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Distribution of oil, grease and polycyclic aromatic hydrocarbons in coastal water and sediments of Suez Bay

by

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Abstract

The permanganate index (PI), oil and grease (O&G), and 17 polycyclic aromatic hydrocarbons (PAHs) were analyzed in surface sediment and water samples collected at 13 sites along the western coast of Suez Bay (SB). PI and O&G in the SB coastal seawater ranged from 9.6 mg O_2 l^{-1} and 17.0 mg l^{-1} to 16.0 mg O_2 l^{-1} and 37.0 mg l^{-1}, respectively. The level of polycyclic aromatic hydrocarbons (PAH) in water and sediment in the SB offshore area was determined by gas chromatography/flame ionization detection. The concentration ranged from 0.574 to 16873.2 ng g^{-1} in the sediment and 0.502 to 43.540 ng l^{-1} in water. The collected data were compared with values reported in the literature. The possible source and origin of pollution was also assessed based on the determined relative PAH levels at the study sites, the ratio of low molecular mass PAHs (LPAHs) to high molecular mass PAHs (HPAHs), and molecular indices of samples.

Key words: permanganate index, oil and grease, polycyclic aromatic hydrocarbons, pollution, coastal water, Suez Bay

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1. Introduction

Although very low content of petroleum hydrocarbons (< 1 ng ml^{-1}) stimulates photosynthesis in seawater, higher concentrations result in a gradual reduction of photosynthesis in algal cultures (O'Brien & Dixon 1976; Witt et al. 2014). Petroleum hydrocarbons can be classified into the following classes: aliphatic, aromatics, resins, and asphaltenes (Steliga 2012). The former are commonly degraded by microorganisms, while large branched aliphatic chains and aromatic hydrocarbons usually persist in the environment (Hasanuzzaman et al. 2007). Polycyclic aromatic hydrocarbons (PAHs) consist of two or more fused aromatic rings and comprise naphthalene (NAP), acenaphthene (ACE), fluorine (FLU), phenanthrene (PHE), and pyrene (PYR), which are considered model compounds due to their common presence in the environment (Ahmed et al. 2020; Chen et al. 2010). Some polycyclic aromatic hydrocarbons (*PAHs*) are hazardous chemical pollutants of the environment (Purcaro et al. 2015). NAP, ACE, FLU, PHE, anthracene (ANT), PYR, fluoranthene (FLA), and benzo[a]pyrene (bPYR) were classified by the United States Environmental Protection Agency (USEPA) and the World Health Organization (WHO) as hazardous pollutants among other PAHs (Yan et al. 2004). Due to their carcinogenic and mutagenic properties, their concentration levels should be monitored periodically in different matrices. They mainly originate from incomplete fossil fuel combustion and the production of crude oil and petroleum products (Ahmed et al. 2015; Szefer 2013). They occur wherever oil is extracted, transported, stored, processed, or used at sea or on land.

The Gulf of Suez (GS) extends for about 320 km from the city of Suez in the north to Shadwan Island in the south. It represents the northwestern stretch of the Red Sea with an average width of 50 km. Suez Bay (SB) is a shallow extension of the GS, roughly elliptic in shape, with its major axis running NE–SW (Fig. 1). Its average length along the major axis is about 13.2 km, while its average width along the minor axis is about 8.8 km. The mean depth is 10 m, and the plane surface area is about 77.13 km^2 (Hamed et al. 2010). SB is connected with the GS through most of its southeastern side, where a channel is dredged to a depth of 20 m to serve navigation purposes, and with the Suez Canal by a 12 m deep dredged channel through the northeastern side of SB (Elmorsi et al. 2020). The circulation in SB can be generally retraced by following the respective characteristics of these two water types. It was found that seawater in SB circulates counterclockwise by entering SB from the GS on the eastern side (Sinai side) and leaving SB on the western side (Abou-El-Sherbini & Hamed 2000). The growing activity of ports on the western side of SB has led to an increase in shipping and municipal waste in the whole region (El Diasty et al. 2017).

The content of PAHs was assessed in the aquatic ecosystem of the GS region. PAHs were analyzed in the surface sediments and in eleven fish species from the Gulf of Suez (Abdallah et al. 2016; El-Agroudy et al. 2007; Elfadly et al. 2017; Younis et al. 2018). Their content ranged from 1667.02 to 2671.27 ng g^{-1}, with the highest levels observed at the towns of Ras Gharib, Aion Mousa, and Abu Zanima. The total concentration of 16 PAHs in collected fish specimens fluctuated between 621 and 4207 ng g^{-1} wet mass. High molecular mass PAHs (HPAHs) dominated compared to low molecular mass PAHs (LPAHs). LPAHs/HPAHs values were less than unity, indicating an anthropogenic origin of PAHs in fish. The presence of PAHs and aliphatic hydrocarbons (AHs) in the GS has been attributed to anthropogenic activity, as well as petrogenic and biogenic sources (Abdallah et al. 2016). Non-aromatic hydrocarbons in the GS have been reported as originating from multiple terrestrial sources, being of biogenic and pyrolytic origin, and include mainly petrogenic and biogenic hydrocarbons (Elfadly et al. 2017). The main sources of petroleum contamination are the port of Al-Attaqa, the Suez oil processing company, the Al-Nasr Oil Company, AL-Kabanon, and EL-Sukhna of Loloha Beach. Chrysene (CHR), bPYR, and FLU were recorded at concentrations

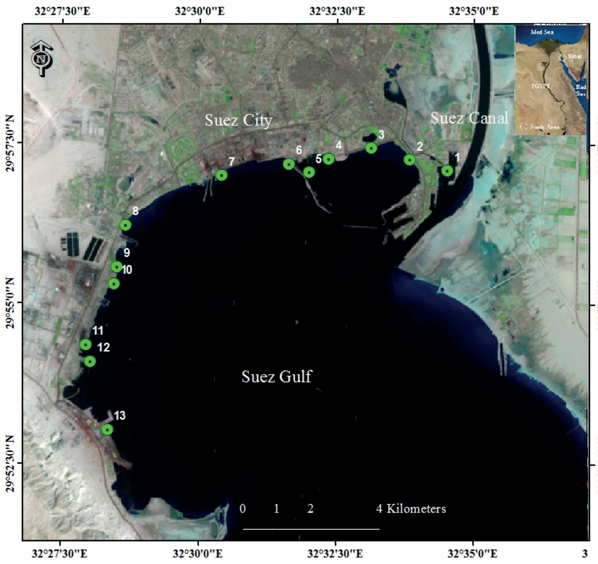

Figure 1

Sampling sites in Suez Bay, Egypt. The map was copied using Google Earth software of 27.610, 9.802 and 4.563 μg l^{-1}, respectively (Said et al. 2001). The content of dissolved/dispersed petroleum hydrocarbons (DDPH) in water of the GS ranged from 3.92 to 363.77 μg l^{-1}, with high concentrations in winter (El-Agroudy et al. 2007). In general, high concentrations of DDPH were recorded in water, as well as in algal and fish samples collected from SB. Total PAHs ranged from 0.033–2.41 μg l^{-1}, 0.006–5.31 μg g^{-1} and 0.358–0.637 μg g^{-1} in water, algae, and fish samples, respectively. Benzo(b)fluoranthene (bbFLA) was the most dominant fraction in water, with 1.634 μg l^{-1} recorded upstream of the port of El-Zeitia.

Such undesirable discharges disturb the ecological balance and deteriorate the quality of water intended for human use. For these reasons, it is necessary to monitor the content of PAHs in SB. This study presents an assessment of the current PAH levels in water and sediments along the western coast of SB.

2. Materials and methods

2.1. Site description

The study area, Suez Bay, is located in the northwestern part of the Gulf of Suez, in the Red Sea (Fig. 1). SB has two important ports, Adabiyah and Tawfik, which receive discharges from anthropogenic, commercial and industrial activities that can affect water quality. SB also receives sewage and waste both from the city of Suez and from ships awaiting transport through the Suez Canal. In addition, it receives waste from the industrial complex south of Suez, including oil refineries, a fertilizer plant, power stations and other industries. All types of waste coming from different sources are directly or indirectly discharged untreated or after treatment into SB. This waste contains a wide variety of chemical residues, including aromatic derivatives (Belal 2019).

2.2. Sampling Procedure

Water and sediment samples were collected from 13 different sites on the west coast of SB in April 2018 (Fig. 1). Surface water samples were collected in triplicates (within a 5 m diameter area) into narrow-necked amber glass bottles with teflon lined caps. Samples were acidified to approximately pH 2 using 10% HCl to inhibit bacterial activity during transportation and storage. Surface sediment (0–5 cm) samples were collected using a Van Veen grab sampler. Offshore sediments (5–6 grabs within a 5 m diameter area) from each site were mixed well and then poured into pre-cleaned wide-mouth glass bottles. Samples were stored in a refrigerator at 4°C and handled immediately upon return to the laboratory according to the recommended techniques (APHA/AWWA/WEF 1999).

2.3. Analytical techniques

All chemicals were of Merck chromatography purity grade. The permanganate index (*PI*), also referred to as the alkaline COD_{Mn} protocol in the Chinese standard method for COD (Chemical Oxygen Demand) in seawater (GB1737.4-2007), was determined as described in the literature (Goh & Lim 2008). In brief, 1 ml of 25% NaOH was added to 100 ml of a water sample in a 250 ml conical flask, and then 10 ml of $KMnO_4$ solution (0.01 M) was added. The mixture was thoroughly mixed, heated for 30 min in a water bath at 96–98°C, and then quenched in an icebox to room temperature. Next, 5 ml of 5 M H_2SO_4 solution and 0.5 g of KI were added to the mixture. It was then kept in the dark for 5 min and unreacted $KMnO_4$ was titrated with 0.01 M $Na_2S_2O_3$ solution using 1 ml of 0.5% starch as an indicator. The volume of thiosulfate solution used was recorded as V_1 (ml). The procedure was repeated replacing the distilled water with a water sample and the volume of thiosulfate solution used was recorded as V_0 (ml). The whole procedure was performed three times and average volumes were used in Eq. (1) to calculate *PI*.

$$PI = \frac{(0.01 \times (V_0 - V_1) \times 8000)}{100} \ (mg\ O_2\ l^{-1}) \qquad (1)$$

Oil and grease (O&G) were analyzed according to the standard method 1664A of the US EPA (U.S. ENVIRONMENTAL PROTECTION AGENCY 1999). For O&G extraction, *n*-hexane (95%) was used in three aliquots of 30 ml added to 1 l of water, and then 20 ml of n-hexane was used for rinsing. The organic phase was collected from each separation and stirred in an Erlenmeyer flask containing 30 g of anhydrous sodium sulfate moistened with *n*-hexane. The extract had a light yellowish color, so procedure 1664A was considered suitable for gravimetric analysis. The extract was filtered in a clean Erlenmeyer flask with silica gel (3.0 g) under magnetic stirring for 5 min. Then the extract was filtered, collected in a pre-weighed (initial mass) beaker, and evaporated in a drying oven at 60°C till constant mass (final mass). The total O&G content was calculated by Eq. (2):

$$Total\ O\&G\ (mg\ l^{-1}) = \frac{1000 \times [final\ mass\ (g) - initial\ mass\ (g)]}{sample\ volume\ (l)} \qquad (2)$$

PAHs were determined using a gas chromatography/flame ionization detector (GC/FID) as described in revised EPA standard method 8015D.

Seawater samples (1 l) were extracted three times with 60 ml of dichloromethane in a separatory funnel according to the US EPA 3510C liquid-liquid extraction technique. Sample extracts were collected and concentrated by rotary evaporation to 5 ml. Samples were then concentrated under a gentle stream of pure nitrogen to a final volume of 1 ml.

Clean-up and fractionation were performed prior to gas chromatography/flame ionization detection (GC/FID). First, 1 ml of the extracted volume was passed through a cleaning column prepared by the slurry packing method using 20 ml (10 g) of silica, followed by 10 ml (10 g) of alumina, and finally 1 g of anhydrous sodium sulfate (dehydrator). Alumina (EPA 3611) and silica gel (EPA 3630) columns are for clean-up, by which the fatty matter is excluded based on polarity, and petroleum hydrocarbons are fractionated into aliphatic and aromatic fractions (Adeniji et al. 2017). Elution was performed using 40 ml of hexane/dichloromethane (90:10), followed by 20 ml of hexane/dichloromethane (50:50). The first elution fraction, containing aliphatic petroleum hydrocarbon was discarded, while the second elution fraction, containing combined PAHs, was used later. Finally, the eluted samples were concentrated under a gentle stream of purified N_2 to about 0.2 ml, prior to injection into GC/FID for PAHs analysis. All samples were analyzed using a Hewlett Packard 5890 series II GC gas chromatograph equipped with a flame ionization detector (FID).

Sediment samples (10–20 g air dried) were extracted in a Soxhlet apparatus with dichloromethane according to US EPA Method SW846 3540. The siphoning cycle lasted about 30 min with at least 10 repetitions. After the process of Soxhlet extraction was completed, the solvent was evaporated to about 1 ml using a rotary evaporator. Activated copper powder was used to remove sulfur compounds from the extract. The final extracted volume (1 ml) of sediment was cleaned and fractionated as described above and then injected into a gas chromatograph (Hewlett Packard, 5890 series II) with a capillary column (25 m long × 0.2 mm i.d. × 0.5 µm thick), Ultra-1, coated with 100% dimethylpolysiloxane. Nitrogen was used as a carrier gas at a flow rate of 4 ml min^{-1}. The temperature programing rate was 8°C min^{-1} from an initial hold of 50°C to a final hold of 290°C. The blank used for the GC analysis was a standard PAH mixture, including 10 ppm NAP, ACE, acenaphthylene (ACEL), FLU, PHE, ANT, carbazole (CAR), FLA, PYR, benzo(a)anthracene (bANT), CHR, bbFLA, benzo(k)fluoranthene (bkFLA), bPYR, dibenzo(a,b)anthracene (dbANT), indeno(1,2,3-c,d) pyrene (inPYR) and benzo(g,h,i)perylene (bPRL) dissolved in n-hexane (Younis et al. 2018).

The GC/FID apparatus was equipped with a spotless injector (3 µl). The detector was maintained at 30°C, while the injection port was maintained at 290°C. The oven temperature program ranged from 60 to 290°C, ramped at 3°C min^{-1}, and maintained at 290°C for 25 min. Nitrogen was used at a rate of 1.2 ml min^{-1}.

Quality Controls: To study the recovery efficiency, three analyses were conducted on PAH standard reference materials (SRM 2974) provided by the National Institute of Standards and Technology (NIST, USA). The analyses showed that the efficiency fluctuated between 90 and 105% with a coefficient of variation (CV) of 6–10% for all 16 PAHs. Quality assurance was also carried out by analyzing blank samples spiked with a known quantity of each PAH standard. The values of PAHs in blank samples were below the detection limit of the instrument (0.01 µg ml^{-1}).

2.4. Apparatus

The examined samples were analyzed using Hewlett Packard 5890 series II GC equipped with a flame ionization detector (FID).

2.5. Statistical evaluation

The two-tailed bivariate Pearson correlation test was used to assess significant differences in the obtained *PI*, O&G, and PAHs results compared with water quality parameters at different study sites

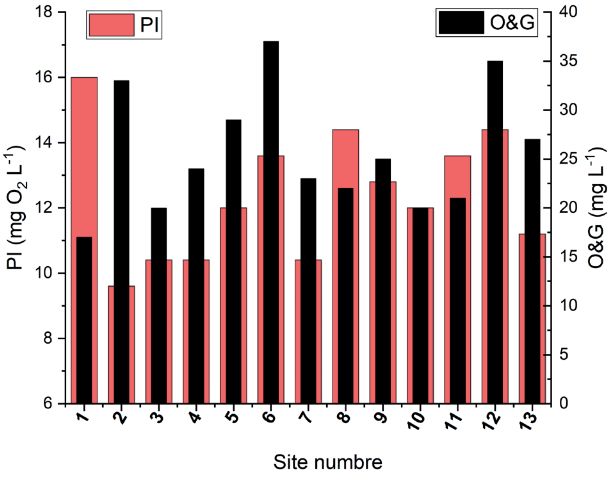

Figure 2

Variation in permanganate indices (*PI*, mg O_2 l^{-1}) and oil and grease (O&G, mg l^{-1}) along the western coastal waters of Suez Bay recently reported (Elmorsi et al. 2020), using SPSS software version 16.

3. Results

3.1. Assessment of the permanganate index and oil and grease in water of Suez Bay

Figure 2 shows the distribution of *PI* and O&G in coastal seawater of SB, which is detailed in Table 1. The highest *PI* value (16.0 mg O_2 l^{-1}) was recorded at site 1, whereas the lowest value (9.6 mg O_2 l^{-1}) at site 2. The mean *PI* value in SB was 12.4 mg O_2 l^{-1}.

The highest O&G value (37.0 mg l^{-1}) was recorded at site 6, followed by sites 12 and 2, whereas the lowest value (17.0 mg l^{-1}) was recorded at site 1. The mean value was 25.6 mg l^{-1}.

3.2. Assessment of polycyclic aromatic hydrocarbons

The PAHs investigated are 17 compounds: NAP, ACE, ACEL, FLU, PHE, ANT, CAR, FLA, PYR, bANT, CHR, bbFLA, bkFLA, bPYR, dbANT, inPYR, and bPRL. PAH values in seawater (Fig. 3) ranged from 0 (below detection limit, BDL) at site 5 near the Pilgrim village and at site 10 near NIOF (National Institute of Oceanography and Fisheries), to 114.0 ng l^{-1} (47.11% of the total PAH content in the study area) at site 12. The 17 PAHs were distributed in water with PYR (34.52%), FLU (28.19%), and CHR (11.46%) having the highest concentrations, while CAR was absent.

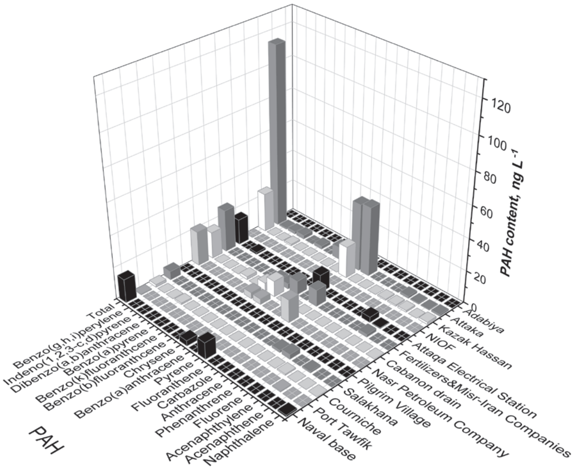

Figure 3

Concentration of PAHs at different sites in the western coastal waters of Suez Bay in 2018 expressed in ng l^{-1}

Table 1

Variation in permanganate indices (*PI*, mg O_2 l^{-1}) and oil and grease (O&G, mg l^{-1}) along the western coastal waters of Suez Bay

Site no.	Site name	*PI* mg O_2 l^{-1}	O&G mg l^{-1}
1	naval base	16.0	17
2	port Tawfik	9.6	33
3	Courniche	10.4	20
4	Salakhana	10.4	24
5	Pilgrim Village	12.0	29
6	Nasr Petroleum Company	13.6	37
7	Cabanon drain	10.4	23
8	Fertilizers and Misr-Iran Companies	14.4	22
9	Attaqa Electrical Station	12.8	25
10	NIOF	12.0	20
11	Kazak Hassan	13.6	21
12	Attaka	14.4	35
13	Adabiya	11.2	27

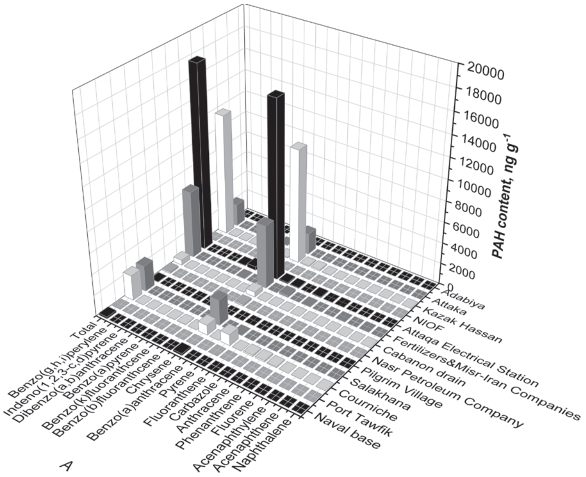

Figure 4

Concentration of PAHs at different sites in the western coastal sediments of Suez Bay in 2018 expressed in ng g^{-1}

The highest values of NAP, ACE, ACEL, FLU, PHE, ANT, CAR, FLA, PYR, bANT, CHR, bbFLA, bkFLA, bPYR, dbANT, inPYR and bPRL in seawater were 1.41, 0.42, 1.80, 3.37, 2.95, 1.47, 0, 43.5, 42.3, 10.2, 9.89, 5.00, 1.96, 1.83, 2.36, 1.63, and 0.82 ng l^{-1}, while their mean values were 0.27, 0.03, 0.41, 0.48, 0.28, 0.11, 0, 5.24, 6.43, 1.45, 2.13, 0.88, 0.15, 0.15, 0.33, 0.21 and 0.06 ng l^{-1}, respectively.

The level of PAHs in the sediments (Fig. 4) ranged from 0 (BDL) at sites 10 (NIOF) and 13 (Adabiya) to 17 669 ng g^{-1} (40% of the total PAH content in the study area) at site 9. The main PAH in the sediments was CHR, accounting for 92% (40141 ng g^{-1}) of the total content of 17 PAHs.

The mean values of NAP, ACE, ACEL, FLU, PHE, ANT, CAR, FLA, PYR, bANT, CHR, bbFLA, bkFLA, bPYR, dbANT, inPYR and bPRL in the sediment samples collected from the SB study sites were 0, 1.36, 0, 1.61, 7.58, 12.49, 19.43, 2.85, 116.91, 17.67, 3087.80, 12.80, 59.15, 11.05, 2.27, 1.76, 4.12 ng g^{-1}, respectively.

3.3. Source diagnostic ratios of PAHs in SB

Low molecular weight PAHs (LPAHs)/high molecular weight PAHs (HPAHs) ratios for seawater and sediment samples collected from the SB sites were below 1 as detailed in Table 2.

According to the results presented in Table 2, the PHE/ANT ratios in water and sediments are mainly below 5 at all sites, except for water at site 12.

3.4. Statistical evaluation

The current content of PAHs in water and sediments of SB were statistically compared with the water quality parameters recently published for the same (Elmorsi et al. 2020). Interestingly, a significant correlation was obtained between total PAHs in the sediments and water temperature. The *PI* was also negatively correlated with chlorophyll-*a* in water. The detailed statistical evaluation is available in the supplementary data provided as S1.

Table 2

Comparison of current mean values of *PI*, O&G, TPAHs in seawater and TPAHs in sediments of SB with previously published data

reference (place, year)	*PI* mg O_2 l^{-1}	O&G mg l^{-1}	TPAHs	
			seawater (ng l^{-1}) dominant PAH	sediment (ng g^{-1}) dominant PAH
this work (SB, 2018)	12.4	25.6	13.6 PYR, FLU, CHR	3359 CHR
Soliman et al. 2017 (SB, 2013–2014)	17.1– 18.87*	14.7–28.0		
Emara et al. 2013 (GS, 2013)	36.8–296*			
Environmental Impact Assessment (EIA) for a Proposed Methanol Facility in Damietta Port (Draft Report), 2006 (Damietta port, 2006)	22.5–585*			
Eed et al. 2016 (port Tawfik – El Ain Sokhna, 2016)		81.7		
State of Oil Pollution and Management in Suez Gulf Region 2008 (SB, 2004–2005)		4–213		
Eed et al. 2016 (GS, 2016)		4–14		
Soliman et al. 2017 (SB, 2013–2014)		14.7–90.9		
Ahmed et al. 2015 (drainage basin of Suez Oil Petroleum Company, 2014)			65–2 338 413 NAP, ACE, FLU, PHE, ANT	65–2 338 413 NAP, ACE, FLU, PHE, ANT
El-Agroudy et al. 2007 (GS, 2004–2005)			33–2410	
El-Agroudy et al. 2007 (GS, 2011)			160 FLU, bANT, PYR, iPYR, bkFLA	103–208 FLU, bANT, PYR, iPYR, bkFLA
Ali et al. 2006 (Suez Canal, 2005)			520–3 393 000 inPYR	586–8593 inPYR
Soliman et al. 2019 (Arab Gulf, 2014–2015)				112 PHE, ANT, CHR
Azab et al. 2012 (SB, 2013)				719 000
Jaward et al. 2012 (an estuary in Mexico, 2007)			9–347 PHE, PYR, NAP	27–418 PHE, PYR, NAP

* $K_2Cr_2O_7$-COD

4. Discussion

4.1. *PI* and O&G

The alkaline *PI* is a good indication of COD in seawater, representing almost > 80% of the total COD in water, including PAHs (Goh & Lim 2008). The approximately salinity-independent results of alkaline *PI* makes it the most reliable indicator of COD in seawater, in contrast to acidic *PI* and $K_2Cr_2O_7$-COD (Li et al. 2016). The highest *PI* value at site 1 may be due to port activities in the naval base. The mean value is slightly lower than the oxidizable organic matter values reported for SB in 2013 (17.1–18.87 mg O_2 l^{-1}; Soliman et al. 2017), but it is much lower than COD values (36.8–296 and 22.5–585 mg O_2 l^{-1}) reported in 2013 in GS and in 2006 at the port of Damietta, respectively [Emara et al. 2013; Environmental Impact Assessment (EIA) for a Proposed Methanol Facility in Damietta Port, Draft Report 2006]. These findings may indicate an improvement in water quality in SB.

The main components of O&G values are non-polar organic materials, which are also known as petroleum-based hydrocarbons and fatty compounds of biological origin (Adeniji et al. 2017). The highest values of O&G can be attributed to the activities of the ports of Tawfik and Attaka and the poorly treated wastewater from Nasr Petroleum Company (NPC). The mean value (25.6 mg l^{-1}) is lower than the values obtained in 2016 (81.7 mg l^{-1}) in the area between the port of Tawfik and the port of El Ain Sokhna (Eed et al. 2016). NPC, in particular, was reported to discharge oily wastewater into the GS at a rate of 360 000 m^3 day^{-1} (Younis et al. 2018). The effluent from Suez Petroleum Manufacturing Co. (SPMC) is almost compliant with the Egyptian effluent standards. However, 6060 kg of O&G was reported to flow daily in receiving waters (State of Oil Pollution and Management in Suez Gulf Region 2008). However, the current values of O&G are within the range of those obtained in SB in spring and summer of 2013–2014 (14.7–28.0 mg l^{-1}; Soliman et al. 2017). These important differences in the 2013–2018 period may indicate increasing water treatment efforts in relation to increasing marine activities during the same 2001–2019 period (Egypt GDP: Suez Canal 2020). However, more efforts should be made to reduce O&G values to levels below the standard value specified for oily mixtures discharged from ships and unclean ballast water discharged from oil tankers, as specified by Law No. 4 (State of Oil Pollution and Management in Suez Gulf Region 2008). Table 2 illustrates a comparison between the current mean values of *PI*, O&G, TPAHs (total PAHs) in seawater and TPAHs in sediments of SB with previously published data.

4.2. PAHs

The highest values of total PAHs in water (114.0 ng l^{-1}, 47.11% in the study area) obtained at Attaka site 12 may be due to fishing boat activities. The highest and mean values of the studied PAHs in water at the SB study sites were lower than those recorded in the Suez Canal (5.74, 2.73, 2.79, 4.85, 7.54, 3.45, 22.50, 16.47, 32.63, 8.82, 7.68, 10.58, 5.10, 16.61, 6.64 and 19.06 ng l^{-1} for NAP, ACEL, ACE, FLU, ANT, PHE, FLU, PYR, bANT, CHR, bbFLA, bkFLA, bPYR, dbANT, bPRL, and inPYR, respectively; Al-Agroudy et al. 2017). The current total PAHs (below the detection limit – 114.00 ng l^{-1}) were also remarkably lower than the values reported from the Suez Canal (992.56 ng l^{-1}) and the port of Alexandria (1364.59 ng l^{-1}), but are still 10 times higher than the values reported from the Sea of Japan (Honda & Suzuki 2020).

The high values of PAHs in the sediments at site 9 may be affected by discharges from the Attaqa Electrical Station. The following concentrations of PAHs in the sediment were previously classified as low, moderate, high and very high contamination: 0–100, 100–1000, 1000–5000, > 5000 ng g^{-1}, respecitvely (Baumard et al. 1998). Therefore, the surface sediments of Suez Bay can be classified as very highly contaminated at sites 8, 9 and 12, whereas the other sites show low contamination.

The sites where PAHs concentrations were low, such as the port of Tawfik and the Pilgrim village, were far from the pollution source. On the contrary, the high concentrations recorded at some sites, such as at NPC, the electrical station and Attaka, could be attributed to the proximity of these sites to pollution sources such as oil tanker transportation and oil drilling activities concentrated in these regions. However, the counterclockwise circulation of surface water in SB is an important factor that spreads pollutants southward from their actual source on the west coast, especially in the sediments (Eladawy et al. 2018).

The current mean values of PAHs in the sediments at the SB study sites were lower than the reported values: 14.03, 28.93, 38.69, 21.94, 87.99, 15.54, 125.08, 68.32, 104.08, 62.99, 35.05, 21.60, 37.43, 18.56, 25.89, and 12.89 μg l^{-1} for NAP, ACE, ACEL, FLU, PHE, ANT, FLU, PYR, CHR, bANT, bPYR, dbANT, bbFLA, bkFLA, bPRL, and inPYR, respectively, in GS (Azab et al. 2012). The current total PAHs (ND – 17 669.00 ng g^{-1}) were also much lower than the values recorded in GS (195.53 – 1189.3 μg g^{-1}; Azab et al. 2012) and in the port of Alexandria (88 to 6338 ng g^{-1}; Nemr et al. 2007) as detailed in Table 2.

When comparing the main PAHs determined in water and sediment, it was observed that CHR ranked as the third highest concentration in water after PYR and FLU compared to sediments where CHR was the major PAH. This may be attributed to the very low solubility of CHR in water (0.002 mg l^{-1}) compared with PYR (0.135 mg l^{-1}) and FLU (0.260 mg l^{-1}; Lu et al. 2008). Seven PAHs were identified as likely human carcinogens: bANT, bPYR, bbFLA, bkFLA, CHR, dbANT, and inPYR, of which CHR is the dominant PAH in both sediment and water. Comparing the present results with reported data, the three dominant PAHs in the present study were reported repeatedly in the SB and GS regions, indicating that this may be a long-term risk to be considered (Table 2). The major PAH in the sediments (CHR) is one of the natural components of coal tar (Neff et al. 2005). It is a 4-ring component, likely produced as smoke during partial combustion of coal, gasoline, garbage, animals and plants, which may explain its presence near the Attaqa Electrical Station (Mojiri et al. 2019).

4.3. Source diagnostic ratios of PAHs in SB

The most important sources of PAHs in the marine environment are either petrogenic or pyrogenic. Petrogenic sources are associated with natural discharge of petroleum or petroleum products into the environment, while pyrogenic sources are associated with the imperfect combustion of fossil fuels (Tobiszewski & Namieśnik 2012). PAHs in the literature were divided into low molecular mass PAHs (LPAHs) and high molecular mass PAHs (HPAHs). LPAHs contain two to three rings, whereas HPAHs contain four to six rings and are extremely carcinogenic (Younis et al. 2018). The LPAHs/HPAHs ratio > 1 indicates a petrogenic source, while the LPAHs/HPAHs ratio < 1 indicates a pyrogenic source (Zhang et al. 2015). In this study, the ratios were below 1 for seawater at all 13 sites, which suggests a predominance of a pyrogenic source of PAHs, except for sites 2 and 4, where no HPAHs were recorded, indicating a petrogenic origin. On the other hand, LPAHs/HPAHs ratios for sediment at all 13 sites are below 1, indicating a pyrogenic origin of PAHs (Table 3).

Furthermore, some molecular indices play an important role in determining the origin of PAHs, e.g. the PHE/ANT ratio in the case of three-ring isomers and the FLU/PYR ratio in the case of four-ring isomers. They were selected according to their thermodynamic stability; PHE and FLU are thermodynamically more stable. Thus, the PHE/ANT ratio of pyrogenic PAH assemblages is usually below 5, while the petrogenic ratio is usually above 5. The FLU/PYR ratio usually approaches or exceeds a value of 1 in pyrogenic assemblages and is usually significantly below 1 in petrogenic PAH assemblages (Neff et al. 2005). According to the results presented in Table 3, the PHE/ANT ratios are usually below 5 at all sites, except for water at site 12, which indicates a dominant pyrogenic origin of PAHs in sediment and water of SB due to industrial as well as shipment activities, which is consistent with the conclusion drawn from the above LPAHs/HPAHs ratios. On the other hand,

Table 3

PAH concentrations in water (W) and sediment (S) samples in SB based on the number of aromatic rings and PAH ratios

site	LPAHs (2–3 rings)		HPAHs (4–6 rings)		LPAHs/HPAHs		FLU/PYR		PHE/ANT	
	W (ng l^{-1})	S (ng g^{-1})	W (ng l^{-1})	S (ng g^{-1})	W	S	W	S	W	S
1	1.019	0.575	13.716	177.261	0.07	0.00	0	-	-	0
2	0.502	1.171	0.000	11.203	∞	0.10	-	0	-	0
3	0.727	334.239	0.937	2069.393	0.78	0.16	-	0	-	0.57
4	5.297	4.252	BDL	2456.395	∞	0.00	-	0	2.01	0
5	BDL	4.318	BDL	31.077	-	0.14	-	0	-	1.21
6	BDL	BDL	21.644	169.064	0.00	0.00	∞	-	-	-
7	BDL	BDL	16.733	492.426	0.00	0.00	-	0	-	-
8	1.796	71.865	24.827	6370.110	0.07	0.01	∞	0.03	-	0.31
9	3.878	130.909	12.342	17 538.434	0.31	0.01	0	0.18	-	1.06
10	BDL	BDL	BDL	BDL	-	-	-	-	-	-
11	3.394	4.834	110.602	11 670.158	0.03	0.00	1.03	0.15	-	0
12	3.892	0.000	20.669	2127.562	0.19	0.00	0	0	∞	-
13	BDL	BDL	BDL	BDL	-	-	0	-	-	0

the FLU/PYR ratios are above 1 only at sites 6, 8 and 11, which confirms the pyrogenic origin of PAHs at these sites, whereas the differences may be due to the continuous counterclockwise circulation of water in SB (Abou-El-Sherbini & Hamed 2000).

4.4. Statistical evaluation

The current content of PAHs in water and sediment of SB was statistically compared with the water quality parameters recently published for the same samples (Elmorsi et al. 2020). A significant correlation was obtained between TPAHs in the sediments and water temperature, which may indicate that the source of PAHs is affected by a heat source such as cooling water. The *PI* was also negatively correlated with chlorophyll-*a* in water. This is an important indication that the presence of oxidizable matter is responsible for a reduction in chlorophyll production (Yang et al. 2008). The detailed statistical evaluation is available in the supplementary data as S1.

5. Conclusion

In this study, *PI*, O&G, and 17 polycyclic aromatic hydrocarbons (PAHs) were analyzed in surface sediment and water samples collected at 13 sites along the western coast of Suez Bay. The levels of the studied pollutants were lower compared to previous reports. The *PI* and O&G in the SB coastal seawater ranged from 9.6 mg O_2 l^{-1} and 17.0 mg l^{-1} to 16.0 mg O_2 l^{-1} and 37.0 mg l^{-1}, respectively. The results also indicate that the total PAH levels in sediment samples ranged from ND to 17 669.00 ng g^{-1} and ND to 114.00 ng l^{-1} in water samples. Based on the results obtained from several diagnostic ratios, the source for PAHs in the analyzed water and sediment samples was identified as pyrogenic. The qualitative and quantitative analysis of water and sediment samples from SB indicates that they are contaminated with PAHs. The statistical evaluation suggests that the presence of oxidizable matter is the cause of reduced chlorophyll production, which is problematic given the tendency of organic matter, especially PAHs, to trigger carcinogenic and mutagenic effects in terrestrial and aquatic biota.

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Supplement 1

Statistical correlation study

environmental parameter	factor	PI	OG	TPAHs in sediment	TPAHs in water	T	pH	TDS	Cl	DO	BOD	NH_4	NO_2	NO_3	PO_4	SiO_4	Chl *a*	TRIX
PI	PCn	1	−0.092	0.231	0.499	0.104	−0.411	−0.114	−0.336	-0.022	−0.1	0.363	−0.067	-0.003	−0.539	−0.101	−0.711(**)	−0.476
	S2t		0.766	0.447	0.099	0.736	0.163	0.71	0.262	0.942	0.746	0.222	0.828	0.992	0.057	0.742	0.006	0.1
	N	13	13	13	12	13	13	13	13	13	13	13	13	13	13	13	13	13
OG	PCn	−0.092	1	−0.21	0.445	0.06	0.447	0.06	0.275	0.157	−0.081	0.064	0.237	0.277	0.502	0.318	0.352	0.478
	S2t	0.766		0.49	0.148	0.845	0.125	0.845	0.362	0.609	0.792	0.835	0.436	0.359	0.08	0.289	0.239	0.099
	N	13	13	13	12	13	13	13	13	13	13	13	13	13	13	13	13	13
TPAHs in sediment	PCn	0.231	−0.21	1	0.072	0.596(*)	0.083	0.487	−0.198	0.211	0.001	0.254	0.167	0.219	−0.046	0.361	−0.255	0.037
	S2t	0.447	0.49		0.824	0.031	0.788	0.092	0.517	0.488	0.996	0.403	0.586	0.472	0.881	0.226	0.401	0.903
	N	13	13	13	12	13	13	13	13	13	13	13	13	13	13	13	13	13
TPAHs in water	PCn	0.499	0.445	0.072	1	0.278	0.164	0.187	−0.059	0.3	0.21	0.243	0.237	0.281	0.169	0.384	−0.322	0.149
	S2t	0.099	0.148	0.824		0.381	0.61	0.561	0.855	0.343	0.512	0.446	0.458	0.375	0.601	0.217	0.307	0.645
	N	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12

* Correlation is significant at the 0.05 level (2-tailed);

** Correlation is significant at the 0.01 level (2-tailed);

a Can not be computed because at least one of the variables is constant;

Pearson Correlation, Sig. (2-tailed) PCn, S2t;

Probability at a level of 0.05 or less was considered significant. Parameters with no data for more than 6 sites were excluded from the statistical analysis