Polycyclic Aromatic Hydrocarbons (PAHs) Levels in Two Commercially Important Fish Species from the Coastal Waters of Ghana and their Carcinogenic Health Risks

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) concentrations were measured by gas chromatography with flame ionization detector (GC/FID) in two fish species, *Sardinella maderensis* (Flat sardinella) and *Galeoides decadactylus* (Lesser African threadfin or Shine-nose or Common threadfin) from Ghanaian coastal waters and the carcinogenic health risks, associated with the consumption of these fishes, estimated. The average concentrations of PAHs ranged from below detection limit of 0.01 µg/kg wet wt to 34.04 ± 0.56 µg/kg wet wt in *S. maderensis,* and from below detection limit (0.01 µg/kg wet wt) to 54.13 ± 5.22 µg/kg wet wt in *G. decadactylus*. Pyrene had the highest mean concentration of 54.13 ± 5.22 µg/kg wet wt in *G. decadactylus* from Tema. Both fish species from Tema and Chorkor showed similar PAH assemblages although the concentrations were different, suggesting common source of PAHs in these coastal environments. *G. decadactylus* accumulated significantly higher ($P < 0.05$) concentrations of total PAHs at all the sites, except at Chorkor. High molecular weight PAHs (HMW-PAHs) were generally predominant compared to low molecular weight PAHs (LMW-PAHs). The LMW-PAH/HMW-PAH ratios were < 1 for both species, indicating anthropogenic, mainly pyrogenic, origin of PAHs in the Ghanaian coastal environment. With the exception of *G. decadactylus* from Ada-Foah, benzo(a)pyrene concentrations in the fish samples analysed exceeded the EU recommended limit of 2 µg/kg wet wt for fish considered safe for human consumption. The estimated carcinogenic potency equivalent concentrations exceeded the screening value for both species from all the study areas, indicating significant carcinogenic health risks associated with the consumption of these fishes. A further study of PAHs and other contaminants in seafood, landed on the coast of Ghana, is recommended in the light of recent discovery and drilling of oil in commercial quantities in Ghanaian coastal waters.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants containing two or more fused benzene rings. They are known to be ubiquitous in both marine and terrestrial environments (Bouloubassi *et al*., 2001). PAHs have received much attention due to their potential adverse human health and ecosystem impacts. Human exposure to these pollutants can result in cancer, mutations and birth defects (Zedec, 1980; White, 1986). Adverse effects of PAHs have also been observed in marine organisms and they include growth reduction (Christiansen & George, 1995), endocrine alteration (Meador *et al*., 2006), malformations of embryo and larvae (Carls *et al*., 2008; Camus & Olsen, 2008) and DNA damage (Caliani *et al*., 2009). Consequently, the United States Environmental Protection Agency (USEPA) and the European Union (EU) have included PAHs in the list of priority pollutants (Bouloubassi *et al*., 2001).

Various anthropogenic activities in coastal areas have contributed to PAH contamination of coastal environments. These activities include the use of creosote-treated wood in

mussel aquaculture (Phillips, 1999), combustion of organic matter on land, offshore oil production and transport, and discharge of industrial effluents into the coastal environment (Law *et al*., 2002; Zhu *et al*., 2004). Ingestion of contaminated food (Meador *et al*., 1995) and diffusion from water across their gills and skin (Gobas *et al*., 1999) are the major routes of PAHs exposure to fish. Due to the lipophilic nature and high chemical stability of PAHs (Bouloubassi *et al*., 2001), they accumulate in the fatty tissues of fish following their uptake (Van der Oost *et al*., 1991). Fishes are, therefore, good indicators of pollution in coastal waters, and they have been used extensively for environmental monitoring (Bouloubassi & Saliot 1993; Bouloubassi *et al.,* 2006). Industrial, agricultural and domestic activities along the Ghanaian coast may lead to PAH contamination of the coastal waters.

A large section of the world's population depends on seafood, especially fish, to meet their nutritional requirements. In Ghana, fish is recognized as the most important source of animal protein, and provides over 60% of animal protein intake (Koranteng *et al*., 2004). Food consumption has been identified as an important pathway of human exposure to many contaminants including PAHs (Cheung *et al*., 2007) and, therefore, PAHs contamination of fish species that are widely consumed among the population may have serious health implications.

Coastal populations, which tend to consume relatively larger quantities of fish, are at greater risk of dietary PAHs exposure (Wei *et al.*, 2006). To safeguard human and ecosystem health, therefore, maximum residual levels of PAHs have been set by regulatory bodies such as the European Commission. Consequently, PAHs have been extensively studied in the coastal environment in many parts of the world (e.g. Zhu *et al.*, 2004; Wei *et al*., 2006; Perugini *et al*., 2007; Said, 2007), as well as their human health risk assessment (e.g. Wei *et al*., 2006; Cheung *et al.*, 2007). Although studies conducted on PAHs in the aquatic environment in Ghana have focused mainly on lagoon sediments (e.g. Gilbert *et al*., 2006), no data exists on the levels of PAHs in fresh fish caught from Ghanaian coastal waters.

The sources of PAHs in the coastal environment are described as either petrogenic (if the source is derived from petroleum, e.g. natural oil seepage and oil spills) or pyrogenic (if the source is derived from the incomplete combustion of organic matter and fossil fuel (e.g. Baumard *et al*., 1998; Abrajano *et al*., 2003). The ratio of high molecular weight PAHs (HMW-PAHs) to low molecular weight PAHs (LMW-PAHs) has been used to characterize the origin of PAHs in the environment. Petrogenic sources of PAHs show characteristically higher proportion of LMW-PAHs such as naphthalene and acenaphthene while pyrogenic PAHs have characteristically higher proportion of HMW-PAHs such as pyrene and benzo(a)pyrene (Helfrich & Armstrong, 1986; Rocher *et al.*, 2004). Thus, petrogenic sources of PAHs exhibit LMW/HMW ratios > 1 whereas pyrogenic sources of PAHs exhibit LMW/HMW ratios < 1 (Rocher *et al*., 2004).

In addition to the LMW/HMW ratios, isomeric ratios of PAHs have been widely used as indices for the identification of PAH

sources in the environment (e.g. Yunker *et al*., 2002). For instance, a BaA/(BaA + Chry) ratio > 0.35 indicates pyrogenic or combustion sources while a ratio < 0.20 has been attributed to petrogenic sources although these sources are indistinguishable for ratios in the range 0.20–0.35 (Yunker *et al*., 2002). Both approaches, which have been used to characterize the sources of PAHs in sediments, were adopted to characterize the sources of PAHs in the fishes analysed. The objectives of the study were therefore to (1) determine the levels of PAHs in two commercially important fish species from Ghanaian coastal waters, namely *S. maderensis* and *G. decadactylus,* (2) identify the sources of the PAHs, and (3) assess the associated carcinogenic health risks.

Materials and method

Study area

Three coastal communities, which are major artisanal landing sites of *S. maderensis and G. decadactylus*, namely, Chorkor (05° 31.18' N, 000° 14.41' W), Tema (05° 38.49' N, 000° 01.22' E) and Ada-Foah (05° 46.45' N, 000° 38.02' E) (Fig. 1), were selected for the present study. Chorkor is noted for poor environmental management practices such as improper disposal of refuse (mainly plastic wastes) directly on the beach (Nunoo & Quayson, 2003). Most of these plastic wastes are usually carried into the sea by waves and tides and come into contact with fish. The Korle lagoon, which carries untreated industrial and domestic wastes, also discharges into the sea near Chorkor. Smoking of fish, burning of refuse and automobile tyres are some anthropogenic activities in the area that can potentially introduce PAHs in the coastal environment.

Tema is characterized by heavy industrial activities, which may impact the coastal environment *via* the discharge of effluents into waterways that eventually enter the coastal area. In addition, shipping activities at the Tema Harbour may impact the coastal environment *via* oil leakage and spillage, most especially during the discharge of oil at the oil berth for onward transfer to the Tema Oil Refinery (TOR). Ada-Foah is also a coastal settler community whose inhabitants engage in artisanal fishing and agriculture. The area is located eastward of Chorkor and Tema, and may be impacted by activities in Chorkor and Tema due to the eastward movement of the Guinea Current. The study areas fall within the southern zone with average climatic conditions, as described by Kortatsi *et al*. (2008).

Sampling and sample preparation

Fresh samples of two commercially important fish species, *S. maderensis* and *G. decadactylus,* were obtained from landing beaches at the selected sites. *S. maderensis* is a pelagic fish while *G. decadactylus* is a demersal fish and, therefore, they are expected to provide some indication about PAHs distribution within the water column. At each site, 30 individual fish of similar size of each species were collected, wrapped with aluminium foil, then kept frozen on ice in an ice-chest, and transported to the Department of Oceanography and Fisheries laboratory, University of Ghana for analysis.

In the laboratory, the fish samples were washed with distilled water and their scales removed. The fish muscles (together with their skin) were then cut off, using a clean stainless steel knife previously rinsed with

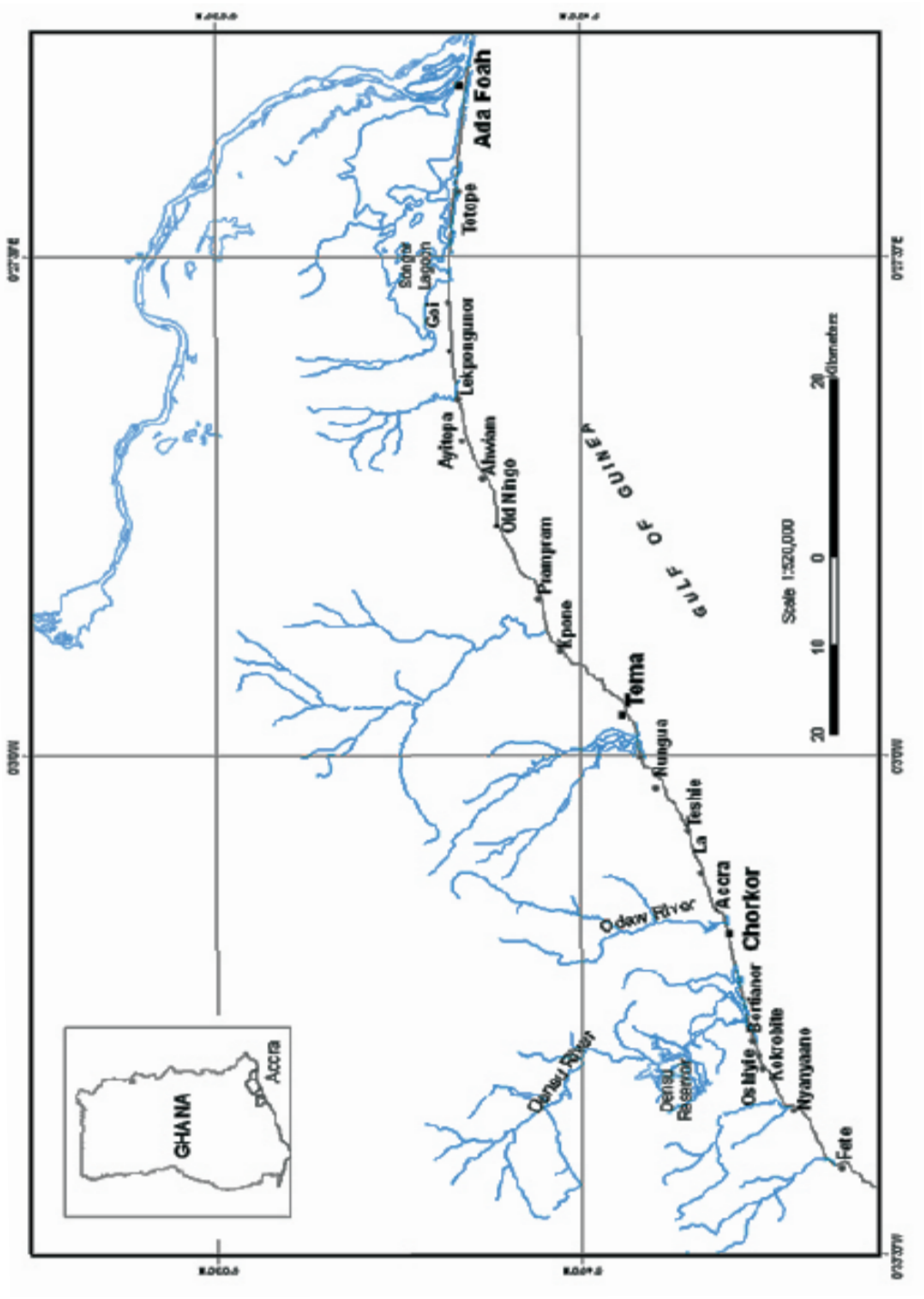

Fig. 1. Map showing locations of the sampling sites along the Ghana coast

acetone, and weighed. The fish tissue samples were then freeze-dried, reweighed and stored in a desiccator.

Prior to extraction, the freeze-dried samples were ground to powder using pestle and mortar to ensure homogenization. The powdered samples were then Soxhlet extracted according to USEPA Standard Method 3540C (USEPA, 1996) and also by Cheung *et al*. (2007), with some modifications. Briefly, 10 g of homogenized samples were weighed into a Soxhlet extraction thimble and extracted with 200-ml acetone/dichloromethane mixture (1:1) for 16 h cycling 5–6 times h^{-1}. About 10 g of anhydrous sodium sulphate was added to each extract to dry the extract. The dry extracts were then transferred into clean and dry 250-ml round bottom flasks, rinsing the sodium sulphate three times with 5 ml hexane and the extracts combined. The dry extracts were evaporated to near dryness on a rotary evaporator maintained at a temperature of 35 °C. The residues were re-dissolved with 2 ml portions of *n*-hexane and transferred into 10 ml graduated test-tubes.

The flasks were rinsed three times with 1 ml portions of *n*-hexane and transferred to the test-tubes to obtain a volume of about 5 ml. The extracts were concentrated further by a gentle stream of pure nitrogen gas to 2 ml. Clean-up and fractionation of extracts in the study were performed following the method by Said (2007). Briefly, 1 ml portions of extracts were passed through silica/alumina columns overlaid by 1 g of anhydrous sodium sulphate. The columns were eluted using 40 ml portions of *n*-hexane, and then 40 ml portions of *n*-hexane/dichloromethane (9:1) mixture, followed by 20 ml portions of *n*-hexane/dichloromethane (1:1) mixture. The combined eluates were then concentrated under gentle stream of pure nitrogen gas to 2 ml, before injecting into a GC/FID for analysis of PAH compounds.

Quality control

High purity (95–99.9%) external standard mixture containing naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene dibenz (a,h)anthracene and indeno (1,2,3-cd) pyrene, and an internal standard mixture containing five deuterated PAHs (biphenyl-d_{10}, anthracene-d_{10}, phenanthrene-d_{10}, pyrene-d_{10}, perylene-d_{12}) were obtained from Chiron, Norway. Analytical grade solvents and reagents (acetone, hexane, dichloromethane and anhydrous sodium sulphate) obtained from Merck (USA) were used for the extraction. Standard and surrogate solutions were prepared in hexane.

To correct for PAH recovery efficiencies, fish samples were spiked with 1 ml of a solution of five internal standards (biphenyl-d_{10}, anthracene-d_{10}, phenanthrene-d_{10}, pyrene-d_{10}, perylene-d_{12}) each at 2 µg/ml in hexane. After spiking, samples were kept in a refrigerator overnight to facilitate equilibration with the sample matrix. Reagent blanks were also prepared and analysed with the samples to test for contamination in the extraction process. Mean recoveries of internal standards ranged from 78 to 94%. Two certified reference materials of soil (CRM 104-100 and CRM

105-100) from the National Institute of Standards and Technology (NIST) were also analyzed in the same way as the fish samples (Cheung *et al*., 2007) with recoveries of 86–92%.

The limits of detection (LOD) and quantification (LOQ) were evaluated on the basis of the noise obtained with the analysis of unfortified blank samples (n = 3). In this analysis, LOD was defined as the concentration of analyte that produced a signal-to-noise ratio of three while the LOQ was defined as the concentration of the analyte that produced a signal-to-noise ratio of 10 (ACS, 1980). Both the LOD and LOQ were then tested experimentally by spiking blank samples at their respective levels. External standard calibration was used for quantification of analytes. The recoveries varied from 82 to 90% with reproducibility less than 10%.

Instrumental analysis

Analysis of PAHs was done using an Agilent 6890N gas chromatograph with flame ionization detector (GC/FID), equipped with an injector fused with a silica capillary column (DB-5ms). Helium was used as the carrier gas with a split ratio of 50: 1, and the temperature set point was maintained at 300 °C. The detector temperature set point was maintained at 300 °C where hydrogen gas was introduced at a rate of 30 ml/min with an inflow of air (neutral air) at a rate of 300 ml/min and make-up gas (helium) was allowed to flow through at 20 ml/min. All injection volumes were 2 µl. The inlet and the column lines were maintained within 290–300 °C. Analyte peaks were identified by their retention times compared to the corresponding retention times of the PAH standards. No independent method of confirmation was applied. Triplicate analyses were performed for all the samples.

Statistical analysis

All concentrations were expressed as µg/kg wet weight. Comparisons of PAHs levels between species within sites were made using student *t*-test while one-way analysis of variance (ANOVA) was performed to compare PAHs levels between species across sites with the statistical package SPSS 14.0.2 (SPSS Inc., Chicago, IL). In order to determine the origin of PAHs in a fish species as petrogenic or pyrogenic, results for each species were also expressed in terms of total PAHs (PAHs), low-molecular weight PAHs (LMW-PAHs) and high-molecular weight PAHs (HMW-PAHs). The LMW-PAHs were naphthalene (Nap), acenaphtene (Ace), acenaphthylene (Acy), fluorene (Fluo), phenanthrene (Phe) and anthracene (Ant), and the HMW-PAHs were fluoranthene (Fl), pyrene (Py), benzo(a)anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BaF), benzo(k) fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h) anthracene (DahA) and indeno(1,2,3,c,d) pyrene (IP).

Human health risk assessment

In estimating the carcinogenic risk from exposure to PAHs in fish, the USEPA guideline, as described by Cheung *et al*. (2007), was followed. By this method, BaP is used as a marker for the occurrence and effect of carcinogenic PAHs in foods and, therefore, the overall carcinogenic health risk from the measured PAHs was estimated

based on toxic equivalency factors (TEFs) derived from the cancer potencies of individual PAH compounds relative to the cancer potency of BaP. Table 1 shows the PAHs and their TEFs (Nisbet & LaGoy, 1992).

TABLE 1
PAHs and their toxic equivalency factors (TEF) relative to the cancer potency of BaP (Nisbet & LaGoy, 1992)

PAH compound	*TEF*
BaP	1
Nap	0.001
Acy	0.001
Ace	0.001
Fluo	0.001
Phe	0.001
A	0.01
Fl	0.001
Py	0.001
BaA	0.1
Chry	0.01
BbF	0.1
BkF	0.1
IP	0.1
DahA	5

The product of the PAH concentration (µg/g) and its TEF gives a BaP equivalent concentration (BaPeq) for each PAH. All the individual BaPeq were then summed up to give a carcinogenic potency equivalent concentration (PEC) of all the PAHs according to equation (1) (Nisbet & Rasmussen, 1992).

$$PEC = \Sigma (TEF \times Concentration) \quad (1)$$

PEC values were then compared with a screening value for carcinogenic PAHs. The screening value was calculated from Equation (2) by Russell *et al.* (1997).

$$SV = [(RL/SF) \times BW]/CR \quad (2)$$

where SV = screening value (µg/g); RL = maximum acceptable risk level (dimensionless); SF = USEPA oral slope factor $(\mu g/g\ day)^{-1}$; BW = body weight (g); CR = consumption rate (g/day).

SV is the threshold concentration of total PAHs in fish tissue that is of potential public health concern; BW is the average body weight (g) and was set to 60000 g (i.e. 60 kg) for the adult population (Jiang *et al.*, 2005); CR is the consumption rate (g/day). Fish consumption rate was set to 68.5 g/day from the annual per capita fish consumption of 25 kg for Ghana (MOFA, 2004). RL is the maximum acceptable risk level (dimensionless), which is set to 10^{-5} (USEPA, 2000) so that the maximum risk would be one additional cancer death per 100000 persons, if an adult weighing 60 kg consumed 68.5 g of fish daily with the same measured concentrations of PAHs for 70 years; SF is the USEPA oral slope factor for PAHs, used to estimate an upper-bound probability of an individual developing cancer as a result of a lifetime (70 years) exposure to carcinogenic PAHs and has a value of 7.30 $(\mu g/g\ day)^{-1}$ (USEPA, 1993). For safety reasons, a consumption rate of 1 g/day was used to estimate the minimum level that a consumer may be protected from the carcinogenic effects of PAHs detected in these fishes.

Results

The average concentrations of PAHs in *S. maderensis* and *G. decadactylus*, total PAHs concentrations (ΣPAHs), LMW-PAH/HMW-PAH ratios and the PEC values are shown in Table 2. A total of 15 PAHs, namely Nap, Acy, Ace, Fluo, Phe, Ant, Fl, Py, BaA, Chry, BbF, BkF, BaP, DahA and IP were detected in the fish samples analysed. Average concentrations of these PAHs ranged from below detection limit of 0.01 µg/kg wet wt to

TABLE 2

PAH concentrations (mean ± SE, µg/kg wet wt.), total mean PAH concentrations (µg/kg wet wt.), PEC values, LMW-PAH/HMW-PAH and BaA/(BaA + Chry) ratios in G. decadactylus *and* S. maderensis *from the study areas*

PAH compound (abbreviation)	*Ada-Foah*		*Tema*		*Chorkor*	
	G. decadactylus	*S. maderensis*	*G. decadactylus*	*S. maderensis*	*G. decadactylus*	*S. maderensis*
Nap	4.19 ± 0.19	1.72 ± 0.82	1.00 ± 0.26	4.03 ± 0.17	3.20 ± 0.69	1.69 ± 0.13
Acy	1.74 ± 0.64	n.d	15.83 ± 1.30	7.98 ± 0.3	2.49 ± 0.35	3.44 ± 0.22
Ace	0.86 ± 0.24	n.d	0.84 ± 0.73	2.55 ± 0.88	2.06 ± 0.38	0.82 ± 0.53
Fluo	3.30 ± 1.43	n.d	0.36 ± 0.15	1.16 ± 0.11	7.31 ± 0.96	1.03 ± 0.32
Phe	2.31 ± 0.22	n.d	2.73 ± 0.65	n.d	2.24 ± 0.15	0.52 ± 0.09
A	n.d	1.33 ± 0.01	6.15 ± 0.55	1.34 ± 0.37	5.97 ± 0.49	9.23 ± 0.83
Fl	7.03 ± 0.24	2.34 ± 1.70	8.20 ± 0.64	0.89 ± 0.10	8.21 ± 0.36	3.35 ± 0.58
Py	9.54 ± 2.22	16.81 ± 1.19	54.13 ± 5.22	24.51 ± 1.62	27.68 ± 3.26	11.73 ± 1.33
BaA	5.26 ± 0.68	2.36 ± 1.20	21.16 ± 3.86	34.04 ± 0.56	12.33 ± 3.83	7.85 ± 2.22
Chry	5.56 ± 0.10	0.05 ± 0.01	11.83 ± 0.58	1.39 ± 0.18	6.61 ± 0.16	7.81 ± 1.83
BbF	6.39 ± 0.11	0.30 ± 0.13	18.37 ± 0.54	6.21 ± 0.17	9.70 ± 0.25	8.29 ± 0.29
BkF	0.36 ± 0.15	0.72 ± 0.31	1.32 ± 0.24	1.93 ± 0.22	0.18 ± 0.06	10.32 ± 0.53
BaP	0.86 ± 0.20	8.80 ± 0.52	7.46 ± 0.37	4.611 ± 0.54	6.59 ± 0.39	17.45 ± 2.33
IP	5.72 ± 0.84	12.18 ± 0.48	11.21 ± 1.04	1.48 ± 0.16	2.89 ± 0.37	11.37 ± 0.33
DahA	10.16 ± 0.37	2.14 ± 0.39	6.20 ± 0.43	7.70 ± 0.54	13.02 ± 0.19	20.66 ± 0.90
PAH	63.29 ± 2.68	48.75 ± 3.00	166.79 ± 2.17	99.87 ± 6.91	110.48 ± 4.27	115.56 ± 5.27
PEC	0.058	0.024	0.047	0.045	0.071	0.120
LMW-PAH/HMW-PAH ratio	0.24	0.07	0.19	0.21	0.27	0.17
BaA/(BaA + Chry) ratio	0.49	0.99	0.64	0.96	0.65	0.50

SE = standard error; n.d = not detected (i.e. below the detection limit of 0.01 µg/kg wet wt.)

34.04 ± 0.56 µg/kg wet wt in *S. maderensis* and from < 0.01 µg/kg wet wt to 54.13 ± 5.22 µg/kg wet wt in *G. decadactylus*. The highest average concentration of 54.13 ± 5.22 µg/kg wet wt was recorded for pyrene in *G. decadactylus* from Tema. ΣPAHs concentrations in *S. maderensis* were 48.75 ± 3.00, 99.87 ± 6.91 and 115.56 ± 5.27 µg/kg wet wt at Ada-Foah, Tema and Chorkor, respectively. The PAH assemblages in *G. decadactylus* at all three sites were similar although the concentrations were different. However, the same can be said about *S. maderensis* at only Tema and Chorkor. ΣPAHs concentrations in *G. decadactylus* were 63.29 ± 2.68, 166.79 ± 2.17 and 110.48 ± 4.27 µg/kg wet wt at Ada-Foah, Tema and Chorkor, respectively. ΣPAHs concentrations in both fish species from Ada-Foah were significantly lower ($P < 0.05$) than total PAHs concentrations in fish from Tema or Chorkor. Between the two fish species, *G. decadactylus* accumulated significantly higher concentrations ($P < 0.05$) of total PAHs at all the sites except at Chorkor.

LMW-PAH/HMW-PAH ratios in *S. maderensis* were 0.07, 0.21 and 0.17 at Ada-Foah, Tema and Chorkor, respectively, and were 0.24, 0.19 and 0.27 in *G. decadactylus* at Ada-Foah, Tema and Chorkor, respectively. The LMW-PAH/HMW-PAH ratios in *S. maderensis* were markedly lower relative to the ratios found in *G. decadactylus* at Ada-Foah and Chorkor. The LMW-PAH/HMW-PAH ratios in both species from all the sites were < 1. BaA/(BaA + Chry) ratios in *S. maderensis* were 0.99, 0.96 and 0.50 at Ada-Foah, Tema and Chorkor, respectively, and were 0.49, 0.64 and 0.65 in *G. decadactylus* at Ada-Foah, Tema and Chorkor, respectively.

The BaA/(BaA + Chry) ratios in *S. maderensis* were, however, markedly higher relative to the ratios found in *G. decadactylus* at Ada-Foah and Chorkor. The BaA/(BaA + Chry) ratios in both species from all the sites were > 0.35. BaP concentrations in all the fish samples analysed exceeded the EU limit of 2 µg/kg wet wt, except in *G. decadactylus* from Ada-Foah. The calculated PEC values were 0.024, 0.045 and 0.12 in *S. maderensis* at Ada-Foah, Tema and Chorkor, respectively, and were 0.058, 0.047 and 0.071 in *G. decadactylus* at Ada-Foah, Tema and Chorkor, respectively. The calculated SV for PAHs in fish was 0.001.

Discussion

The occurrence of PAHs in fish is an indication of PAH contamination in coastal waters. Possible sources of PAHs in Ghanaian coastal waters include oil slicks, accidental discharges of oil from ships and fishing boats, discharges from the Tema Oil Refinery (TOR), burning of garbage on land, dumping of domestic wastes on the coast, and smoke emissions from industries and automobile exhaust. Exposure pathways of PAHs to fish include bioconcentration from water across their gills and skin (Gobas *et al*., 1999) and ingestion of PAH-contaminated particulate matter along with food (Meador *et al*., 1995), as PAHs readily adsorb onto particulate organic matter (Fowler & Knauer, 1986; Raoux *et al*., 1999). PAHs are lipophilic and so they accumulate in the fatty tissues of fish following their uptake (Bouloubassi *et al*., 2001).

Fishes are also likely to be contaminated with PAHs as they come into contact with fishing nets contaminated with oil from oil slicks, and PAH-contaminated plastics dumped into the sea which are usually caught

with the fishes. Although similar PAH assemblages were observed in both species, the concentrations of the PAH assemblages were different. Knutzen & Sortland (1982) found out that different pollution sources give rise to different PAH assemblages, thus, the findings from the study suggest a common source of PAHs in these environments. PAHs are rapidly removed from the water column by settling particles and volatilization (Gsehwend *et al.,* 1982; Broman *et al.,* 1988). As was expected, pelagic fishes such as *S. maderensis*, which live in the surface waters, showed very low levels of total PAHs as compared to demersal fishes such as *G. decadactylus* (Froescheis et al., 2002). This was confirmed at Ada-Foah and Tema, where *G. decadactylus* accumulated significantly higher concentrations ($P < 0.05$) of total PAHs than *S. maderensis*..

At Chorkor, however, *G. decadactylus* accumulated significantly lower ($P < 0.05$) concentrations of total PAHs than *S. maderensis*. This is possibly due to local physical mixing, which can result in re-suspension of bottom sediments and re-distribution of PAHs into the water column (Jurado *et al*., 2007), thereby, exposing both fishes to PAHs irrespective of where these fishes may be found. The observed differences in PAH bioaccumulation in *S. maderensis* and *G. decadactylus* may also be attributed to differences in feeding preferences and general behavior (Fisher, 1995), as well as the mode of feeding in these species (Kong *et al*., 2005). The LMW-PAH/HMW-PAH ratios indicate that the HMW-PAHs were generally predominant compared to the LMW-PAHs. The predominance of HMW-PAHs may be due to the fact that LMW-PAHs are preferentially degraded during PAH transport and burial into sediments (Berto *et al*., 2009).

The concentrations of contaminants in fish reflect the state of contamination of the environment (Lanfranchi *et al.*, 2006) and, therefore, the observed levels of total PAHs in fish indicate high levels of PAH contamination at Tema and Chorkor relative to Ada-Foah. The LMW-PAH/HMW-PAH ratios observed in both species from all the sites were < 1, indicating that the sources of these PAHs in the fish analysed are mainly pyrogenic (Rocher *et al*., 2004), and is a clear indication of anthropogenic pollution of PAHs in the coastal marine environment.

The observed BaA/(BaA + Chry) ratios in both species from all the sites were > 0.35 and also indicated pyrogenic sources of PAHs contamination. This finding also confirms the finding of Gilbert *et al*. (2006), who assessed the sources of PAHs in sediments of the Fosu lagoon along the Ghana coast, and concluded that combustion was the dominant source of PAH input into the lagoon. Possible anthropogenic sources include combustion of petroleum, automobile tyre, and wood and vehicle emission. PAHs may then be transported from their points of release to the coastal environment *via* surface runoff and atmospheric deposition (Lipiatou & Saliot, 1991).

With the exception of *G. decadactylus* from Ada-Foah, average BaP concentrations exceeded the EU limit of 2 µg/kg wet wt for fish, which is recommended to be safe for human consumption. The PEC values also exceeded the SV in all the fish analysed, indicating that consumption of *S. maderensis* and *G. decadactylus* at a rate of 68.5 g/day

can have adverse health effects. Although the estimated fish consumption rate of 68.5 g/day for Ghana is less than the USEPA fish consumption rate of 142.2 g/day for subsistence consumers (USEPA, 2000), the PEC values for both fish species from all sites (0.0239–0.1195) were above the calculated SV (0.0012), about 20–100 times higher. This indicates unacceptable levels of PAHs in *S. maderensis* and *G. decadactylus*. Thus, these fish species could be an important source of PAHs exposure among the Ghanaian population. In a tropical country such as Ghana, fish constitutes a major source of animal protein (FAO, 2004) in the diet.

The coastal people who tend to consume larger quantities of fish (Wei *et al*., 2006) could be at a greater risk. A consumption rate of 1 g/day, however, appears to be protective from the carcinogenic effects of the current PAH levels. This is because the PEC values associated with a consumption rate of 1 g/day are found to be less than the screening value (Russell *et al*. (1997). It is also important to note that the BaPeq-based approach used for carcinogenic risk assessment is limited to a few PAHs that have been monitored in ambient air, and does not account for the toxicity of all PAHs to which the general population is exposed (Chen & Liao, 2006). As PAHs are also known to cause growth reduction (Christiansen & George, 1995), endocrine alteration (Meador *et al*., 2006), malformations of embryo and larvae (Carls *et al*., 2008; Camus & Olsen, 2008) and DNA damage (Caliani *et al*., 2009) in fish, as well as human health effects such as cancer, mutations and birth defects (Zedec, 1980; White, 1986), they may also have adverse impacts on marine life.

Conclusion

The present study shows that PAH levels detected in *S. maderensis* and *G. decadactylus* are high and, thus, consumption of these fishes may pose significant health risk. A consumption rate of 1 g/day may, however, be protective from carcinogenic health risk. High molecular weight PAHs were predominant over low molecular weight PAHs, indicating that PAH contamination in coastal waters of Ghana are mainly from pyrogenic or anthropogenic sources such as combustion of refuse and releases from automobile exhausts along the Ghanaian coast. The results also suggest that fishes from coastal areas away from urban centres are safer for consumption relative to species found in coastal areas close to urban centres. A comprehensive study of PAHs and other contaminants in seafood landed on the Ghana coast is recommended to better understand and control PAH pollution in the Ghanaian coastal marine environment, in the light of the recent discovery and drilling of oil in commercial quantities in Ghana's coastal waters.

Acknowledgement

The work was supported by the International Atomic Energy Agency (IAEA) under the Technical Co-operation Africa Project RAF/7/008 "Enhancing Regional Capability for the Assessment of Contamination in the Marine Environment".

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