Chemosphere 120 (2015) 575–583

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Distribution and composition pattern of polycyclic aromatic hydrocarbons in different tissues of sturgeons collected from Iranian coastline of the Caspian Sea

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HIGHLIGHTS

- 16 PAHs levels determined in *Acipenser persicus* and *Acipenser stellatus* from the Caspian Sea.
- PAHs were analyzed in the liver, kidney, gills and muscle tissues of Caspian sturgeon species.
- *Acipenser stellatus* showed significantly higher levels of heavy PAHs than *Acipenser persicus.*
- PAH levels and lipid content and K_{ow} was the more relevant statistical correlations observed.
- Low molecular weight PAHs predominated in the sturgeons, accounting for 81.89% of the total PAHs.

ARTICLE INFO

Article history:
Received 17 February 2014
Received in revised form 9 September 2014
Accepted 20 September 2014
Available online 18 October 2014

Handling Editor: A. Gies

Keywords:
Acipenser persicus
Acipenser stellatus
Fish
PAHs
Iran

ABSTRACT

The levels of 16 polycyclic aromatic hydrocarbons (PAHs) were determined in the liver, kidney, gills and muscle tissues of Persian sturgeon (*Acipenser persicus*; $n = 16$), and Stellate sturgeon (*Acipenser stellatus*; $n = 7$) collected from coastal waters of the South Caspian Sea from March and April 2011. The distribution and composition pattern of PAHs in the different tissues of sturgeons, and the effects of lipid content in sturgeon tissues and the octanol–water partition coefficient (K_{ow}) of PAHs congeners on them were analyzed. The levels of total PAHs in the various tissues of Persian sturgeon and Stellate sturgeon ranged from 2.095 to 6.587 and 1.942 to 6.206 μg g^{-1} dw, respectively. Stellate sturgeon showed significantly higher levels of heavy PAHs ($\geqslant$4-rings) than Persian sturgeon. The analysis has revealed a high degree of differential accumulation of the studied PAHs in the tissues of the both species. Low molecular weight PAHs predominated in the sturgeons, accounting for 81.89% of the total PAHs. Among the sixteen tested PAHs, naphthalene was the most dominant congener, followed by phenanthrene and fluorene. The PAHs levels and distribution in the tissues of sturgeons are dependent on both the K_{ow} of PAH congeners and the lipid content in these tissues. There was a significant positive relationship ($r = 0.868$, $p < 0.005$) between lipid content and PAHs levels. The statistically significant negative relationships ($p < 0.01$) were found between log K_{ow} and log-transformed PAHs levels for muscle tissues of both sturgeon species.

1. Introduction

The Caspian Sea region is one of the oldest oil-producing regions in the world; surrounded by five countries: Russia Federation, Kazakhstan, Turkmenistan, Islamic Republic of Iran and Azerbaijan. These nations with huge oil and natural gas reserves have attracted the attention of the international oil and gas industry, especially since the collapse of the Soviet Union in 1991 (Effimoff, 2000). The Caspian Sea is estimated to be the world's third largest reservoir of oil and natural gas after the Persian Gulf and Russia (Energy Information Administration, 2010; British Petroleum, 2011). Although Iran has not started any oil production in the Caspian Sea yet, however offshore oil production and land-based sources from other Caspian Sea range states are considered to be the main sources of pollution to the Caspian Sea (Karpinsky, 1992). The sea level, now 27 m below the level of the world oceans, increased by about 2.5 m in the past 20 years (Clauer et al., 2000) and as a result

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http://dx.doi.org/10.1016/j.chemosphere.2014.09.071
0045-6535/

inundation has flooded oil fields, agricultural lands and toxic waste sites, thereby contributing to the pollution burden of the Caspian Sea (Dumont, 1998). By 1900s the Baku region produced about half the world's total crude oil; they are major sources of land-based pollution. These land-based sources, together with offshore oil fields, tanker traffic, and trans-Caspian pipelines, have generated large quantities of toxic waste, run-off, and oil spills to the Caspian Sea (Dumont, 1995; Tolosa et al., 2004).

Today sturgeons live exclusively in the waters of the Northern Hemisphere (Billard and Lecointre, 2001). The Caspian Sea is the home of commercially important and valuable sturgeon species. Caspian Sea sturgeon are often claimed to yield the highest quality caviar, and countries bordering the Caspian Sea have accounted for about 80% of the global trade. Caspian sturgeon populations are imperiled due to a poorly regulated fishery, illegal catch, poaching, over harvesting, spawning habitat loss, water quality, and accumulation of toxic compounds in sediments which disturb the migration and reproduction of the sturgeon species (Billard and Lecointre, 2001). Among these factors, chemical contamination seems to be one of the most significant factors influencing the sturgeon population (Pourkazemi, 2006). As a land-locked system, various pollutants discharged from coastal catchment areas into the Caspian Sea remain trapped within the basin and accumulated in the Sea environment constitute a threat to biological life (Karpinsky, 1992). Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in aquatic ecosystems, and consist of over 100 different chemicals that are components of crude oil (Nef, 1979). Sixteen PAHs are included in the European Union and U.S. Environmental Protection Agency (U.S. EPA) priority pollutant list because of their mutagenic, carcinogenic, teratogenic, and toxic properties, environmental persistence, bioaccumulation and trophic transfer of PAHs in aquatic ecosystem (ATSDR, 1995; European Commission, 2011), and for this reason, the increase in levels of PAH contamination in aquatic systems that has occurred in recent decades is a cause for concern. Sturgeons are at a high potential risk for accumulating PAHs in their tissues due to the high lipid content in their bodies, long lives, long juvenile stage and benthivorous diet (Mashroofeh et al., 2013). As opportunistic bottom feeders, these fish frequently come in contact with sediments that could contain sediment-adsorbed hydrophobic pollutants. In recent years, the level of oil contamination has increased and the average content of petroleum hydrocarbons in the Caspian Sea is several times higher than the maximum permissible pollutant level set up in the USSR (Karpinsky, 1992; Agusa et al., 2004). Tolosa et al. (2004) also reported elevated levels of PAHs in sediments of the Caspian Sea. Furthermore, recent studies have demonstrated the occurrence of multielemental contamination in sturgeon species from the Caspian Sea (Agusa et al., 2004; Pourang et al., 2005; Abtahi et al., 2007; Heydari et al., 2011; Mashroofeh et al., 2012, 2013) and organochlorine pesticides (Kajiwara et al., 2003; Hosseini et al., 2008). However, distributions of PAHs in sturgeons from the Caspian Sea are still not well documented. Previous studies have shown that fish can efficiently metabolize PAHs to more polar compounds (that may be more toxic than the parent PAH) that are then secreted in the bile for elimination (reviewed in Beyer et al., 2010). Thus, fish rarely contain substantial amounts of PAHs in their edible muscle (Hom et al., 2008; Ylitalo et al., 2012). Because the Caspian Sea is landlocked and the PAHs cannot be flushed out, then these fish can be exposed to PAHs via respiration, ingestion of contaminated prey and/or contaminated sediments and dermal exposure to contaminated sediments.

The objectives of the present study are: (1) to investigate the residue levels of PAHs in the tissues of two sturgeon species from the Caspian Sea; (2) to explore the relationships between the residue levels of PAHs in sturgeons and the lipid content in fish tissues as well as the octanol–water partition coefficient (K_{ow}) of PAH congeners; and (3) to compare the obtained results with those from other studies.

2. Materials and methods

2.1. Sample collection

The Iranian Fisheries divided the entire area of the southern Caspian Sea into five sturgeon fishery zones. The Persian sturgeon (*Acipenser persicus*; $n = 16$) and Stellate sturgeon (*Acipenser stellatus*; $n = 7$) were collected from two of the important sturgeon fishery zones in Guilan and Mazandaran Provinces during March and April 2011. The specimens were caught using Gill nets with the standardized mesh and dimensions set by the Iran Fisheries Research Organization. The biological characteristics of the samples including total body length (cm) and weight (kg) were recorded, then individuals were sacrificed with laboratory set and samples of gills, kidney, liver and muscle were quickly removed, washed with distilled water and refrigerated until the extraction process.

2.2. Reagents

All reagents were of analytical grade and the water of Millipore-Q quality. Acetone, methanol, chloroform, *n*-hexane, dichloromethane and potassium hydroxide pellets were purchased from Merck Inc. (Darmstadt, Germany) and all authentic PAH standards were purchased from Dr. Ehrenstorfer Gmbh (Augsburg, Germany). Silica gel 60 (63–230 mesh) was activated at 200 °C for 24 h and deactivated by addition of 5% distilled water and was applied in the cleanup process. Anhydrous sodium sulfate was of analytical grade and was activated for 4 h at 450 °C to remove impurities before using. Glass wool and all glassware was washed with detergent and tap water, rinsed successively with methanol, acetone and distilled *n*-hexane to remove any organic contaminants and dried in an oven at 70 °C before use.

2.3. Extraction and sample clean-up

The lipid content of the samples was determined gravimetrically as described in Hijona et al. (2010). The procedure used for determined concentrations of PAHs has been described previously (Riyahi et al., 2010; Wretling et al., 2010; Mihalca et al., 2011) with some modifications. Briefly, all samples were freeze-dried for 72–96 h and then preserved in a desiccator prior to analyses of PAHs. Approximately 5–10 g (depending on the tissues) of the homogenized powder from each dried sample were weighed into a 250 ml Erlenmeyer flask and spiked with 100 µl of deuterated PAH surrogate internal standard mixture (naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) for ensure the accuracy of analyses. Saponification was carried out by adding 60 ml of 3.5 M methanolic KOH solution (methanol/water 9:1), thoroughly sealing the flask and keeping it at 60 °C in an oven for 2 h (flask was shaken after 1 h). Then 50 ml of *n*-hexane was added to the flask, which was shaken and then cooled to ambient temperature. The contents were transferred to a 250 ml separatory funnel, the flask was rinsed with 30 ml methanol/water (4:1) and the rinsing added to the separatory funnel. This was shaken vigorously. After separation, the aqueous layer was transferred to a second 250 ml separatory funnel and washed with 30 ml *n*-hexane. The *n*-hexane phases were combined and washed with 30 ml MeOH/H_2O (4:1), then with 30 ml MeOH/H_2O (1:1) and finally with 30 ml water. The cleaned *n*-hexane phase was decanted into a 100 ml round-bottomed flask, while carefully avoiding transferring any aqueous droplets, and concentrated to 1 ml in a rotary evaporator. Further clean-up was performed using a 5% H_2O deactivated silica gel column. The first step, eluted with