

Environmental Assessment of Polyaromatic Hydrocarbons in Sediment along Discharge Basin of Suez Oil Refinery Company, Southwest of the Suez Gulf

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ACCORDING to the IMO declaration, the Gulf area is the most sensitive and oil-polluted area in the world. Sediment samples were collected from five stations at different distances along discharge basin of Suez Oil petroleum Company (SOPC), in 2012-2013 and the concentrations of poly-aromatic hydrocarbons were determined by HPLC analysis. The concentrations of Σ PAHs were higher than the guideline value 4022 ng/g, due to the aromatic outlet to discharge basin. The concentration of PAHs in the sediments ranged between 22333.983 and 73597.864 ng/g. dry weights with 43016.278 ng/g. dry weights as the average concentration was greater than the guideline; thus, the study area is classified highly polluted. Concentration of the most PAH components were above the ER-L, ER-M, TEL and PEL values in all the sampling stations. The PAHs profiles showed that the Σ 2-3&4 rings compounds were the major PAHs detected in discharge basin of SOPC. Characteristic ratios of Ant/ (Ant+ Phe), and Flu/ (Flu + Pyr) indicated that PAHs could originate from petrogenic and pyrolytic sources. Petroleum contamination associated with increased industrial processes beside, continuous discharge of the refinery's effluents related by oily smuggling with water to bottom sediments of the discharge basin, without completely treated or degraded easily through weathering processing, which can have side-effects on the ecosystems and human safety, must be controlled.

Keywords: PAHs, SOPC, Bottom sediment, Pyrogenic, Petrogenic, Mixed pyrogenic and petrogenic, ERL, PEL, IMO and Guideline value.

Suez Oil petroleum Company (SOPC) industry was considered as one of the most important industry all over the world. It has too many benefits for our life, they have lots of adverse impacts⁽¹⁾. One of the most important industries in the middle of Egypt which has been constructed in the vicinity of the northwest of Suez Gulf (Fig. 1) and its products are:(aromatics, chemicals, fuel) assemble

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40% from local consuming: as solar, (local, banker, electrical station), benzene (80, 90, 92), botogas, mazote by different types and characterization, sulfur (liquid and solid types) asphalt (60, 70) as a principal production and propane, asphalt, distilled wax as a secondary production.

Discharge basin of petroleum Suez Company is a semi- enclosed aquatic ecosystem with semidiurnal tide and the tidal current has caused (Fig. 2), Suez Gulf to be wholly affected by the discharged pollutants^(2, 3). According to the IMO (International Maritime organization) declaration, the Gulf area is the most sensitive area in the world and DOE (Department of Environment) has reported, Gulf is the most oil-polluted marine area in the world⁽⁴⁻⁷⁾. Many studies showed that the lipophilic characteristics of poly-aromatic hydrocarbons, their tendency to accumulate in sediments, their low degradation rate and high stability, also their potential to manifest the eco-toxicological activity, the concentration of PAH in sediment is an appropriate index of the status of contaminates in marine environment⁽⁸⁻¹¹⁾ and due to these characteristics, it can adsorb to the suspended particulate matter and accumulate in bottom sediments and it can remain unchanged and toxic for long term; therefore, they can have a long term effect on the structure of the benthic community⁽¹²⁾. There upon, according to the sensitivity of Gulf area, several studies have been performed on various pollutants. In 1996, studies showed that the Iranian coastal area (especially the southern region along the Imam Khomeini port) was contaminated with petroleum hydrocarbons and this area was classified as slightly polluted⁽¹²⁾. In 2004, the Research Institute of the Petroleum Industry showed that the most polluted areas in Musa Bay were located in the vicinity of petrochemical industries and Mahshahr oil export terminal and it showed that Musa bay is more polluted than other Arabic coastal areas, some authors⁽¹³⁻¹⁵⁾ provided important data set on PAH levels in sediments along harbor line, Mumbai, India. Refining of oil is the company's main activity to produce petroleum-derivative products like naphtha, kerosene, gasoline, asphalt, at Al -Nasr OIL Company. The company is one of the companies owned by the Egyptian Public Petroleum Corporation and lies in the most northerly tip of the Gulf of Suez south east of El-zait Harbor, the company discharges oily wastewater of 144,000 m³/day into the Gulf of Suez⁽¹⁶⁾. The levels of PAHs in sediment were several folds higher than the other study reports from various countries. The PAH distribution profile indicated potential source dependence, as the levels were generally higher in the vicinity of known inputs such as oil terminals and ports. There are implications for the quality of seafood from many aquaculture areas destined for human consumption. The findings point to the urgent need to establish a monitoring programmed for persistent organic pollutants such as PAHs, not only in sediment but also in the organisms themselves to ensure that any excess in concentrations over environmental quality standards is rapidly reported and necessary actions are taken. Their presence in Gulf sediments combined with other potentially toxic compounds can result in negative effects, which have yet to be investigated to any great extent.

Materials and Methods

The reagents were all analytical reagent grade or chemically pure. All solvents were redistilled and dried before use by standard procedures⁽¹⁷⁾. All the oils-extracted from surface sediment samples were analyzed according to the standard test method IP318/75⁽¹⁷⁾. The apparatus used was water HPLC 600, Auto Sampler 616 Plus, Dual Absorbance Detector 2487, attached to a computerized system with Millennium 32 Software⁽¹⁸⁾.

Area of study on the Suez Gulf

Suez Gulf to be wholly affected by the discharged pollutants (Fig. 1 & 2). Outlet wastewaters of Suez Oil Petroleum Company are located in area about 2-3 km south west of Suez city and closed to the most important and famous international way. The minimum areas and dimensions for discharge basin as a final design: Number of channel (n) is 2, the maximum width, (B) = 55m. Depth, (d) = 3.5 m. Length, (L) = 148m. Sampling station has been selected to appreciate the direct influence of associated oil activities. Suez Gulf relative to a reference background level represented by the discharge basin of (SOPC)⁽¹⁶⁾.

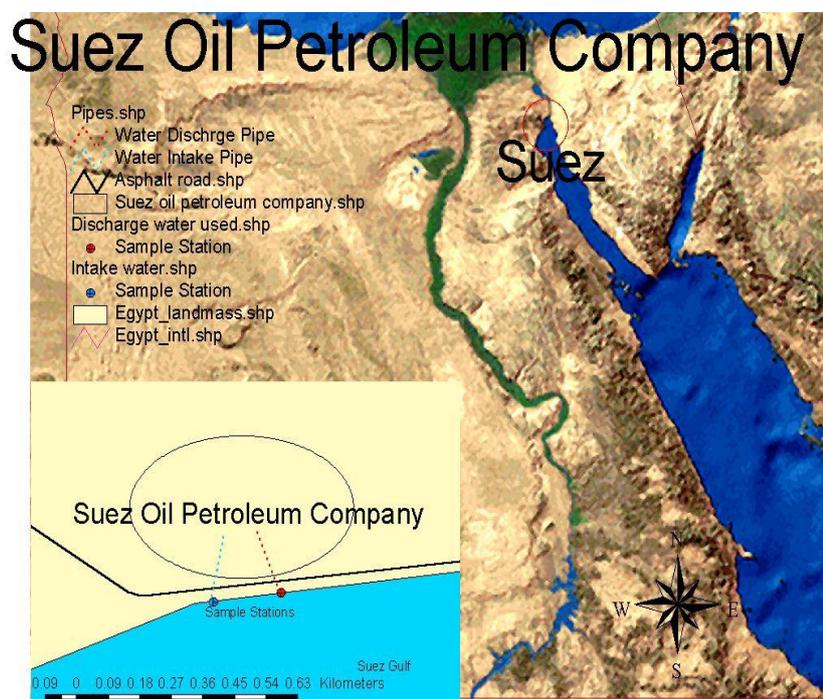


Fig.1. Position of (SOPC) along the Suez Gulf .

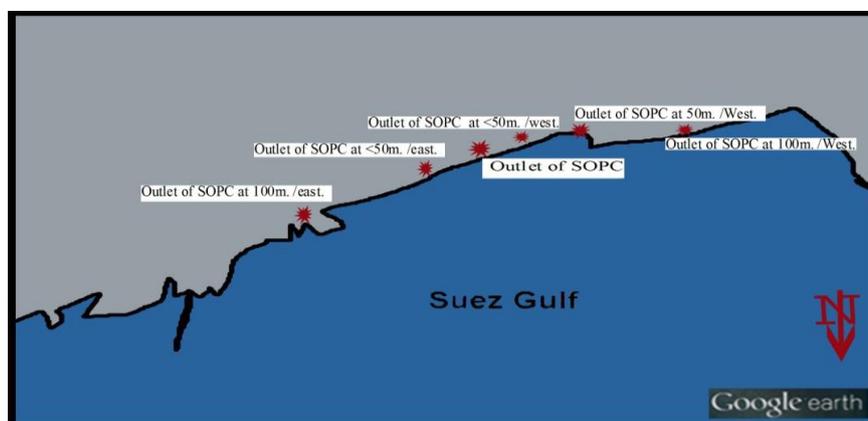


Fig.2. Map of sample stations along the drainage basin of SOPC .

Samples collection and storage

Surface sediment (0-2cm) samples were collected using a stainless steel grab, from different stations along discharge basin of the company, according to activities for each site and distance (Table 1), then mixed and stored in refrigerator in pre – cleaned jars until analysis ⁽¹⁹⁾.

TABLE 1. Studied sites, their locations, activities and distance along the drainage Basin of (SOPC) .

S. No.	Locations	Activities for each site	Distance along drainage basin (m.)
7	Outlet of Suez Oil Petroleum Company at 100m. /west.	Wastes of conversion operations of crude oil to refined products along the west side of the outlet of petroleum drainage of Suez Company with 100 m	100m. /west.
9	Outlet of Suez Oil Petroleum Company at 50m. /west.	Wastes of conversion operations of crude oil to refined products along the west side of the outlet of petroleum drainage of Suez Company with 50m	50m. / west.
8	Outlet of Suez Oil Petroleum Company at <50m. /west.	Wastes of conversion operations of crude oil to refined products along the west side of the outlet of petroleum drainage of Suez Company with 50 m	<50m. /west.
10	Outlet of Suez Oil Petroleum Company at <50m. /east.	Wastes of conversion operations of crude oil to refined products along the east side of the outlet of petroleum drainage of Suez Company with 50 m	<50m. /east.
10*	Outlet of Suez Oil Petroleum Company at 100m. /east.	Wastes of conversion operations of crude oil to refined products along the east side of the outlet of petroleum drainage of Suez Company with 100 m	100m. /east.

M: Meter's

Extraction of petroleum oil from sediment samples

500 g. of dried, sediment were added in round bottom flask with 300 ml, methanol and 15 g. potassium hydroxide. The mixture were refluxed for 1 hr and 30 min then cooled to room temperature. The methanol extracted twice with 25 ml *n*-hexane, then, the extract was filtered through anhydrous sodium sulphate. The volume was reduced to 0.5 ml. The reduced volume was transferred quantitatively to glass vial. The extracted oil was concentrated to approximately 0.2 ml using dry nitrogen. The oil content in sediment was then calculated after removing the solvent till constant wt.⁽²⁰⁾.

High performance liquid chromatography Analysis (HPLC)

PAH identification and quantification in the extracted oil were performed using HPLC technique⁽¹⁸⁾. The apparatus used was water HPLC 600, Auto Sampler 616 Plus, Dual Absorbance Detector 2487, attached to a computerized system with Millennium 32 Software. The following were the HPLC conditions: the sample volume was 100 μ L; the column used was Supelcosil LC-PAHs 15 cm, 4.6 mm ID, 4- μ m particles; mobile phase was achieved using a acetonitrile/water ratio of 60:40 and was changed gradually to 100 % acetonitrile within 20 min. The flow rate was 1.2 ml/min, and the detector used was a UV type, 254 mm.

Results and Discussion*Concentration of total TPAHs in polluted sediments along the drainage basin of SOPC*

The concentrations of PAHs and TPAHs in the sediment of different stations are shown in Table 2 and Fig. 3. The PAHs components were distributed in various stations with different patterns. This difference in PAHs composition might be related to the extent and the nature of inputs along the discharge basin. At all of the stations, the concentration of Σ PAHs was higher compared to the guideline value (4022 ng/g)^(21, 22). The PAHs concentration varied significantly among the SOPC within the discharge basin from 22333.983 up to 73597.864 ng/g dry weights with 43016.278 ng/g dry weights as an average concentration was greater than the guideline, high value represented at site (3)73597.864 ng/g dry weights while, low value at site (10*) 22333.983 ng/g dry weights. This is consistent with the direction of the water currents and winds from the west to the east side's within the discharge basin. On the other hand, a steady decline of the level of poly-aromatic hydrocarbons towards the east, then followed by a rise in poly-aromatic concentration at <50m. /east of outlet of SOPC site recorded 39180.36 ng/g dry weights, this is attributed to the presence of this side from nearby petroleum Nasr Company (outlet), which is closed to Suez Oil Company. Generally, the level of poly-aromatic hydrocarbons in the sediments at all study areas is found to vary widely depending on sites with the west coast of discharge basin recorded

higher values than the east coast ones, this is consistent with the direction of the water currents and winds from the west to the east side's within the basin. The Suez Oil Company takes water from the Suez bay and mixes it with fresh water to utilize in washing the crude oil, after the use of water for this purposes different some oily smuggling occurs for water. Source of salt water necessary for cooling various company in Suez Gulf is characterized by oily water that contains a high proportion of the oil which is caused by refinery production units (Coking - distillation - oils), liquidation warehouses crude and petroleum products, water waste companies neighboring filter wards pumps, Trenchant grids crude and petroleum products. Are assembled this oily water and pushed through a network of lines to basins separated oil. These high values may point out that high residual petroleum fractions are precipitated on sediments. These residual petroleum fractions of oil cannot be completely treated (untreated) or degraded easily through weathering processing, consequently, this leads to accumulation of oil residues in sediments. The drainage basin was under stress from intensive wastes of conversion operations of crude oil to refined products along the east and west sides from it. The deliberate drainage of oil related activities and oily smuggling from the industrial processing cause's continuous inputs and large cumulative loading on the discharge basin water and shore sediments. Also mean, minimum and maximum concentration of PAH components in this area compared to the guidelines ^(23, 24). Concentrations were more than the guideline value in most of the stations (Table 3) and it indicates that occasionally adverse biological effects are likely to accrue for these components in these area average concentrations of Σ PAHs (ng/g) in sampling stations.

TABLE 2. Average concentration of Σ PAHs (ng/g dry weight) in the oil extracted from drainage basin of SOPC.

S.NO.	Location	Conc. Σ PAHs (ng/g)
7	Outlet of Suez Oil Petroleum Company at 100m. /West.	73597.864
9	Outlet of Suez Oil Petroleum Company at 50m. /West.	47384.966
8	Outlet of Suez Oil Petroleum Company at <50m. /west.	32584.224
10	Outlet of Suez Oil Petroleum Company at <50m. /east.	39180.36
10*	Outlet of Suez Oil Petroleum Company at 100m. /east.	22333.983

Conc.: Concentration (ng/g), m.: meter.

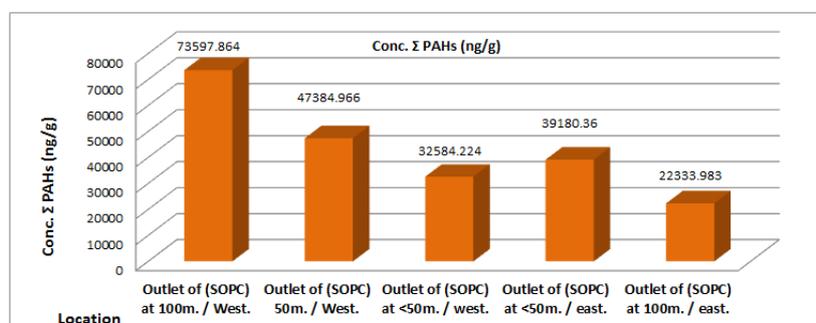


Fig. 3. Average concentration of Σ PAHs (ng/g) in the oil extracted from drainage basin of SOPC .

TABLE 3. Mean minimum and maximum concentration of PAHs (ng/g dry weight) in the oil extracted from drainage basin compared to the guideline.

S.NO.	Total Σ PAHs	Minimum	Maximum	Guideline ¹
7	73597.864	11.141	9628.942	4022
9	47384.966	0.2144	16972.595	4022
8	32584.224	9.416	10578.204	4022
10	39180.36	6.746	15175.524	4022
10*	22333.983	2.0311	10287.232	4022
Mean Σ PAHs	43016.278	0.2144	16972.595	4022

Comparison of literature data about total TPAH concentrations in sediments from various marine sites in the world

Aromatic hydrocarbons were analyzed to reveal the presence of PAHs contamination relative to pyrolytic or petrogenic origins in sediments of discharge basin. Results show that 16 PAHs can be identified at detectable levels, the total amount of PAHs examined ranged from 22333.983 up to 73597.864 ng/g dry weights with 43016.278 ng/g dry weight, as the average concentration (Table 3) . An understanding of the local and global extent and severity of marine environment contamination by fossil fuel hydrocarbons from various sources requires measuring the compounds of interest and comparing them in different regions. The total PAHs concentration measured in the discharge basin indicates that the sediment contamination is important, and comparable to that found in other locations around the world. TPAHs concentration in sediment from various sites in the world, the investigation of the study area in general could be considered as highly contaminated by PAHs. In 2004, the Research Institute of the Petroleum Industry showed that the most polluted areas in Musa Bay were located in the vicinity of petrochemical industries ⁽¹³⁾ and reverse concentration ranged between 537.9 to 2713.33 ng/g ⁽¹⁴⁾. In 2009, concentration of PAHs in the sediments of Imam Khomeini Port were monitored

and the concentration of PAH concentration was (190 - 3520 ng/g) ⁽²⁵⁾. In 1996, the concentration limits of Σ PAHs for marine sediments was considered (4022ng/g) ⁽²²⁾ and Canadian Environmental Quality Guidelines present this value (7071 ng/ g), in 2002 ⁽²²⁾, National comparison revealed, elevated PAH concentrations in the Santander Bay, Spanish 20-34,460 ng/g ⁽²⁰⁾, in the Gulf of Trieste, Northern Adriatic 297-115,854ng/g ⁽²⁶⁾, and in the western Xiamin Sea 2,900-61,000 ng/g ⁽²⁷⁾, and comparable to that found in other locations around the world (Table 4), the comparison showed higher sedimentary concentrations of PAHs in discharge basin compared with those found in the sediment of Persian Gulf, Iran, Busheher 884-4792 ng/g ⁽²¹⁾, 34.67 – 682.29 & 600-800 ng/g in the year 2010 & 2001, respectively ^(28,29), in Alexandria Sea Coasts, Egypt 558.258-2924.273 . Mumbai in India 2608 – 13413 ng/g ⁽¹⁵⁾, Western Xiamen Bay in China 247-480 ng/g ⁽³⁰⁾, Western Baltic Sea 3-30,100ng/g ⁽³¹⁾, San Francisco Bay in USA 2,653-27,680 ng/g ⁽³²⁾, Yangtze Estuary in China 107-633 ng/g ⁽³³⁾, and higher than those found in Kaohsiung Harbor in Taiwan 472–16,207 ng/g ⁽³⁴⁾. The drainage basin was under stress from intensive wastes of conversion operations of crude oil to refined products along the east and west sides from it. The deliberate drainage of oil related activities and oily smuggling from the industrial processing cause's continuous inputs and large cumulative loading on the discharge basin water and bottom sediments, which may explain the observable difference between the concentrations in the sediments. In fact this region is subject to hydrocarbon pollution by industrial processing waste, and other non-point source pollution .

TABLE 4. Comparison of literature data about total PAH concentrations (ng/g dry weight) in sediments by various marine sites in the world .

Location	N ^a	N ^b PAHs	Concentration range ng/g	Method	Preferences
Drainage basin of SOPC , Suez Gulf, Egypt	5	--	22333.983 - 73597.864	HPLC	This work
Gulf of Trieste, Northern Adriatic a	10	24	297-115,854	GC-FID	(26)
Xiamen Harbor, China	9	8	2,900-61,000	GC-FID	(27)
Santander Bay, Spanish	-	-	20-34,460	HPLC, GC/MS	(20)
Gulf of Trieste ,Northern Adriatic	17	22	34.67 – 682.29	GC-MS	(28)
Gulf of Trieste, Northern Adriatic	3	22	600-800	GC-MS	(29)
Western Xiamen Bay, China	8	16	247-480	GC-FID	(30)
Western Baltic Sea	22	14	3-30,100	GC-MS	(31)
San Francisco Bay, USA	16	17	2,653-27,680	GC-MS	(32)
Yangtze Estuary, China	-	-	107-633	HPLC	(33)
Kaohsiung Harbor, Taiwan	17	16	472–16,207	HPLC	(34)
Mumbai, India	27	15	2608 – 13413	HPLC	(15)
Persian Gulf, Iran, Busheher	5	16	884-4792	HPLC	(21)
Alexandria Sea Coasts, Egypt	-	16	558.258-2924.273	HPLC	(3)

N^a: the number of samples, N^b PAHs: the number of PAH compounds analyzed in each study .

Comparing the guidelines of individual poly-aromatic hydrocarbons contaminated sediments

16-US EPA PAHs (Fig. 4) was grouped in four groups according to their number of aromatic rings. The concentration of TPAHs representing 2-3 ring, 4-ring, 5-ring and 6-ring PAHs are shown in Table 5. 2-3 Rings and 4-rings, beside 6-ring, the most abundant PAH compounds in sediment were, acenaphthylene (A), acenaphthene (Ace), phenanthrene (Phe), flourene (F), naphthalene (Nap), anthracene (Ant), fluorantkane (Flu), pyrene (Pyr), benzo [a] anthracene (BaA), chrysene (Chr), benzo [ghi] perlyene (Bp) and indo[1,2,3-cd] pyrene (IP) shown (Fig. 5&6). The high PAHs level was observed at all the stations along the discharge basin and it may be due to the locations of the sampling point of the aromatic in outlet of Basin Company, with the continuous accumulation of effluents pollutants beside, the depth of this station was low. In this research minimum and maximum concentration of PAH components in the area compared to the guidelines^(23,24) and two sets of SQGs including the ERL/ERM and TEL/PEL values, were used as a guideline (Tables 6 & 7). Concentrations of the most PAH components were higher than the ER-L, ER-M, TEL and PEL values in all the sampling stations, and also higher than national sediment quality criteria purposed by USEA⁽³⁵⁾ for fluoranthne (Flu) 3000 ng/g dry wt., phenanthrene (Phe) 2400 ng/g dry wt., acenaphthylene (A) 2400 ng/g dry wt., which might need a more detailed study, the results of this study reverse that banzo (A) anthracene [BaA] concentrations were low than the TEL /PEL and ER-L/ ER-M, in all the stations, in addition chrysene (Chr) was higher than ER-L/TEL values and lower than ER-L/PEL values also dibenzo [a,h] anthracene (DahA) have lower values than ER-L/ ER-M, & PEL and higher value TEL. In fact, the presence of fluoranthene (Flu) and pyrene (Pyr) indicates the importance of pyrolytic inputs since, these compounds are considered as products formed from the condensation of aromatic compounds of low molecular weight at high temperature⁽³⁶⁾. Chrysene is the most important representative toxic PAH, in the discharge basin of SOPC. Chrysene is considered as a preserved biomarker of PAHs and it was selected to be a good marker of petroleum compounds because of its resistance to a biotic factors and bacterial degradation⁽³⁾. Chrysene showed highly concentration in sediment of drainage basin, reflecting a petrogenic contamination. High concentrations of chrysene can be associated with weathering effect in crude oil and chemical composition change. In addition, high concentration of chrysene considered as conservative PAH due to its resistance to weathering and bacterial degradation, indicates petroleum contamination input in the discharge basin. Higher concentrations of perylene could however, result from terrigenous precursors whose diagenetic degradation could lead to the formation of perylene and indicates biogenic contribution⁽³⁶⁾. Similarly, that chronic exposure to sediments contaminated with PAHs known for their carcinogenic, mutagenic and teratogenic properties are benz [a] anthracene and chrysene, benzo [b] fluoranthene, benzo [k] fluoranthene, benzo [a] pyrene, benzo [ghi] perylene, dibenz (a,h) anthracene (C20H14), and indeno (1,2,3-cd) pyrene (C22H12)⁽³⁷⁾.

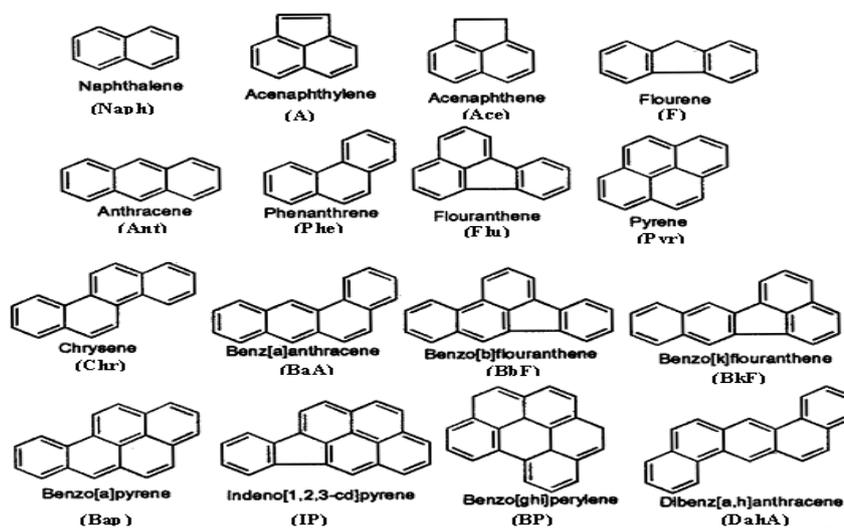


Fig. 4. Nomenclature, chemical structure, and abbreviations for 16 - priority PAHs ⁽³⁾.

TABLE 5. Concentration of individual PAHs (ng/g dry weight) in the oil extracted from polluted sediments of drainage basin .

Locations		S.NO.7	S.NO.9	S.NO.8	S.NO.10	S.NO.10*
2Ring	Nap.	N.D.	7795.9559	N.D.	15175.715	N.D.
	Total	N.D.	7795.9559	N.D.	15175.715	N.D.
3Ring	A.	4729.2815	9766.0046	7854.1056	10207.524	7765.9849
	Ace.	5473.1024	N.D.	N.D.	N.D.	N.D.
	Phe	733.353	1380.4077	999.1343	1115.4698	1161.6265
	F.	9628.942	8357.5658	7234.1061	1681.8082	10287.232
	Ant.	984.088	N.D.	1753.0902	N.D.	N.D.
	Total	61548.766	19503.977	17840.436	13004.801	19214.843
4Ring	Flu.	3041.6255	16972.595	3924.2012	8903.4148	N.D.
	Pyr.	8441.9379	3007.8823	10578.204	514.771	2989.9833
	BaA	37.435	0.2144	11.9342	6.7455	2.3112
	Chr.	37.895	50.7574	64.6989	788.1005	73.648
	Total	11558.893	20031.448	14579.037	10213.031	3065.9425
5Ring	Bbf	12.3729	N.D.	25.6766	42.1285	22.7754
	Bkf	466.695	1.1281	102.7849	N. D.	N.D.
	BAp	N.D.	N.D.	N.D.	N.D.	N.D.
	DahA	N.D.	32.3083	N.D.	700.3045	N.D.
	Total	479.0679	33.4364	128.4615	742.433	22.7754
6Ring	Bp	N.D.	16.4332	26.8753	N.D.	N.D.
	Ip	11.1407	3.717	9.4161	44.3801	30.4232
	Total	11.1407	20.1502	36.2914	44.3801	30.4232
Total PAHs		73597.866	47384.966	32584.225	39180.36	22333.983

Conc.: Concentration (ng/g), N.D. not detected, (under the level of detection).

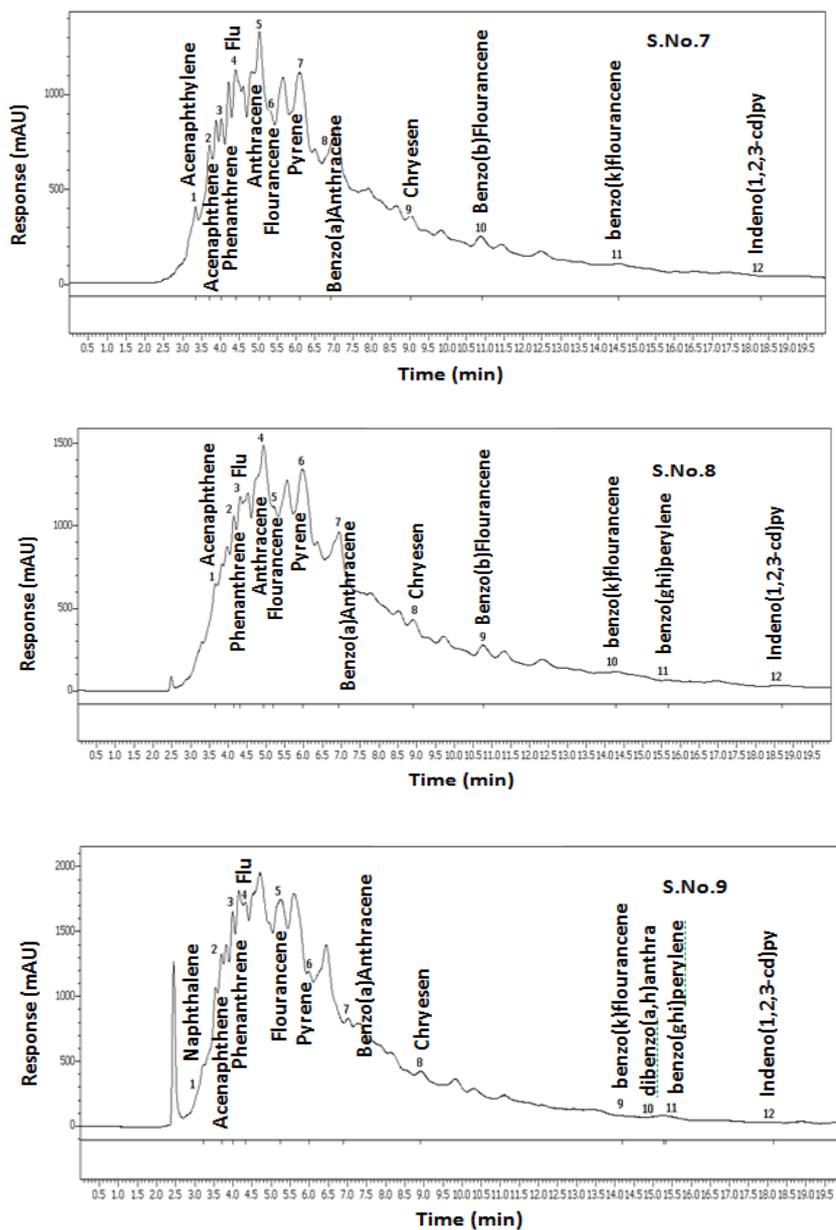


Fig. 5. HPLC chromatograms of extracted oils from discharge basin of SOPC .

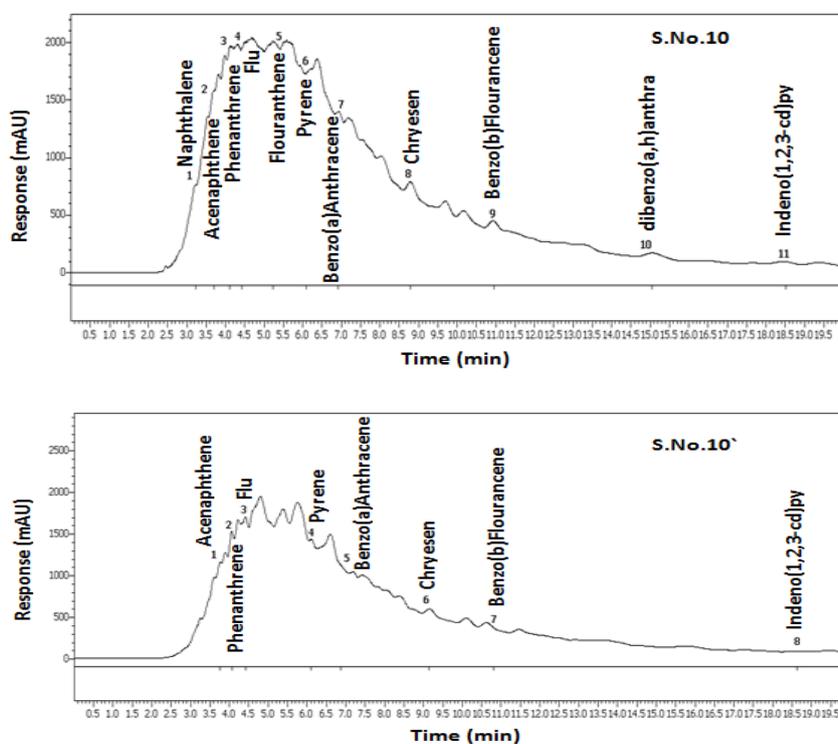


Fig. 6. HPLC chromatograms of extracted oils from discharge basin of SOPC .

TABLE 6. PAHs components (ng/g) and toxicity guidelines .

Samples station	Guideline			
	ER-L	ER-M	TEL	PEL
PAHs compounds				
Naphthalene (Nap)	160	2100	34.6	391
Acenaphthylene (A)	44	640	5.87	128
Acenaphthene (Ace)	16	500	6.71	88.9
Flourene (F)	19	540	21.2	144
Phenanthrene (Phe)	240	1500	86.7	544
Anthracene (Ant)	85.3	1100	46.9	245
Fluoranthne (Flu)	600	5100	113	1494
Pyrene (Pyr)	665	2600	153	1398
Benzo [a] anthracene (BaA)	261	1600	74.8	693
Chrysene (Chr)	384	2800	108	846
Benzo [b] fluoranthene (Bbf)	Na	Na	Na	Na
Benzo[K] Fluoranthene (Bkf)	Na	Na	Na	Na
Benzo[a] Pyrene (BAP)	430	1600	88.8	763
Dibenzo[a,h]anthracene (DahA)	63.4	260	6.22	135
Indo[1,2,3-cd] perlyene (IP)	Na	Na	Na	Na
Benzo[ghi] perlyene (Bp)	Na	Na	Na	Na

ERL: effect range low, ERM: effect range median, TEL: threshold, Affect level, PEL: probable effect Level. Na: not available.

TABLE 7. Minimum and maximum concentration (ng/g), of PAHs in the area compared to the guidelines .

Samples station	Guideline					
	PAHs Comp.	Min.	Max.	ER-L	ER-M	TEL
Nap	7795.959	15175.715	160	2100	34.6	391
A	4729.2815	10207.524	44	640	5.87	128
Ace	N.D.	5473.1024	16	500	6.71	88.9
F	733.353	1380.4077	19	540	21.2	144
Phe	1681.8082	10287.232	240	1500	86.7	544
Ant	984.088	1753.0902	85.3	1100	46.9	245
Flu	3041.6255	16972.595	600	5100	113	1494
Pyr	514.771	10578.204	665	2600	153	1398
BaA	0.2144	37.435	261	1600	74.8	693
Chr	37.895	788.1005	384	2800	108	846
Bbf	12.3729	42.1285	Na	Na	Na	Na
Bkf	1281	466.695	Na	Na	Na	Na
BAP	N.D.	N.D.	430	1600	88.8	763
DahA	32.3083	700.3045	63.4	260	6.22	135
IP	3.717	44.3801	Na	Na	Na	Na
Bp	16.4332	28.8753	Na	Na	Na	Na

ERL: effect range low, ERM: effect range Median, TEL: threshold, Affect level, PEL: probable effect Level, Min.: Minimum, Max.: Maximum, Comp.: Components, N.D. not detected, Na: not available.

PAH compound profiles and origins in polluted sediments of drainage basin

The source analysis results may help us to know about the proportion of pyrogenic and petrogenic origins and it may identify which one is a stronger contributor (Table 8) used to detect the origin of PAHs for the oil extracted from sediment. The sources of PAHs whether from fuel composition (pyrolytic) or from crude oil (petrogenic) contamination, may be identified by ratios of individuals PAH compounds based on peculiarities in PAH composition and distribution pattern as a function of the emission source⁽³⁸⁾. Ratio values such as phenanthrene /anthracene (Phe /Ant) and fluoranthene /pyrene (Flu/Pyr) had been used by previous workers^(39,40). Petroleum often contains more phenanthrene relative to anthracene as phenanthrene that's more a thermodynamically stable tri-cyclic more isomer than anthracene so, Phe/Ant ratio is observed to be very high in PAH petrogenic pollution, but low ratio in pyrolytic contamination cases^(41,42). Some authors^(38,43) suggest that sediments with Phe/Ant >10 were mainly contaminated by petrogenic inputs and Phe/Ant < 10 was typically of pyrolytic sources. However the ratio of individual PAH compounds varied between sediments, indicating that the sources of PAH contamination might be different. Some sediment samples were under the limit of detection otherwise samples 7 (0.745) and 8 (0.570) (Table 8) suggesting that they were pyrolytic – derived PAHs. The different ratios might also be related to its degree of photo-degradation, chemical degradation or biodegradation and also to the granulometry of the sediment samples. In addition to the Phe/Ant ratio, fluoranthene / pyrene ratio also indicated the origin of PAHs⁽³⁹⁾, other author⁽³⁹⁾ suggested that a Flu/Pyr of less than 1 was attributed to petrogenic sources and values greater than 1 were obviously related to a pyrolytic origin, composition of coal

and wood gave Flu/Pyr ratio of 1.4 and 1.0, respectively, while crude oil and fuel oil had values of 0.6 – 0.9⁽⁴⁰⁾, samples 7 (0.360) and 8 (0.371) had values less than 1 except samples 9, 10 had values 5.643 & 17.296, respectively. The small Flu/Pyr ratio values suggest strong petrogenic input. In order to provide a good estimation of PAH sources, sediment samples with Phe/Ant > 10 and Flu/Pyr < 1 showed strong petrogenic origin, sediment samples with Phe/Ant < 10 and Flu / Pyr < 1 were characteristic of mixed pattern of pyrolytic and petrogenic contamination. The benzo [a] anthracene/chrysene (BaA/Chr) ratio has also been suggested to identify PAH sources, and this ratio in sediment tended to increase as petrogenic contribution decrease⁽³⁸⁾, the study area reflects values between 0.004 to 0.988 (Table 8). In addition, (Ant/Ant+Phe) < 0.1 indicates a petrogenic source, while this ratio indicates a combustion source when it is greater than 0.1. The ratio of Flu/Pyr < 1 is characteristic of a petrogenic source and the ratio Flu/Pyr > 1 characterizes a pyrolytic source. Table 8 displays values ranged between 0.360 up to 17.296 indicating multiple sources of Anthropogenic / petrogenic and biogenic PAHs. The ratio (Flu / Flu+ Pyr) differentiates between petroleum, wood, coal and plants combustion. When (Flu / Flu+ Pyr) < 0.5⁽⁴⁴⁾, it is generally associated with petrogenic source as a characteristic of fuel combustion (gasoline, diesel and crude oil), as samples 7(0.265) and 8(0.271), respectively, while when this ratio exceeds 0.5 as samples 9 (0.849) and 10 (0.945), respectively (Table 8), it characterized pyrolytic sources (kerosene, wood, terrestrial plants and coal combustion)⁽³⁶⁾. Phe/Ant and Ant/Ant+Phe ratios indicate that PAHs present in sediment of discharge basin derived from pyrolytic sources. This pyrolytic origin is however not exclusive since the values of Flu/Pyr and (Flu / Flu+ Pyr) ratios show the contribution of oil sources (lubricating oils) in sediment of discharge basin indicating mixed origin of PAHs.

Several studies⁽⁴⁵⁻⁴⁷⁾ reveal that the increased anthropogenic inputs of pyrogenic and petrogenic PAHs in sediments correspond to refinery's effluents and fossil fuel usage in the industrial processes. One of the most used approaches is to compare the sum of several pyrogenic PAHs (4-6-ring PAHs) with a group of petrogenic PAHs (2-3-ring PAHs), since the (2- 3-ring) PAHs are more abundant in petroleum, while highly condensed PAHs (4-6-ring PAHs) are significant combustion products⁽²⁶⁾.

Pyrogenic sources, such as the combustion-derived particles present in urban atmospheric dust, were depleted in low molecular weight 2-3 ring PAHs (LPAHs) and enriched in high molecular weight 4-6 ring PAHs (HPAHs), which led to an LPAHs/HPAHs ratio < 1. Petrogenic sources, such as fuel oil or light refined petroleum products, were dominated by low molecular weight PAHs and have LPAHs/HPAHs ratio > 1. Indeed the higher the LPAHs/HPAHs ratio is, the higher the prevalence of petrogenic sources^(39, 40). The drainage basin of SOPC recorded values ranged between 1.210 - 6.160, Table 8 pointed to multiple sources of anthropogenic / petrogenic and biogenic PAHs, in addition LPAHs/HPAHs ratio < 1 and Flu/ (Flu+Pyr) ratio > 0.4 calculated for the five surface sediments suggest pyrogenic sources. These results reveal that the increased anthropogenic inputs of pyrogenic and petrogenic PAHs in sediments correspond to industrial development and fossil fuel usage in the industrial processes beside, continental discharge of the refinery's effluents to the discharge basin.

TABLE 8. PAHs parameter used to detect the origin of PAHs for the oil extracted from polluted sediments of drainage basin.

Station	Ratio											
	Phe/Ant	Flu/Pyr	BaA/Chr	Chr/BaA	BaP/Bp	Ant/(Ant+phe)	BaA/(BaA+Chr)	Flu/(Flu+Pyr)	IP/IP+BP	6LPAHs/10HPAHs	6LPAHs/10HPAHs	
7	0.745	0.360	0.988	1.0123	N.D.	0.427	0.497	0.265	N.D.	61548.766	12049.1	5.108
9	N.D.	5.643	0.004	236.742	0.013	N.D.	0.004	0.849	0.184	27299.932	20085.034	1.359
8	0.570	0.371	0.184	5.421	0.444	0.637	0.156	0.271	0.259	17840.436	14743.789	1.210
10	N.D.	17.296	0.009	116.834	N.D.	N.D.	0.008	0.945	N.D.	28180.515	10999.845	2.562
10*	N.D.	N.D.	0.031	31.866	N.D.	N.D.	0.0030	N.D.	N.D.	19214.843	3119.14	6.160

N.D.: not detected, concentration: ng/g, LPAHs/HPAHs > 1 petrogenic, < 1 petrogenic, Flu/Flu+Pyr < 0.4 petrogenic, > 0.4 pyrogenic, Ant/Ant + phe < 0.1 petrogenic, > 0.1 pyrogenic, Flu/Pyr < 1 petrogenic, Phe/Ant > 10 petrogenic, < 10 pyrogenic, BaA/BaA+Chr < 0.2 petrogenic, > 0.35 pyrogenic, BaA/Chr 0.9 petrogenic, < 0.4 pyrogenic, Chr/BaA < 1 petrogenic, > 1 pyrogenic, BaP/BP < 0.6 petrogenic, > 0.6 pyrogenic, Flu/Flu+Pyr 0.4-0.5 petrogenic, > 0.5 pyrogenic, IP/IP+BP < 0.2 petrogenic, > 0.2 pyrogenic, IP/IP+BP 0.2-0.5 petrogenic, > 0.5 pyrogenic, Ant: Anthracene; Phe: Phenanthrene; BaA: Benz[a]anthracene; Chr: Chrysene; Flu: Fluoranthene; BP: Benzo [g,h,i] perylene; BaP : Benzo [k] pyrene; LPAHs: Low molecular weight PAHs; HPAHs: High molecular Weight PAHs; IP: Indo (1, 2, 3-cd) perylene; Pyr: Pyrene. ⁽⁴⁸⁾

Distribution of PAHs % in the oil extracted from polluted sediments of drainage basin

Predominance of low molecular weight PAHs LMW-PAHs (2-3 ring PAHs) and also, high molecular weight PAHs HMW-PAHs (4-ring PAHs) in sediment are in accordance with some other studies, ^(49,50). 2-3- ring and 4-ring PAHs showed dominance at all the different distances stations of basin. In addition, 5, 6 ring PAHs with low concentrations PAHs compared to the other rings, (Table 5). 2-3 ring PAHs showed dominance at s.no.10*, 7, 10 and 9 with percentage between 54.75 to 86.03 % (Table 9 & Fig. 7). Beside, four ring PAHs suggests value ranged between 13.73 up to 44.75% percent represented an increasing percentage for 4-ring distribution at s.no.10, 9, 8 & 10* with values 44.75, 42.27, 26.07 and 13.73%, respectively. Penta aromatic ring percentage of higher molecular weight PAHs reverses values between 0.07 – 1.89 %. Indeed, six aromatic ring compounds recorded values ranged between 0.02 to 0.14% from benzo (ghi) perlyene (Bp) and indeno (1, 2,3cd) perlyene at all stations. The dominance of the LMW-PAHs due to (2-3 rings) PAHs not subject to any degradation as results of continental discharged of the refinery's effluents to the discharge basin whereas, the HMW-PAHs (4-ring) can be due to their strong adsorbance by sediments. The composition of PAHs in a particular sample usually reflects the sources that produce the PAH. There are three major types of PAH which differ by their genesis: petrogenic, pyrogenic and biogenic. PAHs with 2-3 rings are generally of petrogenic origin, related to petroleum including crude oil and its refined products ^(27,51). High concentrations of phenanthrene indicate the presence of petrogenic sources. The presence of naphthalene at station 9&10 suggests fresh petroleum pollution ⁽⁵²⁾. PAHs with 4-6 ring hydrocarbons are generally of pyrogenic origin and generated by the combustion of fossil fuels and of recent organic material ⁽²⁷⁾. High concentrations of fluoranthene, pyrene and chrysene found at all stations suggest a pyrogenic origin, as a result of a variety of processing sources and industrial effluents to the discharge basin of SOPC from oily smuggling occurring with water.

TABLE 9. Distribution of PAHs % in the oil extracted from sediment of drainage basin according to the number of aromatic rings .

S.NO.	Location	2-3Rings %	4-Ring %	5-Ring %	6-Ring %
7	Outlet of Suez Oil Petroleum Company at 100m. /West.	83.63	15.71	0.65	0.02
9	Outlet of Suez Oil Petroleum Company at 50m. /West.	57.61	42.27	0.07	0.04
8	Outlet of Suez Oil Petroleum Company at <50m. /west.	54.75	44.75	0.39	0.11
10	Outlet of Suez Oil Petroleum Company at <50m. /east.	71.93	26.07	1.89	0.11
10*	Outlet of Suez Oil Petroleum Company at 100m. /east.	86.03	13.73	0.10	0.14

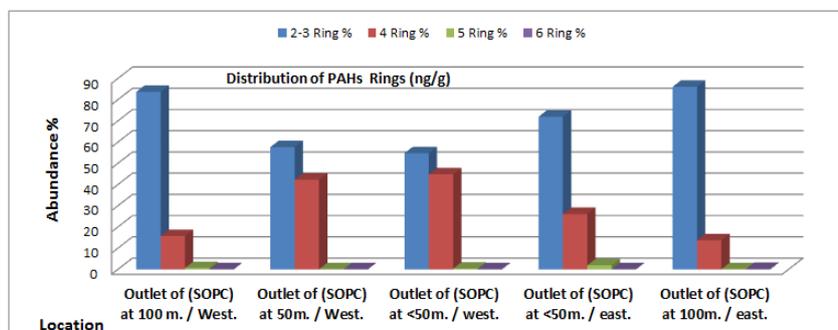


Fig. 7. Histogram representing distribution of PAHs % in the oil extracted from drainage basin according to the number of aromatic rings .

Conclusion and Recommendations

The aim of the present study was to investigate and establish the pollution of PAHs in surface sediment along discharge basin of SOPC. HPLC was applied as screening method for the determination of TPAHs in surface sediment. The concentration of PAHs in the sediments ranged between 22333.983 and 73597.864 ng/g dry weights with 43016.278 ng/g dry weights, as the average concentration was greater than the guideline value (4022ng/g) and also most PAH components were higher than the ER-L, ER-M, TEL and PEL values moreover, higher by comparison with literature data in various sites in the world, this is due to the deliberate drainage of oily smuggling from the industrial processing which causes continuous inputs and large cumulative loading on the discharge basin water and shore sediments without completely treated (untreated) or degraded easily through weathering processing, consequently, this leads to accumulation of oil residues in sediments. The dominance of the LMW-PAHs due to (2-3 rings) PAHs not subject to any degradation as results of continental discharged of the refinery's effluents to the discharge basin whereas, the HMW-PAHs (4-ring) can be due to their strong adsorbance by sediments. The discharge basin receives PAHs from petrogenic sources, while the major part of PAHs originated from both anthropogenic / petrogenic and biogenic PAH hydrocarbons, due to the elevated levels of PAHs compound in the sediment and also, the high concentration of anthropogenic contaminates including industries, processing activities and other non-point source pollution. The findings point to the urgent need to establish a monitoring programme for persistent organic pollutants not only sediment but also in water to ensure that any excess in concentrations over environmental quality standards is rapidly reported and necessary actions are taken. This study recommended that pollution control for some oily smuggling disposing should be improved by separation of oils water before dumping into the discharge basin, must be committed to the decisions of the IMO declaration and the guideline. The present findings suggest that strict regulations and improvements in the existing environmental legislation should be made to avoid adverse effects to public health both within and outside of the country.

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التقييم البيئي للهيدروكربونات العطرية المتعددة الحلقات في الرواسب على طول حوض تصريف شركة السويس لتكرير البترول ، جنوب غرب خليج السويس

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القاهرة – مصر .

يقع مخرج شركة النفط بالسويس في منطقة Zietyia حوالي 2-3 كم جنوب غرب مدينة السويس ، النشاط الرئيسي لشركة السويس للبترول هو تكرير النفط لإنتاج المنتجات النفطية المشتقة مثل النفتالين والكروسين والبنزين والاسفلت والفحم البترولي والكبريت. وتمتلك الشركة خط إنتاج لإنتاج الفحم البترولي من خلال تزويد أبراج بالفحم فضلا عن الكبريت. وتقوم الشركة بتصريف مياه الصرف الصناعي الزيتي في خليج السويس. كمية مياه الصرف إلى خليج السويس هو 360000 day³m فقط. وتفيد التقارير أن نوعية المياه من النفايات السائلة غير متفقة مع حدود معايير النفايات السائلة في مصر؛ حيث يحدث بعض التهربات الزيتية للمياه ، وجد 060، 6 كجم من النفط والشحوم تبرا يوميا في المياه المستقبلية. وتم أخذ العينات من مياه الصرف الصناعي علي إمتداد حوض الصرف. يتراوح تركيز الهيدروكربونات العطرية عديده الحلقات في الرسوبيات على طول حوض التصريف لشركة السويس لزيت البترول ما بين 22333.983 الى 73597.864 ng/g مع متوسط تركيز 43016.278 نانوغرام / غرام ، و كان أكبر من قيمة المبدأ التوجيهي (4022 ng/g) ، ويرجع ذلك إلى أنه يحدث بعض التهربات الزيتية للمياه نتيجة لاستخدام المياه في أغراض التبريد المختلفة ثم يحدث التصريف الى حوض الصرف بشركة السويس للبترول ، وبالتالي، فإن منطقة الدراسة تصنف على أنها شديدة التلوث. بواسطة مقارنة التركيز مع مناطق أخرى من العالم أظهرت المستويات تركيزات أعلى بكثير من التي في البيئات البكر المحدد. قد تشير هذه القيم العالية إلى ارتفاع بقايا النفط في الرواسب ، هذه البقايا البترولية المتبقية من النفط لا يمكن علاجها تماما ، وبالتالي هذا يؤدي إلى تراكم بقايا النفط في الرواسب. وكان حوض الصرف تحت ضغط من النفايات مكثف من عمليات تحويل النفط الخام إلى منتجات مكررة على طول الجانبين الشرقي والغربي منه. الى جانب الأنشطة ذات الصلة بتهيرب النفط الزيتية من مدخلات مستمرة والتحميل التراكمي كبير على رواسب حوض تصريف المياه. مما يؤدي تركيزات أعلى بكثير من السموح به. بمقارنة التركيزات بقيم معايير الجودة البيئية كانت تركيزات معظم مكونات PAH أعلى من قيم ER- TEL و ER-M, ER-L, في جميع المواقع ، ، بالإضافة الى أن تركيز Chrysene (Chr) كان أعلى من قيم ER-L/TEL، وأقل من قيم ER-L/PEL، أيضا Dibenzo anthracene (DahA) (a,h) سجل تركيزات أعلى من قيم TEL و أقل من ER-L/ ER-M, & PEL، ولكن تركيز Banzo (A) Anthracene (BaA) أقل من قيم TEL /PEL و ER-L/ ER-M، في جميع المواقع، وجود الحلقات

على طول حوض تصريف الشركة في الرواسب جنباً إلى جنب مع المركبات السامة المحتملة الأخرى فإن هذا يشير إلى تأثيرات بيولوجية سلبية على منقطة الدراسة. نتائج التحليل قد تساعدنا لمعرفة نسبة مصادر الهيدروكربونات العطرية عذدة الحلقات Biogenic و petrogenic وأن أيهم هو المساهم الأقوى. يتلقى حوض التصريف الحلقات من مصادر petrogenic ، في حين أن جزءاً كبيراً من الحلقات في الرواسب نشأت مزوجة المصدر Biogenic و petrogenic معاً، نظراً لمستويات مرتفعة من المركبات الحلقية في الرواسب. هناك حاجة لدراسات أكثر تفصيلاً لتقييم آثار نفايات حوض التصريف على الرواسب مع المعالجات الصناعية المختلفة من التلوث و الرصد الدورى ينبغى أن يتم بصفة دورية . هذا ؛ وأوصت الدراسة بأن مكافحة التلوث لبعض التهربيات الزيتية ينبغى لتحسين فصل الزيوت عن طريق المياه قبل إلقائها في حوض التفريغ. لقد أصبح تصريف المواد الخطرة مثل البترول والمذيبات الكيميائية على البيئة المائية محور قلق متزايد من منظمات الصحة العالمية بسبب التأثيرات السلبية لهذه المواد على صحة الإنسان والبيئة؛ وقد تبين أن تركيزات منخفضة من البترول (0.1) جزء في المليون أن تكون شديدة السمية. يجب أن تكون هناك قرارات ملزمة للإلتزام بقانون البيئة لسنة 1994 ، والذي يلزم بمعالجة النفايات داخل الشركات قبل تصريفها إلى أحواض الصرف ثم بعد ذلك إلى الخلجان والبحار، والتحكم في منع تسريب المياه الزيتية عن طريق فصل الزيوت منها وأن تخضع التركيزات للمعايير المسموح بها عالمياً.