Bull. Environ. Contam. Toxicol. (1989) 43:864–869
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Bulletin of Environmental Contamination and Toxicology

Distribution of Polycyclic Aromatic Hydrocarbons (PAH's) in Marsh Sediments, Iraq

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Recently there has been a growing concern in the release of harmful organics into the environment. Carcinogenic polycyclic aromatic hydrocarbons (PAH's) are a class of compounds of interset due to their possible harmful effects to man as well as organisms. Anthropogenic PAH's may reach aquatic environment as a result of both industrial and domestic effluents, deposition of airborne particles, surface runoff and oil spillage. Having a relatively low water solubility and high affinity to sorb to the suspended particulate matter, most of the PAH's introduced to the aquatic environment tend to accumulate in bottom sediments (Delaune et al., 1981). Sedimentary PAH's may thus provide a record of the input and history of these pollutants (Wakeham et al., 1980). Consequently, the distribution of PAH's in aquatic sediments have received considerable attention. The purpose of the present work was to establish the distribution of PAH's in the sediments of the marsh region located southern of Iraq.

MATERIALS AND METHODS

Sediment samples were collected from seven stations in Hor al-Hammar marsh (Fig. 1). A van Veen grab sampler together with a phleger type corer were used to furnish these samples. An arbitrary choice of surface (the upper most 2cm) and sub-surface (about 10cm deep layer) have been taken. Surface sediments were carefully removed using a board bladed stainless steel spatula. Precautions were taken to minimize mixing during sampling. The samples were stored in glass-jars and immediately frozen to -20°C. Before analysis, the sediments were freeze-dried, ground finely in an agate mortor and sieved through 62µ metal sieve. The procedure employed for the extraction of PAH's from the sediments

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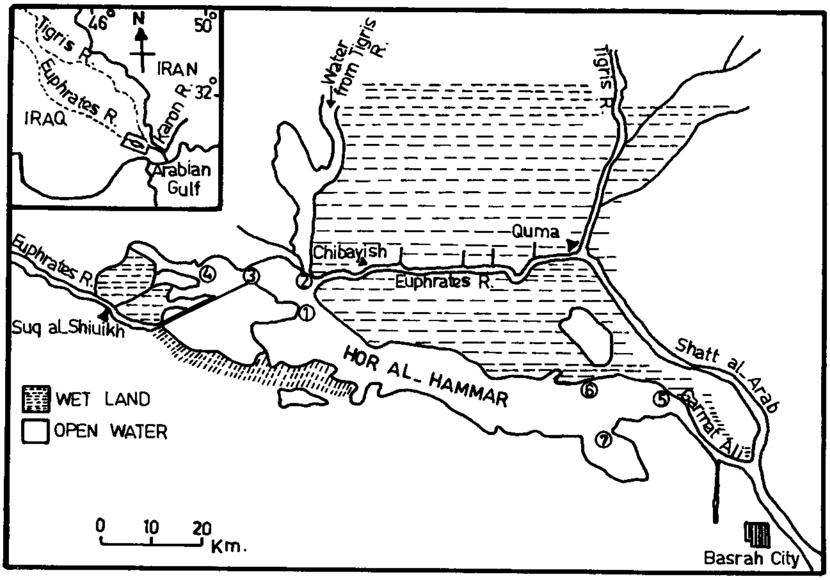

Figure 1. Sampling locations.

was based upon that described by (Risebrough et al., 1983). Briefly, sediments were soxhlet extracted with n-hexane, the extracts were saponified and separated into groups by column chromatography of deactivated florisil (5% w/v water). The PAH's fraction were eluted with 10, 30 and 50% methylene chloride in hexane. The fractions were reduced in volume and analyzed by a Perkin-Elmer sigma 300 capillary gas chromatography. A wall coated open tubular (WCOT) fused silica capillary column (50m X 0.25mm i.d.) with 0.22μ film thickness coated with SE30 (methysilicone)(Supelco S.A.) was used. Operating temperatures were 300 and 310°C for injector and detector respectively. While the column was operated under temperature programmed conditions 4°C/min from 70 to 280°C with an isothermal period (30 min) at the end.

Recovery studies with fortified samples indicated that the recovery efficiency exceeded 85% for all compounds measured. Procedural blanks consisting of all reagents and galssware used during the analysis were periodically determined and the sample values were corrected for procedural blanks.

Total organic carbon (TOC) and grain-size analysis were performed on representative slips of the bulk sediment samples in order to give a better apprisal of PAH's residues. TOC was determined following the procedure of El-Wakeel and Riley (1957). Grain-size analysis of the sediment was carried out using the combined dry sieve and pipette method (Folk, 1974).

RESULTS AND DISCUSSION

Polycyclic aromatic hydrocarbons concentrations observed in the present study are summerized in Table 1. In surface sediments, PAH's contents were found to vary between 0.59 ppb at station 5 to 2.07 ppb dry weight sediment at station 4. As for sub-surface sediments they were found to vary between 0.46 ppb at station 5 to 1.42 ppb dry weight at station 4. The highest levels were at station 4 which may be due to numerous number of small boats moring the area. As a consequence the environment here is constantly subjected to small spillage of fuel oil as well as direct discharge of engine exhaust. This contention was further supported by the detection of both naphthalane and acetonaphene which are reported to be present in No. 2 fuel oil used extensively in this region (DouAbul et al., 1987). Sediments adjacent to large urban areas may contain high concentrations of anthropogenically derived hydrocarbons (Wakeham and Farrington 1980). Areal distribution of PAH's in marshes sediments indicates that contamination is local and thus suggesting that transportation of these pollutants within the sediment is rather slow. Recent evidence, however, showed that both biogenic and anthropogenic hydrocarbons may be transported to a considerable distance from a point source (Wakeham and Farrington, 1980). Iraqi marshes receive water from both Tigris and Euphrates Rivers whom carry tremendous amounts of suspended particulate matter to which organic matter are sorbed. These materials are mostly deposited in the entrance of the marsh i.e. station 4 (Fig. 1) as the water currents of Tigris and Euphrates River drops appreciably. It is reasonable to presume that PAH's represent an important group of detrital organic matter transported by these river, since they drain a considerable urban and industrial areas. The fate of the various chemical components of the detrital organic matter after introduction to aquatic environment depends upon their solubility, particle phase associations and the processes of dispersal for these carrier particles.

The persistence of PAH's in aquatic sediments seem to be related to their molecular weight (Readman et al., 1982). Thus, low molecular weight compounds tend to be volatile and subjected to rapid microbial degradation, hence they have short residence time. On the other hand, high molecular weight PAH's have a high particle affinity and low microbial degradation rate and hence tend to accumulate in sediments. The present results are in a good agreement with these conclusions as the PAH's appears to be divisible into two groups (1) low molecular weight PAH's incorporating naphthalene, biphenyl, acenaphthene, fluorene, phenanthrene and anthracene; and (2) large molecular weight homologues include fluoranthene, pyrene, chrysen, benzo(ghi)perylene and benzo(a) pyrene. Similar findings were arrived at by Al-Saad (1987).

Diagentic processes also produce a mixture of PAH's derived from

Table 1. Concentrations of PAH's in surface and sub-surface sediments (ppb dry weight).

PAH's Location	1	2	3	4	5	6	7
Surface sediment:							
Napthalene	0.04	0.04	0.07	0.09	0.01	0.07	0.08
Biphenyl	0.02	0.03	0.01	0.03	-	0.02	-
Acenaphthylene	0.06	0.07	0.06	0.08	0.06	0.08	0.07
Acenaphthene	0.01	0.02	0.07	0.06	-	0.03	0.02
Fluorene	0.03	0.05	0.03	0.07	0.05	0.08	0.09
Phenanthrene	0.03	0.03	0.02	0.05	0.07	0.06	0.08
Anthracene	0.04	0.04	0.10	0.06	0.06	0.05	0.09
Fluoranthene	0.03	0.06	0.08	0.10	0.06	0.07	0.20
Pyrene	0.03	0.03	0.05	0.08	0.04	0.08	0.07
Chrysene	0.06	0.05	0.07	0.80	0.04	0.09	0.06
Benzo(ghi)perlylene	0.90	0.91	0.92	0.60	0.20	0.08	0.09
Benzo(a)pyrene	0.01	0.06	0.03	0.05	-	0.08	0.09
Total PAH's	1.26	1.39	1.51	2.07	0.59	0.76	0.86
TOC(%)	0.69	0.58	0.79	3.62	0.95	1.38	0.45
Grain size Mdφ	7.10	6.85	7.90	6.10	3.20	6.20	7.00
Sub-surface sediment							
Naphthalene	0.05	0.06	0.02	0.06	-	0.06	0.06
Biphenyl	-	-	-	0.05	-	0.01	0.01
Acenaphthylene	0.06	0.05	0.06	0.10	-	0.09	0.07
Acenaphthene	-	-	-	-	-	-	-
Fluorene	0.04	0.03	0.09	0.09	0.07	0.03	0.05
Phenanthrene	0.01	-	0.07	0.06	0.03	0.02	0.01
Anthracene	0.02	0.02	0.08	0.07	0.08	0.01	0.01
Fluoranthene	0.02	0.07	0.06	0.31	0.09	0.06	0.10
Pyrene	0.05	0.06	0.07	0.21	0.06	0.03	-
Chrysene	0.60	0.40	0.08	0.09	0.02	0.02	0.09
Benzo(ghi)pyrene	0.06	0.09	0.30	0.31	0.10	0.04	0.10
Benzo(a)pyrene	0.01	0.03	0.01	0.07	0.01	0.01	0.03
Total PAH's	0.92	0.82	0.84	1.42	0.46	0.56	0.53
TOC(%)	0.46	0.37	0.63	2.12	0.83	1.23	0.33
Grain size Mdφ	7.00	6.85	7.65	5.70	4.20	8.00	4.30

polycyclic biogenic precursors originating from bacterial lipids, terrestrial higher plant terpenoids and unknown precursors. The marshes of Iraq are surrounded by grass and covered with aquatic plants which may contribute some PAH's to the sediments. Some evidence appear to indicate that PAH's present in soil and recent aquatic sediments are principally derived from natural grass (Youngblood and Blumer 1975). The presence of Benzo (ghi)perlyene, is believed to be produced primarily by biogenesis from unidentified precursor(s) under reducing conditions (Wakeham et al., 1980).

Grain size properties and organic matter content of the sediment may effect the transport and preservation of organic compounds and absolute amount of sedimentary hydrocarbons (Wehmiller and Lethen 1975). However, the mean grain size (Mdø) in stations 5, 6 and 7 was lower than that in station 1,2,3 and 4 while average organic matter as indicated by (TOC) was the reversed. Thus it may be concluded that the settlement of the slit and clay particles enriched by organic matter along the course of the marshes sediments is the principal factor. Photo-oxidation may also degrade oil components (Lee, 1980). Intensive solar radiation coupled with relatively higher water temperature are characteristic features of the climate of the subtropical region of Iraq. Thus the rather low levels of PAH's encountered in the marshes sediments are expected due to their rapid photolysis.

The major conclusions that can be drawn from the present study are that the marshes sediments are presently contaminated with PAH's and the main source of these PAH's are both anthropogenic and biogenic. The low levels of PAH's may be due to processes brought about by bacterial degradation and photo-oxidation.

REFERENCES

Al-Saad HT (1987) Distribution of polycyclic aromatic hydrocarbons (PAH) in surficial sediment from the Shatt al-Arab River and the NW region of the Arabian Gulf.Mar Pollut Bull 18:248-251.
Delaune RD, Patrick WH, Casselman ME (1981) Effect of sediment pH and redox conditions on degradation of Benzo(a)pyrene. Mar Pollut Bull 12:251-253.
DouAbul AAZ, Abaychi JK, Al-Edanee TE, Ghani AA, Al-Saad HT (1987) Polynuclear aromatic hydrocarbons (PAH's) in fish from the Arabian Gulf. Bull Environ Contam Toxicol 38: 546-552.
El-Wakeel SK, Riley JP (1957) The determination of organic carbon in marine mud. J Cons Int Explor Mer 12: 180-183.
Folk RK (1974) Petrology of sedimentary rocks. Hemphill publishing Co., Austin, Texas.
Lee RF (1980) Processes affecting the fate of oil in the sea. In: Marine environmental pollution-1-Hydrocarbons. Geyer RA(ed)

Elsevier oceanographic series. New York, 337p.
Readman JW, Mantoura RCF, Rhead MM, Brown L (1982) Aquatic distribution and heterotrophic degradation of polycyclic aromatic hydrocarbons (PAH) in the Tamar Estuary. Estuar Cstl Shelf Sci 14: 369-389.
Risebrough RW, DeLappe BW, Walkerll W, Simoneit BRT, Grimalt J, Albaiges J, Requeiro GAG, Inolla AB, Fernandez JAG (1983) Application of the mussle watch concept in studies of the distribution of hydrocarbons in the coastal zone of the Ebro delta. Mar Pollut Bull 14: 181-187.
Wakeham SG, Farrington JW (1980) Hydrocarbons in contemporary aquatic sediment. In: contaminants and sediment, Baker RA (ed) Ann Arbor Science Publishers, Ann Arbor, MI 1:3-32.
Wakeham SG, Schaffner C, Giger W (1980) Polycyclic aromatic hydrocarbons in recent lake sediment 1. compounds having anthropogenic origin. Geochem Cosmochem Acta 44: 403-443.
Wehmiller JF, Lethen M (1975) Saturated hydrocarbon material in sediments of the Delware Estuary as determined by gas chromatographic analysis. Univ Delawar, Coll Mar Stud CMS-RANN 3-75, 3-87.
Youngblood WW, Blumer M (1975) Polycyclic aromatic hydrocarbons in the environment homologous series in soils and recent marine sediments. Geochem Cosmochem Acta 39: 1303-1314.

Received October 28, 1988, accepted May 11, 1989.