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Polycyclic aromatic hydrocarbons (PAHs) in surface sediments from the Karachi Harbour and off-Clifton Coast, Karachi: spatial distribution, composition and ecological risk assessment

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Abstract

We reported the distributions and compositions of sixteen polycyclic aromatic hydrocarbons (PAHs) of 13 surface sediment samples of the Karachi Harbour and off-Clifton coast. The total concentrations of the PAHs in surface sediments ranged from 6.47 to 104.462 ng/g dry weights with a mean concentration 27.519 ng/g dry weights. PAHs distribution showed that 2-3- and 4-ring PAHs were predominant in almost all of the samples. On average, 2-3, 4, and 5-6-ring PAHs consisted of 56 %, 42 % and 2% of total PAHs, respectively. The m-ERM-q and Risk Quotient (RQ) were also used to assess the ecological risk of PAHs. The m-ERM-q average values were 0.61 and 0.14 in Karachi Harbour and off-Clifton coast respectively. The value of m-ERM-q indicates that PAHs concentrations are approximately 9-21% and with 30-46% probability of toxicity to benthic organisms of off-Clifton coast and Karachi Harbour respectively. Risk Quotient RQ Σ PAHs (NCs) calculated values were in a range from 5,301 to 32,810. The present study results show that the ecological risk of PAHs in the sediments of Karachi Harbour were very high but there was relatively lower risk in off-Clifton coast sediments. The purpose of this study was to determine the ecological risk of PAHs in marine environment of the Karachi harbor and off-Clifton coastal sediments.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) with two or more fused rings form a large group of organic pollutants. PAHs are formed as incomplete combustion products of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat (Nadal *et al.*, 2004). The subjection of organic material in sediments to a low-temperature (100 to 300°C) environment for long periods of time produces PAHs as coal and oil deposits within sedimentary rock formations (Diagenesis) Neff, (1985) and Grimmer, (1983). Aquatic contamination by PAHs is caused by petroleum spills, discharges, and seepages; industrial and municipal wastewater; urban and suburban surface runoff; and atmospheric deposition (Eisler, 2000).

Karachi is a densely populated city of Pakistan it is located on the northern border of the Arabian Sea. Its population is estimated more than 20 million. More than 10,000 varieties of industries are located in five industrial estates (SITE, West wharf and Federal B area, LITE and KITE). The first three are located along the Lyari River and the next two are along the Malir River. Karachi generates more than 550 MGD of wastewater, approximately 60% of this waste comes from industries and 40 % is domestic. Lyari River receives more than 250 MGD wastewater, while Malir receives 200 MGD wastewater. The Karachi municipal authorities treat only 50-55 MGD waste water (Karachi Water Sewerage Board 2017). Waste water from the Lyari River comes into the marine environment through Karachi Harbour and spreads due to tidal action in Clifton shore and offshore areas.

The Karachi Harbour is one of the biggest seaports of Pakistan. An estimated four thousand five hundred ships visited the Karachi Harbour each year and about four thousand five mechanized boats make their fish landing at Karachi fish Harbour located in the Karachi Harbour area. An estimated 31,000 tons of oil was spilled through accidentally grounded ship Tasman Spirit in July, 2003 in shallow water of the Karachi coast. The most oil impacted coastal area was observed in the Clifton and DHA coast, Karachi Harbour and offshore area adjacent to Clifton and DHA coast (Monawwar *et al.*, 2004). Few studies have been conducted regarding the PAHs in the sediments of Karachi Harbour and Clifton coast, Sanober *et al.*, 2015; Siddiqiet *al.*, 2014. The purposes of this study are to examine the concentration and distribution of

PAHs in the surficial sediments to evaluate the ecological risk of PAHs by using the Risk Quotient RQ ΣPAHs (NCs) and m-ERM-q. The study also aimed to identify the possible sources of PAHs using the diagnostic ratio in the study area and to try to find out the impact of the oil in the study area.

Materials and Methods

Sampling

Surface sediment samples were collected from Karachi Harbour and off-Clifton coast to determine levels of sixteen types of PAHs.

The sampling sites are shown in Fig.1. Thirteen surface sediments, six from Karachi Harbour and seven from off-Clifton coast were collected during 7-8 October, 2008. Global Positioning System (GPS) was used to locate the sampling sites. Surface sediment samples were collected with a Peterson grab sampler, and the top 1cm surface layer was selected and stored in aluminum foil.

Then properly cooled in ice during transportation to the laboratory where they had been stored at (-20)°C before being freeze-dried.

The dried sediment samples in triplicates were mixed thoroughly to make a composite sample in order to minimize the degree of within site variability, and ensure that the sediment samples collected were truly representative of each site.

Extraction and cleanup

About 0.25-0.45gm of homogenized sediment samples were used for extraction. Each sample was added with 25 mL n-hexane-acetone with 7:3 (v/v) ratios in 50mL lined microwave extraction vessels.

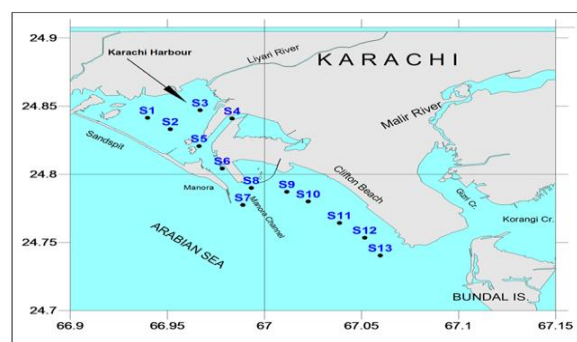


Fig. 1. Map of the study area showing sampling stations.

The samples were extracted by using “Multiwave 3000”, manufactured by Anton Paar (GmbH). The procedure of extraction was adopted from Application Note from Anton Paar website. Each extracted sample was cleaned up using glass column which size was 1.0 x 20.0 cm, packed with activated copper on the top. 2 grams (100-200 mesh) silica gel was added to column. Samples were added in a column with pre-cleaned glass pipette, followed by adding 25 ml of a mixture of Dichloromethane (DCM) and Hexane (3:1). Eluted samples were collected in a 100ml conical flask. Its volume was reduced to 2ml in a rotary evaporator. It was further reduced to 100µL with a gentle stream of ultra-pure nitrogen.

GC analysis

Cleaned extracts were analyzed using gas chromatography with flame ionization detector (GC/FID). 1µL sample was injected into GC model 6890N (Agilent Technologies), set on split less mode equipped with a 7683B series injector (Agilent Technologies) and fitted with a fused silica capillary column Heliflex® AT™-5 (30m x 0.25mm x 0.25µm). The following methods were used for the Ecological Risk Assessment of PAHs in the Karachi coastal sediments.

Mean Effect Range Median Quotient (m-ERM-q)
 m-ERM-q is developed by Long *et al.*, 1998, 2000.
 The mean ERM quotient (m-ERM-q) has been

calculated using the following equation, which calculates the mean quotient for all PAHs:

$$m-ERM-q = \Sigma(C_i/ERM_i)/n$$

Where C_i is the sediment concentration of i compound, ERM_i is the ERM value for compound i and n is the number of compounds.

Risk Quotients (RQ)

Risk Quotients (RQ) can be a useful tool for characterization of PAHs risk to organisms and ecosystem (Peijnenburg *et al.*, 2005; Wu *et al.*, 2011). Kalf proposed the risk measurement of organic substances using Risk Quotients (RQ).

The following formula is applied for Risk Quotients (RQ): $RQ_{NCs} = C_{PAHs} / NCs$

$$RQ_{MPCs} = C_{PAHs} / MPCs$$

Where RQ_{NCs} and RQ_{MPCs} are risk quotients of negligible concentrations (NCs) and maximum permissible concentrations ($MPCs$) of PAHs in water or sediments respectively (Kalf *et al.*, 1997; Li *et al.*, 2015; Cao *et al.*, 2010).

Results and discussion

PAHs concentrations, composition and source

The concentrations and composition of PAHs in the surface sediments from the Karachi Harbour and off-Clifton coast of different sampling stations are given in Table 1.

Table 1. Concentrations (ng/g, dry wt.) of 16 PAHs in surface sediments collected from the Karachi Harbour and off-Clifton coast.

| Target compounds | St-1 | St-2 | St-3 | St-4 | St-5 | St-6 | St-7 | St-8 | St-9 | St-10 | St-11 | St-12 | St-13 |
|--------------------------|-------|-------|-------|------|-------|--------|------|-------|------|-------|-------|-------|-------|
| Naphthalene | 120 | 610 | 310 | 100 | 230 | 1020 | 230 | 850 | 720 | 120 | 250 | 370 | 130 |
| Acenaphthylene | 160 | 720 | 470 | 880 | 110 | 2390 | 640 | 1470 | 290 | 290 | 2450 | 610 | 770 |
| Acenaphthene | 170 | 2780 | 1150 | 240 | 320 | 2350 | 190 | 1050 | 680 | 880 | 1270 | 690 | 830 |
| Fluorene | 15990 | 20971 | 16646 | 3409 | 20073 | 38880 | 370 | 1270 | 2870 | 2266 | 1628 | 5526 | 3200 |
| Phenanthrene | ND | 3000 | 820 | 410 | 920 | 5960 | 520 | 810 | 500 | 170 | 130 | 650 | 410 |
| Anthracene | ND | 3270 | 2680 | 450 | 5250 | 7480 | 160 | 2830 | 990 | 490 | 390 | 1290 | 450 |
| Fluoranthene | 2980 | 6070 | 1590 | 360 | 1380 | 5360 | 340 | 1530 | 1500 | 510 | 340 | 1350 | 610 |
| Pyrene | 1940 | 5230 | 2010 | 530 | 6050 | 2420 | 760 | 4610 | 1080 | 2800 | 1740 | 1850 | 360 |
| Benzo(a)anthracene | 8470 | 2030 | 140 | 990 | 2350 | 590 | 1630 | 1780 | 860 | 270 | 590 | 300 | 550 |
| Chrysene | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Benzo(b)fluoranthene | 610 | 14090 | 2630 | 250 | 2060 | 27520 | ND | 490 | 360 | 940 | ND | 810 | 280 |
| Benzo(k)fluoranthene | ND | 3954 | 7370 | 710 | 5790 | 7722 | ND | 1370 | 1000 | 2630 | ND | 2280 | 780 |
| Benzo(a)pyrene | ND | ND | ND | ND | ND | 990 | ND | ND | ND | ND | ND | ND | ND |
| Indeno(1,2,3,-c,d)pyrene | ND | 1390 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Dibenzo(a,h)anthracene | ND | ND | ND | ND | ND | 1190 | ND | ND | ND | ND | ND | ND | ND |
| Benzo(g,h,i)perylene | ND | 2410 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| ΣPAHs | 30440 | 66525 | 35816 | 8329 | 44533 | 103872 | 4840 | 18060 | 7980 | 11366 | 8788 | 15726 | 8370 |

ND Not Detected.

The concentrations of PAHs in sediments ranged from 4,840 to 103,872 ng g⁻¹ (Dry wt.) with the mean value of 26,983 ng g⁻¹ (Dry wt.). Spatial distribution pattern of total PAHs in the sediments from Karachi Harbour and off-Clifton coast are given in Fig. 2. Generally, higher values of total PAHs were recorded in the Karachi Harbour than the sediments of off-Clifton coast. The highest total PAHs concentration in the Karachi sediments was recorded at St-6, and the lowest at St-4. The highest concentration of PAHs was recorded at St-6 in Karachi Harbour which is most probably due to leakage of combusted and un-combusted fuel from intense boat operation and oil

terminal activities suspended particle mix with oil which facilitates in the sedimentation at this station. Baumard classified the PAHs pollution levels in the sediment as follows (a) low, 0-100 ng/g; (b) moderate, 100-1000 ng/g; (c) high, 1000-5000 ng/g; (d) very high, > 5000 ng/g *et* (Baumard *et al.*, 1998). According to this classification Karachi Harbour sediments lie in the high to very high levels. High levels of PAHs are most probably due to the combined effect of untreated industrial and domestic waste receives in Karachi Harbour via Lyari River from Karachi city. In addition to this Karachi port and Karachi Fish Harbour activities enhance the levels of PAHs of pollution in Karachi Harbour sediments.

Table 2. Total PAHs concentration (ng/g d.w) in sediment at different station in around the world (The pollution level assigned as Low 0-100ng/g d.w, moderate 100-1000ng/g d.w, high 1000-5000ng/g d.w, very high >5000ng/g d.w (Baumard *et al.*, 1998).

| Area | n ^a | Σ PAHs (ng/g d.w) | Level of pollution | Literature |
|------------------------------------|----------------|-------------------|-----------------------|--|
| Karachi Harbour, Karachi | 16 | 8,329-1,03,872 | High to very high | Current study |
| Off-Clifton coast, Karachi | 16 | 4,840-18,060 | High to very high | Current study |
| Kaohsiung Harbour, Taiwan | 17 | 34-16,700 | Low very high | Chen <i>et al.</i> , (2011) |
| Commercial port from Spain | 12 | 260-66,710 | Moderate to very high | Casado-Martinez <i>et al.</i> , (2006) |
| Norwegian Harbour, Norway | 16 | 2000-76,000 | High to very high | Oenet <i>et al.</i> , (2006) |
| Genoa-Voltri Harbour, Italy | 16 | 4,500-20,800 | High to very high | Salvo <i>et al.</i> , (2005) |
| Olbia Harbour, Italy | 16 | 160-770 | Moderate | De Luca <i>et al.</i> , (2005) |
| Western Harbour, Alexandria, Egypt | 20 | 8-131,150 | Low to very high | Notaret <i>et al.</i> , (2001) |
| Hsin-ta Harbour, Taiwan | 30 | 1,156-3,382 | High | Fang <i>et al.</i> , (2003) |
| Boston Harbour, USA | 16 | 7,300-3,58,000 | High to very high | Wang <i>et al.</i> , (2001) |
| Baltimore Harbour, USA | 21 | 2,944-29,590 | High to very high | Pereira <i>et al.</i> , (1999) |
| Incheon Harbour, Korea | 23 | 12-1,400 | Low to moderate | Kin <i>et al.</i> , (1999) |
| Ajaccio Harbour, Corsica | 26 | 20,140 | Very high | Baumard <i>et al.</i> , (1998) |
| Torres Harbour, Sardinia | 26 | 920 | Moderate | Baumard <i>et al.</i> , (1998) |
| Victoria Harbour, Hong Kong | 9 | 1,200-14,000 | High to very high | Hong <i>et al.</i> , (1995) |
| Xiamen Harbour, China | 9 | 2,900-61,000 | High to very high | Hong <i>et al.</i> , (1995) |

n^a# number of PAHs.

Table 3. Negligible Concentration (NCs) and Maximum Permissible Concentration (MPCs) of individual PAHs in the medium of sediment.

| PAHs | PAHs | Negligible Concentration (NCs) | Maximum Permissible Concentration (MPCs) |
|-------------------------|------|--------------------------------|--|
| Naphthalene | Nap | 1.4 | 140 |
| Acenaphthylene | Ace | 1.2 | 120 |
| Acenaphthene | Ace | 1.2 | 120 |
| Fluorene | Fl | 1.2 | 120 |
| Phenanthrene | Phe | 5.1 | 510 |
| Anthracene | Ant | 1.2 | 120 |
| Fluoranthene | Flu | 26 | 2600 |
| Pyrene | Pyr | 1.2 | 120 |
| Benzo(a) anthracene | BaA | 3.6 | 360 |
| Chrysene | Chr | 107 | 10700 |
| Benzo(b)fluoranthene | BbF | 3.6 | 360 |
| Benzo(k)fluoranthene | BkF | 24 | 2400 |
| Benzo(a)pyrene | BaP | 27 | 2700 |
| Indeno(1,2,3-c,d)pyrene | InP | 59 | 5900 |
| Dibenzo(a,h)anthracene | DBA | 27 | 2700 |
| Benzo(g,h,i)perylene | BgP | 75 | 7500 |

As compared to Karachi Harbour PAHs level from Off-Clifton coastal sediment which was found two to four times lower, but the classification level remains high to very high in range. The total PAHs concentration of Karachi Harbour and off-Clifton

coastal sediments were compared with the different world harbours and ports as shown in Table 2. Total PAHs concentration in Karachi Harbour was found highest among those except Boston Harbour (USA) Wang *et al.*, 2001 and Western Harbour, Alexandria

(Egypt) Notar *et al.*, 2001, where maximum concentrations were reported 3, 58,000 and 131,150 ng/g respectively.

The mean compositional profiles of PAHs in the sediments are shown in Fig. 3-4 and it can be seen that 2- and 3-rings of PAHs were more abundant than higher rings PAHs at most of the Karachi Harbour sampling stations (St-1, 3, 4, 5 and 6) except at St-2 where, 4 rings of PAHs dominated. Also at four of Clifton offshore stations St-9, 11, 12 and 13 higher levels were noted, whereas, at three stations St-7, 8

and 10) 4-rings of PAHs dominated. Karachi Harbour and off-Clifton coast sediment compositions 2 and 3-rings of PAHs, 53 and 47% were recorded respectively.

The 4 rings PAHs concentration compositions in the off-shore Clifton sediment were noted higher than the Karachi Harbour sediments which were 47% and 41% on average respectively. 5-6 rings PAHs concentration, composition in the Karachi Harbour was recorded only 2%, but in off-Clifton coastal sediments it was nil.

Table 4. Risk classification of individual PAHs and ΣPAHs concentrations in sediment. (Cao *et al.*, 2010).

| Risk classification | Individual PAHs | | Risk classification | ΣPAHs | |
|---------------------|---------------------|----------------------|---------------------|---------------------|----------------------|
| | RQ _(NCS) | RQ _(MPCs) | | RQ _(NCS) | RQ _(MPCs) |
| Risk-Free | < 1 | | Risk-Free | 0 | |
| | | | Low- Risk | ≥1; <800 | 0 |
| Moderate Risk | ≥ 1 | < 1 | Moderate Risk 1 | ≥ 800 | 0 |
| | | | Moderate Risk 2 | < 800 | ≥1 |
| High Risk | | ≥ 1 | High Risk | ≥ 800 | ≥1 |

Table 5. Mean of individual PAHs values of RQ_(NCS) and RQ_(MPCs) in sediment of Karachi Harbour and off-Clifton coast.

| PAHs | Karachi Harbour | | Off-Clifton coast | |
|-------------------------|---------------------|----------------------|---------------------|----------------------|
| | RQ _(NCS) | RQ _(MPCs) | RQ _(NCS) | RQ _(MPCs) |
| Naphthalene | 285 | 2.8 | 272.4 | 2.7 |
| Acenaphthylene | 657 | 6.6 | 776.2 | 7.8 |
| Acenaphthene | 974 | 9.7 | 665.5 | 6.7 |
| Fluorene | 16107 | 161.1 | 1980.6 | 19.8 |
| Phenanthrene | 363 | 3.6 | 89.4 | 0.9 |
| Anthracene | 2657 | 26.6 | 785.7 | 7.9 |
| Fluoranthene | 114 | 1.1 | 34.0 | 0.3 |
| Pyrene | 2525 | 25.3 | 1571.4 | 15.7 |
| Benzo(a) anthracene | 675 | 6.7 | 237.3 | 2.4 |
| Chrysene | 0 | 0.0 | 0.0 | 0.0 |
| Benzo(b)fluoranthene | 2183 | 21.8 | 114.3 | 1.1 |
| Benzo(k)fluoranthene | 177 | 1.8 | 48.0 | 0.5 |
| Benzo(a)pyrene | 6 | 0.1 | 0.0 | 0.0 |
| Indeno(1,2,3-c,d)pyrene | 4 | 0.0 | 0.0 | 0.0 |
| Dibenzo(a,h)anthracene | 7 | 0.1 | 0.0 | 0.0 |
| Benzo(g,h,i)perylene | 5 | 0.1 | 0.0 | 0.0 |

Different types of PAHs and their ratios have been used to identify different sources that contribute PAHs to the sediments (Soclo *et al.*, 2000; Guinan *et al.*, 2001; Magi *et al.*, 2002; Yunker *et al.*, 2002; Fang *et al.*, 2007; Jiang *et al.*, 2009). A ratio of low (2 and 3rings) to high (4 to 6 ring) PAHs has been used to identify pyrogenic (if ratio <1) and petrogenic (if ratio

>1) sources of PAHs in the sediment samples (De Luca *et al.*, 2005; Chen and Chen, 2011).

A ratio of ΣLPAHs/ΣHPAHs < 1 indicates a pollution of pyrolytic (pyrogenic) origin and >1 suggests a pollution of petrogenic sources (Magi *et al.*, 2002; De Luca *et al.*, 2005). According to the ΣLPAHs/ΣHPAHs ratio sat five sampling stations of Karachi Harbour (St-3, St-4, St-5

and St-6) and also four off Clifton Coast stations (St-7, St-8, St-9 and St-10) originate from petrogenic sources(Fig.5).However, the composition patterns of PAHs in the Karachi Harbour and off-Clifton coast showed no significant difference.

Therefore, Karachi Harbour sediments are originated from petrogenic sources while, mostly off-Clifton coastal sediments originate from petrogenic sources. Another isomeric ratio FLU/ (FLU + PY) described by Yunker *et al.*, 2002, is a useful indicator in assessing the contribution of PAHs in sediment contamination. FLU/ (FLU + PY) ratio <0.4 suggests petroleum sources, ratio >0.5 is attributed to the combustion process, whereas ratios between 0.4 and 0.5 are known to be from petroleum combustion sources

(mixed sources). As shown in Fig. 6, the ratios of FLU/ (FLU + PY) found >0.5at three stations (St-1, St-2, and St-6) of Karachi Harbour, which indicates that PAHs originate from combustion processes, while at other three stations(St-3, St-4, St-5) the values were <0.5,which indicate petroleum sources. According to the result of the isomeric ratio FLU/ (FLU + PY)at four Off-Clifton coast stations (St-7, St-8, St-10 and St-11) the sediments are contaminated with petroleum sources and the sediments in the rest of two stations (St-9, St-13) originate from petroleum combustion sources. In conclusion, PAHs pollution in Karachi and off-Clifton coast sediments were possibly contributed by petroleum and combustion sources (mixed sources) derived from shipping traffic and industrial activities being conducted in Karachi city.

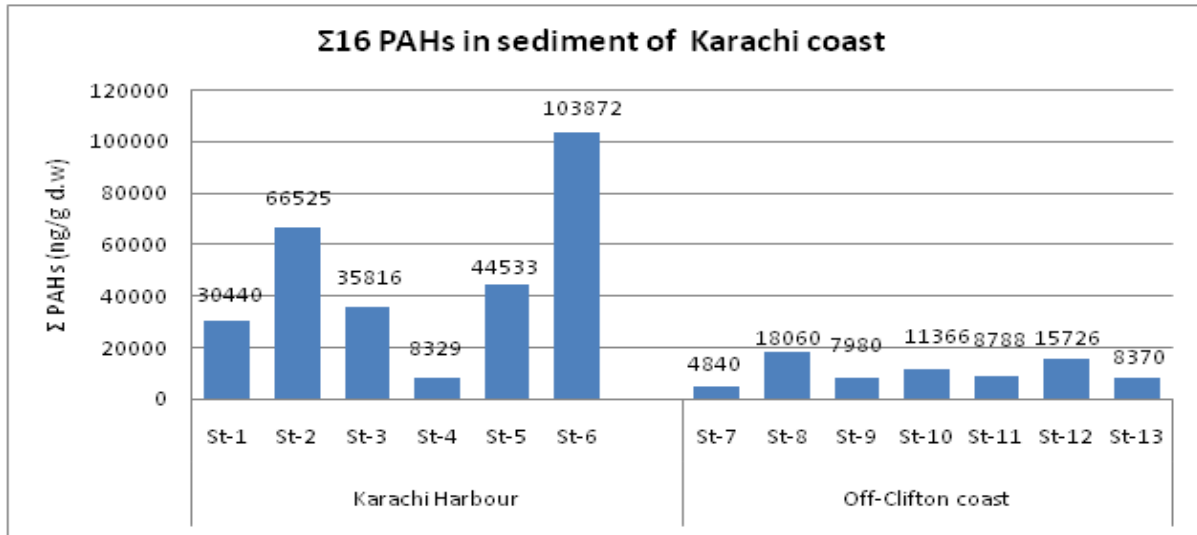


Fig. 2. Spatial distribution pattern of total 16 PAHs in the sediment from Karachi Harbour and off- Clifton coast.

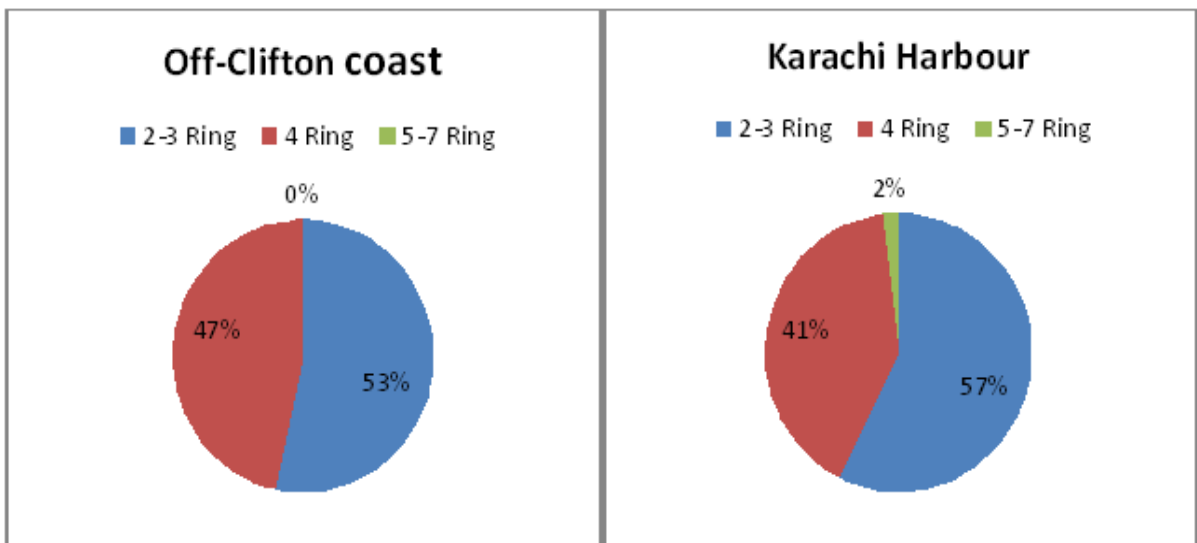


Fig. 3. Percentage composition of high and low ring PAHs in the surface sediment of Karachi Harbour and off-Clifton coast.

Mean effect range median quotient (m-ERM-q)

Another approach to assess the possible Ecotoxicological effects on marine organisms through individual chemicals, by comparing the chemical concentrations with the limit concentrations, is the mean ERM quotient (m-ERM-q).

The m-ERM-q has been associated with the probability of toxicity, according to the matching of chemicals and toxicity data from the USA estuaries (Long *et al.*, 1998, 2000). The m-ERM-q can be classified into four groups including lower than 0.1, 0.11 to 0.51, 0.51 to 1.5 and more than 1.5 which represent 11%, 30%, 46% and 75% probability of toxicity, respectively (Long *et al.*, 2000).

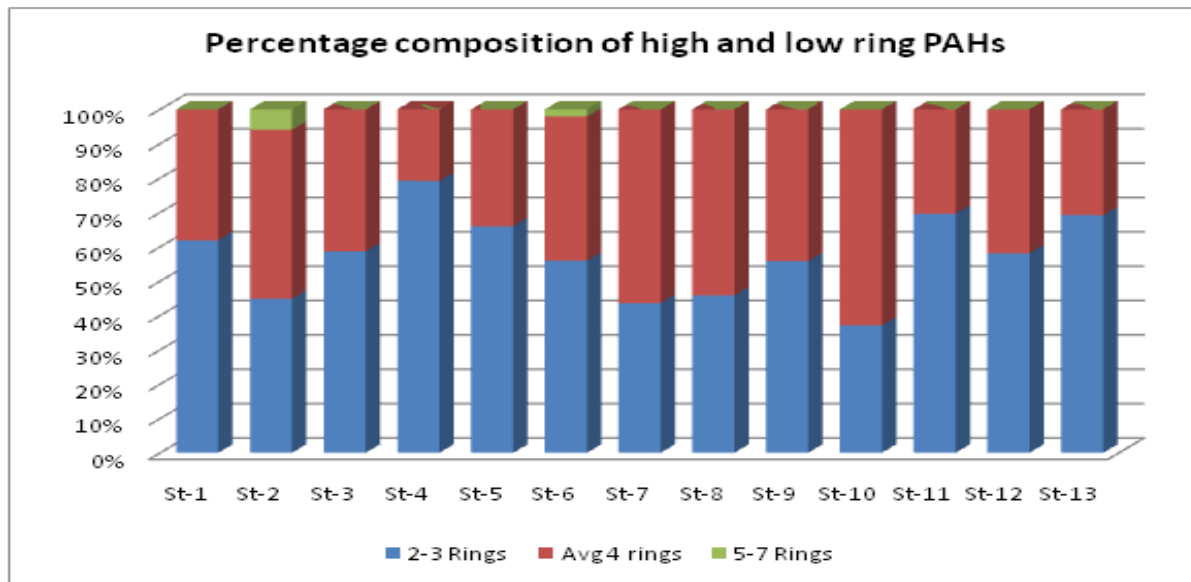


Fig. 4. Percentage composition of high and low ring PAHs in the surface sediment of 13 Stations.

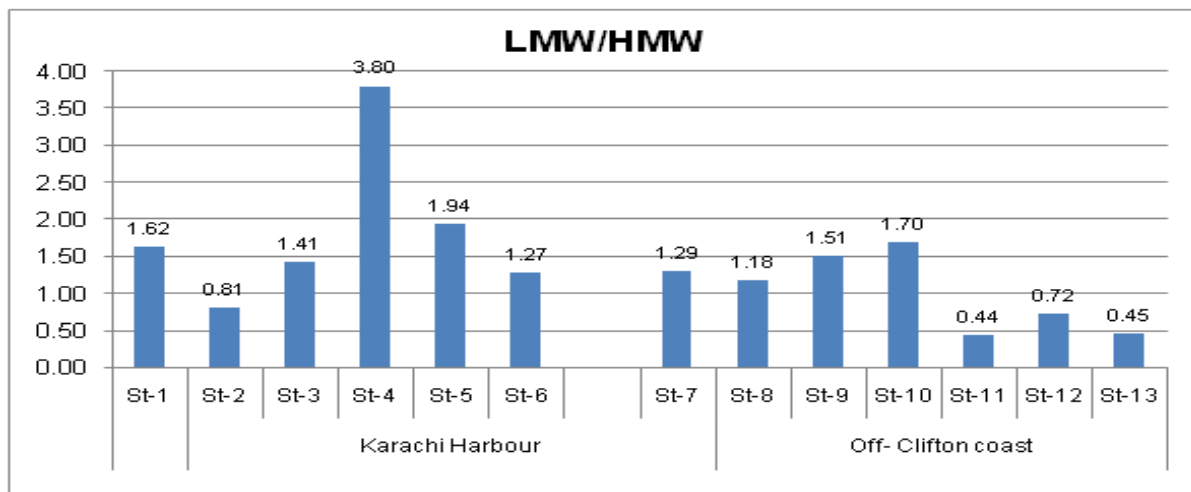


Fig. 5. High and low ring ratio of PAHs in the surface sediment of Karachi Harbour and off-Clifton coast.

In the present study m-ERM-q values ranged from 0.14-0.91 and 0.1-0.37 while, average values were 0.61 and 0.19 in the Karachi Harbour and Off-Clifton coast respectively (Fig.7). According to this classification, the probability of toxicity in Karachi Harbour was in the range 30-46%, whereas in Off-Clifton coast toxicity was in the range 11-30%. Based on above m-ERM-q values, it was concluded that the ecological risk of PAHs in the sediments of Karachi

Harbour was medium to high, while PAHs in Off-Clifton coast were observed to be low to medium.

Risk Quotients (RQ)

Kalf (1997) proposed the risk measurement of organic substances using risk quotients (RQ). The proposed NCs and MPCs values of different PAHs in sediments are given in Table 3. Risk classification was proposed by Cao *et al.*, 2010 as shown in table 4. According to

this classification $RQ_{NCs} < 1$ shows that individual PAHs might probably be of negligible concentrations, while $RQ_{MPCs} > 1$ indicates that contamination of individual PAHs might be severe. However, $RQ_{NCs} > 1$ and $RQ_{MPCs} < 1$ show moderate level of PAHs

contamination. In the case of $\Sigma PAHs$, values interpreted as: $RQ_{NCs} < 1$ shows very low risk; $1 \leq RQ_{NCs} < 800$ and $RQ_{MPCs} < 1$ indicate low to moderate risk; $RQ_{NCs} \geq 800$ and $RQ_{MPCs} \geq 1$ reveal high risk.

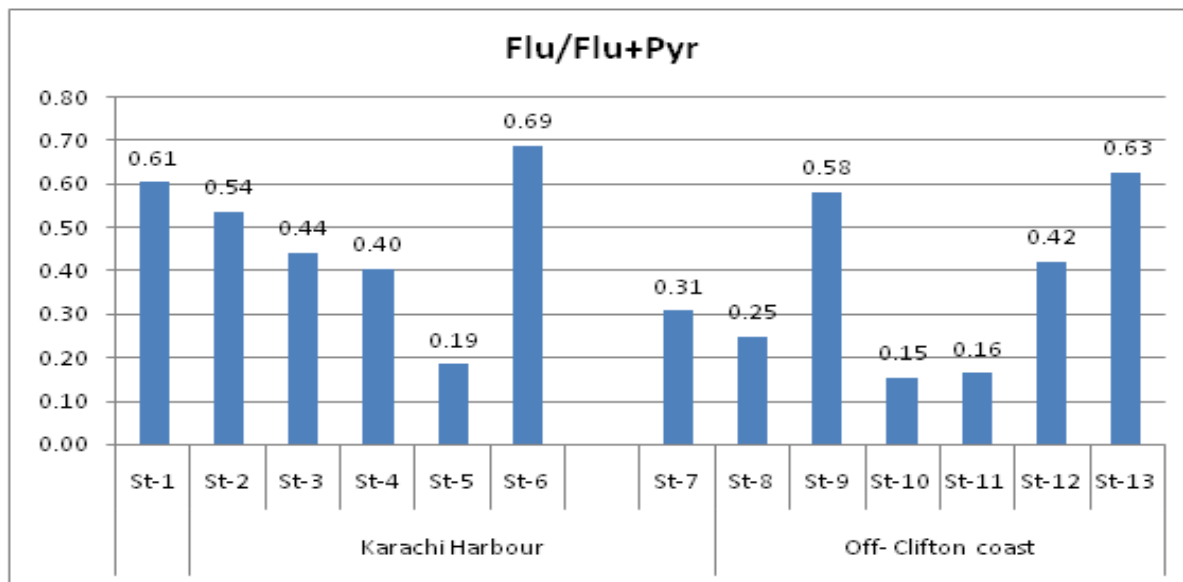


Fig. 6. Ratios of FLU/ (FLU + PY) in the surface sediment of Karachi Harbour and off-Clifton coast.

The mean individual PAHs values of $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ in the sediments of Karachi Harbour and Off-Clifton coast are presented in Table 5. Mean values of $RQ_{(NCs)}$ for most individual PAHs in Karachi Harbour and Off-Clifton coast were found to be greater than 1.00, with the exception of Chrysene (not detected) at both sites while, Benzo(a)pyrene and Indeno(1,2,3-c,d)pyrene also not detected in the Off-Clifton coast sediment.

The calculated $RQ_{(MPCs)}$ values in eleven individual PAHs (Nap, Ace, Ace, Fl, Phe, Ant, Flu, Pyr, BaA, BbF and BkF) and eight individual PAHs (Nap, Ace, Ace, Fl, Ant, Pyr, BaA and BbF) were higher than 1.00 in Karachi Harbour and Off-Clifton coastal sediments respectively. The above mentioned individual mean values of $RQ_{(MPCs)}$ and $RQ_{(NCs)}$ indicate that both sides of sediments have a high ecological risk of the ecosystem. The values of $\Sigma PAHs RQ_{(NCs)}$ and $\Sigma PAHs RQ_{(MPCs)}$ were also calculated from each sampling site and presented in Fig. 8 and 9. All sampling site values of Karachi Harbour were recorded two to five times higher than the off-Clifton coast. By comparing of the RQs for $\Sigma PAHs$ with the classification system given in Table 4, it is concluded that that ecological risk associated with $\Sigma PAHs$ at all sites is very high but, in the off-Clifton coast it is relatively lower than in the Karachi Harbour.

Therefore, it is suggested that higher level PAHs should be controlled, and remedial actions should be implemented to decrease the high levels of PAHs.

Conclusion

In the present study, PAHs distribution shows that 2, 3 and 4 ring PAHs are dominant in almost all of the samples. On average, 2-3, 4, and 5-6-ring PAHs consisted of 56 %, 42 % and 2% of total PAHs, respectively. According to Baumard (1998), classification of PAHs concentration in the Karachi Harbour sediments lies in the high to very high levels range. The profile of PAHs showed that 2 to 3-ring and 4 rings PAHs dominated in all stations of the study area. Isomeric ratio FLU/ (FLU + PY) indicates that Karachi and off-Clifton coastal sediments are possibly contributed by petroleum and combustion sources (mixed sources) most probably due to the shipping traffic and industrial activities being conducted in Karachi city. Ecosystem risk assessment on the basis of m-ERM-q values show that the ecological risk of PAHs in the sediments of Karachi Harbour were medium to high while, in off-Clifton coast they were observed in low to medium range. Risk Quotients $RQ_{\Sigma PAHs (NCs)}$ at all sites is very high, but in the off-Clifton coast it is relatively lower than the Karachi Harbour.

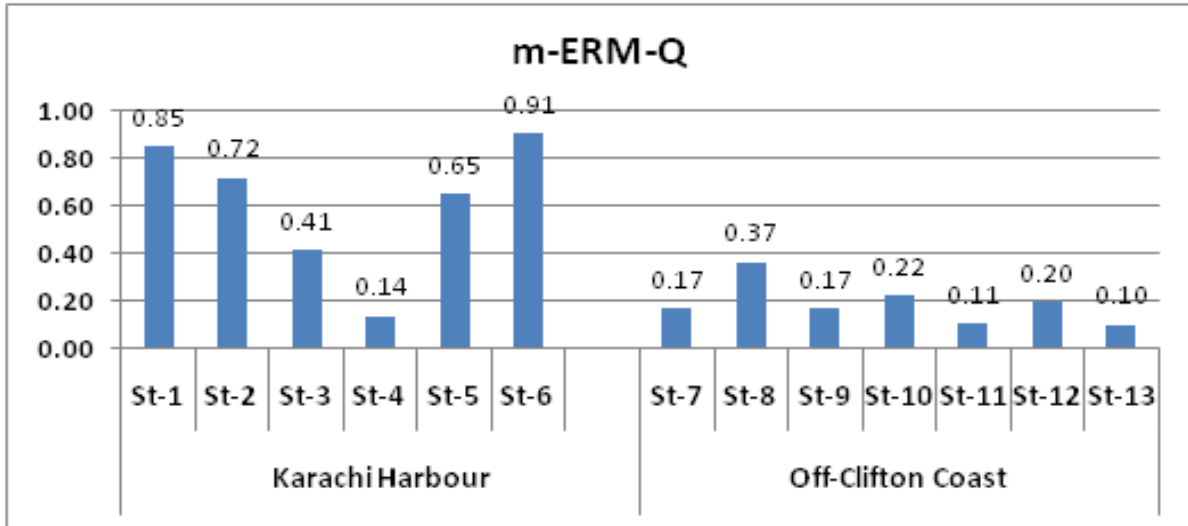


Fig. 7. Distribution of m-ERM-Q values in the surface sediment of Karachi Harbour and off-Clifton coast.

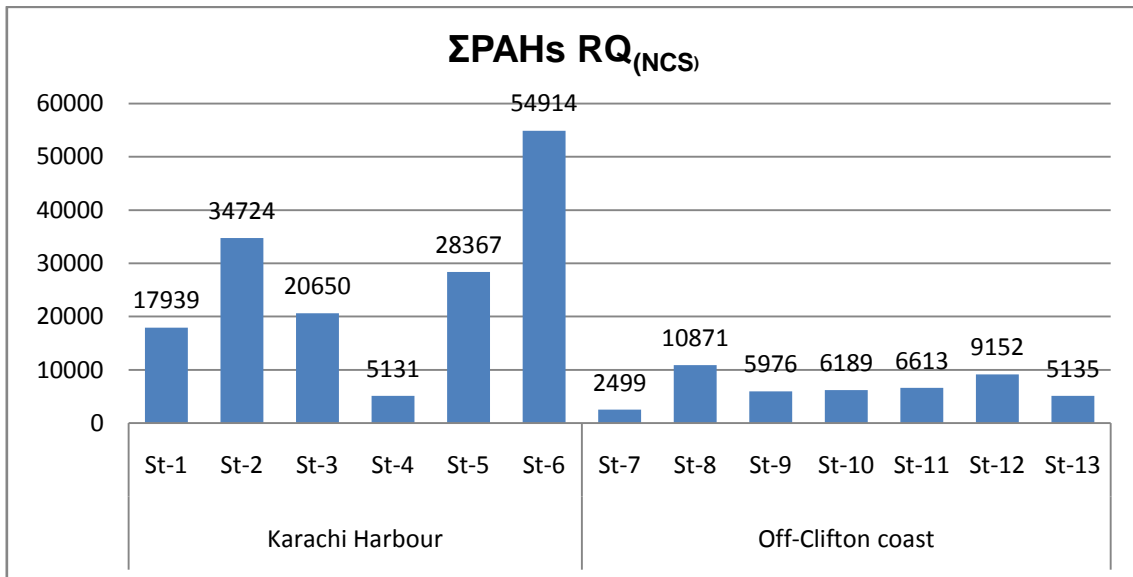


Fig. 8. Distribution of ΣPAHs RQ(NCS) values in the surface sediment of Karachi Harbour and off-Clifton coast.

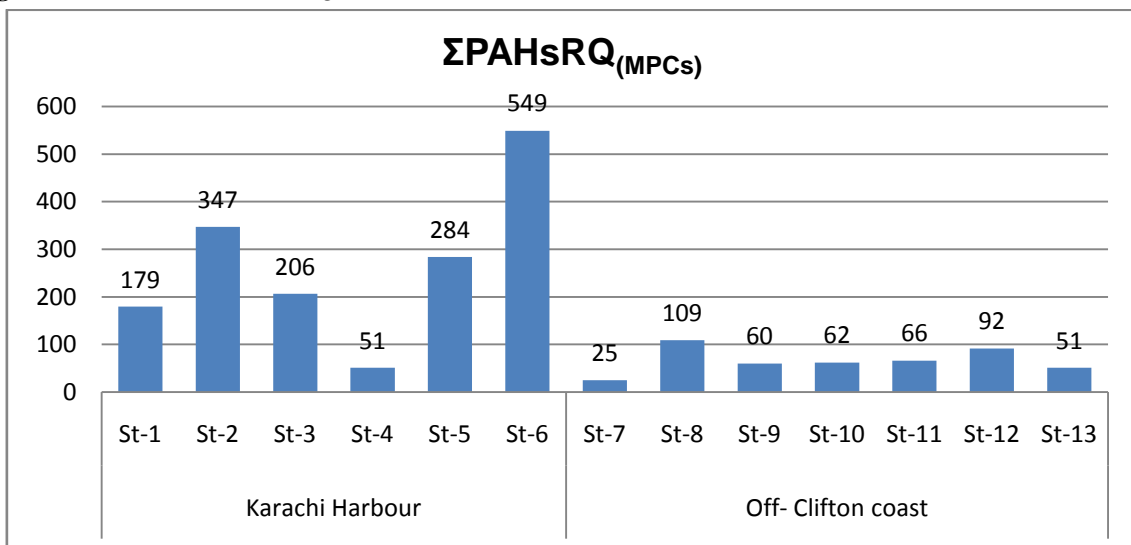


Fig. 9. Distribution of ΣPAHs RQ(MPCs) values in the surface sediment of Karachi Harbour and off-Clifton coast.

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