Concentrations of Petroleum Hydrocarbons Residual in Seawater of Aden Coasts, Yemen

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Abstract

The environmental quality along Aden coasts is affected by the anthropogenic pressure of Aden city. A field work has been carried out to investigate the occurrence of petroleum pollution along Aden coasts. To determine the status of aliphatic hydrocarbons (AHs) (n-C10 to n-C34) and polycyclic aromatic hydrocarbons (PAHs) pollution in seawater, twenty seven surface seawater samples were collected in July, December 2014 and March 2015 and analyzed for AHs and PAHs by using gas chromatography-mass spectrometry (GC-MS) to determine their concentrations and sources. The concentration of AHs ranged from 0.12 µg/l (station 9) to 0.90 µg/l (station 3). The concentrations of PAHs were in the range between 0.45 µg/l (station 5) and 14.70 µg/l (station 3). Concentrations of petroleum hydrocarbons (PHs) were in the range between 0.68 µg/l (station 5) and 15.89 µg/l (station 9). The study showed that the level of PHs in coastal seawater within the allowed limits. The major sources of the pollution were petrogenic origin based on the indices of AHs and PAHs. This pollution is a result of localized oil operation and/or heavy ship traffic in Gulf of Aden. The results will be used to assess the ecosystem quality. Environmental control is recommended to reduce the marine pollution in Aden coasts.

Keywords: Aden; Coastal seawater; Gulf of Aden; Petroleum pollution; Yemen

Introduction

The coastal ecosystem is one of the most important global ecosystems. It provides numerous ecosystem services, such as the food supply, biodiversity, and recreation. Hence, maintaining the habitat quality and ecosystem health of the coastal system is highly significant [1]. Coastal environments are very important areas for recreational and industrial activities for the people living their [2]. They are considered as places of high ecological risk due to the complex biogeochemical processes and the intensive human activities such as terrestrial urban, agricultural runoff, industrial effluents and aquatic chemical spills with rapid economic development [1,3]. These activities discharge different kinds of pollutants to these ecosystems such as AHs and PAHs.

Petroleum is a complex mixture of hydrocarbons and non-hydrocarbons (metal porphyrins, acid and organometallic compounds) [4]. It is one of the most common pollutants released into marine environments [5]. PHs are coming from biogenic, petrogenic, and/or pyrogenic sources [6]. They enter to marine environment from many sources including industrial discharges, ships’ operations, accidental spills, atmospheric fallout, oil and gas exploration and domestic and industrial effluents, etc. [7-9].

AHs and PAHs are the major components of crude oil, which is one of the main pollutants in coastal environments. The AHs consists of about 80% of crude petroleum and, hence, they are widely used as geochemical markers of oil contamination [8,10]. A high concentration of AHs is a potential source of pollution and may cause adverse effects on ecosystem [11]. Despite of their anthropogenic sources, AHs have also different natural sources, such as, marine phytoplankton and bacteria and biomass combustion [12]. PAHs are a wide group of compounds with two or more aromatic rings containing solely hydrogen and carbon [13]. They are group of ubiquitous pollutants in the marine environment [14] and produced by pyrogenic, natural processes and/or anthropogenic activities [15]. PAHs are also derived from crude oil and its derivatives [15]. They are highly insoluble and persist in the environment [16].

The scientific community was aware of the high concentrations of PAHs in seawater, sediments and biota and consequently, of their deleterious effects on the marine environment [17]. Some compounds of PAHs are considered to be the most toxic components in crude oil, with carcinogenic, teratogenic, and mutagenic effects in aquatic animals and humans [18].

The pollution of the marine environment by organic and inorganic pollutants in the Gulf of Aden and Arabian Sea is a major concern of all countries in the region. The coastal water of Yemen are characterized by its high productivity making it a basic feeding and nursery ground for marine species [19]. More than 600 species of marine organisms have been recorded in Yemen seawater [20].

Petroleum pollution threatens the coastal area through; oil transport, oil spillage, ballast water and untreated sewage. Untreated domestic wastewater, industrial wastewater and agricultural drain water, run-off during rainy periods, ship and boat traffic, oil transportation, oil spillage, and atmospheric fallout are all potential sources of pollution [21]. In the water environment, pollutants quickly spread over large distances from the sources of pollution.
Gulf of Aden is among the busiest tanker route. Most of the oil produced in the region is exported via sea and pipelines, while local consumption refineries are located in the coastal area. The widespread oil pollution in Gulf of Aden are not surprising [22,23]. The increases of sewage and industrial effluent discharged into Gulf of Aden have seriously endangered the ecosystem [24]. On the other hand, Gulf of Aden is characterized by a high water temperature (>25ºC) and surface water salinity varies between 33.7% to 37% which provide favorable conditions for oil degradation [25].

Aden coast, which comprises the biggest and most important harbors in Yemen. It is vital for marine activities, fisheries and tourist attraction. Aden coast is receives considerable amounts of petroleum along with its products. The usually common pollutants in the coastal line of Aden originate from discharges from desalination power generation, sewage, and wastewater treatment plants in addition to hydrocarbons and trace metal compounds [24].

The aims of this study are to evaluate the concentrations of AHs and PAHs, and to identify the sources of these pollutants in surface seawater collected along Aden coasts, Yemen. The results obtained will provide insight on the pollution levels of PHs in Aden coasts, which could contribute to the prevention and control of pollution of PHs.

Material and Methods

Study area

Aden city is located on the coast of the Gulf of Aden in the south Yemen. It is bounded by latitudes 12.7°-12.9° N and longitudes 44.78°-45.08° E (Figure 1). It is the economic capital of Yemen and the second most important after the Yemeni city of Sana’a. Aden is the largest coastal city and famous for transit trade, boat building, ship repairs and bunkering. Before the closure of the Suez Canal in 1967, Aden was the third largest bunkering port in the world. Besides port related activities, major economic resources in the coastal zone are fisheries, maritime traffic, oil and gas exploitation. Crude oil is supplied by pipeline from the shore and then transferred from the vessel to tankers. A large boat is available for transport of ship based garbage and oily waste, which is carried by lorries to a municipal landfill where it is burned. The port and entrance channel are dredged regularly and dredge spoil is dumped offshore [26].

Figure 1: Location map of study area and selected sampling sites.

Sampling technique

Twenty seven surface seawater samples (2.5 l) were collected 1 m depth with a glass bottle held in a metal frame to cover the coastal area of Aden which is considered as an area of intense industrial and urban activities. These samples were taken during July, December 2014 and March 2015 from selected nine stations (Figure 1). A reference station of surface water sample was collected from station 5 at Goldmoor area which is far from any expected oil pollution and considered as a natural protected area (Figure 1). Global Positioning System (GPS) was used to determine the coordinates of the sampling points. The samples were analyzed according to UNEP techniques [27]. The procedure used for extraction and analysis of AHs and PAHs in surface water samples was performed according to conventional procedures [28]. The concentrations of the AH and PAH were calculated three times (July, December 2014 and March 2015) and the mean values were taken. In this work, gas chromatography (GC-MS) a Shimadzu GC-2010 C.N. 1134102760 Sa, with split/splitless injector furnished with a 60 m × 250 mm × 25µ fused silica capillary with a chemically bonded gum phase DB-wax, was used. Blank determinations were carried out by repeating the procedure with pre-extracted sample. Using a calibration with Marib export blend crude oil and the detector
response was 45.8 mV at 360 nm emission wavelength. Samples were extracted and analyzed at the Yemen Standardization, Metrology and Quality Control Organization, Sana'a, Yemen.

### Results and Discussion

The temperature, salinity and pH of the seawater were in the range of 27°C-29.5°C, 37%-38% and 7.8-8.03, respectively (Table 1).

<table>
<thead>
<tr>
<th>Station No.</th>
<th>pH</th>
<th>Temp (°C)</th>
<th>Salinity (%)</th>
<th>Pr (µg/l)</th>
<th>Ph (µg/l)</th>
<th>Pr/Ph</th>
<th>n-C17/Pr</th>
<th>n-C18/Ph</th>
<th>Sq (µg/l)</th>
<th>UCM (µg/l)</th>
<th>CPI (µg/l)</th>
<th>ΣAHs (µg/l)</th>
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<tr>
<td>1</td>
<td>8.01</td>
<td>28.1</td>
<td>37.2</td>
<td>0.01</td>
<td>0.013</td>
<td>0.77</td>
<td>1.15</td>
<td>0.89</td>
<td>0.03</td>
<td>0.5</td>
<td>1</td>
<td>0.41</td>
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<tr>
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<td>0.025</td>
<td>1.08</td>
<td>0.56</td>
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<td>0.04</td>
<td>1.5</td>
<td>1.1</td>
<td>0.19</td>
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<td>37.1</td>
<td>0.03</td>
<td>0.04</td>
<td>0.75</td>
<td>0.78</td>
<td>0.28</td>
<td>0.03</td>
<td>1.3</td>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
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<td>29.5</td>
<td>37.5</td>
<td>0.003</td>
<td>0.008</td>
<td>0.38</td>
<td>2.75</td>
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<td>0.016</td>
<td>0.63</td>
<td>0.6</td>
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<tr>
<td>6</td>
<td>7.8</td>
<td>28.3</td>
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<td>0.035</td>
<td>0.025</td>
<td>1.4</td>
<td>0.23</td>
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<tr>
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<tr>
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<td>37.1</td>
<td>0.003</td>
<td>0.008</td>
<td>0.38</td>
<td>0.02</td>
<td>0.06</td>
<td>ND</td>
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<td>0.3</td>
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<tr>
<td>Max.</td>
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<td>29.5</td>
<td>38.1</td>
<td>0.043</td>
<td>0.04</td>
<td>1.6</td>
<td>2.75</td>
<td>2.31</td>
<td>1</td>
<td>2</td>
<td>1.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Average</td>
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<td>28.41</td>
<td>37.42</td>
<td>0.025</td>
<td>0.023</td>
<td>1.04</td>
<td>0.85</td>
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<td>0.87</td>
<td>0.31</td>
<td>0.014</td>
<td>0.01</td>
<td>0.42</td>
<td>0.84</td>
<td>0.69</td>
<td>0.34</td>
<td>0.62</td>
<td>0.38</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 1: pH, temperature, salinity, Pr, Ph, Sq, UCM, CPI and ΣAHs concentration in surface seawater samples from Aden coasts.

The isoprenoids Pr and Ph are common components of crude oil. Ph originates from petroleum hydrocarbons, but Pr can be generated by biogenic processes in the absence of pollution due to petroleum hydrocarbons [10,30]. The ratio between Pr/Ph is used to determine the relative contribution of oil to seawater pollution, where values close to or <1 indicate oil pollution, and values between 3 and 5 are characteristic of non-polluted seawater [30]. In this study, Pr/Ph ratio varied between 0.38 (station 4) and 1.60 (station 8), which is indicating petroleum pollution (Table 1).

The degree of oil degradation in the environment was evaluated by the ratios between n-C17/pr and n-C18/ph, since the n-alkanes chains degrade more quickly than the branched ones [31]. Values <2 indicate the presence of degraded oil while values ≥ 2 suggest recent oil pollution [32,33]. The values for the n-C17/Pr were <2 in all stations except station 4 (2.75) (Table 1). The n-C18/Ph ratio presented similar results except for samples of station 6 (2.31) (Table 1). These results show that there is a mixture of degraded and recently introduced oil at these stations.

Samples from station 4 were collected in front of area for cutting scrap ships, where they are carrying out cutting different types of scrap vessels and this cutting leads to the disposal of quantities of bunker, remains of greases, oil products. Sometimes there is a leakage of ships fuel from the marine pipeline which passes along of Al-Omal Island, because the pipeline has become old. Stations 6 continuously receive cooling water directly without any kind of treatment from the Al-Hiswah steam station of electricity.

Concentration of Sq ranges from ND µg/l (station 5) to 1.00 µg/l (station 9), with an average of 0.17 ± 0.34 µg/l (Figure 2, Table 1). Sq is
a major organic constituent in polluted surface seawater, was intimately correlated with anthropogenic sources of hydrocarbons [34]. This compound was encountered in all seawater samples of Aden coasts. This may help to indicate the nature of pollution of Aden coasts. Burns et al. [29] reported elevated values of Sq in some seawater samples, which is constantly subjected to chronic oil pollution. Concentrations of unresolved complex mixture (UCM) ranges from 0.2 µg/l (station 5) to 2 µg/l (station 9), with an average of 1.22 ± 0.62 µg/l (Table 1). The UCM represent components resistant to weathering and bacterial breakdown and its presence in chromatograms has frequently been taken as strong evidence for petroleum pollution in seawater samples [28,35]. The anthropogenic contribution of petroleum hydrocarbons (PHs) is evident from the presence of the UCM in all of the samples analysed (Table 1).

The ratio of odd to even carbon numbered n-alkanes is called carbon preference index (CPI). The CPI for the seawater samples ranged from 0.30 µg/l (station 5) to 1.60 µg/l (station 9), with an average of 1.16 ± 0.38 µg/l (Table 1). It is the most common index for determination of the sources of AHs. CPI values <3 indicates petrogenic hydrocarbons inputs to the seawater, while natural inputs have values >3 [36,37]. The results of CPI of Aden coastal seawater reflect that all samples are polluted with petrogenic hydrocarbons (CPI <1.6).

The linear regressions between UCM and CPI parameters show good significant correlation (R2=0.69) (Figure 3).

The results of ΣAHs in surface seawater samples of Aden coasts are given in Table 1 and shown in Figure 4. The concentration of ΣAHs ranges between 0.12 µg/l (station 9) to 0.9 µg/l (station 3), with an average of 0.44 ± 0.26 µg/l. Station 5 is considered as background level for this study. Little or no pollution is considered to exist when ΣAHs concentration is 100 μg/l [38]. Hence, all stations exhibited values <0.9 µg/l, clearly indicating surface seawater in Aden coasts are considered low polluted.

The concentrations of ΣPAHs in Aden coasts seawater ranges between 0.45 µg/l (station 5) and 14.7 µg/l (station 9) with an average of 5.69 µg/l (Figure 4, Table 2). Unpolluted seawater contains less than 0.1 ΣPAH [39]. Hence, Aden’s coastal seawater is low polluted with PAHs (values ≤ 14.70 µg/l). In this study, higher concentrations of ΣPAH were recorded at stations 7,8 and 9. The possible sources of PAH in these stations were due to oil leakage, refinery, port area and shipping operations.

The main sources of PAHs in aquatic system originate mainly from pyrolytic or petrogenic sources [40,41]. Pyrolytic PAHs which derived from combustion contains four or more aromatic rings, while petrogenic PAHs derived from petroleum contains less than four aromatic rings [42].

The Flu/Pyr and Flu/(Flu+Pyr) ratios are useful indicators for evaluating the attribution of PAH pollution in seawater. PAH isomers of masses Flu and Pyr are widely used to differentiate between pyrolytic and petrogenic sources. If the ratio Flu/Pyr <1, PAHs will be from petrogenic source but when the ratio >1, its source is from pyrolytic source [43]. Moreover, if Flu/(Pyr+Flu) <0.5, it is generally associated with petrogenic source as a characteristic of fuel combustion, while when this ratio exceeds 0.5 it characterized pyrolytic sources (grass, coal and wood combustion) [42]. This implies that the source of PAHs in surface seawater could be mainly polluted by petrogenic inputs. All stations exhibited values of the Flu/Pyr ratio ≤ 1 and Flu/(Flu+Pyr) ratio ≤ 0.5 (Table 2), clearly indicating a petrogenic origin and reflecting a petroleum combustion origin (Figure 5).
### Table 2: Concentration of PAHs in seawater samples from Aden coasts (in µg/l).

The distribution of PAHs in the seawater samples from Aden coasts are summarized in Table 2. The PAHs consists of two groups: low molecular weight PAHs (naphthalene, biphenyl, phenanthrene and anthracene) and large molecular weight (fluoranthene, pyrene, chrysene, benzopyrene and perylene).

![Figure 6: Distributions of ΣPHs in sampling stations along Aden coastal area.](image)

Some countries (e.g. China and Russian Federation) use maximum allowed concentration of 50 µg/l as seawater quality standard [49]. Hence, the measured concentrations of ΣPH in our study were within the allowed limit (<16 µg/l, Figure 6 and Table 3). Generally, the ΣPHs concentration in seawater which can induce harmful effect on the aquatic organisms is in the range of 50 µg/l. Gordon and Prouse [50] reported that oil concentrations in excess of this value can retard phytoplankton photosynthesis.

![Table 3: ΣPHs concentration in surface seawater samples from Aden coasts.](image)

The concentration of total petroleum hydrocarbons (ΣPHs) as the sum of ΣAHs and ΣPAHs in the seawater samples are given in Table 3 and shown in Figure 6. It's ranged from 0.69 µg/l (station 5) to 15.89 µg/l (station 9), with an average of 6.33 µg/l. Oppenheiner [44] has suggested that if the concentration of PHs in the seawater has exceeded the value of 100 µg/l should be considered to be polluted. The ΣPH concentrations <1 µg/l are considered typical of seawater without significant petroleum pollution [45-48]. Hence, Aden’s coastal seawater is low polluted with PHs and stations 1 and 5 are unpolluted.
In this study, the highest concentration of ΣPHs was detected at the station 9 followed by station 8 and station 7 (Figure 6).

The possible source of ΣPH in these stations was due to oil leakage during the loading and unloading of oil ships in the refinery area (especially in station 9, oil harbor), weakness of surface sea currents, close these stations to the international maritime corridor, discharge of ballasting water and throwing oil waste into marine environment illegally.

Conclusion and Recommendations

Surficial seawater samples from Aden coasts, Yemen were analyzed for AHS and PAHs to determine the distribution, concentration, composition and source of organic matter in Aden’s coastal areas. ΣAHS concentrations ranged from 0.12 µg/l in station 9 to 0.90 µg/l in station 3, with an average value of 0.44 µg/l. ΣPAHs concentrations ranged between 0.45 µg/l in station 5 and 14.70 µg/l in station 9, with an average value of 5.69 µg/l. ΣPH concentrations ranged from 0.69 µg/l in station 5 to 15.89 µg/l in station 9, with an average value of 6.33 µg/l. The observed Sg, UCM, CPI, Flu/(Flu+Py) ratio and Flu/(Flu+Py) ratio indicating pollution by petroleum hydrocarbons.

The study showed that the concentration of PHs in seawater of Aden coasts within allowed limits. The pattern of the distribution of PAHs in the seawater appears to be governed mainly by its proximity to potential oil pollution sources. This study provides useful data for assessing the effect of marine petroleum pollution control measure from the view of human health.

It is recommended that, continuous monitoring programme for the Aden city coasts; Yemen and Red Sea and Gulf of Aden region should be formulated and conducted to ensure that the concentration of PHs is within the base line level established in the present study.

References


