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FULL LENGTH ARTICLE

A new record for aliphatic and polycyclic aromatic hydrocarbon accumulation in the surficial sediments of El Mex Bay, Alexandria, Egypt after 19 years from the first one

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KEYWORDS

Surficial sediments; *n*-alkanes; PAHs; Diagnostic ratios of PAHs sources Abstract Petroleum hydrocarbons were identified and quantified in the surficial sediments of El-Mex Bay, Alexandria during 2013 and 2014. The results were compared with a previous study in 1995. Contamination by aliphatic hydrocarbons in the sediments of the Bay was found to be magnified by about 3 folds from the former study. It was found that the two *n*-alkanes C21 and C32 were the highly concentrated aliphatic among all the other alkanes with mean concentrations approaching 300 ng g⁻¹ dry wt., while PAHs in the surficial sediments appeared to be clearly magnified to about 17-fold. The total PAH concentrations at the different stations in the Bay ranged between 1123 and 8654 ng g⁻¹ dry wt. Various PAH concentration diagnostic ratios: LMW/ HMW, Fluo/Py, Fluo/[Fluo + Py] and the isomeric ratios BbF/BaP against BkF/BaP were applied to identify the source of pollution by PAHs in the sediments of the Bay. All the above mentioned ratios were indicating pyrolytic origin of PAHs in the sediments with very weak evidence of petrogenic sources at few sites. Natural *n*-Alkanes Ratio (NAR) was used to assess the origin of aliphatic hydrocarbons.

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Introduction

Petroleum hydrocarbons in the sea are considered among the most dangerous organic compounds particularly aromatics. Hydrocarbons enter the sea at high and low levels of concentrations as a result of their sources. Such sources include minor

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spills from offshore oil production and accidents of oil tankers which may release huge quantities on minor spills from oil into the sea. Meanwhile, other sources of hydrocarbon contamination that affect the coastal areas during the whole year include industrial discharge, ballasting and deballasting operations of oil tankers, effluents of sewage outfall and atmospheric rain. The last sources bring to the coastal areas moderately lower levels of contamination in comparison with the former one (Martínez-Lladó et al., 2007). The last sink of petroleum hydrocarbon pollution is sufficial coastal sediments, which are considered the main nursing area of fisheries and their

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contributing species of vertebrate and invertebrate animals. It is found that the annual water discharged through El-Mex pump station into the Mediterranean Sea is $2547.7 \times 10^6 \text{ m}^3/$ year (Abdallah, 2007). EL-Max Bay is a semi closed marine basin suffers from the discharges of different sources. Its waters are contaminated with many agricultural wastes, industrial wastes and some oil contaminates (Shreadah et al., 2014, 2015). The free connection between the bay and the Western Harbor of Alexandria facilitates the passage of petroleum contaminants arising from ships into the bay. The newly established Dekheila harbor and the discharge of wastes of many petroleum companies of the petroleum complex through Wadi Al-Kamar drain provide other sources of oil pollution to the Bay. Aliphatic and polycyclic aromatic hydrocarbons were detected and identified in the surface sediment samples of the Bay in the year 1995 (El-Deeb, 1998).

This paper aimed to study the accumulation of hydrocarbons for the last period (about 19 years), and their contaminations in El Mex Bay sediments.

Materials and methods

Surface sediment (0–3 cm) samples were collected using a stainless steel grab sampler from 8 sites during Two trips in 2013 and 2014 (Fig. 1) and stored in pre-cleaned aluminum containers frozen at -20 °C for analysis. Subsamples of sediments were air dried and subjected to grain size analysis according to Folk (1974), total organic carbon (%TOC) using



Figure 1 Sampling stations.

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method described by Gaudette et al. (1974) and total carbonates (CaCO₃) were estimated as described by Molnia (1974).

Extraction of sediment samples

Following freeze-drying samples were sieved through vibration stacked stainless steel sieves with mesh sizes from 250 μ m to 1000 μ m and homogenized prior to extract according to (UNEP/IOC/IAEA, 1992). Samples were Soxhlet extracted for 8 h with 250 ml of hexane: methylene chloride (1:1, v/v). The extracts were concentrated to a few milliliters in a rotary evaporator at low temperature (35 °C) followed by concentration with N₂ gas stream down to a volume 1 ml.

Clean-up and fractionation were performed by passing the extract through a silica/alumina column in which the silica and alumina were activated first at 200 °C for 4 h and partially deactivated with 5% water. The chromatography column was prepared by slurry packing 10 ml of silica, then 10 ml of alumina and finally 1 g of anhydrous sodium sulfate. Elution was performed using 40 ml of hexane to yield the first fraction (aliphatic hydrocarbon), then 40 ml of hexane/methylene chloride (9:1), followed by 20 ml of hexane/methylene chloride (1:1) (Which combined contain PAHs). Copper powder was added to the obtained fractions and the change of the copper color from brassy red into black was taken as an indication of sulfur removal that interfere in GC-MS analysis (Sundberg et al., 2005). Finally, eluted samples were concentrated with N₂ gas stream down to a volume 0.2 ml.

Instrumental analysis

All samples were analyzed using Gas Chromatograph-Mass Spectrometer; Trace-Ultra coupled to DSO-II MS (thermo electron S.P.A.) equipped with splitless injector and a fused silica capillary column; Thermo TR-35 MS (30 m, 0.25 mm and 0.25 µm) with 35% phenyl polyphenylenesiloxane. Helium was used as carrier gas at 1.5 ml/min. The oven temperature program was 60 °C (1 min) ramped at 8 °C/min to 100 °C, held for 1 min then ramped at 5 °C/min to 300 °C maintaining about 20 min. The injection and the transfer line temperature were maintained at 280 and 300 °C, respectively. The response factor of individual PAH compounds to the internal standard was measured and calculated at least three times at the beginning, in the middle and at the end for each batch of GC injections (15 samples). Identification and quantification of 15 out of 16 EPA-PAH compounds were based on matching their retention times with a mixture of PAH standard,

St. no.	Grain size a	nalysis (%)		Sediment type	CaCO ₃ (%)	TOC (%)
	Sand	Silt	Clay			
1	77.50	10	12.5	Fine sand	55.87	0.22
2	80.20	11.27	8.53	Fine sand	38.87	1.39
3	47.00	28.73	24.27	Medium silt	40.12	0.09
4	7.00	46.53	46.47	Fine silt	58.75	0.27
5	80.27	11.53	8.2	Fine sand	44.75	1.17
6	83.86	10.96	5.18	Fine sand	55.62	0.78
7	79.00	12.8	8.2	Fine sand	38.12	1.42
8	100.0	0	0	Coarse sand	58.62	0.22

Table 2 M	ean valı	nes of n	-alkane	concen	trations	$(ng g^{-1})$	dry we	ight of H	El Mex I	Bay sed	iments.										
Compound Station	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28	C29	C30	C31	C32	$\sum n$ -alkane	NAR
1	103	29	108	72	88	149	222	581	366	57	80	130	78	22	28	60	18	279	240	2710	0.106
2	39	169	109	9	57	160	100	324	26	22	18	15	34	312	28	45	58	47	36	1605	0.51
3	0	106	16	9	99	102	40	33	134	38	2	29	56	0	41	28	192	69	0	1033	-0.217
4	110	209	151	38	103	110	152	314	34	12	13	33	6	10	30	45	53	11	1176	2613	-0.466
5	65	85	211	50	124	341	67	113	209	53	47	64	12	22	19	24	15	20	50	1591	0.206
9	30	18	14	6	10	39	21	56	28	4	12	3	18	47	4	80	90	8	34	525	0.068
7	140	68	214	39	142	83	234	307	52	78	15	65	7	141	43	160	76	197	667	2728	-0.03
8	44	49	14	4	45	141	93	595	16	24	e	13	18	88	1365	60	43	540	105	3260	-0.059
\sum aliphatic	531	733	912	224	635	1125	929	2323	865	288	190	352	232	642	1558	502	545	1171	2308	16,065	
Mean	99	92	114	28	79	141	116	290	108	36	24	44	29	80	195	63	68	146	289	2008	

Quality assurance/quality control

Appropriate blanks were analyzed with each set of samples, together with sediment reference material HS-5 (sediments) provided by NRC-IMB of Canada as well as samples spiked with a mixture consisting of 2 μ g each of PAHs. The recovery efficiency ranged from 92% to 96% for HS-5 and 93% to 105% for the spiked samples.

Statistical analysis

All analyses were done using IBM SPSS Statistics 20 and Excel 2010 software for windows.

Results and discussion

Table 1 shows the grain size analysis, $CaCO_3\%$ and TOC% of El-Mex Bay sediments. The texture of these sediments varied between fine silt and coarse sand which is arbitrary facilitates the accumulation of organic contaminants between its grains. The total organic carbon (TOC%) content in El-Mex Bay sediments was generally low. They ranged from 0.09% at station 3 and 1.42% at station 7 with an average value of 0.7%. Values above 1.0% were observed in stations 2, 5 and 7.The Bay receives a heavy load of wastewater both directly from industrial outfalls, El-umum Drain and indirectly from lake Mariut via El-Mex pumping station and EL-umum drain The mean *n*-alkane values (2013 and 2014) and the mean PAHs concentrations (2013 and 2014) at the different stations respectively are represented in Tables 2 and 3.

Figs. 2 and 3 illustrate the distribution of mean *n*-alkanes and the mean PAH profiles. It is clear that the two n-alkanes C21 and C32 are the highly concentrated aliphaties among all other alkanes with mean concentrations approaching 300 ng g^{-1} dry wt. The distribution of *n*-alkanes showed a wide range of the concentration, the mean ranged between 50 and 300 ng g^{-1} dry wt., while some n-alkenes had low levels less than 50 ng g^{-1} (C17, C23,C24 and C26). On the other hand, the range of total aliphatic hydrocarbon concentrations $(\sum C_{14}-C_{32})$ of El-Mex Bay was varying between 525 and 3260 ng g^{-1} dry wt with a mean concentration of 2008 ng g^{-1} dry wt. observed at stations 6 and 8. Thus, it was very clear that the high concentrations of n-alkanes are found at the off shore of the Bay sediments. El-Deeb (1998) recorded total aliphatic hydrocarbon content in the surficial sediments of El-Mex Bay that varied between 200 and 1000 ng g^{-1} dry wt. In the present study, accumulation of aliphatic hydrocarbons in the sediments of the Bay seems magnified by about 3 folds from the previous study. However, total *n*-alkanes are lower than those found in El Mex Bay during 2010 (Abd El-Moneim, 2011) which ranged from 1545 to 9457 ng g^{-1} (dry wt.) with a mean concentration of 4135 ng g^{-1} (dry wt.), while, El-Nemr et al. (2013) reported high concentrations of total aliphatic hydrocarbons in surface sediments varied between 1621 and 9069 ng g^{-1} (dry wt.) at the shore areas close to Alexandria of the Egyptian Mediterranean coast.

The natural *n*-alkanes ratio (NAR) is used to estimate the proportions of natural and petroleum *n*-alkanes. The NAR is defined as follows: (Mille et al., 2007)



Figure 2 Mean concentrations of *n*-alkane in El-Mex Bay sediments (2013–2014).



Figure 3 Mean concentrations of PAHs in El-Mex Bay sediments (2013–2014).

NAR =
$$\frac{\sum n - alk(C_{19-32}) - 2\sum even \ n - alk(C_{20-32})]}{\sum n - alk(C_{19-32})}$$

for petroleum hydrocarbons and crude oils origin the natural n-alkanes ratio (NAR) is close to zero and for higher terrestrial plants or marine plants the NAR is closed to 1. In most cases n-alkanes in the range C₁₉–C₃₃ have petroleum origin.

All stations except station 2 have NAR values around zero (-0.446 to 0.106) which indicate the predominance of petroleum hydrocarbons. NAR of station 2 (In front of El-Umum drain) is 0.51 revealed the existence of a mixture of petroleum and higher plant hydrocarbon origins.

The most frequently occurring PAHs in the sediments are: Chrysene, Acenaphthene, dibenzanthracene and Benzo(a)anthracene, with mean values of 863, 568, 494 and 470 ng g⁻¹ dry wt. respectively. The total PAH concentrations at the different stations in the Bay ranged between 1124 and 8652 ng g⁻¹ dry wt. at stations 3 and 5 consecutively. Ecological risk assessment based on the ERL and ERM (Liu et al., 2009a) reveals that, the total PAHs of sediment samples have a concentrations between ERL and ERM, Table 3, suggesting a limit potential ecological hazards from PAHs in the coastal sediments of El Mex Bay.

In the year 1995 the results of total PAHs content in the El-Mex Bay sediments ranged between 26 and 530 ng g^{-1} dry wt. (El-Deeb, 1998). The present study clarifies that the accumulated PAHs in the sediments of the Bay is clearly magnified to about 17-fold.

Applying the correlation coefficient of total PAHs with both the clay percentage and total organic carbon, the correlations coefficient (r) were 0.004 and 0.396 (at $\rho = 0.05$) for the clay% and TOC%, respectively. Several studies have demonstrated that TOC is a key property influencing PAH concentration in sediments (Li et al., 2012), and sedimentary TOC is a crucial factor for determining the sorption, sequestration, and fate of PAHs. In the present study, there was no significant correlation between the concentrations of PAHs and TOC content (r = 0.396), ruling out the sedimentary TOC as controlling factor in the study region. As a literature review (Table 5), the recorded concentration levels in El-Mex Bay in some studies are smaller than those observed in the present study (Barakat et al., 2011; El-Nemr et al., 2013). The PAHs

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Hydrocarbons accumulation in surficial sediments of El Mex Bay

Table 3 Mean values of PAHs concentrations (ng g^{-1} ; dry wt.) of El Mex Bay sediments.

Compound ^a Station	Naph	Acthy	Ace	Phe	Ant	Fluo	Flue	Pyr	BaA	Chr	BbF	BkF	Bap	Inp	DBA	B (ghi) p	\sum_{Aromatic}
1	160	58	170	196	171	22	120	513	331	409	200	670	341	24	280	422	4087
2	10	67	390	190	51	6	29	346	779	1323	720	9	5	312	365	50	4652
3	0	0	110	0	90	24	6	66	525	33	20	0	2	28	192	28	1124
4	20	392	1440	282	202	66	464	87	417	1201	50	136	35	117	233	85	5227
5	0	77	1220	447	552	202	900	840	327	3134	260	250	186	26	113	118	8652
6	0	63	540	43	44	58	40	50	220	329	30	1	23	12	17	23	1493
7	40	130	580	16	360	55	234	614	388	239	120	261	77	632	2623	367	6736
8	0	53	90	29	117	53	20	24	769	233	100	8	6	102	125	49	1778
∑PAHs	230	840	4540	1203	1587	486	1813	2540	3756	6901	1500	1335	675	1253	3948	1142	33,749
Mean	29	105	568	150	198	61	227	318	470	863	188	167	84	157	494	143	4219
PAHs																	
ERL ^b	160	16	44	240	853	600	190	665	261	384	320	280	430	-	63	430	
ERM ^b	2100	500	640	1500	1100	5100	540	2600	1600	2800	1880	1620	1600	-	260	1600	

^a Naph: Naphthalene, Acthy: Acenaphthylene, Ace: Acenaphthene, Phe: Phenanthrene, Ant: Anthracene, Fluo: Fluoranthene, Flue: Flueare, Pyr: Pyrene, BaA: Benzo(a)anthracene, Chr: Chrysene, BbF: Benzo(b)fluoranthene, BkF: Benzo(k)fluoranthene, Bap: Benzo(a)pyrene, Inp: Indeno(1,2,3cd)pyrene, DBA: Dibenz(a,h)anthracene, B(ghi)p: Benzo(ghi)perylene, PAH: Polycyclic aromatic hydrocarbons, ERL: Effects range low, ERM: Effect range median.

^b Liu et al. (2009a).

Table 4	Five diagnostic ratio	os between individu	al PAHs concentrations.			
St. no.	Phe/Ant	Fluo /Pyr	Fluo/[Pyr + Fluo]	BbF/BaP	BkF/BaP	LMW/HMW
1	1.15	0.04	0.04	0.59	1.96	0.48
2	3.73	0.02	0.02	144.00	1.80	0.19
3	0.00	0.36	0.27	10.00	0.00	0.23
4	1.40	0.76	0.43	1.43	3.89	0.31
5	0.81	0.24	0.19	1.40	1.34	0.50
6	0.98	1.16	0.54	1.30	0.04	0.33
7	0.04	0.09	0.08	1.56	3.39	0.29
8	0.25	2.21	0.69	16.67	1.33	0.18
Average	1.05	0.61	0.28	22.12	1.72	0.31

Table 5	Comparison	of PAI	Is cond	centrations	$(ng g^{-1};$	dry
weight) w	ith that record	ded in p	revious	studies.		

Region	∑PAH	References
El Mex	1123-8654	Present study
El Mex	1020	El-Nemr et al. (2013)
El Mex	925-2010	Barakat et al. (2011)
El Mex	26-530	El-Deeb (1998)
Egyptian Mediterranean	88-6338	El-Nemr et al. (2007)
coast		
Abu Qir Bay	MDL-	Khairy et al. (2009)
	2660	
Red Sea coasts	ND-442	Aly Salem et al.
		(2014)

in present study are also higher than those found in Abu Qir Bay (El-Deeb et al., 2007; Khairy et al., 2009) and that reported in Egyptian Mediterranean Coast by El-Nemr et al. (2007) (88–6338 ng/g). The results of PAHs content in El-Mex Bay sediments were less contaminated than Mediterranean coastal sediments ranging from 100 to 13,000 ng g⁻¹ dry wt. (Raoux, 1991; Raoux and Garrigues, 1993).

The PAH patterns differ according to the emission sources (Benner et al., 1995; Wang et al., 1999) and several PAH concentration diagnostic ratios have been extensively used to identify and quantity the contribution of each source of contamination to specific environmental regions (Bouloubassi et al., 1997; Kavouras et al., 2001). The estimated ratio of PAHs should be used cautiously due to the interaction of physical and biochemical processes which may alter PAH profiles during processes of transport and flux. The fingerprints of PAHs from pyrolytic or petrogenic origin maybe used to differentiate these origins using molecular indices based on ratios of selected isomers of PAHs concentrations (Colombo et al., 1989). Five significant PAH ratios were drawn from the correlation and calculated for the studied samples: Phe/Ant, Fluo/ Py, Fluo/[Fluo + Py], BbF/BaP, BkF/BaP in addition to the less significant ratio of: LMW/HMW = (Ph + Ant + Py + Fluo)/(Ba A + Chry + BbF + BkF + DBA).

To identify the source of pollution by PAHs in surficial sediments of the Bay, the LMW/HMW ratio (sum of the low molecular weight PAH levels versus sum of higher molecular weight concentration) was undertaken as a primary index in the investigation. Muel and Saguen (1985) reported that PAHs of high molecular weight was dominated in mostly pyrolytic

5

Variable	Component			
	PC1	PC2	PC3	PC4
C14	.480	.192	.607	.550
C15	219	.181	119	.737
C16	.294	.640	.505	.332
C17	.844	.389	.162	.261
C18	.376	.576	.552	.354
C19	.247	.888	178	0
C20	.641	0	.579	.424
C21	.459	166	0	.225
C22	.908	.240	177	199
C23	.552	.352	.653	175
C24	.922	.279	106	0
C25	.947	.206	.199	0
C26	.702	330	298	230
C27	196	126	.329	0
C28	275	0	0	131
C29	0	187	.914	0
C30	333	326	0	118
C31	.184	172	.155	176
C32	0	0	.318	.925
Naph	.958	234	0	0
Acthy	0	.139	0	.969
Ace	0	.647	0	.655
Phe	.299	.774	314	.326
Ant	.226	.879	.372	0
Fluo	0	.948	0	0
Flue	.116	.929	0	.259
Pvr	.503	.688	.409	155
BaA	252	0	0	0
Chr	0	.902	201	.103
BbF	0	.151	0	0
BkF	.961	.132	.160	0
Bap	.940	.277		0
Inp	0	0	.907	.167
DBA	0	0	.985	0
Bghip	.819	0	.555	0
TOC	132	.398	.587	124
% of Variance	26.27	21.04	16.53	11.4
Cumulative%	26.27	47.32	63.84	75.24

Fable 6 Varimax-rotated component matrix of El Mex Bay sedin	ments.
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Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.

Rotation converged in 8 iterations.

Values greater than 0.7 (Bold Italic) are significant.

PAHs contaminate, while Berner et al. (1990) reported that PAHs of the low molecular weight predominance as an indication of petrogenic origin. The values of LMW/HMW ratio were lower than 1 (ranged between 0.15 and 0.65 with a mean value of 0.33) indicating pyrolytic origin. Also, during low temperature maturation of organic matter the higher molecular weight PAHs (Benzo anthracene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene and dibenzanthracene) are dominated over the lower molecular pyrolytic, origin of PAHs could be accepted (Garrigues et al., 1993). Most of the site sediments in the study area are characterized by Fluo/Pry values < 1 which is an indication of pyrolytic input ranging between 0.02 and 2.21 (ave. 0.61). The high ratio of Fluo/ Pyr 2.21 noticed at the offshore (station 8) the Bay revealed petrogenic origin which is of very little effect on the origin of PAHs in the Bay sediments.

The ratio of Phen/Ant < 10 was typical of sediments impacted by combustion residues (Unlü and Alpar, 2006). In the present study, Phe/Ant ratio (<10) is recorded in all stations (Table 4). The ratio of Fluo/(Fluo + Pyr) was calculated for all the sampling sites (Table 4) and found to be between 0.02 and 0.69 with an average of 0.28 suggesting combustion of liquid fossil fuel as a major source of PAHs in El-Mex Bay sediments which is in agreement with Tsapakis et al. (2003) who reported that the ratios of Fluo/(Fluo + Pyr) in sediment samples from the Eastern Mediterranean were < 0.50. The low ratios observed at stations 1, 5 and 6 suggest pyrolytic origin of PAHs, as lower molecular weight of PAHs easily undergoes pyrolysis than higher molecular weight aromatics. The relatively high ratios calculated in sediments of stations 4 and 7 (i.e. Western and Dekheila harbors, respectively) may indicate petrogenic sources of PAHs.



Figure 4 Scree plot showing the Eigen values.

Principal component analysis (PAC) of hydrocarbons

Principal component analysis (PCA) was used to distinguish between samples to assess the different origin of AHs and PAHs in the present study Table 6, Figs. 4 and 5. The four factors (PC1, PC2, PC3, PC4) (eigenvalue > 1) with cumulative covariance of 75.24% of the total variance in analysis of AHs of sediments. After the rotation, the first factor (PC1), accounted for 26.27% of the total variance indicating moderate to long chain *n*-alkanes (C17–C26) while, the second factor (PC2) displayed 21.04% of the total variance and had high loading of C19. PC3 representing covariance of 16.53% of the total variance had a high loading of C29. The NAR, PC1, PC2 and PC3 can be used to discriminate the contribution of weathered/fresh hydrocarbons and petrogenic/petrogenicbiogenic hydrocarbons. Furthermore, PCA was also performing on the matrix of the PAHs concentrations in sediment. The first three Varimax rotated components matrix is given in (Table 6). PC1 was responsible for 26.27% of the total variance predominantly indicating 4, 5 and 6 rings PAHs; BkF, Bap and B(ghi)p related to petroleum combustion and refined petroleum products. High loading of naph is also recorded. Most naphthalene is derived from coal tar. PC2 explained 21.07% of the total variance and was dominated by Phe, Ant, Fluo, Flue and Chr related to mix sources of PAHs such as petroleum pollution or incomplete combustion (Sofowote et al., 2008; Liu et al., 2009b; Deng et al., 2013). Finally PC3 indicated 16.53% of the total variance, correlated to PAHs with 5 rings (Inp and DBA) and related to both gas and diesel engine emissions (Vehicular emission sources).



Figure 5 Component plot in rotated space.

Conclusion

Our findings assure the pyrolytic origin of PAHs accumulated with surficial sediments of El Mex Bay. Most of these petroleum hydrocarbon compounds are clearly arising from pyrolysis of petroleum fractions and internal combustion in the engines. The critical situation of the Bay arising from accumulation of the most hazardous PAHs in its sediments to about 17 folds during 19 years reveals that, the area is subjected to

intensive organic pollution. Most locations have concentrations between the ERL and ERM. The current excessive discharge now will result in a more than 17-fold in the following years. Hence there is an urgent need to find applicable management techniques that have the ability to remove or biodegrade the studied pollutants from the wastewater before discharging.

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