WFL Publisher
Science and Technology
Meri-Rastilantie 3 B, FI-00980
Helsinki, Finland
e-mail: info@world-food.net

Journal of Food, Agriculture & Environment Vol.7 (1) : 9-15. 2009 *www.world-food.net*

Dietary exposure to polycyclic aromatic hydrocarbons from commercially important seafood of the Arabian Gulf

Husam Alomirah [1*], Sameer Al-Zenki [1], Adnan Husain [1], Nisar Ahmed [2], Amal Al-Rashdan [2], Bondi Gevao [3] and Wajih Sawaya [1]

*[1]Biotechnology Department, [2]Central Analytical Laboratory, [3]Department of Environmental Science, Kuwait Institute for Scientific Research, P.O. Box 24885, 13109 Safat, Kuwait. *e-mail: omirah@safat.kisr.edu.kw*

Received 29 September 2008, accepted 12 December2008.

Abstract

In order to assess the dietary intake of polycyclic aromatic hydrocarbons (PAHs) by Kuwaiti population, concentrations of PAHs were determined in edible tissues of commercially important seafood (fish and shrimp) samples collected from fish markets in 2005. Naphthalene, phenanthrene, fluoranthrene, pyrene, benz[*a*]anthracene and chrysene were routinely detected in all samples analyzed. The concentrations of ΣPAHs ranged between 30 and 247 ng/g dry wt. with yellowfin seabream imported from Iran exhibiting the highest concentration followed by Nile tilapia imported from Egypt (218 ng/g dry wt.) and then by locally caught silver pomfret (142 ng/g dry wt.) and Jinga shrimp (139 ng/g dry wt.). The PAHs pattern was dominated by the presence of high molecular weight compounds with pyrene as the most prevalent compound (59.1% of the total). The mean exposure for the average adult Kuwaiti consumer to ΣPAHs and benzo(a)pyrene equivalents (BaPEs) was estimated to be 1.3 µg/day and 0.0013 µg/day, respectively. The concentration and composition of PAHs found in this study are similar to those reported for fish from the Arabian Gulf basin in other studies over the past two decades, suggesting that the sources of pollution might have remained relatively unchanged. Nevertheless, the levels of exposure to PAHs through seafood consumption in the Northern Arabian Gulf environment, particularly in Kuwait, do not represent an unacceptable health risk due to the fact that these exposure levels were below the reference dose established by the European Union law.

Key words: Polycyclic aromatic hydrocarbons (PAHs), seafood, benzo(a)pyrene equivalents (BaPEs), Arabian Gulf.

Introduction

Polycyclic or polynuclear aromatic hydrocarbons (PAHs) are a group of more than 100 different hydrophobic compounds with two or more fused aromatic rings in linear, angular or clustered arrangements [1]. PAHs are widely distributed in the environment and can be introduced via natural (volcanic eruptions and forest fires) and anthropogenic (automobiles, municipal waste incineration, power generation, asphalt production, etc.) combustion processes [2]. Petroleum sources (e.g. oil production, transportation and spill) generally generate low molecular weight (LMW) PAHs (< 200 MW or ≤ 3 aromatic rings), while high temperature incomplete combustion processes generally generate high molecular weight (HMW) PAHs (> 200 MW or ≥ 4 aromatic rings) [2]. Many of the HMW PAHs are suspected to have carcinogenic and mutagenic properties [3]. Therefore, the occurrence of PAHs in different environmental matrices (e.g. air, water, sediment and dust) and in the diet is of concern and should be routinely assessed. The diet is the primary source of human exposure to PAHs, contributing to more than 90% of total exposure to PAHs [4]. In fact, besides smokers and the occupationally exposed population, most individuals are exposed to PAHs predominately from dietary sources [5].

The 1991 Gulf War resulted in the catastrophic pollution of the northern Arabian Gulf environment. Two major sources triggered such pollution: a) direct release of large amount of oil into the Gulf waters (6 to 10 million barrels) and b) oil field fires emitted/ignited some 500 million barrels [6-8]. The potential of such large-scale contamination from those sources generated concerns over the possible extent and impact of petroleum pollution in the region. These concerns are supported by the fact that the Arabian Gulf marine ecosystem is fragile and already stressed [9]. The northern region of the Arabian Gulf is shallow with limited circulation and high salinity and temperature. Moreover, the Arabian Gulf receives continuous inputs of petroleum hydrocarbons from industrial effluent and shipping activities as one-third of the world's oil is produced around the Arabian Gulf [10]. Therefore, PAHs generated from oil degradation and/or incomplete combustion tend to accumulate in bottom sediments and may constitute a continuous source to benthic organisms. The distribution among different marine environmental compartments may reach human receptors through the consumption of seafood which may result in long-term public health risks from these chemical food safety hazards, especially in communities consuming large quantities of fish, like in the Arabian Gulf region.

The levels of PAHs found in unprocessed foods, like raw fish, reflect the background contamination, which originates from long-distance airborne transportation of contaminated particles and natural emissions along with land based discharges. In this context, a survey of PAHs in raw fish was conducted in Kuwait 15 years ago and no recent information is available. Thus, the need exists for more current information. The aim of this study was to investigate the levels of PAHs in edible tissues of 10 commercially important seafood (fish and shrimp) samples collected from

Kuwait fish market during the month of August 2005. No bivalves were included in the survey as they are not commonly consumed by the Kuwaiti populations. Based on the levels of PAHs established in this study and data for the average daily consumption of fish and shrimp by Kuwaiti adults reported previously [11], an estimate of the average daily intake of ΣPAHs was derived and used to assess the exposure to PAHs by the Kuwaitis through fish consumption. In addition, the results could be used to address food safety concerns of fish consumption by the Kuwaiti and Arabian Gulf populations where fish is a popular food.

Materials and Methods

Chemicals and materials: All solvents used in this study were of high-performance liquid chromatography (HPLC) grade and purchased from Merck (Darmstadt, Germany). Silica gel 60 (0.063-0.200 mm) for column chromatography and potassium hydroxide pellets (min. 85% purity) and anhydrous sodium sulphate (≥ 99.0% purity) of analytical grade were also purchased from Merck (Darmstadt, Germany). Analytical standards were purchased from Supelco (PAH mix Quebec Ministry of Environment, Cat. No. 502065, PA, USA) while deuterated internal standard solution (Acenaphthalene-d10, Phenanthrene-d10, Chrysene-d12 and Perylene-d12, 2000 µg/ml, Cat. No.8500-6076) was obtained from Agilent (Foster City, CA, USA). Certified standard reference material SRM 2977 (mussel tissue) was obtained from the National Institute for Standardization (NIST) (Gaithersburg, MD, USA). Distilled water was used throughout the experiments. Before use, all glass-ware was soaked in 2% liquinox soap solution overnight followed by washing and rinsing with distilled water and heated overnight at 400ºC. The experiments were conducted away from direct sunlight, and amber screw-cap vials (Wheaton, Cat. No. 225153-03, NJ, USA) were used to store the final extract.

Sampling: Local and imported seafood samples (fish and shrimp) were purchased from the main fish market located in Kuwait city during the month of August 2005. Targeted commercially important fish species were selected according to the following spatial distribution: i) fish species shared among countries of the northern Arabian (Persian) Gulf (e.g. silver pomfret and Hilsa shad); ii) fish species that are distributed throughout Kuwait's coastal territorial waters (e.g. yellowfin seabream and tigertooth croaker) and iii) fish species that are distributed in the deeper areas of eastern and southern sea areas (e.g. javelin grunter and orange-spotted grouper). Table 1 shows the trophic/ecological characteristics of selected fish and shrimp samples. The selected commercially important seafood belonged to different families and had different trophic/ecological characteristics including pelagic plankton feeders (Hilsa shad), pelagic carnivores (tigertooth croaker), pelagic carnivore/plankton feeders (silver pomfret), demersal top carnivores (orange-spotted grouper, javelin grunter, sobaity seabream and yellowfin seabream), pelagic herbivores (Klunzinger's mullet), farm-raised fish (Nile tilapia) and benthic omnivores (shrimp). These seafood samples take up pollutants from the water column and from their diets; shrimp (rubyan) also takes up pollutants by intimate contact with the sediments. Typically, three different pooled samples were analyzed for each fish type (i.e. 48 samples), and each sample was analyzed in duplicate (i.e. 96 tests).

Sample preparation: Field handling and sample preparation procedures were carried out according to the US Environmental Protection Agency (EPA) guidelines for assessing chemical contaminant data for use in fish advisories [12]. Briefly, the samples were weighed and their length recorded (Table 2). The length for silver pomfret samples was for fork length (cm), i.e. the length from the tip of the mouth to the tip of the fork of the tail, for shrimp (rubyan) it was for the head-carapace (mm) using a vernier caliper and for all other fish samples for the total length (cm), i.e. the length from the tip of the mouth to the tip of the tail. The edible portions, separated by dissection, were individually wrapped in a pre-cleaned aluminum foil and their moisture content was determined. Before the analysis, edible portions of fish of similar type and origin were pooled (Table 2), homogenized (Robot Coupe, S.A., France), freeze-dried (Unitop 800 L, Virtis Company, Gardiner, NY, USA) and stored in the dark at -18°C in tightly sealed glass bottles.

Table 1. Trophic and ecological characteristics of selected seafood in Kuwait.

English name	Local name	Scientific name	Family	Trophic characteristics
Tigertooth croaker	Nuwaibi	*Otolithes ruber*	Sciaenidae	Pelagic, carnivore, close to sea bottom
Silver pomfret	Zobaidy	*Pampus argenteus*	Stromateidae	Pelagic, carnivore/zooplankton feeder, inshore over muddy bottoms
Klunzinger's mullet	Maid	*Liza klunzingeri*	Mugilidae	Pelagic, shallow coastal waters, feed on algae and detritus on the bottom
Hilsa shad	Suboor	*Tenualosa ilisha*	Clupeidae	Pelagic, zooplankton feeder in shallow coastal waters
Yellowfin seabream	Sheim	*Acanthopagrus latus*	Sparidae	Demersal, carnivore, close to the bottom in shallow coastal waters
Javelin grunter	Nagroor	*Pomadasys kaakan*	Haemulidae	Demersal, carnivore, in shallow coastal waters and coral reefs
Orange-spotted grouper	Hamoor	*Epinephelus coioides*	Serranidae	Demersal, carnivore, in shallow coastal waters and coral reefs
Sobaity seabream	Subaiti	*Sparidentex hasta*	Sparidae	Demersal, carnivore, in shallow coastal waters to moderate depths
Nile tilapia	Bulti	*Oreochromis niloticus niloticus*	Cichlidae	Aquacultured
Green tiger shrimp	Rubyan, Amnearah	*Penaeus semisulcatus*	Penaeidae	Benthic, selectively omnivore, offshore coastal water
Jinga shrimp	Rubyan, Shaamiya	*Metapenaues affinis*	Penaeidae	Benthic, selectively omnivore, offshore coastal water

Extraction and clean-up: Sample extraction and clean-up were performed as reported previously [13] with some modifications. A 5 g portion of the homogenized freeze-dried sample was weighed into a round bottom flask (500 ml). The sample was spiked with 1 ml of deuterated internal standard (1 µg/ml) followed by the addition of 100 ml of a 2 M solution of potassium hydroxide in water-ethanol mixture (1:9, v/v). The mixture was boiled under reflux in the dark (the electro-mantle was first set to 60ºC and reduced to 30ºC when the mixture started boiling). After completion of saponification (1.5 h), pre-weighed cyclohexane (100 ml) was added slowly through the condenser. After 15 min, the mixture was cooled by adding cold distilled water (100 ml) through the condenser. After 30 minutes the flask was capped tightly, shaken thoroughly and the mixture was allowed to stand overnight in the dark. A maximum volume of the clear upper cyclohexane layer was then collected into a pre-weighed round flask (250 ml), and the weight of the cyclohexane extract was measured for recovery calculation. The extract was then concentrated to near dryness (2 ml) on a rotary evaporator at 30ºC. The concentrate was subjected to purification by silica gel chromatography, as described elsewhere [14]. The eluent in cyclohexane was re-concentrated to 1 ml using a rotary evaporator at 30ºC and transferred to 2 ml amber screw-cap vials. The vials were stored at -20ºC until they were ready for analysis by gas chromatography-mass spectrometry (GC-MS).

Analysis: The sample extracts were analyzed using a Hewlett-Packard (HP) 5890 Series II gas chromatograph interfaced with an HP 5972 mass spectrometer. Chromatographic resolution was achieved using splitless injection (2 µl injection volume and 290°C injection port temperature) on a 30 m DB-5 capillary column (J&W Scientific, Folsom, CA) (250 µm i.d., 0.25 µm film thickness) with helium (99.999%) as carrier gas. The oven was programmed at 45°C for 2 min, ramped at 10°C min^{-1} to 290°C and held for 8 min. The mass spectrometer was operated in the electron ionization (EI) mode (295ºC and 70 eV) with quadrupole analyzer and was turned on after a 4.0 min solvent delay. PAHs were analyzed by GC-MS using selected ion monitoring (SIM) and quantitated using the method of internal standards. Ions monitored were 128, 152, 154, 164 (IS), 166, 178, 188 (IS), 202, 228, 240 (IS), 252, 256, 264 (IS), 268, 276, 278, and 302. The compounds included in the analyses were the US Environmental Protection Agency's (US EPA) 16 priority pollutants and benzo[*c*]phenanthrene, benzo[*j*]fluoranthene, 7,12-dimethylbenz[*a*]anthracene, 3-methylcholenthrene, dibenzo[*a,h*]pyrene, dibenzo[*a,i*]pyrene and dibenzo[*a,l*]pyrene. Prior to analyzing a sample set, the GC-MS system performance and calibration were verified for all analytes, and solvent blank (hexane) was injected to insure that the system was free from contaminants or interfering peaks. The average limit of detection (LOD) and the limit of quantitation (LOQ) were 0.1 ng/g and 0.3 ng/g in the basis of signal-to-noise ratio (S/N) of 3, respectively.

Analytical quality assurance: Analytical quality assurance measures for PAH determination involved inclusion in each batch of 10 samples, a blank sample and one certified standard reference material (SRM 2977 - Mussel tissue). The samples were spiked with the deuterated internal standard mixture prior to extraction, to monitor recoveries. Batches of samples were deemed acceptable, if quality control samples (SRM) indicated ≥ 85% recovery rate. The relative standard deviation (RSD) between a calibration standard and a performance standard was monitored to be within 20%. The precision of the analytical method was determined by spiking blanks with the calibration standard and carried through the entire extraction and clean-up process as for samples. The standard deviation for triplicate analyses was 2-5% for LMW PAHs and 10-18% for the HMW ones.

PAH quantitation was carried out in duplicate analysis for three individual edible portions of the same pooled sample under the same condition, with the mean result used for interpretation. In cases where the difference between duplicate analysis was greater than 10% of the mean results, the analysis was repeated. A peak was positively identified if it was within ± 0.05 min of the retention time in the calibration standard and quantified only if the S/N ≥ 3, and the ratio of the target ion to its qualifier ion was within ± 20% of the theoretical value. All samples showing no response or less

Table 2. Sample pooling protocol for seafood samples.

Sample name	Origin	Length range (cm)	Weight range (g)	Number pooled
Tigertooth croaker	Kuwait	40 - 41	630 - 655	3
Tigertooth croaker	Iran	44 - 45	770 - 905	3
Silver pomfret	Kuwait	20 - 22 [1]	270 - 445	3
Silver pomfret	Iran	23 - 25 [1]	430 - 470	3
Klunzinger's mullet	Kuwait	18 - 30	74 - 113	100
Hilsa shad	Kuwait	38 - 45	600 - 940	3
Yellowfin seabream	Kuwait	39 - 43	1060 - 1280	3
Yellowfin seabream	Iran	27 - 30	370 - 490	3
Javelin grunter	Kuwait	53 - 56	2100 - 2315	3
Javelin grunter	Iran	45 - 54	1360 - 2130	3
Orange-spotted grouper	Kuwait	73 - 75	6780 - 7450	3
Orange-spotted grouper	Iran	67 - 76	4240 - 7630	3
Sobaity seabream	Kuwait	44 - 54	1230 - 2070	3
Nile tilapia	Egypt	25 - 31	330 - 570	6
Green tiger shrimp	Kuwait	32 - 64 [2]	20 - 22	200
Jinga shrimp	Kuwait	30 - 65 [2]	20 - 22	200

[1]The measurements are for the fork length which is the length from the tip of the mouth to the tip of the fork of the tail. [2]The measurements (mm) are for the length of the head-carapace only, using a vernier caliper.

than the quantitation limit (0.3 ng/g wet wt.) were reported as none detected.

Toxicity and intake estimation: Benzo[*a*]pyrene (BaP) has been well characterized toxicologically and is the most potent carcinogenic PAH after dibenz[*a,h*]anthracene. Therefore, usually the total PAH contamination is expressed as benzo[*a*]pyrene equivalents (BaPEs) to illustrate the toxicity [15]. The BaPEs was calculated as the sum of the $BaPEs_i$ value for individual PAHs. The $BaPEs_i$ value was calculated for each PAH from its concentration in the sample (C_{PAHi}) multiplied by its toxic equivalency factor (TEF_{PAHi}) as proposed earlier [16].

$$BaPEs = \Sigma(BaPEs_i) = \Sigma(C_{PAHi} \times TEF_{PAHi})$$

To express the PAH concentrations in ng/g of wet tissue, the PAH concentrations expressed in ng/g of freeze-dried tissue were multiplied by a conversion factor of 0.24. This factor was calculated based on the observation that the average percentage of water content in the edible seafood tissues was 76.4 ± 3.8%.

For the estimation of average daily intake of ΣPAHs and BaPEs, data for the average daily consumption of fish and shrimp by Kuwaiti adults, derived from a year-long study of 1066 households, were adopted [3]. A randomly selected adult within each household was queried about species and quantities consumed as well as frequency of consumption during the preceding seven days. All seafood species under this investigation were included in the adopted daily intake of the seafood except for Nile tilapia. For similar fish but of different origin (tiger tooth croaker, silver pomfret, yellowfin seabream, javelin grunter and orange-spotted grouper) or species (shrimp), an average PAH concentration was applied for the intake estimation. For the estimation of PAH and BaPEs daily intake (ng/day), an individual approach was applied using the mean concentration of PAHs detected in seafood sample and its expressed BaPEs value with the individual data for the average daily intake.

Results and Discussion

Levels and composition pattern of PAHs: The mean PAHs concentrations (LMW and HMW) determined in the edible portion of seafood samples from Kuwait's fish market are shown in Table 3. The mean composition (expressed as percentage of the total) for each class of quantified compounds is also reported. Naphthalene, phenanthrene, fluoranthrene, pyrene and chrysene were routinely detected in all samples analyzed. The other LMW and HMW PAHs included in the analyses were present in some samples at concentrations lower than the LOQ (0.3 ng/g, dry wt) and thus have been excluded from further discussions.

The mean concentration of ΣPAHs in the edible tissue was 96.1 ng/g, dry weight, with a range of 31.9 to 247 ng/g dry weight. This mean of ΣPAHs is similar to those reported by Fowler *et al.* (80.7 ng/g dry weight) [8] and Al-Yakoob *et al.* (105.3 ng/g dry weight) [17] but lower than that reported by Saeed *et al.* (224 ng/g dry weight) [9] for similar species collected from the Arabian Gulf during May 1993.

In comparison with international data, the mean ΣPAHs in this study (96.1 ng/g dry wt.) is lower than that reported for four fish species (191 ng/g dry wt.) from central Adriatic Sea, Italy [15], for ventral muscle of 10 marine fish species (312 ng/g dry wt.) from Hong Kong [18], for two fish species (83.7-656 ng/g dry wt.) from Egypt [19] and for 10 fish species (250-13,600 ng/g dry wt.) from Hiroshima Bay, Japan [3]. The mean ΣPAHs (96.1 ng/g dry wt.) found in this study is, however, higher than those reported for nine fish species (21.7 ng/g dry wt.) and shrimp (67.6 ng/g dry wt.) from Catalonia, Spain [5] and for trout (32.3 ng/g, dry wt.) from Canadian Great Lakes [20] (converting factor of 4.25 was used to calculate the dry weight basis).

Among the fish species examined, yellowfin seabream imported from Iran had the highest ΣPAHs (247 ng/g dry wt.), followed by Nile tilapia imported from Egypt (218 ng/g dry wt.). The ΣPAH concentration in yellowfin seabream determined in this study (247 ng/g dry wt.) is comparable to concentrations in samples collected from the Northern Arabian Gulf region, reported previously by Al-Yakoob *et al.* (208 ng/g dry wt.) [17] and Saeed *et al.* (368 ng/g dry wt.) [9]. The highest ΣPAHs in local species was for silver pomfret and jinga shrimp with 142 and 139 ng/g (dry wt.), respectively. The lowest ΣPAH concentration was in Sobaity seabream (31.9 ng/g dry wt.). In all other fish samples, ΣPAHs ranged from 39.6 to 95.8 ng/g dry wt. It is interesting to note that local pelagic carnivore fish samples (tigertooth croaker and silver pomfret) had higher ΣPAHs (65.0 and 141.9 ng/g) compared to those imported from Iran (39.6 and 51.8 ng/g). On the contrary, demersal carnivore fish samples (yellowfin seabream, javelin grunter and orange-spotted grouper) imported from Iran had higher ΣPAH concentrations (247, 94.8 and 95.8 ng/g) compared to those locally caught (76.3, 65.5 and 39.9 ng/g). This may suggest that the pollutant concentrations are linked to the trophic characteristics of the fish species.

Of all PAHs measured in this study, pyrene, a HMW compound, was detected in all samples and constituted the highest burden in the edible tissue (59.1% of the total PAHs) of the analyzed seafood samples. However, the concentration varied widely from 15.9 to 157 ng/g (dry wt.), with a mean concentration of 56.8 ng/g (dry wt.). Both Iranian yellowfin seabream and Egyptian Nile tilapia showed significant levels of pyrene with a concentration of 157 and 156 ng/g (dry wt.), respectively. The mean concentration of pyrene was quite elevated as compared to the levels of pyrene reported for edible portions of seafood (21.9 ng/g dry wt.) sold in Kuwait's fish market during May 1993 [9] but was comparable to Kuwaiti fish samples (62.6 ng/g dry wt.) collected during April 1992 [17]. Pyrene is normally produced through combustion, and elevated levels of pyrene may be indicative of high temperature combustion/urban runoff [2].

Phenanthrene, a LMW PAH, was also present in significant quantities in all fish samples. Phenanthrene levels ranged from 8.0 to 55.9 ng/g (dry wt.). The mean level of phenanthrene in the edible tissues (25.3 ng/g dry wt.) is less than that reported by Saeed *et al.* (47.2 ng/g dry wt.) [9]. Naphthalene and fluoranthene were also present in all samples, however, with low concentrations of 6.2 and 5.7 ng/g, respectively. Similarly, chrysene was present at low levels (mean 2.1, range 0.7-7.1 ng/g dry wt.) but was not detected in five samples of locally caught Klunzinger's mullet, Sobaity seabream, green tiger shrimp and jinga shrimp and tigertooth croaker imported from Iran. Benz[*a*]anthracene was detected only in locally caught yellowfin seabream at trace levels of 0.4 ng/g dry wt.

The mean ΣPAH concentration in locally caught seafood samples was 79.1 ng/g, dry wt (38.2% LMW and 61.8% HMW)

Table 3. Levels of PAHs (ng/g, dry wt.) in edible tissue of seafood samples from Kuwait's fish markets.

Sample name	Origin	LMW [1]		HMW [2]				ΣPAHs
		Naphthalene	Phenanthrene	Benzo[*a*] anthracene	Fluoranthene	Pyrene	Chrysene	
Tigertooth croaker	Kuwait	5.1	23.2	ND[3]	3.6	32.1	1.1	65.0
Tigertooth croaker	Iran	7.2	15.2	ND	1.4	15.9	ND	39.6
Silver pomfret	Kuwait	10.6	33.4	ND	10.3	84.4	3.2	141.9
Silver pomfret	Iran	8.3	9.2	ND	3.9	28.8	1.6	51.8
Klunzinger's mullet	Kuwait	6.1	25.2	ND	2.4	40.0	ND	73.6
Hilsa shad	Kuwait	8.8	21.5	ND	2.7	31.1	4.6	68.7
Yellowfin seabream	Kuwait	2.8	19.7	0.4	4.9	46.1	2.4	76.3
Yellowfin seabream	Iran	9.3	54.7	ND	18.5	157.4	7.1	247.0
Javelin grunter	Kuwait	4.9	22.5	ND	3.8	33.3	1.0	65.5
Javelin grunter	Iran	9.2	21.6	ND	5.5	56.1	2.5	94.8
Orange-spotted grouper	Kuwait	3.9	12.2	ND	1.8	21.4	0.7	39.9
Orange-spotted grouper	Iran	4.3	22.3	ND	6.3	59.7	3.2	95.8
Sobaity seabream	Kuwait	4.0	8.0	ND	2.0	17.9	ND	31.9
Nile tilapia	Egypt	8.4	33.4	ND	14.4	155.5	6.3	218.1
Green tiger shrimp	Kuwait	2.2	27.4	ND	3.9	56.4	ND	89.8
Jinga shrimp	Kuwait	4.9	55.9	ND	5.4	72.4	ND	138.5
Average		6.2	25.3	0.03	5.7	56.8	2.1	96.1
% of total		6.5	26.3	0.03	5.9	59.1	2.2	100

[1] Low molecular weight PAHs (≤ 200 MW or ≤ 3 aromatic rings); [2] High molecular weight PAHs (≥ 200 MW or ≥ 4 aromatic rings) [3] The levels of PAHs were below the limit of quantitation (0.3 ng/g dry wt.).

while the ΣPAHs of fish imported from Iran and Egypt was 106 ng/g (30.5% LMW and 69.5% HMW) and 218 ng/g (19.2% LMW and 80.8% HMW), respectively. It is apparent from these results that the edible tissue of the seafood samples from Kuwait's fish market has higher concentration of HMW PAHs (benz[*a*]anthracene, fluoranthene, pyrene and chrysene) than that of LMW PAHs (naphthalene and phenanthrene). Such patterns of accumulation are characteristic of PAHs generated from high temperature combustion. Other HMW PAHs, especially PAHs with five and six aromatic rings (e.g. benzo[*a*]pyrene, perylene, benzo[*g*,*h*,*i*]perylene), were present at concentrations lower than the LOQ (0.3 ng/g dry wt.).

The mean levels of PAHs (ng/g, dry wt.) detected in the edible tissue of fish samples from the northern west coast of the Arabian Gulf after the 1991 Gulf War is presented in Table 4. On the basis of our study and other studies presented in Table 4 (except for shark samples, Study 4), our ΣPAH concentrations in seafood are generally low. The ΣPAH concentrations ranged from 80.7 to 224 ng/g (dry wt.), which is within the range of those from relatively unpolluted areas with <2.5-740 ng/g (dry wt.) [21-22]. With the exception of one study (No.3), the studies presented in Table 4 showed similar PAHs composition pattern with the dominance of HMW pyrene and LMW phenanthrene. Generally, the similarity in ΣPAH concentration and composition between this study and those carried out nearly 15 years ago (Table 4) indicates that the sources of PAHs in the Arabian Gulf remained relatively unchanged over this period. It has been reported that intensive solar radiation and relatively high water temperature of the Arabian Gulf could lead to rapid photolysis of some PAHs [10]. This together with capabilities of fish for PAHs bio-transformation [2, 23] may explain the lack of any significant bio-magnification of PAHs in the Arabian Gulf aquatic food chain. It is worth mentioning that different species of sharks caught in the Arabian Gulf contained noticeable levels of PAHs which may pose a risk to shark meat consumers (Table 4, Study 4) [24]. This could be related to the fact that sharks are wandering predators covering long distances and varied depths of the sea.

Intake and exposure: Since February 2005, the Commission of the European Communities recommended the maximum allowable concentration for BaP in fish muscle at 2 ng/g wet weight [25]. In this study, the concentration of BaP was below the detection limit

Table 4. Levels of PAHs in the edible tissue of seafood from the Northern West coast of the Arabian Gulf after the 1991 Gulf War.

Serial No.	Sampling date	No. of samples	Mean (ng/g dry wt.)			% of total		Prevalent compound		References
			LMW [1]	HMW [2]	ΣPAHs	LMW	HMW	LMW	HMW	
1	1991	14 [3]	34.9	45.8	80.7	43.2	56.8	Phenanthrene	Pyrene	8
2	1992	19	32.5	72.8	105.3	30.8	69.2	Phenanthrene	Pyrene	17
3	1993	19	161.11	62.90	224.01	71.92	28.08	Naphthalene	Pyrene	9
4	1997-1998	11 [4]	3,053 [5]	17,145	20,198	15.11	84.88	Phenanthrene	Indeno-(1,2,3-cd) pyrene	24
5	2005	16	31.6	64.5	96.1	32.8	67.2	Phenanthrene	Pyrene	Present study

[1] Low molecular weight PAHs (≤200 MW or ≤ 3 aromatic rings).[2] High molecular weight PAHs (≥200 MW or ≥4 aromatic rings).[3] Only fish samples collected from Kuwait, Saudi Arabia and Bahrain were considered.
[4] Samples are different species of sharks only.[5] Original data were reported in wet weight basis and converted to dry weight basis using the average moisture of 76.4 ± 3.8 % determined in the present study.

Table 5. Mean daily intake of ΣPAHs and BaPEs (µg/day, wet wt.) for average adult Kuwaiti seafood consumer.

Fish species [1]	Mean daily consumption (g/day)	Mean ∑PAH content (ng/g wet wt.) [2]	Mean BaPEs (ng/g wet wt.) [3]	Mean daily intake of ∑PAH (µg/day)	Mean daily intake of BaPEs (µg/day)
Yellowfin seabream	64.1	38.8	0.05	2.5	0.00321
Shrimp	75.6	27.4	0.03	2.1	0.00227
Silver pomfret	75.8	23.2	0.03	1.8	0.00227
Javelin grunter	62.4	19.2	0.02	1.2	0.00125
Klunzinger's mullet	63.3	17.7	0.02	1.1	0.00127
Hilsa shad	57.2	16.5	0.03	0.9	0.00172
Orange-spotted grouper	68.9	16.3	0.02	1.1	0.00138
Tigertooth croaker	64.4	12.6	0.01	0.8	0.00064
Sobaity seabream	65.7	7.6	0.01	0.5	0.00066
Mean	66.4	19.9	0.02	1.3	0.00133

[1] Average PAHs data were used for similar fish but of different origin (Yellowfin seabream, Silver pomfret, Javelin grunter, Orange-spotted grouper and Tigertooth croaker) or species (Shrimp).
[2] Converting factor of 0.24 was used to calculate the wet weight basis. [3] Calculated on the basis of TEFs proposed previously [16].

in all samples analyzed (0.3 ng/g dry wt.), and well below the values established by the European Union. The results are similar to recent reports [15, 18] which indicated that BaP levels were below the instrumental detection limit (0.25 ng/g dry wt.) in all marine organisms from the Adriatic Sea, Italy and Hong Kong. Furthermore, a previous study revealed that edible portions of fish from unpolluted seas generally do not contain detectable levels of BaP [21].

The mean daily consumption of seafood and ΣPAHs expressed as benzo[*a*]pyrene equivalents (BaPEs) (ng/g wet wt.) together with the daily intake of ΣPAHs and BaPEs (µg/day wet wt.) for the average Kuwaiti adult seafood consumer are shown in Table 5. In general, results indicated that fish samples with high ΣPAHs contamination contributed to higher levels of BaPEs. This is mostly due to the fact that the bulk of PAH burden in analyzed seafood samples consisted mainly of pyrene (59.1%) and phenanthrene (26.3%) and to less extent of naphthalene (6.5%) and fluoranthene (5.9%), all of which have a same TEF value of 0.001. In the present study, the mean level of BaPEs was 0.02 ng/g (wet wt.) which was below the screening value of 0.67 ng/g (wet wt.) for human consumption set by the US EPA [12] and is lower than 1.32 ng/g (wet wt.) and 0.094 ng/g (wet wt.) reported for marine fish tissues from Italy [15] and Hong Kong [18], respectively.

The estimated mean daily consumption of seafood by the Kuwaiti adult population was 66.4 g/day [11]. This average consumption is higher than that of the average fish and shrimp intake (4.4 g/day) by the Spanish adult male population [5] but lower than that set by the US EPA (142.2 g/day) for subsistence consumers [12] and that for an average person from Hong Kong (164.4 g/day) [26]. The mean exposure to ΣPAH via seafood for the average Kuwaiti consumer is 1.3 µg/day (Table 5). More than half (53.3%) of this intake originated from the consumption of yellowfin seabream, shrimp and silver pomfret, which accounted for 36% of the seafood intake. The estimated contribution of seafood to dietary intake of ΣPAH by the Kuwaiti population (1.3 µg/day) was over a factor of two higher than that estimated in the Spanish adult population (0.52 µg/day) [27].

Similarly, the calculated BaPEs indicated that yellowfin seabream, shrimp and silver pomfret were again the main contributors (52.8%) to the total burden of relative carcinogenic potency of individual PAHs. The mean exposure for the average Kuwaiti consumer to BaPEs was 0.00133 µg/day which is only 0.1% of the ΣPAH concentrations. This BaPEs exposure is approximately six times lower than that reported for the Spanish adult population (0.00882 µg/day) [27] and much lower than that estimated for Kuwaiti consumers at 0.15 µg/day [28] and 0.0167µg/day [9] conducted in the year of 1994 and 1995, respectively. It has been concluded that an average American consumed between 1 and 5 µg/day of carcinogenic PAHs and the contribution of seafood to this exposure was 0.5 to 0.6 µg/day [1]. The levels obtained in this study are well within the lower range of daily intake levels reported for an average American consumer.

In conclusion, it can be deduced from the present results that the exposure to PAHs through seafood consumption is not currently an unacceptable health risk for Kuwaiti consumers. Further studies are required to ascertain if these contamination levels of PAHs in seafood remain the same in the incoming years, especially in seafood, because the Arabian Gulf is constantly exposed to PAHs contamination from oil spills as this is an active oil exploration and transportation area.

References

[1]Menzie, C.A., Potocki, B.B. and Santodonato, J. 1992. Exposure to carcinogenic PAHs in the environment. Environ. Sci.Technol. **26**:1278-1284.

[2]Baek, S.O., Field, R.A., Goldstone, M.E., Kirk, P.W., Lester, J.N. and Perry, R. 1991. A review of atmospheric polycyclic aromatic hydrocarbons: Sources, fate and behaviour. Water Air Soil Pollut. **60**: 279-300.

[3]Deb, S.C., Araki, T. and Fukushima, T. 2000. Polycyclic aromatic hydrocarbons in fish organs. Mar. Pollut. Bull. **40**:882-885.

[4]Scientific Committee on Food (SCF) 2002. SCF/CS/CNTM/PAH/29 ADDI Final 4 December 2002. Polycyclic Aromatic Hydrocarbons-Occurrence in Foods, Dietary Exposure and Health Effects. Background Document to the Opinion of the Scientific Committee on Food on the Risks to Human Health of Polycyclic Aromatic Hydrocarbons in Food. Scientific Committee on Food, Brussels. Available: http://europa.eu.int/comm/food/fs/sc/scf/index_en.html.

[5]Llobet, J.M., Falcó, G., Bocio, A. and Domingo, J.L. 2006. Exposure to polycyclic aromatic hydrocarbons of edible marine species in Catalonia, Spain. J. Food Prot. **69**:2493-2499.

[6]United Nations Environment Programme Report (UNEP) 1991. UN Interagency Plan of Action for the Regional Organization for the Protection of the Marine Environment (ROPME) Region: Phase 1: Initial Survey and Preliminary Assessment. Oceans and Coastal Areas Programme Activity Centre, (UNEP), Nairobi, Kenya.

[7]Literathy, P. 1992. Environmental consequences of the Gulf war in Kuwait. Impact on water resources. Water Sci. Technol. **26**:21-30.
[8]Fowler, S.W., Readman, J.W., Oregioni, B., Villeneuve, J.P. and McKay, K. 1993. Petroleum hydrocarbons and trace metals in near shore gulf sediments and biota before and after the 1991 war: An assessment of temporal and spatial trends. Mar. Pollut. Bull. **27**:171-182.
[9]Saeed, T., Al-Yakoob, S., Al-Hashash, H. and Al-Bahloul, M. 1995. Preliminary exposure assessment for Kuwaiti consumers to polycyclic aromatic hydrocarbons in seafood. Environ. Int. **21**:255-263.
[10]DouAbul, A. A.-Z., Abaychi, J.K., Al-Edanee, T.E., Ghani, A.A. and Al-Saad, H.T. 1987. Polynuclear aromatic hydrocarbons (PAHs) in fish from the Arabian Gulf. Bull. Environ. Contam. Toxicol. **38**:546-552.
[11]Al-Yakoob, S., Saeed, T., Khordagui, H., Saif, M., Al-Matrouk, K. and Al-Hashash, H. 1995. Estimation of Risk Associated with Consumption of Oil-Contaminated Seafood by Kuwait's Population. Report No. KISR4631. Kuwait Institute for Scientific Research (KISR), Kuwait.
[12]US Environmental Protection Agency (US EPA) 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Fish Sampling and Analysis. Vol. 1. 3rd edn. EPA/823-B-00-007.
[13]De Vos, R.H., van Dokkum, W., Schouten, A. and De Jong-Berkhout, P. 1990. Polycyclic aromatic hydrocarbons in Dutch total diet samples (1984-1986). Food Chem. Toxicol. **28**:263-268.
[14]Grimmer, G. and Boehnke, M. 1975. Polycyclic aromatic hydrocarbons profile analysis of high-protein foods, oils and fats by gas chromatography. J. AOAC **58**:725-733.
[15]Perugini, M., Visciano, P., Giammarino, A., Manera, M., Di Nardo, W. and Amorena, M. 2007. Polycyclic aromatic hydrocarbons in marine organisms from the Adriatic Sea, Italy. Chemosphere **66**:1904-1910.
[16]Nisbet, I.C.T. and LaGoy, P.K. 1992. Toxic equivalency factor (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Reg. Toxicol. Pharmacol. **16**:290-300.
[17]Al-Yakoob, S., Saeed, T. and Al-Hashash, H. 1993. Polycyclic aromatic hydrocarbons in edible tissue of fish from the Gulf after the 1991 oil spill. Mar. Pollut. Bull. **27**:297-301.
[18]Cheung, K.C., Leung, H.M., Kong, K.Y. and Wong, M.H. 2007. Residual levels of DDTs and PAHs in freshwater and marine fish from Hong Kong markets and their health risk assessment. Chemosphere **66**: 460-468.
[19]Loutfy, N., Fuerhacker, M., Tundo, P., Raccanelli, S. and Tawfic, A. M. 2007. Monitoring of polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons in food and feed samples from Ismailia city, Egypt. Chemosphere **66**:1962-1970.
[20]Zabik, M.E., Booren, A., Zabik, M.J., Welch, R. and Humphrey, H. 1996. Pesticides residues, PCBs and PAHs in backed, charbroiled, salt boiled and smoked Great Lakes lake trout. Food Chem. **55**:231-239.
[21]Rainio, K., Linko, R.R. and Routsila, L. 1986. Polycyclic aromatic hydrocarbons in mussels and fish from the Finnish archipelago sea. Bull. Environ. Contam. Toxicol. **37**:337-343.
[22]Landlot, M., Kalman, D., Nevissi, K., Ness, V. and Hafer, F. 1987. Potential toxicant exposure among consumers of recreationally caught fish from urban embayments of Puget Sound. Technical NOAA Memorandum, NOS OMA-33, National Oceanic and Atmospheric Administration, Rockville, Maryland, USA.
[23]Baumard, P., Budzinski, H., Garrigues, P., Dizer, H. and Hansen, P.D. 1999. Polycyclic aromatic hydrocarbons in recent sediments and mussels (*Mytilus edulis*) from the Western Baltic Sea: Occurrence, bioavailability and seasonal variations. Mar. Environ. Res. **47**:16-47.
[24]Al-Hassan, J.M., Afzal, M., Rao, C.V.N. and Fayad, S. 2000. Petroleum hydrocarbon pollution in sharks in the Arabian Gulf. Bull. Environ. Contam. Toxicol. **65**:391-398.
[25]European Commission (EC) 2005. Commission Regulation (EC) No 208/2005 of 4 February 2005 amending Regulation (EC) No 466/2001 as regards polycyclic aromatic hydrocarbons. OJEUL **34**:3-5.
[26]Dickman, M.D. and Leung, K.M.C. 1998. Mercury and organochlorine exposure from fish consumption in Hong Kong. Chemosphere **37**: 991-1015.
[27]Ibáñez, R., Agudo, A., Berenguer, A., Jakszyn, P., Tormo, M.J., Sanchéz, M.J., Quirós, J.R., Pera, G., Navarro, C., Martinez, C., Larrañaga, N., Dorronsoro, M., Chirlaque, M.D., Barricarte, A., Ardanaz, E., Amiano, P. and Gonzálezi, C.A. 2005. Dietary intake of polycyclic aromatic hydrocarbons in a Spanish population. J. Food Prot. **68**:2190-2195.
[28]Al-Yakoob, S.N., Saeed, T. and Al-Hashash, H. 1994. Polycyclic aromatic hydrocarbons in fish: Exposure assessment for Kuwaiti consumers after the gulf oil spill of 1991. Environ. Int. **2**:221-227.