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Polychlorinated Biphenyls in Sediments from Bizerte Lagoon, Tunisia

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Polychlorinated biphenyls (PCB) are a class of synthetic organic chemicals that have biphenyl nucleus with up to ten chlorine atoms; 209 combinations are possible. 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 (Maruya and Lee, 1998). Benthic organisms in a lower trophic level may be exposed by these hydrophobic compounds in contaminated sediments and then transferred to higher trophic levels. PCBs appear to have a potential to biomagnify in both freshwater and marine food webs. Suedel *et al.* (1974) reported that in 87% of reviewed data, PCBs showed biomagnification through the aquatic food chain. Therefore, sediment contamination is of great concern.

In the last few decades, the economic situation along the Mediterranean coastline and lagoons has developed in northern Tunisia. The concentration of many industrial units around these lagoons has increased as well as the population. It's also very common to see in Tunisia that lagoon basins and streams flowing into the lagoons or sea have been used as open-dumping type disposal sites. Bizerte Lagoon is one of such lagoons located in the northern Tunisia. It's extended for about 150 km^2, limited by the outer geographic co-ordinates 37° 08' N, 9° 48' E and 37° 14' N, 9° 56' E and connected to the Mediterranean Sea and Lake Ichkeul by straight channels. The exchanges of winter between the sea and lake control the salinity of the lagoon, which varies between 32.5 and 38.5 partial salinity units (psu). The water temperature is between 10°C during water and 29°C during summer. The Bizerte Lagoon is located in a highly populated area and is subjected to environmental pollution by sewage, industrial and aquaculture waste, agricultural run-off and other human activities.

To our knowledge there are no studies of PCBs in coastal sediments in Bizerte Lagoon. This work is aimed to elucidate the source and distribution of PCBs and to evaluate PCBs contamination in sediments from Bizerte Lagoon.

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MATERIALS AND METHODS

Surface sediment (0–2 cm) samples were collected in December 2001 from the locations shown in Figure 1 and Table 1 using a stainless-steel grab.
Individual sediment samples were well mixed and stored frozen (-20°C) in pre-cleaned glass jars on board the boat used for sampling. In laboratory the samples were air-dried, ground with mortar and pestle, filtered by a sieve of 0.5 mm mesh and stored at 4°C until analysis.

The analytical procedure of PCB in sediments is a modification of the method described by Montone et al (2001). 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 sulfur removal by activated copper, the solution was reduced to 2 ml and added to a column (i.d.=10 mm), slurry packed with 5 g of activated florisil. The extract is 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.

Table 1. Site description of the Bizerte Lagoon stations.

Site Number	Sampling location	Depth (m)	Site Number	Sampling location	Depth (m)
1	37° 15.314' N - 9° 52.004' E	3.1	9	37° 10.569' N - 9° 10.569' E	2.8
2	37° 13.900' N - 9° 49.490' E	3.5	10	37° 13.156' N - 9° 55.207' E	2.9
3	37° 13.000' N - 9° 49.000' E	9.9	11	37° 13.300' N - 9° 51.000' E	4.5
4	37° 12.310' N - 9° 48.067' E	3.2	12	37° 11.000' N - 9° 49.000' E	9.7
5	37° 11.181' N - 9° 47.230' E	2.9	13	37° 11.000' N - 9° 50.000' E	10.3
6	37° 08.348' N - 9° 50.066' E	3.2	14	37° 11.000' N - 9° 52.000' E	9.5
7	37° 08.279' N - 9° 50.095' E	2.8	15	37° 11.000' N - 9° 53.000' E	8.9
8	37° 09.049' N - 9° 53.140' E	2.7	-	-	-

Gas chromatography analysis was carried out on Agilent 6890 Series apparatus equipped with ^{63}Ni electron capture detector (GC-ECD) operated by HP Chemstation software. The column used for analysis was fused silica capillary PTE-5 (30 m x 0.32 mm i.d. x 0.32 μm 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 (constant flow) 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 identification of compounds was deduced from their retention times and quantification was based on peak area measurement as well comparison with responses of a mixed PCB standard reference material (SRM 1493) from the National Institute of Standard and Technology (USA), including PCB8, PCB18,

PCB28, PCB44, PCB52, PCB66, PCB77, PCB101, PCB105, PCB118, PCB126, PCB128, PCB138, PCB153, PCB170, PCB180, PCB187, PCB195, PCB206 and PCB209 in IUPAC number. In this paper, ΣPCB was presented as sum of the concentrations of 20 PCB congeners.

Confirmation of peak identify was obtained for selected extracts using GC with ions trap mass spectrometry (GC-MS) (Varian Saturn III). However, it should be noted that PCB concentration reported in table 2 are based on the assumption that most of the chromatographic peaks contain only one PCB congener. There are several congeners that have the same retention times as the 20 PCB congeners studied, and despite the use of the mass spectrometry, several coeluting congeners can not be quantified separately, i.e., PCB 138 with PCB163 and PCB164; PCB66 with PCB80. Thus, the concentration of these 20 PCBs are likely to be over estimated somewhat. For example, the concentration of PCB 163 generally contributes approximately 20-30% to the concentration of PCB138 (Larsen et al. 1993).

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%.

RESULTS AND DISCUSSION

The analytical results, based on dry sediment weight, are summarized in Table 2. It can be observed that ΣPCB concentrations in the surface sediments in this study ranged from 0.89 to 6.63 ng g^{-1}. Figure 1 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. For the coastal sites, the highest PCB concentrations ranged from 4.39 to 6.63 ng.g^{-1} were detected at the northern part covered sites 1, 2, 3 and 11 and at southwest zone (site 6). The stations 1, 2 and 3 were located in the channel connecting the Lagoon with Mediterranean Sea. This area are high populated and characterized by industrial activities including lead and cement manufacturing. In addition, the station 1 is located near Bizerte Harbour where heavy traffic of tankers and commercial cargo boats are common. PCBs inputs are also probably attributed to the several municipal waste water discharges in the channel and to the incineration landfill close site 2. Site 11 is located near an urban zone (Menzel Abderrahman city) and pollution is affected by a high urban impact with heavy contamination due to the input of untreated sewage. Site 6 is located near Menzel Bourguiba city where an intensive activity is carried out: metallurgic industry, naval construction and tire production. Sediments collected from the other coastal sites are slightly contaminated (ΣPCB ranged from 0.89 to 2.58 ng g^{-1}). These sites are located in agricultural zone and industrial and urban activities are limited. Relatively high PCBs concentrations were also found in samples collected from sites 12, 13, 14 and 15. These stations are located in the

central zone of the lagoon and they are the deepest. The Highest levels of ΣPCB can be related to: sedimentological characteristics; amount of fine-grain sediment; content, distribution, and nature of organic matter; and biological productivity associated with upwelling processes, as well as to the predominant flow and transport of the current system in this area.

Table 2. Concentrations (ng g^{-1}, dry weight) of studied PCBs in surface sediments of the Bizerte Lagoon.

Chlorinated Congener	Site														
Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Bi-															
8	0.23	0.31	0.28	0.50	0.46	0.18	0.33	0.40	0.34	0.36	0.76	0.69	0.86	1.38	0.96
Tri-															
18	-	-	0.19	-	-	-	-	-	-	0.48	0.31	0.37	0.31	0.80	0.45
28	0.15	0.22	0.20	-	0.24	-	-	0.23	0.19	0.22	0.35	0.32	0.31	0.52	0.32
Tetra-															
52	0.11	0.44	0.22	-	0.15	-	0.07	0.09	0.07	0.08	0.32	0.36	0.13	0.10	0.08
44	-	0.21	-	-	-	-	0.06	-	-	0.10	0.11	0.12	0.10	0.10	0.06
66	-	0.10	0.36	0.09	-	0.03	-	0.06	-	0.11	0.17	0.20	0.12	0.15	0.07
77	-	-	0.44	-	-	-	-	-	-	0.41	0.29	0.99	0.18	0.26	0.09
Penta-															
101	0.32	0.64	0.31	-	0.15	0.19	0.06	0.07	-	0.07	0.25	0.23	0.37	0.11	-
118	-	0.54	0.38	0.26	0.09	0.09	-	-	-	0.17	0.17	0.27	0.16	0.12	0.07
105	0.15	0.23	0.15	0.15	0.08	0.07	0.02	-	-	-	0.06	0.08	-	0.08	-
126	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hexa-															
153	0.80	0.73	0.91	0.09	0.40	1.09	0.23	0.10	0.08	0.10	0.51	0.76	0.62	0.37	0.34
138	0.95	0.85	0.72	-	0.38	1.01	0.19	0.08	0.07	-	0.40	0.58	0.40	0.32	0.25
128	0.17	0.29	0.08	-	-	0.18	0.03	-	-	-	0.04	0.04	0.04	0.07	0.08
Hepta-															
187	0.22	0.15	0.55	0.11	0.12	0.36	0.07	-	-	0.06	0.22	0.40	0.27	0.22	0.19
180	0.70	0.34	1.18	0.19	0.23	0.94	0.15	-	0.05	0.25	0.41	0.76	0.55	0.27	0.23
170	0.50	0.20	0.44	0.12	0.15	0.57	0.07	-	-	0.06	0.18	0.27	0.16	0.14	0.12
Octa-															
195	0.09	0.09	0.09	-	0.10	-	-	0.09	0.08	-	0.05	0.04	0.03	0.02	0.02
Nona-															
206	-	-	0.03	-	-	-	-	-	-	-	0.01	0.03	0.01	-	-
Deca-															
209	-	-	0.10	-	0.04	0.07	-	-	-	-	0.08	0.10	0.09	0.09	0.07
ΣPCB	4.39	5.34	6.63	1.51	2.58	4.77	1.29	1.12	0.89	2.48	4.68	6.62	4.69	5.13	3.40

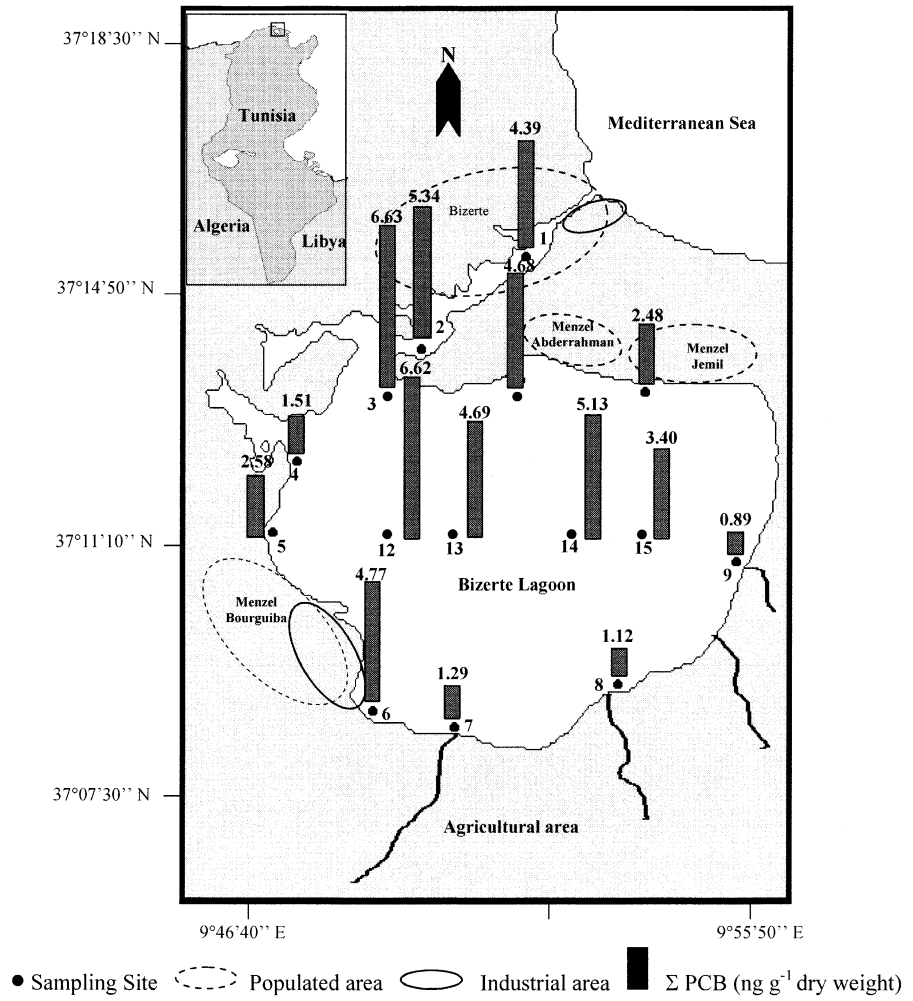

Figure 1. Spatial distribution of ΣPCB in surface sediment from Bizerte Lagoon.

The results of individual PCB congeners showed that greatest number of congeners was found at sites 11 and 12 with 19 and the lowest at sites 9 with 7 (Table 2). 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 Figure 2.

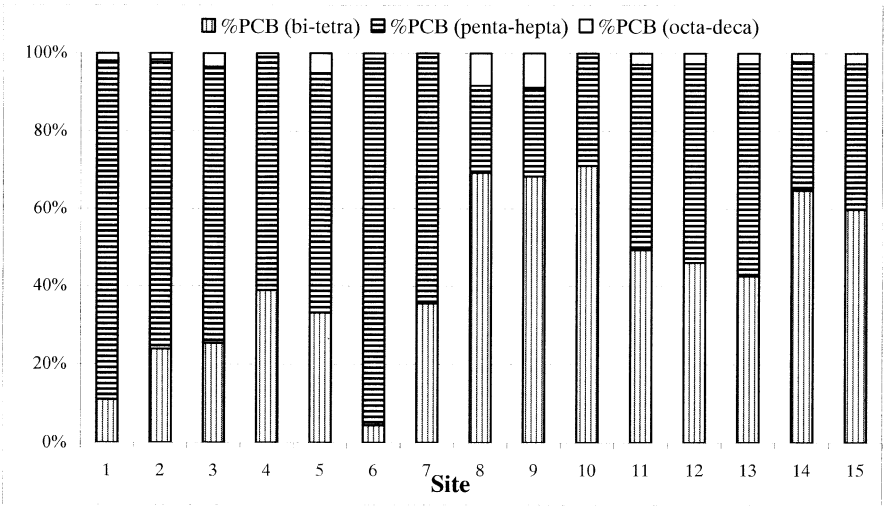

Figure 2. Relative contribution of low-, mid- and high chlorinated PCB congeners to the ΣPCB in Bizerte Lagoon sediments.

Sediment collected at locations 8, 9, 10, 14 and 15 contained great proportions of di-, tri-, and tetra-PCBs, whereas those from locations 1, 2, 3, 4, 5, 6 and 7 had higher proportions of penta-, hexa-, and hepta-PCBs. For the other sites (11, 12 and 13), no significantly difference between the low- and mid-chlorinated PCB congeners. This suggested that sites with the highest PCBs concentrations were characterized by predominance of the mid-chlorinated congeners, whereas the remote sites had higher proportions of the low molecular weight PCBs. That might explain that highly chlorinated PCBs with high K_{ow} are likely to be absorbed to suspended particulate material than low chlorinated PCBs. These materials then probably settle onto the bottom sediment near the source area. The more water soluble low chlorinated PCBs are probably transported a further distance from the source than the highly chlorinated PCBs.

Amongst the PCBs studied, the low-chlorinated congeners were dominant due to the prevalence of congeners 8, 28 and 52. The highest concentration of the individual congeners was detected in site 14 for PCB 8. However, it should be noted that general predominance of mid-chlorinated congeners might result from the stronger dominance of the PCB153, 180 and 138 then 187 and 170. The concentrations of dominant PCB congeners vary respectively from <0.04 to 1.09 ng g^{-1} (Table 2). For the high-chlorinated congeners, PCB195, 206 and 209, are the least abundant with recorded concentrations are lower than 0.1 ng g^{-1}. Although the observed trends in PCB congeners composition were similar in some sediment sample (i.e. between site 12 and 13 and between site 14 and 15). The distribution patterns of PCB congeners are, in general, different among the sediments of this study area, which may indicate different input sources and the establishment of a correlation between the congener profiles and the sources is

difficult, especially when the distance between the source and the sampling site is large. In addition the usage of PCB in Tunisia is not well established, but the use of PCBs in transformers, electrical, and other industries is common.

As regards the results obtained for dioxin-like PCBs (77, 126, 105 and 118) the concentrations for the PCB 77, 105 and 118 vary from < 0.02 ng g^{-1} to 0.99 ng g^{-1} and only PCB126 is not detected for all sediment samples. Moreover, in the lower contaminated site (8 and 9) all the studied dioxin like PCBs were not found. The ratios between these levels and those of the total PCBs were dissimilar in all the locations studied; the dioxin-like PCBs accounted for 0-23% of the total PCBs in these samples.

Table 3. PCB concentration in sediments selected literature data

Area	PCBs (ng g^{-1})	References
Coast of France	29 - 181	Piérard et al. (1996)
Italian coast	0.6 - 3200	Picer (2000)
Bosphorus, Black Sea, Turkey	0.4 - 4.4	Fillmann et al. (2002)
Xiamen Harbour, China	0.05 - 7.2	Hong et al. (1995)
Alexandria Harbour, Egypt	0.9 - 1210	Barakat et al. (2002)
Catalonian coast, Spain	1.1 - 311	Eljarrat et al. (2001)
Venice Lagoon, Italy	4.05 - 239.15	Moret et al. (2001)
Mar Chiquita Lagoon, Argentina	1 - 3	Menone et al. (2000)
Vistula Lagoon, Baltic	0.1 - 0.99	Sapota (1997)
Tongaputa Lagoon, Australia	0.85 - 5.33	Harrison et al. (1996)
Szczecin Lagoon, Baltic	10 - 150	Kowalewska et al (2003)
Bizerte Lagoon, Tunisia	0.89 - 6.63	This study

The comparison of ΣPCB concentrations from various regions was shown in Table 3. Levels of PCBs in surface sediments in this study were lower than in any other sediment from Mediterranean coastal areas including Alexandria harbour, Italian and Catalonian coasts. The residues of PCBs in Bizerte Lagoon were similar to those of other area in the world such as Bosphorus and Xiamen Harbour. However, the concentrations of total PCB in Bizerte Lagoon are generally lower compared to other lagoons over the world include Szczecin and Venice. The contamination level was similar to the Tongaputa and Mar Chiquita lagoons and one to six order of magnitude higher than Vistuela lagoon.

In order to determine the sources of the observed contaminants, intense localized sampling and analysis of effluents and runoff patterns would be needed. To determine sediments quality, bioassays of sediments at suspected sites should be conducted to directly assess the potential for biological impacts.

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