Risk assessment of Polycyclic Aromatic Hydrocarbons on edible fish (Scomberomorus commerson and Parastromateus niger) in Persian Gulf

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Abstract: Background and purpose: Polycyclic Aromatic Hydrocarbons (PAHs) due to their high toxicity are known as priorities of organic compounds pollution in the world which are considered as indicators of pollution. Due to the presence of oil wells in the Persian Gulf, these compounds are considered as one of the sources of pollution. These compounds are pollutants of soil and water ecosystems and are very dangerous and life threatening for fish. The aim of this study was to evaluate 16 combinations of PAHs (pollutants of petroleum compounds index) for Scomberomorus commerson and Parastromateus niger in Persian Gulf. Material and Methods: PAHs: In edible samples, Scomberomorus commerson and Parastromateus niger fishing from the northern part of the Persian Gulf (Bushehr Province) were evaluated using gas chromatography (GC-FID). Findings: Total concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in Scomberomorus commerson was 275 mg/g of fish dry weight and in Parastromateus niger was 180 mg/g of fish dry weight. Origin of both of them was from oil. Conclusion: The total concentration of carcinogen (PEC) for PAHs in Scomberomorus commerson and Parastromateus niger were 42.76 and 26.76, respectively.

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1. Introduction

Persian Gulf has very fragile and vulnerable climatic conditions and the lowest emissions in it would have devastating effects on the health of the fish and organisms. Persian Gulf biodiversity is high.

Persian Gulf as an important economic resource and a valuable oil and gas reserves in the world is important and about 40% of the world's oil and gas reserves in the Persian Gulf are the most crowded of the world for oil and non-oil tankers (GEO, 2000; Khan, 2002). Over the years this area has undergone events such as wars, oil contamination and the resulting environmental disaster is huge. The oil spill in the Persian Gulf waters through the discharge oil tankers during the cleaning of oil tankers, discharging ballast water of ships, rigs, exploitation of oil wells and accidents such as collisions and accidents, destruction and fire tankers and oil rigs, water the severe oil pollution in the Persian Gulf put (ROPME, 1996; Munawar et al., 2002).

PAHs compounds are pollutants as toxic, mutagenic and carcinogenic compounds known (Johnsona et al., 2005). These compounds are environmental carcinogens is that the natural conditions of the environment will not be removed easily. With increasing molecular weight aromatic compounds to break down their resistance is higher (Zahed and Mohammad Dashtaki, 2000).

Polycyclic aromatic hydrocarbons into two categories, light and heavy two to three rings or four rings are more divided. The combination of low solubility in water and fat are friends. Most PAHs of low vapor pressure and particles are absorbed. As a result of incomplete combustion of organic matter there and all contain carbon and hydrogen compounds could act as a precursor. These compounds during paralysis to break down into smaller parts are unstable free radicals and then combined with each other in the presence of heat, PAHs are produced. Temperature 500-700 °C and consists of oxygen, the pressure is intensified (Ivani et al., 2012).

It's reported that a large proportion of human cancers such as lung cancer and prostate cancer, related to food (Ambrosini et al., 2008; Shen et al., 2008). Certain groups of people may be exposed to higher risks of exposure to PAHs in the diet than the general population exist (Martí-Cid et al., 2008). In a study of Persian Gulf three species of fish, mullet, glass Willie exposure to polycyclic aromatic hydrocarbons in amounts of 0.3, 0.6 and 1.2 ppm during 96 hours and 8 days. The total amount of PAHs in mullet-dose and within 96 hours was 0.6

(Mohajeri, 2004). In another study of the origin of 14 PAH compounds was studied in Bushehr. Because of the wide geographic distribution of oyster reefs and feed value in the diet of people are Bushehr were evaluated. PAHs compounds in sediment and clams recovery of more than 65 percent. The total concentration of 14 PAHs in the soft tissue of mussels combined 268 ng per gram dry weight of the composition. 14 concentrations of PAHs in the soft tissue of mussels from 146.9 to 268.1 ng per gram dry weight of sediment between 41.7 to 227.6 ng g dry weight was measured. Oyster rocky coast of Bushehr province in terms of these pollutants was low (Mirza et al., 2010). Anyakora (et al. (2003 reported that 16 aromatic compounds in water, sediments and fish in the Niger Delta region of Nigeria was significantly high.

Table 1. Formula and chemical structure and physical properties of some compounds, polycyclic aromatic hydrocarbons

Order	Compound name	Formula	Mol. wt. (g mo l^{-1})	CAS number	Vapor pressure at 25 °C (Pa)	Boiling point (°C)	Structure
1	Naphthalene	$C_{10}H_8$	128	91-20-3	11.9	218	
2	Acenaphthylene	$C_{12}H_8$	152	208-96-8	3.86	280	
3	Acenaphthene	$C_{12}H_{10}$	154	83-32-9	0.50	279	
4	Anthracene	$C_{14}H_{10}$	178	120-12-7	3.4×10^{-3}	340	
5	Phenanthrene	$C_{14}H_{10}$	178	85-01-8	9.07×10^{-2}	339–340	
6	Fluorene	$C_{13}H_{10}$	166	86-73-7	0.432	295	
7	Fluoranthene	$C_{16}H_{10}$	202	206-44-0	1.08×10^{-3}	375–393	
8	Pyrene	$C_{16}H_{10}$	202	129-00-0	5.67×10^{-4}	360–404	
9	Benzo(a)-anthracene	$C_{18}H_{12}$	228	56-55-3	6.52×10^{-7}	435	
10	Chrysene	$C_{18}H_{12}$	228	218-01-9	1.04×10^{-6}	441–448	
11	Benzo(a)-pyrene	$C_{20}H_{12}$	252	50-32-8	6.52×10^{-7}	493–496	
12	Benzo(b)fluoranthene	$C_{20}H_{12}$	252	205-99-2	1.07×10^{-5}	168	
13	Benzo(k)fluoranthene	$C_{20}H_{12}$	252	207-08-9	1.28×10^{-8}	217	
14	Benzo(ghi)-perylene	$C_{22}H_{12}$	276	191-24-2	1.33×10^{-8}	525	
15	Dibenz[a,h]anthracene	$C_{22}H_{14}$	278	3-70-3	2.80×10^{-9}	262	

Materials and methods:

In this study, statistical and laboratory methods used to study the composition of the 16 main compounds polycyclic aromatic hydrocarbons recommended United States of America Environmental Protection Agency (EPA) is used. So that the data were analyzed statistically using. Each sample was repeated three times. Sampling of fish, milk and black pudding was in the spring of 2014 along the coast of Bushehr. For the measurement of PAHs in two species of fish from 28 to 30 fish, with an average length of 183 cm Scomberomorus

commerson and 52 cm of Parastromateus niger were harvested. Caught fish into a bucket of stainless steel and to remove mud or sand attached to them were irrigated with seawater. Samples were completely covered with aluminum foil and freezer containing crushed ice until analysis laboratory and were stored at -20 ° C (Cortazar et al., 2008).

Chemicals, solvents and standards

Chemicals used in this study were obtained from Merck Germany, a list of the substances listed in the table below:

Table 2. Solvents and equipment needed to test

Solvent	**Tool**
Aston	test tube 250
Cyclohexane	Meyer flask 100
Hexane	Baker 50
Methanol	50-100 hopper and the hopper separator 250, 500
Toluene	Cylinder 100 and 1000
Potassium hydroxide	Pipette

The first part of sample preparation of fish tissue from other parts separated by a steel blade and were crushed by a mixer (Moopam, 1999). After mixing soft tissue Hr4-3 fish (of a species) together and homogenization, the samples were dried by a freeze dryer. In order to digest and extract PAHs 5 g sample of soft tissue dried fish with 200 ml of methanol and 11 ml phenyl 16 micrograms per milliliter, as the internal standard (EPA, 1986) for a period of 16 hours within the system Soxhlet was placed. Then 20 ml of 2 M potassium hydroxide to digest fat content of the solvent added to the flask and were continued for 2 hours Soxhlet. After cooling, the mixture is poured into a separator funnel and 30 ml of distilled water and 90 ml of normal hexane was added and after shaking and mixing perfect funnel to separate the organic and aqueous phases of the base was to be separated. Extracting with two 50 ml of hexane was repeated. All the organic phase separated and concentrated by rotary evaporator passes through the cleaning column, evaporator again by rotating the volume of 5 ml. The samples were graded into vials and then complete evaporation of the solvent, in an ml solution for injection to prepare a GC.

Analysis method

All fish samples obtained were analyzed using Gas Chromatography Varian -3400 models. The device has a column HP-5MS, with a length of 30 meters and inner diameter of 0.32 mm and 0.25 micrometer thin film installed on the gas chromatograph ion Sazshlh was revealed. Split-split injection device by using helium gas flow of 1.5 ml per minute under international standards was carried out. The GC condition, at 280 ° C and a voltage electron injection was equivalent to 2000 eV. The initial temperature was kept at 70 ° C for 2 minutes. Then increase the temperature to 30 ° C per minute to 150 ° C, 4 ° C per minute to 310 ° C, and the temperature was set to 10 minutes remained constant.

Table 3. Table of device condition for analysis

Gas Chromatography	
Detector	FID
Column	Capillary with a thin layer of 1.2 micrometers
Column length	25 meters
Internal diameter	0.32 mm.
Carrier gas	Nitrogen purity 99.999%
Carrier gas speed	

In order to ensure quality control of the work schedule announced by the Environmental Protection Agency has used America. The preparation and analysis of all the tools and equipment needed with a mixture of n-hexane and dichloromethane were washed. All solvents from Merck Germany were also up for chromatography. Solvents controlled once per day before the start of the trial and analysis Instrument blank as a solvent to ensure a clean solvent and the device was used. Per 20 samples a solvent extraction system, the main operating like it was done on the health and injection machine equipment, reactants and the extraction procedure to be established. This operation is called Extraction Blank. The study also Surrogate standard was used. Recovery test was performed every 10 samples. That's a whole fish samples previously studied PAH in the absence of detectable amounts, in this case, the

combination of 5ppm of polycyclic aromatic hydrocarbons was added and all the main types of operations such as those carried on. The results show levels of recovery for each compound among 68% to 99% was variable. Reproducibility was among 85% and 100% respectively. Due to the toxicity and carcinogenesis number of compounds PAH, in all testing guidelines (OSHA, 1990), was observed. The laboratory has a valid certificate from the Department of Environment and standard operated procedure was written.

Findings:

PAH results in Scomberomorus commerson

Scomberomorus commerson is from Scomberidae families which make up the skeleton is a saltwater fish (Fakhri et al., 2011). The fish caught in the Persian Gulf and the environment. Kind of fish is flaked meat is very delicious. The fish in a large area in south-east Asia and the Middle East, China, Japan, Australia and the east coast of Africa is found. Scomberomorus commerson is bigger than Indo-Pacific king mackerel but its shape is as like as Indo-Pacific king mackerel. Scomberomorus commerson is from Scomberidae families and caudal two branches of the important features of this fish. The body of this fish is spindle-shaped cross-section it is oval. The length of this fish is between 120 and 240 cm. Feed of this fish is from smaller fish and marine planktonic forms (Bolgvad and Lopentin, 1998).

Total concentrations of polycyclic aromatic compounds in fish, 275 micrograms per gram dry weight of the fish. Benzo (g, h, i) perylene Benzo (g, h, i) commerson fish in any of the samples (Table 4.1) 16 combined concentration of PAH as follows:

Benzo(a)anthracene< Pyrene <Benzo(b)fluoranthene< Fluoranthene< Phenanthrene< Benzo(a)pyrene <Fluorene< Anthracene< Acenapthene< Chrysene< Naphthalene< Naphthalene< Acenapthalene< Acenapthalene< Dibenzo(a,h)anthracene< Benzo(g,h,i)perylene.

The average concentration of benzo (a) Payrn, the most effective combination of carcinogenic PAH in these fish was 23 micrograms per gram dry weight. Average concentrations of polycyclic aromatic compounds in the range from 0 to 36µg / g dry weight was recorded the highest average concentration in fish, is commerson composition of benzo (a) anthracene.

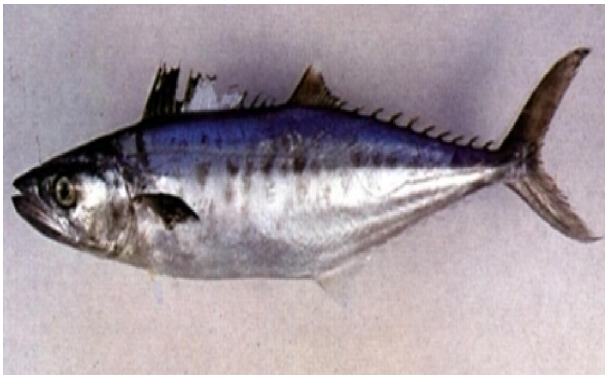

Fig 1. Scomberomorus commerson

Table 4 - 16 levels of polycyclic aromatic hydrocarbons in soft tissue in Scomberomorus commerson

Polycyclic aromatic hydrocarbons	Concentration of 4 micrograms per gram dry weight per fish							Ave.	S.D.
Naphthalene	15	0	20	21	0	0	19	11	10
Acenapthalene	6	10	0	9	5	8	11	7	4
Acenapthene	15	27	25	0	0	18	24	16	11
Fluorene	0	18	28	31	38	26	23	23	12
Phenanthrene	30	19	26	23	22	17	28	24	5
Anthracene	17	14	23	15	13	16	31	18	6
Fluoranthene	34	31	17	28	23	22	21	25	6
Pyrene	21	40	26	41	20	45	19	30	11
Benzo(a)anthracene	19	83	40	22	18	41	26	36	23
Chrysene	32	10	25	13	10	23	0	16	11
Benzo(b)fluoranthene	0	51	47	32	32	39	0	29	21
Naphthalene	0	15	18	0	25	12	0	10	10
Benzo(a)pyrene	23	15	33	50	16	14	13	23	14
Dibenzo(a,h)anthracene	0	8	0	0	7	0	5	3	4
Benzo(g,h,i)perylene	0	0	0	0	0	0	0	0	0
Acenapthalene	9	0	0	0	10	0	10	4	5

PAH results in Parastromateus niger

Pamous argenteus is from bone black pudding and white pudding. Pamous argenteus is commonly found in sea and sea come in the winter and early autumn. Parastromateus niger and fish is wide and compact body. Terminal mouth and upper and lower back and slightly to the front edge of the eye is closed. The fish jaws has a row of tiny teeth are conical. Dorsal fin spines with 4 to 5 short with a radius of 41 to 44 soft rays hard and lasting. Direct the lateral line scales poorly with 8 to 19, which formed the stem tail blade is weak, anal fin has two spines are covered and not visible in adults and 35 to 39 soft rays to a spur leads. Ventral fins in specimens larger than 10 cm is not visible, long, sword-shaped thoracic are small scale and are soon off. Body color of adult fish a gray - silver and brown is blue and fins with black edges, in young people with abdominal jugular, black and dark vertical lines on both sides of the body. A pelagic fish that usually found in the area of the continental shelf at depths of 15 to 40 meters can be seen on the muddy ground. Days near the bed and near the water surface at night to feed the zooplankton, crustaceans and small fish. The maximum body length is 55 centimeters (Sadeghi, 2001, Asadi and Dehghani, 1996).

Total of 16 polycyclic aromatic compounds in fish, black Pamous argenteus is in accordance with the table (4-2), and 180 micrograms per gram dry weight of the fish. Benzo (g, h, i) perylene (Benzo (g, h, i)) and the two (1, 2, 3-cd) pyrene (Indeno (1, 2, 3-cd) in any of the samples fish. The highest concentrations of benzo (a) anthracene (Benzo (a) anthracene) in the range of the average concentration of 23 micrograms per gram dry weight of the fish was found. The average concentration of benzo (a) pyrene is 15 micrograms per gram dry weight of the fish.

Fig. 2. Parastromateus niger

Table 5. Concentrations of polycyclic aromatic hydrocarbons in fish tissue

Polycyclic aromatic hydrocarbons	Concentration of 4 micrograms per gram dry weight per fish,							Ave.	S.D.
Naphthalene	12	0	0	12	18	0	15	8	8
Acenapthalene	24	0	4	2	6	0	0	5	9
Acenapthene	18	10	0	0	14	16	18	11	8
Fluorene	15	24	16	32	12	15	23	20	7
Phenanthrene	0	17	28	19	21	13	0	14	11
Anthracene	13	11	0	16	0	11	22	10	8
Fluoranthene	26	20	19	24	8	16	20	19	6
Pyrene	12	28	18	22	19	24	21	21	5
Benzo(a)anthracene	14	33	25	32	24	0	30	23	12
Chrysene	9	14	0	17	0	0	12	7	7
Benzo(b)fluoranthene	41	26	22	14	18	12	15	21	10
Benzo(k)fluoranthene	23	0	0	6	0	0	9	5	9
Benzo(a)pyrene	16	15	12	15	13	17	14	15	2
Dibenzo(a,h)anthracene	0	5	0	0	0	2	4	2	2
Benzo(g,h,i)perylene	0	0	0	0	0	0	0	0	0
Indeno(1,2,3-cd)pyrene	0	0	0	0	0	0	0	0	0

Pollution risk assessment of PAHs in Scomberomorus commerson and Parastromateus niger

To estimate daily in- take (EDI), the relationship (1) was used (Conti et al., 212):

(1) EDI= (IR*C)/BW

IR: the ingestion rate daily or meal size

C: the metal concentration

BW: the body weight

Comparison of total concentrations of polycyclic aromatic hydrocarbons in two species of fish shows that eating more Scomberomorus

commerson and daily intake of polycyclic aromatic compounds to more Parastromateus niger. So you have to use the fish in sensitive populations such as children and pregnant women should consider carefully. Falco et al. (2003), calculated daily intake of 16 polycyclic aromatic compounds in food samples from the general population of Catalonia, Spain calculated the seven cities. In their study, daily intake for young men was 8.418, 8.199 adolescents, 7.365 children, 6.330 older people and young women were 6.285 micrograms per day. The resulting PAH concentrations (mcg/g) and TEF gives concentration of the BAP (BaPeq) for each of PAH. Then all individual BaPeq summarized the power of carcinogen concentration (PEC) of all of PAHs according to equation (2):

(2) PEC = ∑ (TEF *Concentration)

PEC: carcinogenic potency equivalent concentration

TEFs: Toxic equivalence factors

Table 6. Factor of toxicity for different PAHs

Combination	TEF	The concentration of carcinogen (PEC) in µg / g	
		Scomberomorus commerson	Parastromateus niger
Dibenz[a,h]anthracene	5	15	10
Benzo[a]pyrene	1	23	15
Benz[a]anthracene	0	0	0
Benzo[b]fluoranthene	0.1	2.9	1
Benzo[k]fluoranthene	0.1	1	0.5
Indeno[1,2,3-cd]pyrene	0.1	0.4	0
Anthracene	0.01	0.18	0.1
Benzo[g,h,i]perylene	0.01	0.16	0
Chrysene	0.01	0.007	0.07
Acenaphthene	0.001	0.016	0.005
Acenaphthylene	0.001	0.025	0.011
Fluoranthene	0.001	0.023	0.019
Fluorene	0.001	0.024	0.02
Phenanthrene	0.001	0.03	0.014
Pyrene	0.001		0.021

According to the above equation, the concentration of carcinogen (PEC) for total PAHs in Scomberomorus commerson and Parastromateus niger was 42.765 and 26.76 micrograms per gram, respectively. Research in Mumbai, India in 2006 and 2008 on different species of fish concentrations of carcinogenic PAHs compounds BaA, BbF, BkF, BaP, InP and DbA were 9.49 to 31.23 nanograms per gram fresh weight was calculated (Dhananjayan and Muralidharan, 2012).

Determine the source of contamination in Scomberomorus commerson and Parastromateus niger

The study compared the combination of light and heavy components (LMW/HMW>1) LMW / HMW: Low molecular weight to High molecular weight greater than one, indicating the source of contamination in the fish oil is PAH compounds. The source of contamination in Scomberomorus commerson and Parastromateus niger would be estimated by measuring the ratio of Fluoranthene to Pyrene, it's proved that this ratio in Scomberomorus commerson is 0.83 and in Parastromateus niger is <1.

Conclusion:

Persian Gulf and semi-closed due to low mobility and exchange of water with the Indian Ocean, the lack of specific annual rainfall water is not entering the environment with excessive water evaporation, normally in the distribution and pollution remediation, capacity is limited. Persian Gulf as a unique ecosystem and a vital international waterway traffic in addition to the damages caused by oil tankers and oil extraction from the sea, Persian Gulf Wars I and II, as well as in terms of urbanization, development industrial and irrational exploitation of resources located under the sea to the discharge of large amounts of municipal and industrial wastewater has become. The pollution of coastal areas that are fertile ground for breeding, spawning and growth of particular species of edible fish are affected. Among several organic pollutants Aromatic hydrocarbons and chemical properties due to biological effects should be considered more than others.

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