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Polynuclear Aromatic Hydrocarbons (PAHs) in Fish from the Arabian Gulf

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Emphasis has been placed upon the identification and qualification of compounds with potential adverse health effects on humans. Prominent among this group are polynuclear aromatic hydrocarbons (PAHs), several of which are known or suspected carcinogens (NAS 1972). Much recent attention has been focused on the occurrence of PAHs in the hydrosphere (Black 1982, Readman et at. 1982). PAHs enter the marine environment from a variety of sources including petroleum pollution, industrial and domestic effluents, atmospheric particles, and biosynthesis by plants and micro organisms (Dunn & Fee 1979). Although one-third of the world's oil is produced around the Arabian Gulf (DouAbul 1984) yet, to date no detailed analysis have been conducted to determine PAHs in this region.

The high molecular weight and nonpolar nature of PAHs afford compounds of low solubility in water (Sorrell et al. 1980). Nevertheless, numerous investigations have shown the ability of marine organisms including fish to accumulate PAHs from solution or dispersion in seawater (Lee et al. 1972, Andelman & Snodgrass 1974). When fish are harvested, a human health hazard may result. In the present communication, high performance liquid chromatography (HPLC) was used to identify and measure sixteen PAHs "priority pollutants" issued by U.S. Environmental Protection Agency (EPA) in fourteen species of commercially significant fish from the NW Arabian Gulf.

MATERIALS AND METHODS

HPLC grade n-hexane, methylene chloride and acetonitrile were obtained commercially and were used as received (Merck, Darmstadt, W. Germany). High purity (99+%) analytical standards of PAHs and their related compounds as well as the remaining chromatographic supplies were provided by Supelco S.A., Switzerland. Supelcosil ATF 60/100 mesh (lot No.061) was extracted with methylene chloride for a minimum of 36h in a soxhelt apparatus prior to use.

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Composite samples of fourteen fish species have been collected from the NW Arabian Gulf during July 1985. Generally, each composite consisted of at least 10 uniform size of adult fish of the same species. Edible tissues only were pooled and then macerated in a food chooper from which at least 5 replicates of 60g were freeze-dried, ground and sieved through a 1mm metal sieve. The extraction and fractionation procedures employed in this work were based upon that of Risebrough et al. 1983, PAHs identification and quantification was carried out according to that of Sorrell & Reding (1979). For this purpose a Perkin-Elmer (Norwalk, Connecticut, U.S.A.) series 4 high performance liquid chromatograph equipped with a microprocessor controlled solvent delivery system and fitted with a Reodyne 7125 injection valve was used. The detection system was composed of a Perkin-Elmer 560S scanning fluoresence spectrophotometer and an LC 75 variable wave length spectrophotometric detector with auto-control. Quantification of peaks and identification of PAHs in chromatograms was achieved by an LCI-100 laboratory computing integrator (Perkin-Elmer). Samples extracts (10µl) were injected into a Perkin-Elmer analytical LC-PAH 0258 column (250mm X 5mm i.d.) with acetonitrile-distilled water gradient elution at a flow rate of 1ml/min. Results of HPLC analysis were confirmed in about 10% of the samples by injecting into a Perkin-Elmer sigma 300 capillary gas chromatogaph equipped with a flame ionization detector and a split/splitless injection port. A wall coated open tubular (WCOT) fused silica capillary column (30m x 0.25mm i.d.) with 0.22u film thickness coated with SE-52 was used. Operating temperatures for the detector and injector were 350° and 300° C respectively, while the column was operated under a temperature program conditions (4°C/min) from 80 to 300°C with isothermal period (20 min) at the end. Accurately 1ul of the concentrated extracts were injected splitless (60s splitless period), the carrier gas was helium with a linear velocity of 75cm/s. Recovery studies with fortified samples indicated that recovery efficiency exceeded 70% for all compound measured, however, results were not adjusted for percent recovery. The detection limits were between 10 to 50pg for the 16 PAHs studied. Procedural blanks consisting of all reagents and glassware used during the analysis were periodically determined. No interfering compounds which possess the same retention times of that of PAHs under investigation were detected in the blank, therefore, the sample values were not corrected for procedural blanks.

RESULTS AND DISCUSSION

Of the 16 PAHs studied viz. acenaphthene, flouranthene, naphthalene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, acenaphthylene, anthracene, benzo(ghi)perylene, fluorene, phenanthrene, dibenz(a,h)anthracene, indeno (1,2,3-cd)pyene

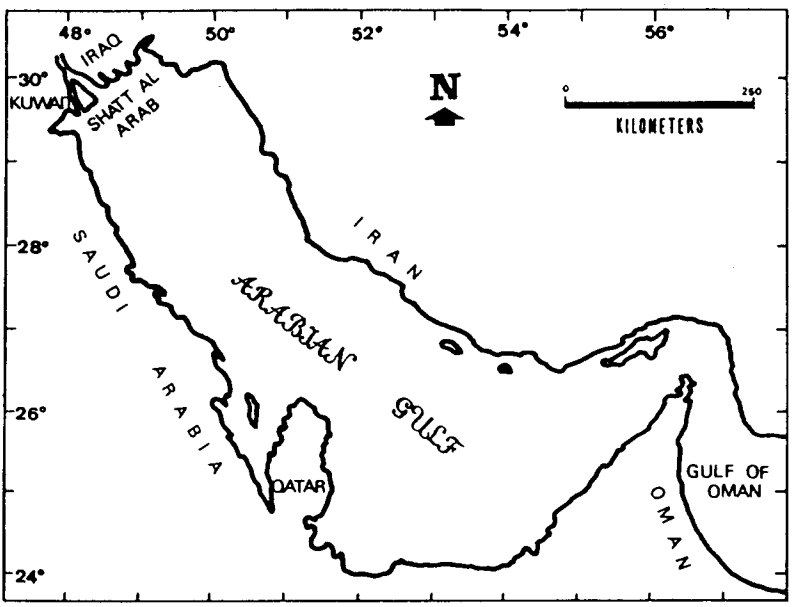

Figure 1. Map of the Arabian Gulf.

and pyrene. Our analysis have confirmed residues of naphthalene and acenaphthene only in fish from the NW Arabian Gulf.

Mean concentrations of these two compounds in muscle tissues are summarized in (Table 1) the range is also given for each species and is bracketed. In addition to the PAHs, lipid contents are reported in this table as percentage by weight of muscle tissues. All samples showing no response, or less than the detection limit are reported as nd = non detected and are taken as 0.7 X limit of detection for the calculation of the mean (Nicholson 1980). Naphthalene was the most prevalent compound detected in all of the samples examined (average concentrations ranged from 14 µg/kg wet weight in sea catfish to 106µg/kg in forktail needlefish). This is undoubltly due to the fact that naphthalene is present in No. 2 fuel oil used extensively in this region. Furthermore, naphthalene is some-what more water soluble and has lower particulate affinity than the larger molecular weight aromatic hydrocarbons. In common with our findings, studies on PAHs have indicated that naphthalenes are the compounds accumulated to highest concentrations by marine organisms (Neff et al. 1976). Acenaphthene was less frequent, thus average percentage occurrence was approximately 40% with mean concentrations ranged between 1 µg/kg wet weight in sea catfish, indian flathead, yellowfin seabream and mullet to 69µg/kg in largescale tongue sole. Variations in naphthalene and acenaphthene concentrations among different groups may be due to the rate of aromatic hydrocarbons accumulation being highly species-dependent. On the basis of total PAH residues, the fourteen fish species examined could be

arranged thus; fourfingered < threadfin < needlefish threadfin < sea catfish < hamiltons thryssa < mullet < indian flathead < croker and yellowfin seabream < silverbanded croaker < elongate ilisha < silvery grunt < indian shad < forktail needlefish < largescale tounge sole.

It is well documented that, in the environment, PAHs are often associated with sediments (Rossi & Neff 1978). Analysis of the Arabian Gulf surficial sediments have similary revealed the presence of both naphthalene and acenaphthene (average concentrations were 54 and 4µg/kg dry weight respectively. However, in addition residues of fluoranthene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, benzo(ghi)fluoranthene, fluorene, phenanthrene and pyrene were also detected (average concentrations were 5, 3, 3, 4, 2, 2, 2, 3, 2 and 2µg/kg dry weight respectively). Intensive solar radiation is a characteristic weather feature in the Arabian Gulf region coupled with relatively high water temperature. Thus the rather low levels of PAHs found in the gulf sediments are expected based upon the rapid photolysis of some PAHs (Mill et al 1981) and the surprisingly high evaporation rates of low solubility compounds in aqueous solutions (Mackay & Leinonen 1975). Bearing that in mind, it would seem that rapid metabolism of PAHs by fish have led to a steady state tissue levels of these compounds, and account for the failure of the present study to demonstrate detectable levels of most PAHs in the examined samples. There is evidence that fish are capable of metabolizing PAHs and excreting them as water-soluble metabolites (Payne 1975, Neff et at. 1976).

In order to gain some informations on the probable source of PAHs (Hites et al. 1980), sediment extracts were subjected to capillary gas chromatography/mass spectrometry. To investigate oil contamination (Neff 1979), the following compound specifictions were selected; m/z 128, 142,156,170 - naphthalene and alkyl-naphthalenes: 166, 180, 194 - fluorene and alkyl - fluorenes: 178, 192,206,220 - phenathrene and alkyl-phenanthrenes; 184, 198,212, 226-dibenzothiophene and alkyl dibenzothiophenes. In the Arabian Gulf sediments the only disernible parent and alkyl-substituted species are for phenanthrene and in particular dibenzothiophenes which represent evidence for some petrogenic contamination (Hites et al. 1877).

To investigate combustion/urban runoff the molecular ions for the typical "parent" (unsubstituted) PAHs (Blumer & Youngblood 1975, Herrmann 1981) were selected: m/z 178-phenanthrene/anthracene; 202-fluoranthene/pyrene; 228-benzoanthracene/chrysene; 252-benz-fluoranthenes/benz-pyrenes; 276-benz(ghi) perylene/indeno (1,2,3,-cd) pyrene. It is apparent that these compounds are present in the Arabian Gulf sediments thus indicating combustion/urban runoff.

Table 1. Mean concentrations (ug/kg wet weight, edible tissues) and ranges of PAHs in fish from the NW Arabian Gulf.

Species		Fat	Naphtha-	Acena-
Scientific name	Common name	%	lene	phthene
Arius thalassinus	Sea catfish	5.8 (5.6-5.9)	14 (9-19)	1 (nd-2)
Eleutheronema tetradactnum	Fourfingered threadfin	2.9 (2.8-3.1)	nd	nd
Johnieops sina	Croaker	2.1 (2.0-2.1)	31 (19-43)	nd
Cynoglosus arel	Large scale tongue sole	4.6 (4.5-4.6)	49 (28-59)	69 (59-83)
Platycephalus indicus	Indian flathead	2.1 (2.1-2.2)	28 (11-38)	1 (nd-3)
Pomadasys argenteus	Silvery grunt	2.5 (2.4-2.5)	61 (43-78)	4 (nd-6)
Ilisha elongata	Elongate ilisha	4.1 (4.0-4.3)	64 (40-78)	nd
Tylosurus strongylurus	Forktail needlefish	2.6 (2.4-2.6)	106 (89-117)	2 (nd-3)
Nematalosa nasus	Threadfin shad	6.0 (5.9-6.0)	6 (nd-10)	nd
Thryssa hamiltonii	Hamilton thryssa	5.7 (5.6-5.7)	20 (10-27)	3 (nd-5)
Acanthopagrus luteus	Yellowfin seabream	5.9 (5.8-5.9)	30 (22-45)	1 (nd-3)
Liza dussumeiri	Mullet	5.9 (5.7-6.0)	27 (18-33)	1 (nd-3)
Otoliths argenteus	Silverbanded crocker	6.1 (6.0-6.1)	54 (40-61)	nd
Tenualosa ilisha	Indian shad	6.2 (6.1-6.2)	80 (66-91)	nd

Bracketed figure underneath the mean is the range. nd = None detected.

The major conclusion that can be drawn from the present study is that, although the Arabian Gulf marine environment is presently contaminated with PAHs including some of the carcinogenic homologues, yet detoxification mechanisms exist which allow effective removal of these compounds from fish tissues.

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