



Annual variations in the concentrations of total petroleum hydrocarbons in water, sediments, and biota of Shatt Al-Arab River and its estuary, 2010-2020

Faris J. M. Al-Imarah*, Zainab J. Muosa, Abbas A. Hantoush,
and Luma J. M. Al-Anbar,

Department of Chemistry and Marine Environmental Pollution, Marine Science
Center, Basrah University, Basrah - Iraq.

* Author for correspondence: alimarahfaris1951@gmail.com

Abstract

- Shatt Al-Arab River is liable to pollution by crude oil and its derivatives due to its location at an oil rich area which release different hydrocarbons to the land, air, and water. Moreover, it is surrounded by petroleum refineries' which release huge amounts of petroleum hydrocarbons to the atmosphere then directed to the river by rain or particulate fall. Different levels of petroleum hydrocarbons were reported in atmosphere and soil of Basrah City and water, sediments, and fishes of Shatt Al-Arab River. Samples of fallen rain at basrah city, soil and waters from over all Basra province were collected. Pollutants of different kinds such as petroleum hydrocarbons, major ions, heavy and trace metals, pesticides, and radioactive materials arises from industrial, agricultural, domestic, petroleum, as well as military wastes, were detected analytically in the laboratories by GC, AAS, Flame photometry, spectrofluorometry, radiation counts, and other tools. The atmosphere, land, and water of Shatt Al-Arab River are all polluted to a certain level by petroleum hydrocarbons, particulates, and radioactive materials. Most of measured petroleum hydrocarbons are toxic which have different effects upon clarity of environment and finally upon the health of human being

Key Words: PHC, Shatt Al-Arab River, Water, Sediments, Fishes.

Introduction:

Aquatic pollution referred to introduction of certain materials either naturally such as flow of water or fall of particulates which carries different pollutants or anthropoginically via industrial, agriculture, and domestic which are classified as waste discharge that contains all expected pollutants in the environment. Pollution in the Shatt Al-Arab river arises from discharge of water via Tigris and Euphrates rivers at the northern sector then at the eastern part from Al-Hewaizh marsh via Al-Suwaib river, and at the western sector

from Al-Hammar marsh via Al-Shafy river, as well as Garmatt Ali River, At the middle sector water from Basrah City via Shatt Al-Arab river most polluted tributaries, Al-Jubailah, Al-Rubat, Al-Khandak, Al-Ashar, Al-Khorah, Al-Saraji, within Basrah city, Then by Karun river from the Iranian territories. An increase in the levels of petroleum hydrocarbons in water, sediments, and biota of Shatt Al-Arab River causing a certain level of pollution Figure (1) shows the location of Shatt Al-Arab River at Southern

part of Iraq. This pollution is reflected upon all users of its water, residences, navigators, All kind, aquatic living organisms, recreation. Swimming's, and more. For the last decade Shatt Al-Arab River faced severe threats among

which is increase in pollutant due to shortage of fresh water supply from Northern parts as well as increase of discharge of waste waters from the cities located on its banks.

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Figure 1. Map of Shatt Al-Arab River showing position of water supply from Tigris, Euphratis, Al-Suwaib, Al-Shafi, Garmatt Ali and Al-Karun rivers as well as Shatt Al-Arab River tributaries.

Materials and Methods:

Most studies for the determination of petroleum hydrocarbons concentration in different media of Shatt Al-Arab River were conducted for the sites which stretches from Qurna at the Northern part where Tigris and Euphrates are met to form Shatt Al-Arab River down to the

estuary of Shatt Al-Arab River where it is opened to Northern Arabian Gulf. Figure (2) shows the selected sites for study: 1) Al-Qurna; 2) Al-Dear; 3) Al-Sinbad Island; 4) Al-Ashar; 5) Abu Al-Khaseeb; 6) Abu Floos Port; 7) Al-Seebah; and finally, 8) Al-Fao city.

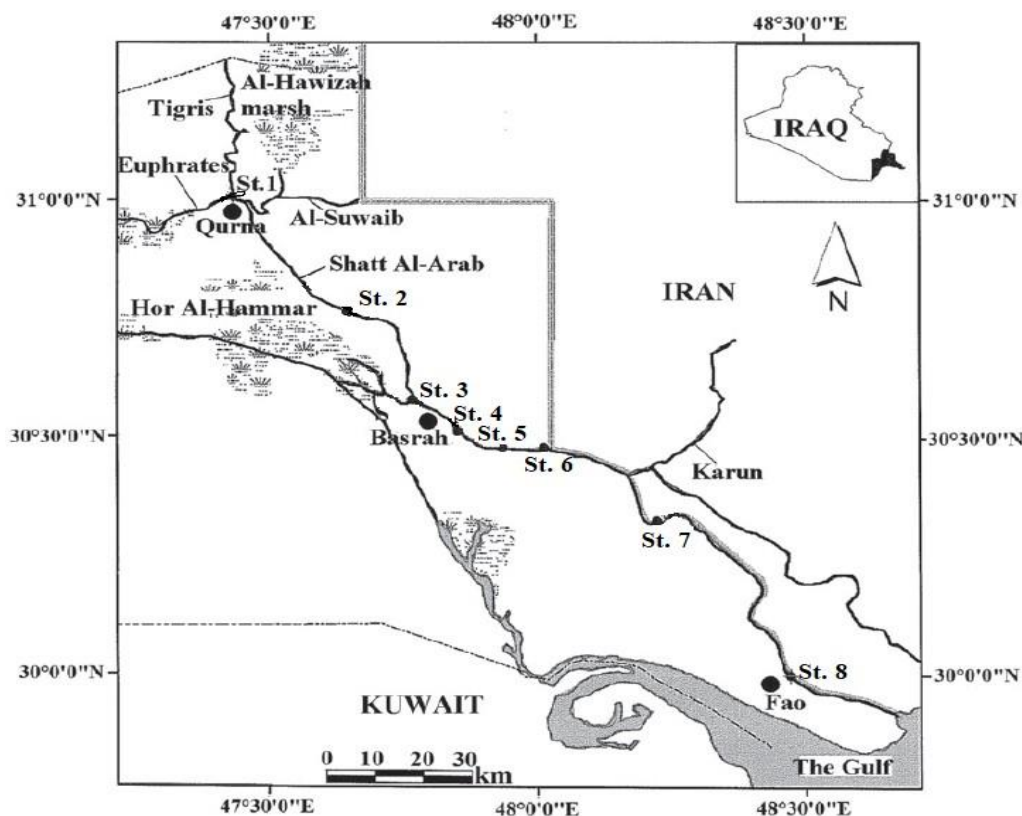


Figure 2. Location map of Shatt Al-Arab River showing the sampling sites (1-8).

Sampling and Extraction:

Several methods of extraction and analytical determination for total petroleum hydrocarbons (TPHC's) in aqueous and solid samples are reviewed. Infrared spectroscopy is one of the efficient methods that are being replaced today pursuant to getting rid of some halogenated solvents classified as ozone-depleting substances. The gravimetric method which uses n-hexane as an extraction solvent for the determination of oil and grease, as well as the nonpolar materials, has become a preferred choice, despite being not suitable for volatiles because of the mandatory evaporation step. Other frequently used methods include gas chromatography with a flame ionization detector (FID) or mass spectrometric detector (MSD) which has the capacity to reveal the type of hydrocarbons present and is applicable to both volatile and semi volatile samples. Ultraviolet fluorescence is another method that is

available both as a portable field device and as off-site laboratory equipment. Each of the methods has its own advantages and disadvantages; hence, the choice of method is guided by the type of data needed as discussed in detail in this review. The distribution of TPHC in water and sediments across the globe and the factors influencing the distribution were also reviewed.

Petroleum Hydrocarbons in Water:

Water samples from middle center of Shatt Al-Arab River were collected by means of water sampler (Fig. 3). Fitted on the board of the ship, samples were kept in ice cold box and transferred to the labs in Marine Science Center / University of Basrah, In the lab an aqueous sample, the EPA liquid-liquid extraction is the most commonly used extraction method for TPH's (Adeniji *et al.*, 3017). The liquid-liquid extraction (LLE) technique involves the use of a separator funnel for multiple extraction

of the sample with an organic solvent of choice with the intent of achieving good recovery of the desired analytes. The technique requires strong shaking of the liquid sample with an organic solvent in a funnel shaped piece of glassware for a couple of minutes.

Petroleum Hydrocarbons in Sediments:

Sediment samples were collected from the middle sector of the river by means of van veen Grab sampler (Fig. 4). Samples were transferred to the lab in the Marine Science Center, the petroleum hydrocarbons were isolated from the sediments by saponification with alcoholic KOH for 2 hours then extraction with n-hexane, then petroleum hydrocarbons were estimated using Spectrofluorometric technique, following IOC (1982). Basrah light crude oil was used as an external standard (Fig. 5).

Petroleum Hydrocarbons in Fishes:

Assorted fishes as commonly available in Shatt Al-Arab Waters were collected from the river by means of net (Fig. 6), kept in ice box and transferred to the lab in marine science center/Basra University, stored frozen prior to analysis. In the lab fishes were thawed, cleaned, and muscles were cut from the side, Muscle samples were freeze dried. then sample was ground, and a certain amount was packed in a thimble (Whitman) and desiccated overnight prior to extraction. The desiccated thimble was loaded in a Soxhlet apparatus and extracted with Methanol: Benzene for 24 hrs. according to the methods described by Al-Ali *et al.* (2016). The solvent was reduced and TPHs was estimated by UV Fluorescence, using Basrah crude oil as standard. Spectra and calibration curve is shown in Figure (5). Quantification was performed at 310 and 360 nm as excitation and emission wavelengths respectively (Al-Ali *et al.*, 2016).



Figure 3. Water sampler for Collecting water samples



Figure 4. van veen Grab sampler for collecting sediments

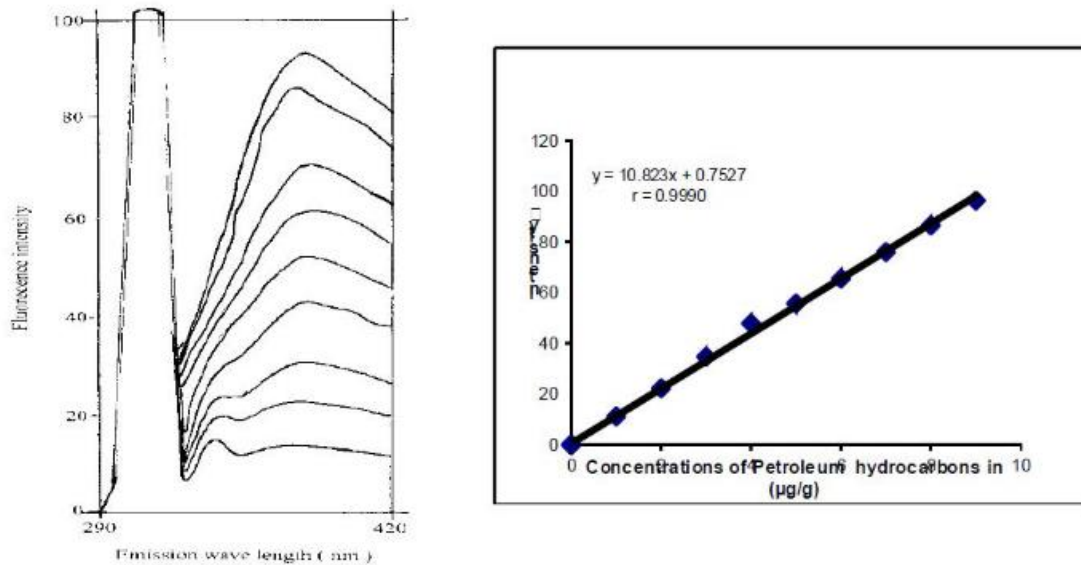


Figure 5. Spectra for standard Basra crude oil and the calibration Curve, Excitation and emission wavelengths were 310 and 360 nm, respectively



Figure 6. Fish caught by net

Result:

As a reflection of petroleum hydrocarbons existence in different sites along Shatt Al-Arab River from Al-Ashar to Al-Fao. Total petroleum hydrocarbons were determined by Gas Chromatography and found ranged between 21.49-31.91 ng/g (Al-Bydhani *et al.*, 2020).

Ali *et al.* (2013) estimated that petroleum hydrocarbons are distributed in Bacteria and Fungi from Shatt Al-Arab River and suggested that the origin of petroleum hydrocarbons were biogenic.

Total petroleum hydrocarbons in water samples from stations along

Shatt Al-Arab River from Al-Qurna (St. 1) to Al-Fao (St. 8) were estimated and reported in water as 2.03-19.58 µg/l while in the sediment's values ranged as 10.15-30.16 µg/g (Mehdi, 2015).

Contamination of water and sediments of Shatt Al-Arab River by petroleum hydrocarbons were investigated during 2012 and 2013. Levels recorded were 5.18-37.58 µg/l in water (Al-Hejuje, 2015a) and 4.76-45.24µg/g in the sediments (Al-Hejuje, 2015b).

Analysis showed that total petroleum hydrocarbons in aquatic fishes caught during 2015 at Shatt Al-

Arab River were reported in the range 4.62-10.67 $\mu\text{g/g}$ and showed seasonal variations (Al-Imarah *et al.*, 2016).

Existence of petroleum hydrocarbons as dissolved in water of Shatt Al-Arab River were found to have a toxic effect to a certain extent even if they showed a certain resistance to crude oil components (Farid *et al.*, 2016a).

Petroleum hydrocarbons in the column of Shatt Al-Arab River are exposed to precipitation to the bottom of the river by the aid of existent particulate matter, Farid *et al.* (2016b) reported levels of petroleum hydrocarbons in different sizes of bottom sediments from Shatt Al-Arab River ranged between 30.86-87.79 $\mu\text{g/g}$ and these levels were related to % TOC which were recorded in the same area and ranged between 0.32-1.64 %, as well as related to grain size of the sediments of the same site too.

The presence of petroleum hydrocarbons in the water column of Shatt Al-Arab River lead to accumulation in core sediments and their concentrations in the core layers were used to estimate the expected pollution by petroleum hydrocarbons during the past years. Total petroleum hydrocarbons in the core sediments of Shatt Al-Arab River in positions started from Al-Qurna (St. 1) towards Al-Fao (St. 8) were ranged being lower at Al-Qurna and higher at Al-Ashar (St. 4) (Al-Muhana *et al.*, 2016).

A degree of oil pollution in water and sediments of Shatt Al-Arab River was estimated by determination of total petroleum hydrocarbons spectrofluorometrically in samples along Shatt Al-Arab River and its estuary. Levels detected were range from 3.09 to 30.87 $\mu\text{g/l}$ in water samples, while in sediments levels were higher and reported in range of 19.43 to 49.09 $\mu\text{g/g}$ (Al-Saad *et al.*, 2017).

Due to its location, Shatt Al-Arab River is liable to pollution by petroleum hydrocarbons. crude oil around Shatt Al-Arab River was discovered since 1908 in the city Masjid Suleiman within the Iranian territories and crude oil is transferred by suitable vessels to Abadan Refinery through Karun River (Al-Imarah *et al.*, 2017).

Aromatic hydrocarbons in water and sediments of Shatt Al-Arab River showed great effect on the biochemical components of mud carb, *chiromants boulegeri* (Calmen, 1920). Levels recorded of total aromatic hydrocarbons in water, sediments, and tissues of carb *boulegeri* were 38.88-23.36 g/l in water, and 24.03-12.46 $\mu\text{g/g}$ in sediments and 26.48-14.17 $\mu\text{g/g}$ in *boulegeri* carb from Shatt Al-Arab River, respectively (Al-Tae *et al.*, 2018).

Detected petroleum hydrocarbons in water from Al-Qurna (St. 1) were change seasonally from 0.33 $\mu\text{g/l}$ during summer to 2.39 μl during winter in water (Al-Talal *et al.*, 2019).

Leakage of petroleum hydrocarbons to the middle sector of Shatt Al-Arab through Garmatt Ali River causing an increase of pollution by petroleum hydrocarbons. In a study during 2019, concentrations of petroleum hydrocarbons in sediments from Al-Hammar marsh were reported in a range between 2.05-14.94 $\mu\text{g/g}$ which were comparable to levels reported earlier at 1982 in the same area (Al-Gizzi *et al.*, 2021), spatially or temporally. they concluded that Shatt Al-Arab River was within the permissible limit, ie. there were no significant differences.

Discussion:

One of the most powerful factors for pollution of aquatic environment of Shatt Al-Arab River is the petroleum industries represented by oil refineries

exist in the area, Al-Shuaibah oil refinery inside Iraqi land, and Abadan oil refinery within the Iranian land. Oil refineries release petroleum hydrocarbons either to the atmosphere or to the water effluents (Wake, 2005). Moreover Shatt Al-Arab River is exposed to pollution by crude oil derivatives leaking from sinking ships since the Iraqi-Iranian war 1980-1988 (Al-Imarah *et al.*, 2017). A certain concentrations of total petroleum hydrocarbons were recorded in six commercial fishes caught at Shatt Al-Arab River, the range was 2.47-21.52 µg/g (Al-Saad *et al.*, 2017). Earlier survey has been conducted to evaluate pollution by petroleum hydrocarbons in water, sediments, and living organisms of Shatt Al-Arab River which revealed that petroleum hydrocarbons are exist in water as dissolved and particulate and in sediments as exchangeable and residual as well as in all organs of fishes (Al-Imarah *et al.*, 2007).

Urban environment, water, air, and soil, of Basrah Province were contaminated to a certain level with petroleum hydrocarbons. Al-Hassan *et al.* (2013) reported levels of 0.4-1905 µg/l in water, 20-29.3 ppm in ambient air samples, and 0.56-41.58 µg/g in soil samples. The contamination of Shatt Al-Arab waters by a certain levels of petroleum hydrocarbons were reflected upon their effects to aquatic organisms living nearby (Al-Saad *et al.*, 2011).

Distribution of petroleum hydrocarbons in water, and sediments from northern parts of Shatt Al-Arab River were investigated and studied temporally and spatially for stations stretches from Qurnah to Basrah city (Al-Imarah *et al.*, 2010). Moreover, Euphrates River to the Northern West of Shatt Al-Arab River releases contaminates of petroleum hydrocarbons towards Shatt Al-Arab

River (Ali, 2012). In addition to that, tributaries of Shatt Al-Arab River play a great role in contamination of its water in which levels recorded in the water of these tributaries were range between 7.1-27.5 µg/l (Hamza, 2012).

Bacteria and fungi as a living organism in Shatt Al-Arab River were contaminated to a certain level by n-Alkane's hydrocarbon released from different sources (Ali *et al.*, 2013). During the year 2013, Farid *et al.* (2014) recorded total aliphatic petroleum hydrocarbons ranged between 16.77-42.6 µg/l while aromatic petroleum hydrocarbons levels were ranged 7.19-22.47 ng/l in the water column of Shatt Al-Arab River. Existence of petroleum hydrocarbons in the water of Shatt Al-Arab River is reflected by accumulation of petroleum hydrocarbons in different organs of living organisms such as *Liza subviridis*. Levels of petroleum hydrocarbons in the range 6.3-9.75 µg/g were recorded in different organs of *Liza subviridis* caught in the Shatt Al-Basrah Canal during 2008-2009 (Atti, 2014).

Petroleum hydrocarbons in the marine environment come from naturally (biogenic or diagenetic) and anthropogenic (petrogenic or pyrogenic) sources (Wu *et al.*, 2001). Biogenic source hydrocarbons refer to those hydrocarbons produced by living organisms (e.g., planktons, algae, and bacteria) or through biological processes involving terrestrial plants. The anthropogenic hydrocarbons are usually more in the environment than the natural ones. They are commonly generated from various human activities like industrialization, urbanization, transportation, oil utilization, operations and storage, shipping, and fishing (Sakari *et al.*, 2008).

Petroleum hydrocarbons (PHC's) are prominent among organic contaminants which are frequently disposed into the marine environment in lower concentrations in the form of urban runoffs, automobile wastes, storm water, industrial effluents, or domestic wastes and occasionally in higher concentrations as a major oil spill (Tahrani *et al.*, 2012; Ahmed *et al.*, 2015).

Petroleum hydrocarbons consist majorly of three groups of compounds,

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- Conclusion:**
- Shatt Al-Arab River faced pollution by petroleum hydrocarbons from different sources since the early years of the last century. Levels reported were ranged from 2.6 µg/l up to 5.6 µg/l along the whole length of the river.
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