

The fluctuations in concentrations, origins and sources of Polycyclic Aromatic Hydrocarbons (PAHs) in water (dissolved and particulate fractions) of the Shatt al Arab River and its branches/Basra-Iraq

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Abstract - The present study was performed to determine the concentrations, sources and origins of Polycyclic Aromatic Hydrocarbons in water (dissolved and particulate fractions) of Shatt Al-Arab river and its branches . Samples were collected seasonally from six stations during the period from August 2014 to September 2015. The concentrations of PAHs compounds as dissolved ranged from (0.003)ng/l at station 3 during Sping to (250.7) ng/l at station 5 during Autumn ,while as particulate from (0.15)ng/g at station 1 during Summer to (908.919) ng/g at station 5 during winter. The highest concentrations of PAHs as dissolved fraction recorded were in Acenophthylene , Banzo(a) Anthracecne and Anthracene respectively. And, the lowest was in Indeno (1,2,3-cd)Pyrene .The highest concentrations of PAHs as particulate fraction recorded were in Anthracene, Acenophthylene ,and Acenophthlene respectively, while the lowest was Indeno in (1,2,3-cd) Pyrene. The more dominant PAHs compounds as dissolved and particulate fractions fraction recorded was Benzo(a) Anthracene and the less was Indeno(1,2,3-cd)Pyrene . The index that had been used showed that the main sources of PAHs compounds were pyrogenic and petrogenic .

Key words : Pollution of PAHs , Water , Shatt Al-Arab river , PAHs , Dissolved &Particulate fraction .

I. INTRODUCTION

PAHs are a widespread type of organic pollutants in the atmosphere and are mainly formed and emitted as a result of incomplete combustion of organic matter such as fossil fuel and biomass(Kafilzadeh et al .,2011;Wu et al.,2014). PAHs are classified as LMW-PAHs if they have two or three fused rings , or HMW-PAHs if they have four or more fused rings(Stogiannidis and Laane ,2015). LMW-PAHs are more water's soluble and volatile, therefore they are more available than HMW-PAHs and the latter are classified as semivolatile organic pollutants (Bakhtiari et al , 2009; Wick et al .,2011), while the HMW-PAHs show higher hydrophobicity than the LMW-PAHs (Zuydam,2007).

There are two sources, the anthropogenic and natural processes (Morillo et al., 2008). Natural sources of PAHs include seeps from deposits of crude oil, erosion of ancient sediment, volcanoes ,forest fires, diagenetic processes and natural vegetation fires.The main anthropogenic sources of PAHs emitted into the environment are industrial emissions (formed at the processing of organic raw materials at the high temperature), domestic waste and fossil fuels burning. Other sources are from oil spillage and waste discharge , automotive transport (more than 150 PAHs were detected in automobile exhaust), aviation, shipping, mining and transportation of oil(Tsymblyuk et al ., 2011).

Aromatic hydrocarbons are the most toxic major classes of petroleum compounds . USEPA(2009) designated sixteen PAHs as priority environmental pollutants because they exhibit properties such as persistence, bioaccumulation, mutagenicity , carcinogenicity, teratogenicity , toxicity , hepatotoxicity and potenly for wide-

range environmental transportation to a certain extent (IARC 2003; Tao et al., 2010 ;Ali et al., 2012). These compounds include benzo(a)pyrene the most toxic and the most studied and Benzo(b)fluoranthene ,Benzo(a)anthracene ,Benzo(k)fluoranthene,Chrysene, Dibenzo(a,h)anthracene and Indeno(1,2,3,cd)pyrene are considered to be probable carcinogens for human (Badjo et al., 2015).The aim of the present study is to measure the concentrations of PAHs , and identifying the major sources of PAHs compounds as dissolved and particulate fractions to give baseline data for further work in Shatt Al-Arab river.

II. MATERIAL AND METHODS

A. Sampling –

Collection of Samples and their measurements were done seasonally during the day for the period from August 2014 to September 2015 at different stations of Shatt Al- Arab and its channels (Abu khasib, Hamza, Hamdan, Mhajeran , Cornish and Garmat Ali canals) during low tide , as shown in Figure (1) .

B. Extraction of PAHs from dissolved fraction –

Is extracted according to the method described in UNEP (1989) by using CCl₄ . The samples were detected with HPLC for polynuclear aromatic hydrocarbons (PAHs) .

C. Extraction of PAHs from particulate fraction –

Is extracted according to the method described in UNEP (1992) by using hat extraction soxhle . The samples were detected by HPLC for polynuclear aromatic hydrocarbons (PAHs).



Fig.(1): The study stations

III. RESULT AND DISCUSSION

PAHs in water (dissolved and particulate fractions)

The results that showed the highest concentrations of some individual PAHs as dissolved fraction were for Acenophthylene, Banzo(a)Anthracene , Anthracene , while as particulate fraction for Anthracene, Acenophthylene, Acenophthlene. The lowest concentrations recorded was for Indeno (1,2,3-cd)Pyrene as dissolved and particulate fractions .The percentages of 16PAHs compounds showed that the 3-ring PAHs represent (92 % and 79 %) ,while low percentage were recorded for 2-ring PAHs (0% and 1%) of the total PAHs as dissolved and particulate fraction respectively. The composition of PAHs followed a gradient of (3-ring>4-ring>5-ring>6-ring>2-ring) as shown in Fig.(1)(2). The results showed Significant differences ($P < 0.01$) among compounds , the highest mean (32.53) was recorded for Acenophthylene and the lowest (0.17) for Banzo(b)Fluoroanthene as dissolved fraction ,while the highest mean (142.61) was recorded for Anthracene and the lowest mean (2.12) for Banzo(g,h,i)Perylene as particulate fraction (Table 2) . This results showed that the source of 3-ring PAHs was not dependent only on domestic and agricultural effluent or atmospheric deposition from industrial emissions and/or biomass burning, but also depend on different petroleum related activity (petrogenic source).Whereas , 4,5,6-rings are less prone to degrade and are also more likely to be

carcinogenic. This suggests that they would be more likely the cause of ecological risk in this region, similar explanation was reported by Ekpo *et al.* (2012). The more dominant 16 PAHs were Benzo(a) Anthracene, Anthracene and Fluoranthene and the less were Indeno(1,2,3-cd)Pyrene, Benzo (g,h,i) Perylene as dissolved fraction, while the more dominant compounds were Benzo(a) Anthracene, Chrysene, and Acenophthylene and the less was Dibenzo (a,h) Perylene as particulate fractions. The highest concentration for all 16 PAHs was (1014.3 ng/l) recorded for Acenophthylene and the lowest (0.03 ng/l) for Indeno(1,2,3-cd)Pyrene as dissolved fraction, while the highest concentration (1180.5) was recorded for Anthracene and the lowest (2.06 ng/g) for Banzo(a)Pyrene as particulate fractions (Table 2). PAHs distributions were dominated by 3 and 4-rings PAHs as dissolved and particulate fraction. These findings in the present study are in agreement with those found in Chen *et al.* (2006). This may be explained by the fact that the surface water receives direct PAHs inputs, such as shipping, oil spill, dry and wet atmospheric deposition, air-water exchange etc, another explanation may be due to that the LMW-PAHs have the ability to solubilized in water more than HMW-PAHs, and the resuspension process of HMW-PAHs(4 or more benzene ring) occur in water column because these compounds are resistant to biodegradation and photooxidation (Mohammed,2007 ;Al-Khatib ,2008). The results of this study showed a significant differences ($P < 0.01$) among stations, the highest mean (11.54 ng/l) was recorded at station 5 and the lowest mean (0.99 ng/l) at station 2 as dissolved fraction, while the highest mean (51.05 ng/g) was recorded at station 5 and the lowest (13.80 ng/g) at station 3 as particulate fractions (Table 1). This may be due to the exposure to different anthropogenic activity at stations, however the variation of PAHs concentrations among stations may be attributed to the proximity of the source, type of source and anthropogenic activity at stations (Doong and Lin ,2004). In addition to the anthropogenic activities that represent the major source of PAHs in addition to natural source, the proximity to sewage discharge and domestic waste, human waste discharge as well as that of fishing boats. A similar conclusion was reached by Maktoof *et al.* (2014). While, a low concentrations of PAHs at station 2 and 3 as dissolved and particulate fractions may be due to density of plants in this stations which play an important role in removing PAHs from water by adsorption and accumulation (Hus,2004). **PAHs pollution indices:** LMW/HMW and Fluoranthene /Pyrene ratios were used to describe the origin sources of PAHs compounds in water samples (Table 3). It is clear from the results that the distribution of PAHs in the Shatt Al-Arab and its branches may had the origin from different sources (petrogenic and pyrogenic).

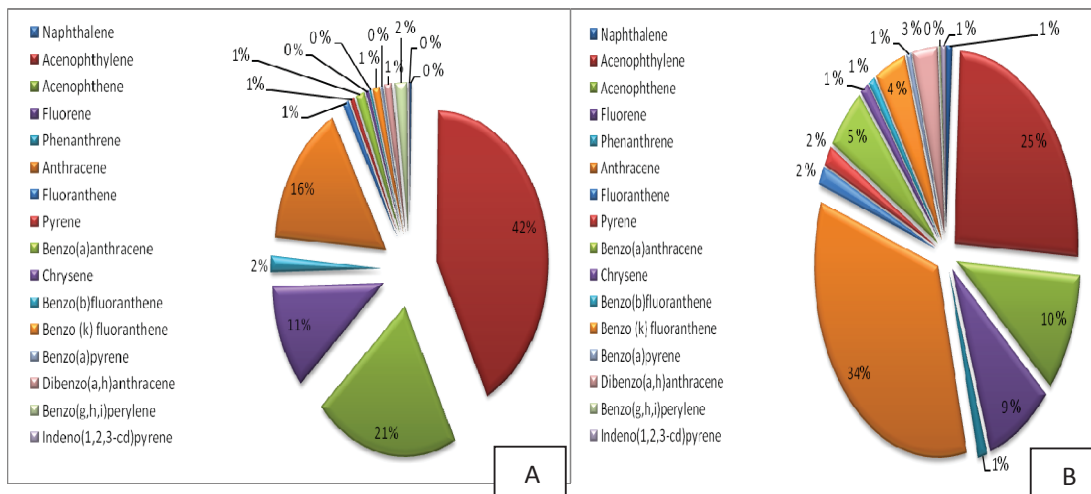


Fig.(1) : (A) :The PAHs compounds percentage in dissolved fraction ,(B): The PAHs compounds percentage in particulate fraction

IV. CONCLUSION

The composition pattern of PAHs during the study period as dissolved and particulate fractions were dominated by 3-4 rings PAHs (Benzo(a)Anthracene), (Benzo(a)Anthracene and Chrysene). And, the highest concentration

were recorded for LMW-PAHs (Acenaphthylene), (Anthracene and Acenaphthylene) respectively , which were a petrogenic source.

REFERENCES

- [1] Ali AZD, Farid WAA, Al-Saad HT, AlMaarofi SS(2012)Hydrocarbons in soil from Basra oil-rich governorate . American Journal of Environmental Science. 8 (5):563-568.
- [2] Al-Khatib FM (2008)" Determination the concentrations , origin and distribution of hydrocarbon compounds in water , sediments and some biota of Hor Al-Howaiza ,south of Iraq and their sources ".Ph.D.Thesis. University of Basrah, college of science, 228P. (In Arabic)
- [3] Badjo ATD, Guéro Y, Lamso ND, Idder T, Echevarria G, Sterckeman T(2015)Assessment of polycyclic aromatic hydrocarbons contamination in urban soils from Niamey, Niger .*Journal of Biodiversity and Environmental Sciences* 6(1): 275-281.
- [4] Bakhtiari AR,Zakaria MP,Yaziz MI,Lajis MNH, Bi X (2009) Polycyclic Aromatic Hydrocarbons and n-alkanes in Suspended Particulate Matter and sediments from the Langat river ,peninsular Malaysia.*Environment, Asia* 2:1-10.
- [5] Doong R, Lin Y(2004)Characterization and distribution of Polycyclic Aromatic Hydrocarbome contamination in surface sediment and water from Gao-Ping river.Taiwan.*Water Research* 38:1733-1744.
- [6] Ekpo BO,Oyo-Ita OE,Offem JO,Adie PA(2012)Anthropogenic PAHs in Sediment-Dwelling Biota from Mangrove Areas of the Calabar River, SE Niger Delta, Nigeria. *Environment and Natural Resources Research* 2(4): 1927-0496.
- [7] Hus S(2004)Removal Polycyclic Aromatic Hydrocarbons (Phenanthrene&Pyrene) in aquatic phase by Ceratophyllum demorsum &Naja gramunea .M.Sc.thesis .Marine Environment &Engineering.chnese.
- [8] IARC (International Agency for Research on Cancer)(2003) <http://www.iarc.fr>.
- [9] Kafilzadeh F, Shiva AH, Malekpour R(2011)Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Water and Sediments of the Kor River, Iran. *Middle-East Journal of Scientific Research (MEJSR)*10 (1): 01-07
- [10] Chen SJ, Luo XJBX,Mai GY, Sheng JM, Zeng EY(2006) Distribution and Mass Inventories of Polycyclic Aromatic Hydrocarbons and Organochlorine Pesticides in Sediments of the Pearl River Estuary and the Northern South China Sea. *Environmental Science and Tech* 40(3): 709-714.
- [11] Maktoof AA,ALKhafaji BY,Al-janabi ZZ(2014)Evaluation of Total Hydrocarbons Levels and Traces Metals in Water and Sediment from Main Outfall Drain in Al-Nassiriya City/Southern Iraq. *Natural Resources* 5:795-803.
- [12] Morillo E,Romero AS,Maqueda C,Madrid L,Ajmone-Marsan F, Grcman H, Davidson CM, Hursthouse AS, Villaverde J(2008) Soil pollution by PAHs in urban soils: a comparison of three European cities. *Journal of Environmental Monitoring* 9(9):1001–1008.
- [13] Mohammed AB(2007) Studies of some Polycyclic Aromatic hydrocarbons (PAHs) and Limnology of Euphrates river. From Al-Hindiya Barrage to Al-Kifil city. Iraq. Ph.D.Thesis. University of Babylon, 247P.
- [14] Stogiannidis,E. and Laane,R.(2015). Source Characterization of Polycyclic Aromatic Hydrocarbons by Using Their Molecular Indices: An Overview of Possibilities. *Springer International Publishing Switzerland* . 234.
- [15] Tao S, Zhang D, Lu Y, Li L, Ding J, Yang Y, Wang X, Liu W, Xing B(2010)Mobility of Polycyclic Aromatic Hydrocarbons in the Gastrointestinal Tract Assessed Using an in Vitro Digestion Model with Sorption Rectification.*Environmental Science & Technology* 44(14):5608–5612.
- [16] Tsyblyuk KK, Den'ga YM, Berlinsky NA, Antonovich VP(2011)Determination of 16 priority polycyclic aromatic hydrocarbons in bottom sediments of the Danube estuarine coast by GC/MS. *Geo-Eco-Marina* .17.
- [17] UNEP(United Nation Environmental Program)(1989)" Comparative toxicity test of water accommodated fraction of oils and oil dispersant's to marine organisms. Reference methods for marine pollution" No. 45, 21PP.
- [18] USEPA(2009)Information on the Toxic Effects of Various Chemicals and Groups of Chemicals. <http://www.epa.gov/R5Super/ecology/html/toxprofiles.htm>.
- [19] Wu SP, Yang BY, Wang XH, Yuan CS, Hong HS(2014)Polycyclic Aromatic Hydrocarbons in the Atmosphere of Two Subtropical Cities in Southeast China: Seasonal Variation and Gas/Particle Partitioning. *Aerosol and Air Quality Research* 14: 1232–1246.
- [20] Wick AF, Haus NW, Sukkariyah BF, Haering KC, Daniels WL(2011) Remediation of PAH-Contaminated Soils and Sediments: A Literature Review. Review <http://landrehab.org/> ,24061:102pp .
- [21] Zuydam CSV(2007)Determination of polycyclic aromatic hydrocarbons (PAHs) resulting from wood storage and wood treatment facilities for electricity transmission in Swaziland,M.Sc.Thesis,Univesity of South Africa,112P.