

## Distribution of polycyclic aromatic hydrocarbons in sediments from Bizerte lagoon, Tunisia

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Introduction Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the aquatic environment. This stems from the fact that they form during incomplete combustion of organic matter and consequently have numerous sources. Sources of anthropogenic combustion include combustion of fossil fuels, waste incineration and production of coke, carbon black, coal tar pitch, asphalt and petroleum cracking<sup>1</sup>. Apart from combustion processes, another common anthropogenic source of PAHs is spillage of fossil fuels including unrefined (crude oil) and refined products (e.g. petrol). PAHs also stem from natural combustion sources such as forest fires, and certain compounds (perylene and retene) are thought to be produced diagenetically<sup>2</sup>. The occurrence and fate of polycyclic aromatic hydrocarbons and their derivatives in the environment attract the public concern because some of these compounds are known to be highly mutagenic and carcinogenic<sup>3</sup>. As a case study, we have chosen an area of highly environmental interest-Bizerte lagoon. The Bizerte lagoon is located in the northernmost part of Tunisia, between latitudes N°37 08' and N° 37 16' and consists of a depression having a surface area of about 150 km<sup>2</sup> and maximum depth of 12 m. This lagoon is known for its geo-strategic position since it links the Mediterranean Sea to an internal lake (Ichkeul), which is classified as a national park and world heritage. Since many decades, the lagoon is known as a fishery and aquaculture park related to the presence of three mytiliculture sectors especially Menzel Jemil park which is the more productive site. Since many years, the lagoon's banks have been subjected to both urbanization and industrialization. Manufacturing facilities such as iron and steel complex, the naval construction and tyre production; urban wastewater and open-dumping-type municipal or industrial solid waste landfills scattered around the lagoon could have led to the ecological perturbation to this fragile environment. The purpose of this study is to evaluate the levels of 16 PAHs nominated by the US Environmental Protection Agency (USEPA) as priority pollutants. Materials and Methods Sediment samples were collected in December 2001 at 10 sites in the Bizerte Lagoon (Figure), using a Van Veen grab. An aliquot (500 g) of the top sediment sample was placed in an aluminum container and frozen on dry ice, then transferred to the laboratory with no exposure to light. In the laboratory, samples were defrosted and dried, then the sediments were passed through a stainless steel sieve (0.5mm mesh). The analytical procedure used for PAHs was a modification of the method described by Kelly<sup>4</sup>. Briefly, 20g of dried sediment was extracted using alkaline saponification with KOH/MeOH (2N, 100ml). Digests were filtered and extracted with n-hexane, and dried over previously roasted Na<sub>2</sub>SO<sub>4</sub>. After sulphur removal by activated copper, the solution was reduced to 2ml and added to a column (i.d. = 10mm), slurry packed with 2g of activated silica gel 60, then eluted with a sequence of 15ml hexane (fraction 1 which was discarded) and 30ml hexane: dichloromethane (9:1; fraction 2) which contained the PAHs. The eluate was concentrated to 0.5ml in a micro-Kuderna-Danish evaporator under a gentle stream of nitrogen. Gas chromatography (GC) analysis was carried out using an Agilent 6890 Series apparatus equipped with a HP1 fused silica column (30m length 0.32 mm i.d., 0.25 µm film thickness) and flame ionisation detector (FID). The oven temperature was held at 50°C for 1min, then programmed at 20°C/min to 150°C and then at 8°C/min to 280°C and held at 280°C for 15 min. The injector was maintained at 280°C and the detector at 300°C. Helium was used as the carrier gas. PAHs were identified and quantified by comparison with known standards injected under the same conditions. Certified standard reference marine sediment (EC-7, National Water Research Institute, Canada) was used in the evaluation of the analytical method. The mean recovery of certified PAHs in the extract was 86%. The following compounds were included in this study: naphthalene (Naph), acenaphthylene (Act), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Ft), pyrene (Py), benzo[a]anthracene (B[a]an), chrysene (Chy), benzo[k]fluoranthene (B[k]ft), benzo[b]fluoranthene (B[b]ft), benzo[a]pyrene (B[a]py), indeno[1,2,3-cd]pyrene (Ind), dibenzo[a,h]anthracene (D[a,h]an) and benzo[ghi]perylene (B[ghi]pe). Figure: Geographic setting and location of sampling sites. Dashed circles are the areas of populated zones and solid circles are of industrial zones Results and Discussion The table shows quantitative PAH concentrations (dry weight basis) obtained at each station for each individual PAH. Total PAHs in sediments from all stations ranged from 83.3 to 447.08 ngg<sup>-1</sup> dry wt with a mean value of 218 ngg<sup>-1</sup> dry wt. Acenaphthylene, fluorene and benzo[ghi]perylene are found only in station 8, while phenanthrene, acenaphthene and anthracene are detected in sediments of all the stations. The other PAHs were found in at least two stations. For most of the stations, more than 70% of the total PAH concentrations were represented by PAHs with three and four fused aromatic rings. The stations showing the highest total concentrations of PAHs were numbers 8 and 9 with values of 447 ngg<sup>-1</sup> dry wt and 396 ngg<sup>-1</sup> dry wt respectively. These stations were located near Menzel Bourguiba city, where intensive industrial activity is carried out, including the metallurgic industry, naval construction and tyre production. In addition, there are several local wastewater discharges in this

area. The sediments of stations 1 and 2 were classified as fairly contaminated with total PAH concentrations of 294 ngg-1 dry wt and 234 ngg-1 dry wt respectively. Station 1 is localised in a channel near Bizerte Harbour. PAH inputs in this area are most likely related to the intensive traffic of boats and industrial activities. Station 2 is near a base of the Tunisian Military Marine and a solid waste landfill. In the other stations the levels ranged from 83.3 ngg-1 dry wt to 208 ngg-1 dry wt, with a mean value of 136 ngg-1 dry wt. The highest concentration of 208 ngg-1 dry wt was found at station 6, located near the mouth of Gharek Wadi where pollution is affected by agricultural inputs.

Table: Levels of PAHs\* (ng g-1 dry wt) in coastal superficial sediments of Bizerte Lagoon Stations 1 2 3 4 5 6 7 8 9 10

Station	Naph	Ac	Fl	Py	B(a)an	B(a)py	B(k)ft	B(b)ft	Chy	D(a,h)an	Ind	Bz	Ben	Flu	Ph	Per	Di	Ac	Fl	Py	B(a)an	B(a)py	B(k)ft	B(b)ft	Chy	D(a,h)an	Ind	Bz	Ben	Flu	Ph	Per	Di	Tot PAHs																																																																																																																					
1	5.42	6.69	12.82	Nd	Nd	Nd	3.15	10.02	3.44	3.26	Ace	0.28	0.29	0.44	0.27	4.45	1.15	0.58	0.24	0.88	0.89	Phe	30.85	13.08	27.19	13.93	4.99	17.3	11.56	54.64	27.1	26.61	An	2.8	1.75	6.4	3.49	8.43	16.58	6.07	30.68	13.72	7.72	Ft	44.2	26.37	17.34	11.23	54.04	61.25	Nd	45.86	70.09	Nd	Py	91.99	26.89	9.51	14.1	33.24	49.74	Nd	176.06	33.7	21.7	B(a)an	38.47	Nd	Nd	Nd	Nd	Nd	33.04	Nd	Nd	Chy	27.8	106.49	Nd	72.78	Nd	Nd	Nd	Nd	140.94	Nd	B(k)ft	32.33	48.77	34.8	Nd	48.83	56.39	Nd	Nd	60.73	Nd	B(b)ft	Nd	4.16	Nd	Nd	Nd	5.41	Nd	Nd	8.72	Nd	B(a)py	20.18	Nd	18.96	Nd	Nd	Nd	35.54	36.67	39.56	Ind	Nd	Nd	Nd	Nd	Nd	61.94	42.31	Nd	Nd	D(a,h)an	Nd	Nd	13.61	Nd	15.02	Nd	Nd	3.11	Nd	Nd	Tot PAHs	294.32	234.49	141.07	115.8	169	207.82	83.3	447.08	395.99	99.74	Nd: not determined (below detectable limit)

\* Act, Fl and B[ghi]pe were detected only at station 8 with values 1.45, 7.8 and 6.44 ng g-1 dry wt respectively

Our results were compared to certain already published studies in the Mediterranean. These values are slightly higher than those measured in Majorca (Western Mediterranean) where total PAHs ( $\Sigma 18$ PAHs) ranged from 0.3 to 100 ngg-1 dry wt<sup>5</sup>. Gogou et al.<sup>6</sup> have reported total values for PAHs ( $\Sigma 28$ PAHs) in the Cretan Sea between 14.6 and 185.5 ngg-1 while concentrations from 48.1 to 86.5 ngg-1 ( $\Sigma 14$  PAHs) have been reported for coastal areas in the northwest Mediterranean Sea<sup>7</sup>. However, the values of total PAHs in sediments from the Bizerte lagoon appear particularly low if compared with data reported for Porto Torres Harbor (Southern Sardinia, Italy) ( $\Sigma 16$ PAHs ranged from 70 to 1210 ngg-1)<sup>8</sup>

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