highly chlorinated (penta- and heptachlorobiphenyls) congeners. No significant correlation was found between the total PCB concentrations and organic carbon content suggesting that sediment organic carbon content did not play an important role in controlling the PCBs levels in the sediments. PCB levels in sediments were compared with Sediments Quality Guidelines (ERM–ERL indexes) for evaluation probable toxic effects on marine organism. The PCBs concentrations were lower than ERM and ERL values for all the collected samples.

Keywords Polychlorinated biphenyls · Sediments · Organic carbon · Grain size · Ghar El Melh lagoon Tunisia · Tunisia

Polychlorinated biphenyls (PCBs) are a group of persistent organic pollutants (POPs) (Johnson et al. 2000) that have been, for a long-time, the focus of great attention by the scientific community due to their impact on public health

and the environment. PCBs have been used as constituents in a variety of products and in several industrial applications. PCBs are hydrophobic compounds that tend to adsorb onto suspended material and sediments. Hence sediments can be considered a pollution reservoir and may be a source of contaminants to aquatic biota. They are carried from terrestrial sources to the aquatic ecosystems through various pathways, such as atmospheric and fluvial transports. Their high lipophilicity and environmental stability make them persistent in the environment for long periods, becoming geographically widespread and bioaccumulating in the fatty tissues of living organisms through the food web, especially in aquatic ecosystems (Borga et al. 2001). Therefore, sediment contamination is of great concern. PCB mixtures can elicit various toxicities, such as dermal lesions, body weight loss, hepatotoxicity, immunosuppression, reproductive and developmental toxicity, endocrine disruption, neurotoxicity, and carcinogenicity, despite the cessation of PCB exposure (Covaci et al. 2001; Negoita et al. 2003; Schuhmacher et al. 2004; Zhang et al. 2004; Borghini et al. 2005). Previous studies revealed the presence of heavy metal (Walid et al. 2010; Chouba et al. 2007) and PAHs (Ameer et al. 2010) in sediments of Ghar el Melh lagoon, but there is no study about PCB in sediments of this lagoon.

The Ghar El Melh lagoon is a Mediterranean coastal lagoon, situated in North-Eastern Tunisia, on the North Western side of the Gulf of Tunis. This lagoon is 34 km² in surface area; it extends over a length of 7 km and a width of 4.5 km and limited by the outer geographic coordinates 37°07'N, 10°08'E and 37°11'N, 10°14'E.

The purpose of this study was to evaluate PCB contamination in sediments from Ghar El Melh lagoon. To our knowledge, this study documents the first analysis of PCBs in sediments in Ghar El Melh lagoon.

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Materials and Methods

A total of 12 surface sediments located by GPS were collected in November 2006 (Fig. 1). The sediment sample was placed in an aluminum container and frozen on dry ice, then transferred to the laboratory protected from light. In the laboratory samples were defrosted, dried, then the sediments were passed through a stainless steel sieve (0.5 mm mesh) and stored at 4°C until analysis.

Acetone and n-hexane were purchased from Fisher (UK). Hydrochloric acid, phosphoric acid and sulphuric acid were obtained from Biotechnica. Florisil (60–100 mesh size) was obtained from Merck (Darmstadt, Germany), activated at 650°C and retreated at 130°C for 5 h. The anhydrous sodium sulfate heated overnight at 150°C and the potassium dichromate was supplied from Fluka. PCB standard reference material (SRM 1493) containing PCB 8, 18, 28, 44, 52, 66, 77, 101, 105, 118, 126, 128, 138, 153, 170, 180, 187, 195, 208 and 209 was purchased from the National Institute of Standard and Technology (USA).

PCBs in sediment samples were analyzed according to the method described by (Derouiche et al. 2004). Briefly, 30 g of dried sediment were extracted with 300 mL of n hexane in a soxhlet apparatus for 12 h. The sample extracts were treated with sulphuric acid (98%) and then with sodium bicarbonate (5%) in a separatory funnel. After sulphur removal by activated copper, the solution was reduced to 2 mL and added to column (i.d. = 10 mm), slurry packed with 5 g of activated florisil. The extract was eluted with 40 mL of hexane. The eluate was concentrated to 1 mL in a micro-Kuderna-Danish evaporator under a gentle stream of nitrogen.

The analysis of PCBs was performed on an Agilent Model 6890 Gas Chromatograph equipped with a ^{63}Ni electron capture detector (GC-ECD). The column used was fused silica capillary PTE-5 (30 m length 0.32 mm i.d.,

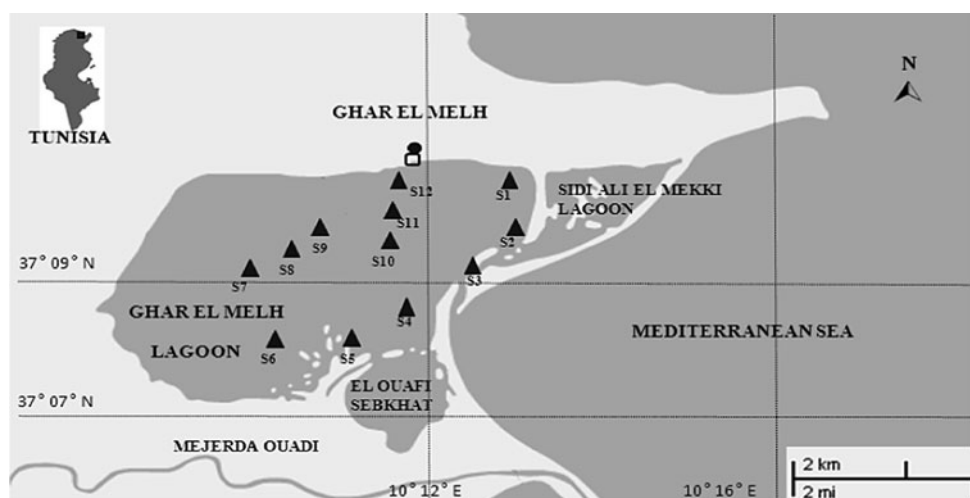
0.25 μm film thickness). The operating conditions were as follows: Injector temperature 250°C; detector temperature 300°C; oven temperature: initial 50°C for 2 min, programmed to 160°C at 5°C/min, followed at 2°C/min to 260°C, final 260°C for 10 min; carrier gas: helium at a flow rate of 1.5 mL/min; detector make-up gas was nitrogen at a flow rate of 60 mL/min; sample injection volume 2 μL ; injection mode: splitless for 1 min. The quantification of compounds was based on peak area measurement as well comparison with responses of a mixed PCB standard reference material (SRM 1493).

The whole analytical procedure was validated by analyzing EC-3 sediment reference materials from National Water Research Institute (Canada). The recoveries of studied PCBs in the extract using the same methodology were >90%. All samples were analyzed in triplicates, and the relative standard deviation ($n = 3$) was less than 20%. The instrument detection limits (IDLs) were determined by assessing the injection amount that corresponded to a signal-to-noise ratio of 3:1. IDL values were between 0.09 and 0.3 pg.

The organic carbon (OC) contents were measured by means of the method described previously (BSI 1990). Briefly, 2 g dried sediment was treated with 10 mL of 1.000 N potassium dichromate followed by the rapid addition of 20 mL of concentrated H_2SO_4 containing 0.5 g silver sulphate, to precipitate chloride ions. Samples were allowed to cool uniformly to room temperature for 30 min (at 20°C), then the mixture was diluted by 200 mL of double-distilled water, and 10 mL of phosphoric acid was added. Finally, the excess dichromate was back titrated with iron (II) sulphate solution using barium diphenylamine sulphate as an indicator.

The percentage of finer grain size fractions (% <63 μm) of each sediment sample was determined gravimetrically after wet sieving. The percentage of finer grain size

Fig. 1 Location of sampling sites



fractions (% <63 μm) of each sediment sample was determined gravimetrically after wet sieving (Savinov et al. 2000).

Statistical treatment of data was performed using the STATISTICA 6.0 Analysis System, version 5. The Pearson correlation was used to analyze relationships between PCBs and both organic carbon percentage (%) and the pelite.

Results and Discussion

The analytical results, based on dry sediment weight, are summarized in Table 1. Total PCB concentrations, as sum

of the 20 congeners, ranged from not detected to 3.940 ng/g dry weight with a mean value of 1.275 ng/g dry wt.

Figure 2 shows the geographic distribution of PCB concentrations. In the whole of the lagoon system, the contents of total PCB in the sediment vary from a site to another. This result reflects a zonation of the level of contamination. The highest PCB concentrations ranged from 2.939 to 3.987 ng/g and were detected at the east part of the lagoon site S3 and at site S6. The station S3 is near the fishing harbour, while station S6 is located in the southwest zone of the lagoon characterized by agricultural activities and water stagnation; this explains the high level of PCB in the sediments of this site.

Table 1 Levels of PCBs (ng/g dry wt), percentage of organic carbon (OC) and percentage of finer grain size fractions (% <63 μm) in surface sediments of the Ghar El Melh lagoon

Chlorinated congener group	Site											
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
<i>Bi-</i>												
8	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x
<i>Tri-</i>												
18	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x
28	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x
<i>Tetra</i>												
52	<x	<x	<x	<x	<x	0.480	<x	<x	<x	<x	<x	<x
44	<x	1.206	<x	<x	<x	0.491	<x	<x	<x	<x	0.173	<x
66	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x
77	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x
<i>Penta-</i>												
101	<x	<x	0.453	<x	<x	0.733	<x	<x	0.595	0.631	<x	<x
118	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x
105	<x	<x	<x	<x	<x	0.296	<x	<x	0.278	<x	0.564	0.498
126	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x
<i>Hexa-</i>												
153	<x	<x	1.656	<x	<x	0.636	0.454	<x	<x	<x	0.239	0.258
138	<x	<x	0.905	0.282	<x	<x	<x	<x	<x	<x	<x	<x
128	<x	<x	0.047	<x	<x	0.014	<x	<x	<x	<x	0.034	0.246
<i>Hepta-</i>												
187	<x	<x	0.140	<x	<x	0.078	<x	<x	<x	<x	<x	<x
180	<x	<x	0.114	0.136	<x	0.159	<x	<x	<x	<x	0.115	0.026
170	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x
<i>Octa-</i>												
195	<x	<x	<x	0.019	<x	<x	<x	<x	<x	0.149	<x	<x
<i>Nona-</i>												
206	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x	<x
<i>Deca-</i>												
209	<x	<x	<x	0.335	<x	<x	<x	0.210	<x	<x	<x	<x
$\sum$ PCB	<x	1.206	3.987	0.772	<x	2.939	0.454	0.458	1.225	1.190	1.125	1.954
%OC	3.10	2.74	2.36	2.01	4.78	3.10	2.35	3.37	3.31	2.74	2.23	3.12
% <63 μm	98.90	65.40	5.30	98.10	95.40	79.10	87.70	68.60	94.20	91.30	92.50	96.70

x IDL value

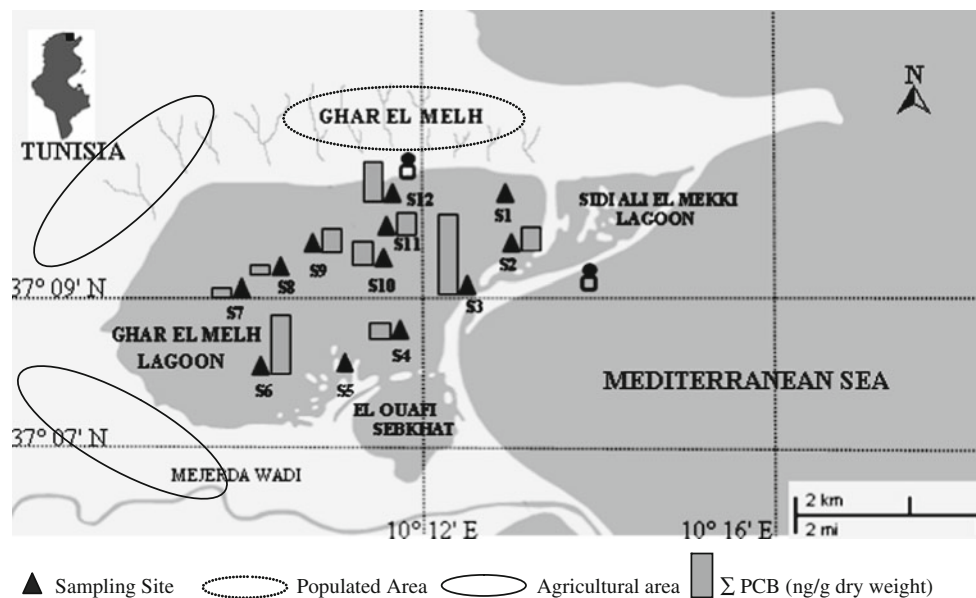


Fig. 2 Spatial distribution of Σ PCB in surface sediment from Ghar El Melh lagoon

Stations S2, S9, S10, S11 and S12 were classified as fairly contaminated with total PCB concentrations ranging from 1.125 to 1.954 ng/g. Stations S11 and S12 were located in area where pollution is affected by fishing harbour associated with artisanal fishing, such as small boats maintenance and painting. Stations S9 and S10 were near Ghar El Melh city, where there are several local wastewater discharges.

Stations S4, S7 and S8 were classified as weakly contaminated. S7 and S8 are near the Ghar El Melh city where the environment is affected by agriculture inputs and several municipal waste water discharges. PCBs were not detected in sediment samples collected from the sites of S1 and S5.

The results of individual PCB congeners showed that greatest number of congeners was found at site S6 with nine congeners and the lowest at sites S2 and S7 with one congener (Table 1). Congeners PCB-8, PCB-18, PCB-66 + 77, PCB-118 + 126, PCB-170 and PCB-206 were not detected in any station. Tetra chlorinated biphenyls represented by PCB-52 and PCB-44 were detected only in the sediments collected at locations S2, S3 and S6.

The percentage compositions of low chlorinated congeners (di-, tri- and tetra-PCBs), mid-chlorinated congeners (penta-, hexa- and hepta-PCBs) and high-chlorinated congeners (octa-, nona-, and deca-PCBs) to the total PCB concentrations are given in Fig. 3. Sediment collected at locations S4, S6, S7, S8, S9, S10 and S12 contained penta-, hepta-, octa-, and deca-PCB. The highest concentration of the individual congeners was detected in site S2 for PCB 44. For the lower chlorinated congeners, PCB 52, and PCB 44 were the most abundant in superficial sediments.

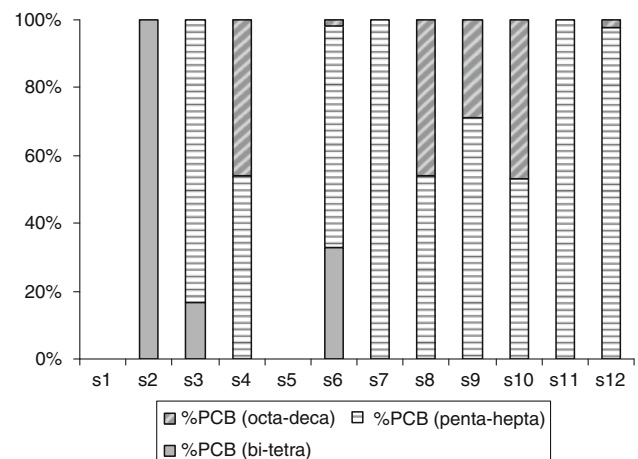


Fig. 3 Relative contribution of low-, mid- and high chlorinated PCB congeners to the Σ PCB in Ghar El Melh lagoon

Polychlorinated congeners contribution according to the degree of chlorination to the observed total PCB concentrations, revealed that tetrachlorobiphenyls, pentachlorobiphenyls, hexachlorobiphenyls, heptachlorobiphenyls, octachlorobiphenyls and decachlorobiphenyls accounted for 16%, 25%, 24%, 4%, 2%, and 13% respectively. The variation of PCB congeners may be attributed to sedimentary characteristics such as TOC contents and the fraction of pelite.

As regards the results obtained for dioxin-like PCBs (77, 126, 105 and 118), the concentrations for the PCB 105 vary from 0.278 to 0.564 ng/g and PCB 77, PCB 126, PCB 118 were not detected in all sediment samples.

Table 2 shows comparisons with other international sites. These comparisons demonstrate that levels of PCBs

Table 2 Comparison of sediment PCB concentrations (ng/g dry wt) measured in this study with those in other countries

Area	PCBs (ngg ⁻¹)	References
Coast of France	29–181	Pierard et al. (1996)
Italian coast	0.6–3200	Picer (2000)
Alexandria Harbour, Egypt	0.9–1210	Barakat et al. (2002)
Venice lagoon, Italy	4.05–239.15	Moret et al. (2001)
Yeongil Bay, Korea	2.85–26.5	Chul-Hwan Koh et al. (2006)
Bizerte lagoon, Tunisia	0.89–6.63	Derouiche et al. (2004)
Ghar El Melh lagoon, Tunisia	0.454–3.987	This study

in surface sediments in this study were significantly lower compared to the other Mediterranean sediments, such as Alexandria Harbour, Egypt (Barakat et al. 2002). Levels of PCBs in surface sediments in this study were lower than sediments collected from the Italian coast (Picer 2000). The concentrations of total PCBs in Ghar El Melh lagoon are generally lower compared to Venice lagoon (Moret et al. 2001). The contamination level was similar to Bizerte lagoon (Derouiche et al. 2004) and higher than Vistula lagoon (Sapota 1997).

Sediment chemistry data can be evaluated to identify the potential hazards on aquatic organisms by using Sediment Quality Guidelines (SQGs). Effect range low (ERL) and effect range median (ERM) guidelines for PCBs concentrations in sediments (Long et al. 1995, 1998) can be used to assess the potential hazard to biota. ERLs and ERMs corresponded respectively to the 10th and 50th percentiles of chemical concentrations associated with adverse biological effects in a large database of matching chemical and biological data.

Concentrations equal to or above the ERL, but below the ERM, represent a probability range within which effects would occasionally occur. The concentrations equal to or higher than the ERM value represent a probability range within which effects would frequently occur (Long et al. 1995). The measured concentrations of PCBs were compared with ERL (22.7 ng/g) and ERM (180 ng/g) (Long et al. 1998). The 12 surficial samples we collected did not exceed the ERL and the ERM guidelines. Thus concentrations of PCBs found in this study are not expected to be a threat to benthic marine organisms.

Many important factors, such as organic carbon content, and particle size can control the PCBs levels in the sediments (Karickhoff et al. 1979; Pierard et al. 1996). Organic carbon contents ranged from 2.0% to 4.78% in the study area (Table 1). Organic matter contents of sediments appeared especially high (>3% of dry weight) in some locations (S1, S6, S8, S9 and S12). These stations are generally located in the extension of urban agglomeration. However, the highest concentration (4.78%) was recorded in station S5. This station is adjacent to El Ouafi Sebkh, whereas Organic carbon contents are relatively low in the eastern part of the lagoon.

whereas Organic carbon contents are relatively low in the eastern part of the lagoon.

The pelite (fraction of the sediment having a grain size <63 µm (silt + clay)) is given in (Table 1). The samples from Ghar El Melh lagoon show large variations in sediments type, from very coarse to very fine grained. Except station S3, all sampled sediments had a predominantly mud-sand composition and after grain-size analysis, the mainly part is composed of particles below 63 µm. The station S3 is located in an area characterised by sandy sediments. This later station is localised near the old communication between this lagoon and the Mediterranean Sea.

Fine grain particles in sediment usually act as effective collectors and carriers of micropollutants from the water column to the sediments and thus elevate concentration of micropollutants in sediment. In Ghar El Melh lagoon, 55% to 65% of the sediment by dry weight was represented by fine particles diameter 40 µm or less (SCET 1999). The abundance of fine particles were assumed to be due to anthropogenic input associated with erosion of upstream agricultural areas and setting out in the lagoon where water currents are generally low.

In the present study the regression analysis was completed to investigate the relationship between the concentration of $\sum$ PCBs and the percentage of organic matter and fine fraction. The linear regressions between these parameters show no significant correlation of $\sum$ 20 PCBs with organic carbon content ($r^2 = 0.0992$) or silt-clay content ($r^2 = 0.0006$). Mostafa et al. 2003 demonstrated similar results of no significant correlation for sediments from the western harbour of Alexandria.

These results indicate that the observed distribution of PCBs was not governed by sedimentary characteristics such as OC contents and the fraction of pelite (grain size less than 63µm), but, it might be due to the localised sources inputs (industrial or urban).

Analyses of twelve surface sediment samples from the Ghar El Melh lagoon showed PCB levels ranging from not detected to 3.940 ng/g dry weight, with a mean value of 1.275 ng/g dry weight. Penta-PCBs and hepta-PCBs were

predominant in the sediments of the Ghar El Melh lagoon. PCBs in the sediment seem to have originated mostly from runoff from wastewater discharges and urbanized areas. Compared to PCB concentrations reported in sediments from other parts of the world, Ghar El Melh lagoon can be considered low to moderately contaminated. The PCBs levels in our sediment samples do not exceed ERM and ERL values. Adverse effect to benthic communities is not expected at the levels of PCBs contamination observed from this lagoon.

No significant correlation was found between the total PCB concentrations and organic carbon content suggesting that sediment organic carbon content did not control the PCBs levels in the sediments.

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