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Original Article

Concentration of total petroleum and total aromatic hydrocarbons in tar balls collected from the Red Sea coast of Yemen

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Abstract

The Red Sea is one of the main traffic routes of oil tankers, resulting in environmental damage and marine resource pollution due to the spillage. Quantitative analysis of tar ball was used to detect the concentrations of total petroleum hydrocarbons (TPHs) and total aromatic hydrocarbons (TAHs). In this study, six stations across the Red Sea coast of Yemen were selected according to their suitability and accessibility. An ultraviolet fluorescence technique was used to analyze the TPHs and TAHs after being extracted by an ultrasound-assisted solvent extraction procedure. The concentrations of TPHs ranged from 175.67 ± 11.20 mg/g to 708.55 ± 6.57 mg/g, and for TAHs were from 16.06 ± 1.89 mg/g to 48.25 ± 1.76 mg/g. The highest values of TPHs and TAHs were noticed in Ras Isa-II station, which reflected a continued oil spill from the Safir oil loading terminal. The study revealed significant environmental and health risks to marine organisms and humans.

Keywords: Tar ball; Petroleum Hydrocarbons; Aromatic Hydrocarbons; Red Sea; Yemen

1. Introduction

The rapid development of Yemen as an oil-producing country and its geographic position as one of the world's busiest shipping routes means a high risk of oil pollution in various forms. There are 25,000-30,000 ship transits annually in the Red Sea, and more than 100 million tons of oil are transported through the Red Sea annually [1]. There are no oilfields located along the coast of Yemen's Red Sea. Still, there are many petroleum service installations, such as the Safir terminal supertanker used for oil storage. Crude oil is supplied by pipeline from the Mariab oilfield to the Safir tanker and then transferred from it to other vessels, which causes oil spills or leakage during the loading process. A recent oil spill accident on the coast of Yemen occurred in October 2002 by a Lumburge oil tanker, spilling more than 17,000 tons of discharges to the Gulf of Aden [2]. Yemen, like many countries of the world, could be affected by oil pollution due to its position in the busiest shipping route.

Tar balls are stranded oil residues that include a complex mixture of hydrocarbons, aliphatic, aromatics, and heterocyclic compounds. Tar balls have been used as an indicator of the impact of oil pollution [3]. Tar balls are fragments or lumps of oil weathered to a semi-solid or solid consistency, sticky to the touch, and are difficult to remove from contaminated surfaces [4]. During oil spills, the components of crude oil, particularly the heavier refined products, float on the ocean surface. It will undergo several physical, biological, and chemical processes, reaching the shoreline as tar balls [5]. The tar balls can be found in several sizes, from a few millimeters to tens of centimeters, and are generally spherical in shape [4].

Tar balls on the beaches can originate from both land and/or sea. Land-based sources comprise atmospheric input, storm sewer runoff, refineries, and oil waste. Marine-based sources include offshore petroleum production, drilling, onshore bulk oil storage or production facilities, marine transportation discharges, which comprise vessels pumping bilges and tank cleaning, and pipelines. In addition, the natural seepage from the ocean/sea floor is considered a source of tar balls [6,7].

Petroleum hydrocarbons (PHs) in the marine environment originate from crude oils, their different refined derivatives, and from combustion products of crude oil and other fossil fuels. There is a broad range of substances, from harmless n-alkanes to toxic and partly carcinogenic aromatic and heterocyclic compounds, e.g., benzo(a)pyrene and benzo(a)anthracene [8]. Aromatic hydrocarbons (AHs) have been presented in the environment as complex mixtures. Sixteen polyaromatic hydrocarbon compounds (PAHs) have been identified by USEPA as serious pollutants due to their toxic, mutagenic, and carcinogenic characteristics [9]. AH compounds are unusually more stable and unsaturated; their stability permits them to be important constituents of oil pollution [10]. Moreover, aromatic hydrocarbons can be divided into two groups based on their properties and molecular weight: the low molecular weight AHs with two or three benzene rings and the high molecular weight AHs with four to six aromatic rings [10].

To the best of the researcher's knowledge, only a few studies on the total petroleum hydrocarbons and aliphatic fraction have been done on tar balls and sediments on the Red Sea coast of Yemen [6,11,12,13,14,15,16]. Abu Bakr [15] studied the distribution of n-alkanes in recent sediments on the Red Sea coast of Yemen from 1995 to 1997. The concentration of *n*-

alkanes in sediments from non-detectable to 1651 ng/g dry weight expressed as Kuwait crude oil equivalent. Al-Shwafi [16] identified the occurrence of oil and oil-products pollution along the Red Sea of Yemen. The concentration of aliphatic hydrocarbons ranged between 2.46 to 22.8 µg/g dry weights in sediment. In the tar ball samples from the same area, the Aliphatic concentrations were between 0.100 and 1.560 ug/g [6]. For the total Aromatic hydrocarbons (TAHs), there is no data available for tar balls from the Red Sea coast of Yemen. Moreover, the toxic effect of aromatic hydrocarbons to aquatic organisms are more serious than aliphatic. Therefore, the present study determined the concentrations of TPHs and TAHs in tar balls from the Red Sea Coast of Yemen to know the current state of oil pollution in this area of the Red Sea.

2. Materials and Method

2.1 Study Area

The sampling stations were between Khawidah and Alsallif (latitude 42°67.0 E 16°15.3 N and longitude 43° 23.0 E 13°55.0 N, Figure 1). These stations cover the coastal lines of Hodeidah city across the Red Sea of Yemen**.**

2.2 Samples collection

The tar ball samples were collected carefully by spoon and cleaned from debris like sand or coral using a brush. They were then wrapped in aluminum foil and then kept in plastic bags (Ziploc) and stored in a dark place for transport to the laboratory. The tar ball samples were stored under -5 ºC until analyzed.

2.3 Chemical analysis

Extraction of extractable organic matter (EOM) and analysis of total petroleum hydrocarbons (TPHs) and total aromatic hydrocarbons (TAHs) were performed following the procedure described by Hegazi [17]. The tar ball (100 mg) was mixed with approximately 250 mg of anhydrous sodium sulfate Na_2SO_4 (activated at 400ºC for 2 hours) and then extracted with 20 ml of *n*-hexane/dichloromethane (DCM) (1:1 v:v) for 15 mins using the ultrasound-assisted solvent extraction technique (sonication bath) to obtain the liquid layer. The extraction was repeated twice. The combined extracts were filtered by a Glass Fiber Filter (GF/F) of 0.45µm to remove any particulates from the solution. The extracts were concentrated to approximately 5 ml using rotary evaporation. The EOM was transferred to 10 ml of a pre-weighed vial and then dried under nitrogen steam. The constant weight of the vial to obtain the EOM was recorded. The EOM was redissolved in a 25 ml volumetric flask with an n-hexane solvent. The sample extracts, which include the TPHs and TAHs, were measured using an ultraviolet fluorescence technique (UVF, Perkin Elmer model LS 55-Luminescence spectrometer) at excitation and emission wavelengths of 310 and 360 nm, respectively. The Marib light crude oil was used as the equivalent standard in Yemen for measuring TPHs [6]. The chrysene standard was used as equivalent standard for measuring TAHs in tar balls.

2.4 Quality control and data analysis

Quality control and quality assurance were applied to all data. Replicate samples were analyzed for each station to calculate the precision of measurements. Procedural blanks were used between each batch of two samples to prevent contamination and detect interference. The density measurement of samples was minimized from the interference density detected in the blank. Detection limits of the ultraviolet fluorescence technique were between 1 ppm and 5 ppm, according to the Naval Facilities Engineering Command [18]. Thus, the extracts were diluted to give a reading within detection limits and the linear calibration range of the fluorimeter. Marib light crude oil equivalent and Chrysene standard calibration standards were run at the beginning of each working day before analyzing samples to estimate the regression equations used to calculate the concentration of TPHs and TAHs in the tar balls, respectively. Linear relationships were obtained with correlation coefficients (r) from the linear regression of r = 0.99 for Marib light crude oil equivalent and r = 0.9914 for Chrysene. Regression equations obtained an r value of ≥ 0.99 are acceptable according to the Environmental Protection Agency.

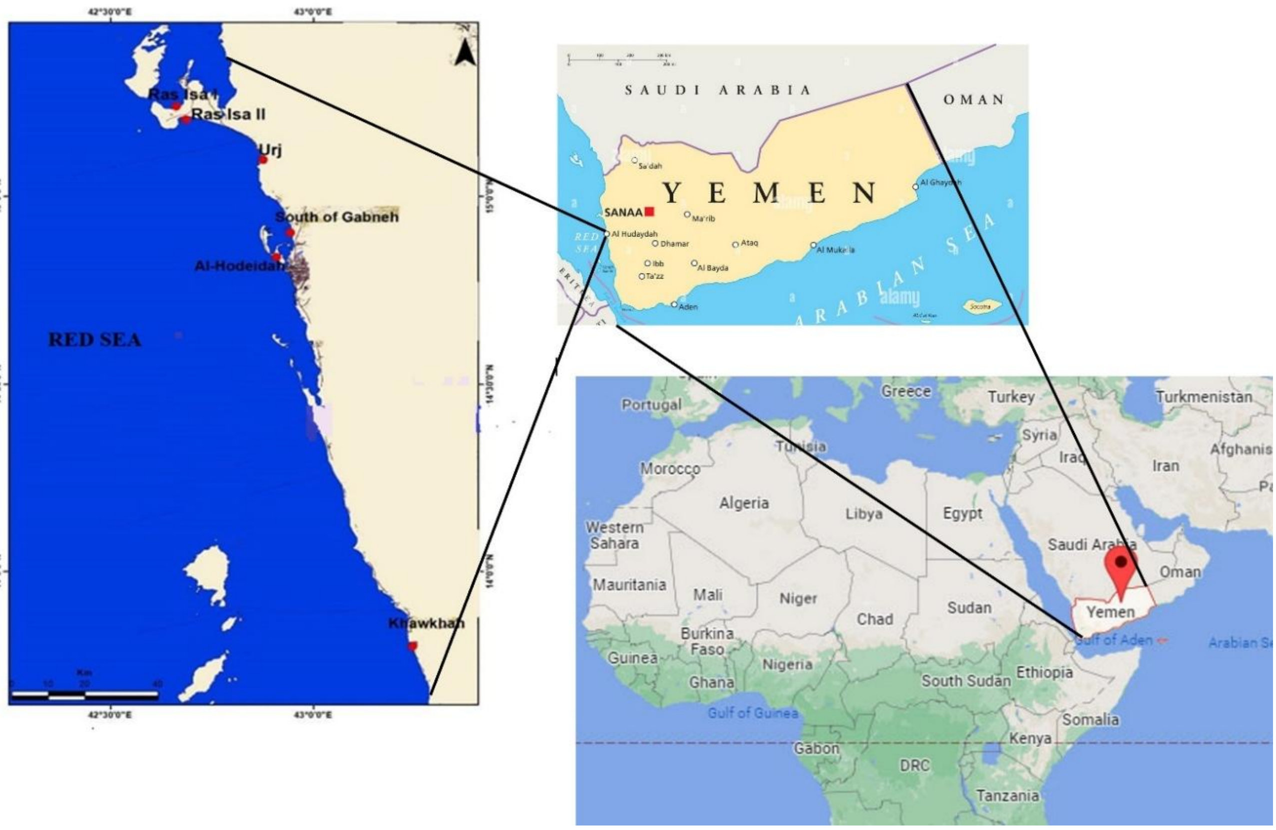

Figure 1: Sampling stations in the Red Sea coast of Al-Hodeidah, Yemen.

3. Results and Discussion

3.1 Total Petroleum Hydrocarbons (TPHs) in Tar Balls

Figure 2 shows the concentrations of TPHs by Marib light crude oil equivalent in the tar ball samples. The concentrations of TPHs vary to a wide range: from 175.67 ±11.20 mg/g at Ras Isa I station to 708.55 ±6.57 mg/g at Ras Isa II station, the mean concentration of which was 444.75 ±17.42 mg/g. The high concentration was found at Ras Isa-II station, which was expected due to the continuous deposition of petroleum hydrocarbons derived from different sources. For example, the oil spill that occurred during the load and transport of crude oil from the Safir oil loading terminal or from an adjacent area to a fuel storage depot at the coastal line is one of the important sources of oil pollution in this area. The same station, Al-Salif or Ras Isa –II, showed a high concentration of aliphatic in the tar ball found by Alshawfi [6]. The same input source was concluded: the Ras Isa oil loading terminal, which affected the area. Moreover, under favorable wind and currents, a portion of the oil leakage was deposited along the coastal stretch around Ras Isa II station. Furthermore, from the field observations, the gentle slope of the shoreline can increase the accumulation of tar balls on it. The slope of the shoreline was so high that it may have saved the tar balls from the weathering factors. The concentrations of TPHs in other stations, Urj, South of Gabaneh, Hodeidah, and Khawkhah samples were 487.69 ± 34.39, 364.45 ± 5.52, 463.41 ± 16.79 and 468.72 ± 30.02 respectively. Variations of concentration in these stations were slight and may be due to their similar sources of petroleum hydrocarbons or similar activities, which include fishing boats, changing engine oil, and discharging dirty ballast water from tankers before reaching the oil loading terminal. In contrast, the low concentration was 175.67 ±11.20 mg/g at Ras Isa -I station, which could indicate the low oil spill or may be due to low activities in the Alsalaf port. Petroleum hydrocarbons in the tar balls and sediments of Yemen and other regions of the Red Sea pose significant environmental and health risks. Research shows that these petroleum hydrocarbons can severely impact marine life, leading to bioaccumulation in the food chain and causing physiological and reproductive issues in aquatic organisms [19]. The socio-economic impacts of petroleum hydrocarbons in the tar balls include loss of fish and crustaceans, eutrophication of water bodies, abandonment of fishing grounds and associated livelihood pursuits, degradation of aquatic resources, and ecological damage [20]. The tourism sector is affected by tar ball pollution, which causes tourists to migrate from the beach and causes economic losses.

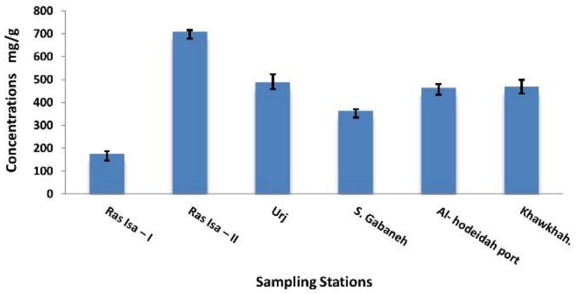

Figure 2: Concentrations of Total Petroleum Hydrocarbons (TPHs) in the tar balls.

3.2 Total Aromatic Hydrocarbons (TAHs) in Tar Balls

Chrysene standard was used widely to reveal the total aromatic hydrocarbons (TAHs) in the sample extracts by an ultraviolet fluorescence technique [21]. Figure 3 shows the concentrations of TAHs in the tar ball samples. The concentration range of TAHs was between 16.06 ± 1.89 mg/g at South of Gabaneh station to 48.25 ± 1.76 mg/g at Ras Isa II station, and the mean concentration was 28.98 ±1.36 mg/g. The same station, Ras Isa-II, recorded high concentrations of TAHs and TPHs, which represented the same source of oil pollution. Clearly, the continuous deposition of petroleum hydrocarbons derived from the oil spill that occurred during the load and transport of the crude oil from the Safir oil loading terminal or from an adjacent area to a fuel storage depot at the coastal line was considered the main sources of TAHs and TPHs. In the second station for the same location that Ras Isa labeled, I recorded a concentration of 39.50 ± 0.70 mg/g, close to that of Ras Isa II station. Both of these stations reflected the same sources of oil pollution. The concentrations of TAHs in Urj, Hodeidah, and Khawkhah samples were 25.13 ±1.55, 19.73 ±0.39, and 25.28 ±1.82 mg/g, respectively. The concentrations in these stations were slightly different, which may indicate the similarity of the oil pollution sources or/and their effect by the same level of weathering factors. The possible sources of TAHs in these stations could result from continuous deposition of PAH derived from heavy, light crude oil spills and/or used crankcase oil of fish boats and water balance from tankers. Similar possible sources have been found worldwide in many tar ball samples [22, 23, 17]. The same sources were suggested by DouAbul [24] when high concentrations of polyaromatic hydrocarbons were found in fish of the Red Sea. The impact of aromatic hydrocarbons on aquatic environment lei on their toxicity. The other types of toxicities that TAHs cause on aquatic organisms and from them to human society are developmental toxicity, genotoxicity, immunotoxicity, oxidative stress, and endocrine disruption, and the most concerning toxicity is their carcinogenicity [25].

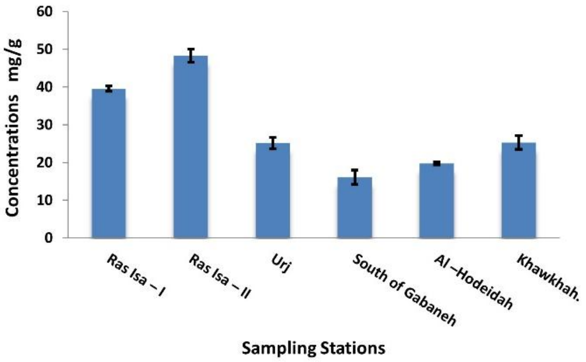

Figure 3: Concentrations of Total Aromatic Hydrocarbons (TAHs) in the tar balls.

3.3 Extractable organic matter (EOM) in tar ball

Figure 4 shows no strong correlation between the EOM of the tar balls and the concentration of TPHs. Indeed, the hydrocarbons in the samples were not related to the concentration of EOM (R^2= 0.21). Likewise, the relationship was positive, but the correlation was not strong between the EOM and TPHs, suggesting that the organic matter does not govern the observed distribution of petroleum hydrocarbons associated with tar balls; therefore, they may be controlled by various sources of inputs and/or differing transport processes [26,27].

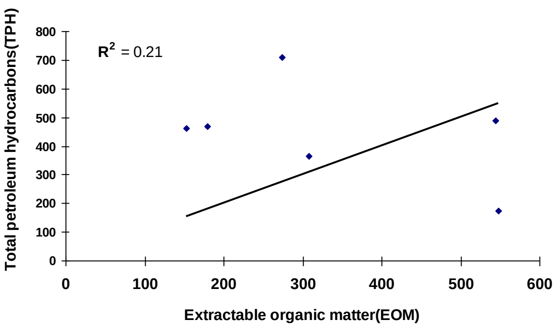

Figure 4: Correlation of total petroleum hydrocarbons against extractable organic matter for tar balls.

Figure 5 shows the concentrations of EOM in tar ball samples. The concentrations of EOM ranged from 153.00 ±9.00 to 548.00 ±54.00 mg/g, with the mean concentration 334.42 ±31.08 mg/g. The significant concentrations were found in Ras Isa I (548.00 ±54.00 mg/g) and Urj (544.50 ±75.50 mg/g). These high results could be affected by both natural (plants, animals, and microorganisms) and anthropogenic input (oil spill, sewage, agricultural drainage). Notably, the lowest value was observed in Al-Hodeidah station (153.00 ± 9.00 mg/g). The reasons for the high or low concentrations of EOM in the several stations were probably caused by sea grass, algae, mangroves, and plankton as natural sources or may be due to untreated sewage, port activities, and/or adjacent fuel storage depot at the coastal area. Other reasons can be due to the contaminated sediments and water, which are likely to enter the sea as well as be deposited in the shoreline through valley run-offs during seasonal rainfall [2].

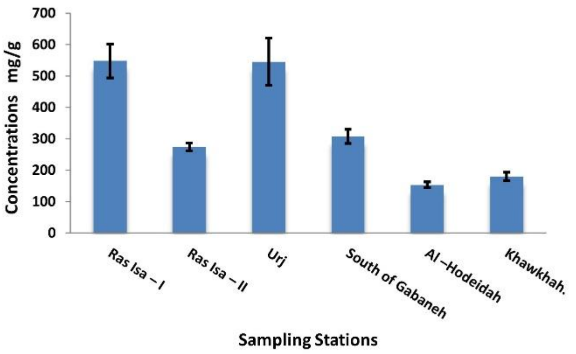

Figure 5: Concentrations of extractable organic matter (EOM) in the tar balls.

4. Conclusion

The concentrations of hydrocarbon partitions, total petroleum hydrocarbons (TPHs), and total aromatic hydrocarbons (TAHs) were measured in tar balls collected from the Red Sea coast of Al-Hodeidah, Yemen. The high concentrations of TPHs and TAHs in some sampling stations were due to the continued deposition of crude oil that occurred during the load and transport of the crude oil from the Safir oil loading terminal and oil spill from other tankers. The concentrations of TPHs and TAHs can pose significant environmental and health risks to marine organisms and humans. Annual monitoring of oil pollution on the coast of the Red Sea by using water, sediments, tar balls, and local fish is encouraged to protect and sustain the Red Sea resources.

Data Availability

The datasets used and analyzed during the current study are available from the corresponding author upon reasonable request.

Conflict of Interest

The authors declare no conflict of interest.

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