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Levels of Organotin Compounds in Selected Fish Species from the Arabian Gulf

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Abstract In the present work, data on the levels of hazardous Organotin compounds in eight commercially important fish species, caught from Arabian Gulf, has been reported. Highest levels of tributyltin (TBT) (98.5 ng/g dry weight) were detected in *Epinephelus Tauvina* whereas minimum (43.7 ng/g) were found in *Acanthoparagus Bifasciatus*. Highest levels of triphenyltin (TPT) were detected in *Lethrinus Miniatus* (107.5 ng/g) whereas lowest were encountered in *Acanthoparagus Bifasciatus* (64.9 ng/g). Highest value of total butyltin compounds (∑BT) were found in emperors (*Lethrinus Miniatus*) (228.4 ng/g) whereas minimum was found in *Acanthoparagus Bifasciatus* (126.4 ng/g). Similarly highest value of total phenyltin compounds (∑PT) was encountered in *Epinephelus Tauvina* (281.9 ng/g) followed closely by *Acanthoparagus Bifasciatus* (281.7 ng/g). In addition, the estimated daily intake (EDI) of the local population from consumption of these fish was also evaluated. Highest EDI was found to be 10.8 ng/kg bw/day for *epinephelus microdan*. The data are also compared internationally.

Keywords Arabian Gulf · Fish · Organotin compounds · Risk assessment

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Organotin compounds are a large class of compounds with widely varying properties, and for the past few decades, they have been extensively used for many different applications. Tri-substituted organotins, tributyltin (TBT) and triphenyltin (TPT) compounds have a wide range of uses associated with their strong biocidal activity towards aquatic organisms. Thus, these are extensively used in antifouling paints, wood preservatives, molluscicides and fungicides in agricultural activities (Hoch 2001). Due to the widespread use of the OTC, considerable amounts of these compounds entered into marine ecosystems. Recent studies have shown that OTC's are evidently released into the aquatic environment from various sources. Therefore, these harmful substances represent a potential risk for aquatic and terrestrial ecosystems (Diez et al. 2005). From an environmental perspective, most attention has been given to widespread TBT and TPT pollution of waters and aquatic biota resulting from their use in antifouling paints in boats and ships (Antizar-Ladislao 2008; Rantakokko et al. 2008; Ruedel et al. 2007). High concentrations of organotins have been detected in water and sediments, and pose an ecotoxicological threat to marine organisms (de Mora et al. 2003).

An antifouling paint consists of a film-forming material with a biocide ingredients and a pigment. TBT was originally designed for use on the hulls of large ships to reduce the build-up of barnacles and to improve on speed as well as economic efficiency. It works by releasing small amounts of the biocide from the painted hull into the water, forming a thin envelope of highly concentrated TBT around the boat. Once released from an antifouling coating, TBT is rapidly absorbed by organic materials such as bacteria and algae or adsorbed onto suspended particles in the water. The nature of the Arabian Gulf is mainly characterized by its oil production and the tremendous movement of the oil tankers through its sea routes. According to Organization of Petroleum Exporting Countries, Saudi Arabia is the biggest exporter of oil, and the volume it produces is close to a record. State-run Saudi Arabian Oil Co., known as Saudi Aramco, ships about 20 percent of all oil cargoes at sea globally, and it is going to expand its fleet to meet rising demand for its crude.

Organotin patterns of accumulation vary with life style of marine organisms. Phenyltin concentrations were found to be higher in benthic fish while butyltin levels were higher in pelagic ones (Stab et al. 1996). Takahashi et al. (1999) have found that butyltins were higher in migratory fish species. Similarly, shallow water organisms have also been found to contain higher butyltin compounds as compared to deep dwellers. Most studies concerning the uptake of these pollutants by aquatic organisms deal with TBT because of its extreme toxicity to several organisms. It has been shown that some marine bacteria display a remarkable ability to accumulate this contaminant. Research on TBT accumulation by aquatic invertebrates has been mostly confined to molluscs (bivalves) and crustaceans (decapods) because these groups are important seafood resources and are ecologically dominant in many habitats (Martina et al. 2012; Furdek et al. 2012). Human beings are mostly exposed to organotins through three ways namely dermal contact, inhalation and ingestion. Out of these dietary consumption through contaminated sea food is regarded as major contributor of OTC intake in the human body. A French study on the levels of OTCs in seafood and their association to health risk, have shown that fish are generally main sources of OTCs in human diet (Guerin et al. 2007; Kannan et al. 1995). Rantakokko et al. (2008), have shown high levels of organotin compounds in the blood of Finnish fishermen and their families consuming contaminated fish. Similar studies have shown OTCs in fish and their implications for human health risk (Ho and Leung 2014; Martina et al. 2012; Jadhav et al. 2011; Rantakokko et al. 2010; Rikka et al. 2010; Santos et al. 2009; Lee et al. 2005).

The GCC (Gulf Cooperation Council) region has seen a substantial rise in per capita seafood consumption. The average per capita consumption for the Middle East in general was 9.9 kg per year in 2010, which now has increased to 14.4 kg per year (FAO 2014). However, no efforts, so far, has been made to assess the level of contamination of locally available seafood for OTC contamination. The present study was conducted to monitor the levels of OTCs in locally consumed fish species and possible risk to consumers.

Materials and Methods

Fish samples of eight commercially important fish species were collected from the Arabian Gulf, coastal line Qateef, Eastren Province, Saudi Arabia. The sampling location was chosen to elucidate the influence of maritime activities and tanker traffic on the contamination of marine environment by OTCs. Depending upon the expected density of tanker traffic sampling stations were selected. Alkhazar Fisheries (26°33′09. 49°57′27.0″E, Tarout) is the biggest fish factory in the area and their fishermen were contacted for sample provision. All the samples were procured afresh from the fishermen at the spot as soon as their boats landed. Samples were packed on ice and brought to lab as soon as possible. In the laboratory, the standard length and total body weight of each fish were measured before dissection (Table 2). In order to avoid degradation of OTCs, samples were immediately dissected. Muscle samples were collected from the left side of the fish, above the lateral line, and between the dorsal fin and caudal fin. The samples freeze-dried, homogenized and then stored in labeled amber glass vials under refrigeration before chemicals analysis.

About 2.0 g (dry weight) of fish samples were extracted with about 10 mL of 1.0 M HCl (Fluka Buchs Switzerland) and 40 mL of 0.1% tropolone-acetone (Fluka Buchs Switzerland) at 30°C for 30 min followed by re-extraction with 50 mL of 0.1% tropolone-benzene. The extracts were dried with anhydrous sodium sulfate and concentrated to 3–5 mL with evaporation and transferred to a 250 mL separating funnel containing 50 mL of acetonitrile saturated with *n*-hexane. After shaking for about 15 min, OTCs were extracted with 100 mL of 10% benzene-hexane mixture. The extract was concentrated to nearly dryness and made up to 1 mL by diluting with *n*-hexane. Alkylation of the concentrated extract was done with 1 mL of Grignard reagent (pentyl magnesium bromide, Sigma-Aldrich) in an ice bath for half hour. Excess of the Grignard reagent was decomposed with 2 mL of 1.0 M HCl and the derivatized samples were recovered with *n*-hexane and concentrated to 1 mL by evaporation. The concentrated samples were passed through a packed column (Florisil) and 2 g of anhydrous sodium sulfate, and then eluted with 50 mL of 10% benzene-hexane for clean up. The clean eluted samples were concentrated to about 1 mL under a gentle stream of pure nitrogen gas and then spiked with tetrabutyltin as an internal standard to check GC-MS performance (Lee et al. 2005). For the determination of lipid contents, 50 g of fish tissues were extracted with 100 mL of dichloromethane for 24 h. After evaporation, the extractable organic materials were weighed with an analytical digital balance.

A Bruker GC-MS with B6 column was used to assay OTCs in the processed samples. The temperature of the column oven was programmed from an initial value of 100°C to a final value of 300°C at a rising rate of 20°C per minute. Temperature of both injector and detector was set at 250 and 300°C, respectively. Helium gas was used as carrier at a flow rate of 1 mL per minute. TBTs and TPTs were identified by assigning peaks in samples to the corresponding peak of internal standard. Individual organotin compounds were quantified by using peak areas and the results were corrected for the recovery of internal standard.

The quality of the obtained data was assured by spiking known amounts of butyltin and phenyltin compounds (Fluka Buchs Switzerland) in blank fish tissue and later carrying out same procedure as described above. A sample blank was also processed to ensure against any background impurity at the low concentration during the course of experiments. Procedural blanks were included with every batch of samples to check for interfering compounds and to accordingly correct the sample values, if necessary. Average recoveries and method detection limits are presented in Table 1.

In order to relate the ingestion of Organotin compounds with food habits of local population and calculate EDI, a survey was used (Khan et al. 2016). The survey was conducted in highly urbanized cities of the Kingdom. The survey was extended to included information related to age, gender and body weight with the likeness of a particular fish species and other foods. The data obtained is referred to in Table 3.

Results and Discussion

The levels of butyltin compounds (ng/g dry weight) in different fish species are presented in Table 2. Data pertaining to fish length, weight and lipids is also presented in Table 2. Figure 1 depicts the cumulative levels of total butyltin and phenyltin compounds. Highest levels of TBT (98.5 ng/g) were detected in greasy grouper whereas minimum (43.7 ng/g) were found in double bar bream. Relatively lower levels of DBT and MBT were detected in all the fish species studied. Highest levels of TPT were detected in emperors (107.5 ng/g) whereas lowest were encountered in double bar bream (64.9 ng/g). Highest value of total butyltin compounds (∑BT) were found in emperors (228.4 ng/g) while minimum was found in double bar bream (126.4 ng/g). Similarly highest value of total phenyltin compounds (∑PT) was encountered in greasy grouper (281.9 ng/g) followed closely by double bar bream (281.7 ng/g) and rabbit fish (281.4 ng/g). The variation in ∑BT levels may be attributed to different living patterns of fish species. Lee et al. (2005) have reported much higher levels of TBT in narrow barred Spanish mackerel (129.7 ng/g) from Taiwan, as compared to present work (98.5 ng/g). Comparably, DBT and MBT values are on the higher side for Taiwan fish as compared to levels in the present study. An international comparison of the data is presented in Table 4.

Table 1 Average recoveries (%) and detection limits (ng/g) for OTCs

OTCs	Recoveries (%)	Detection limits (ng/g)
TBT	76.3 ± 13	10.8
DBT	92.7 ± 7	11.9
MBT	89.3 ± 5	8.7
TPT	90.5 ± 11	7.8
DPT	86.4 ± 9	11.0
MPT	78.9 ± 16	13.1

The estimated daily intake (EDI) of metals from consumption of these products was evaluated using the formula:

$$EDI(ng/kgbw/day) = \frac{MI \times CM}{BWA}$$

where MI mass of product ingested per day. CM concentration of ∑OTC in the product. BWA body weight (70 kg for adult).

The results of EDI are mentioned in Table 3. Highest EDI was found to be 10.8 ng/kg bw/day for grouper (*epinephelus microdan*), whereas lowest value (5.6 ng/kg bw/day) corresponded to double bar bream (*acanthopagus bifasciatus*).

The consumption of seafood varies greatly among the countries. Therefore, in order to explain the risk involved in the consumption of seafood contaminated with organotin compounds, it is important to take into consideration overall fish consumption habits. The suggested way to achieve this is to calculate tolerable average residue levels.

Tolerable average residue levels (TARL) were suggested by Belfroid et al. (2000) to be basis for the concerned authorities to derive the maximum residue limit (MRL) of TBT and TPT in seafood. It can be a tool to ensure the health of the population by comparing the TARL values directly with measured residue levels of TBT and TPT in seafood. TARL was calculated as follows.

$$TARL = \frac{TDI(tolerable\ daily\ intake) \times 70\ kgBW}{Average\ daily\ seafood\ consumption}$$

where TDI of 0.25 µg/kg BW/day was used for TBT and that of 0.5 µg/kg BW/day for TPT (Santos et al. 2009). The average daily fish consumption is estimated to be10.7 g/day in Saudi Arabia. As a result, TARLs were 13.7 µg/g for TBT and 27.4 µg/g for TPT. Due to the use of different levels of body weight (60 kg) and of different average seafood consumption of 0.163 kg/day, a lower TARL value (92 ng/g wet wt) for TBT in Taiwan was provided by Belfroid et al. 2000.

Current research data further indicates highly contrasting results with some samples showing OTCs below

Table 2 Levels of OTCs (ng/g dry weight) with standard deviations for eight fish species

Specie	Common name	n	Length (cm)	Weight (g)	Lipid (%)	DBT	MBT	TPT	DPT	MPT	ΣBT	ΣPT
Scarus ghabon	Bluebarred parrot fish	7	36.6–71.6	357.8–565.6	2.1–3.4	62.7 ± 11.2	36.5 ± 17.4	89.9 ± 12.3	45.5 ± 13.8	106.3 ± 18.3	172.4	241.7
			51.2 ± 14.2	560.4 ± 32.2	2.4 ± 0.2							
Epinephelus microdon	Grouper	5	35.4–48.4	357.9–778.9	0.9–2.3	34.7 ± 8.5	25.3 ± 11.3	67.4 ± 32.4	63.8 ± 17.8	72.4 ± 17.3	147.9	203.6
			37.6 ± 11.8	418.5 ± 78.9	1.3 ± 0.7							
Epinephelus coioides	Orange spotted grouper	8	43.7–51.0	420.7–679.6	0.3–3.1	77.3 ± 21.7	31.8 ± 3.8	86.9 ± 43.9	77.3 ± 18.9	107.3 ± 16.3	165.8	271.5
			49.2 ± 10.3	544.8 ± 65.6	1.7 ± 0.3							
Epinephelus tauvina	Greasy grouper	9	42.9–55.3	515.7–657.3	1.3–3.2	59.5 ± 30.7	12.7 ± 2.7	73.8 ± 8.2	84.5 ± 10.3	123.6 ± 15.3	170.7	281.9
			45.9 ± 12.0	585.7 ± 88.9	2.1 ± 0.6							
Acanthoparagus bifasciatus	Doublebar bream	5	25.8–42.6	267.8–378.5	1.7–3.2	38.8 ± 14.7	43.9 ± 21.6	64.9 ± 12.4	98.4 ± 7.3	118.4 ± 36.2	126.4	281.7
			37.9 ± 14.3	320.5 ± 56.6	1.8 ± 0.3							
Siganus canaliculatus	Rabbit fish	7	15.1–19.0	93.2–318.7	1.2–2.7	38.6 ± 12.9	45.9 ± 13.0	94.7 ± 8.4	91.5 ± 13.7	95.2 ± 18.6	137.2	281.4
			14.2 ± 1.8	123.5 ± 36.3	1.8 ± 0.2							
Lethrinus miniatus	Emperors	6	25.4–30.9	228.7–265.9	0.9–2.3	76.8 ± 5.9	84.7 ± 12.5	107.5 ± 13.7	84.8 ± 11.4	56.9 ± 13.2	228.4	249.2
			26.7 ± 5.2	245.6 ± 34.6	1.6 ± 0.6							
Lethrinus nebulosus	Spangled emperor	7	21.6–32.4	198.6–245.8	0.8–1.8	36.9 ± 16.7	85.9 ± 5.9	84.1 ± 8.4	69.5 ± 9.2	72.7 ± 12.8	211.7	226.3
			25.3 ± 5.1	220.2 ± 19.6	0.9 ± 0.7							

n sample number

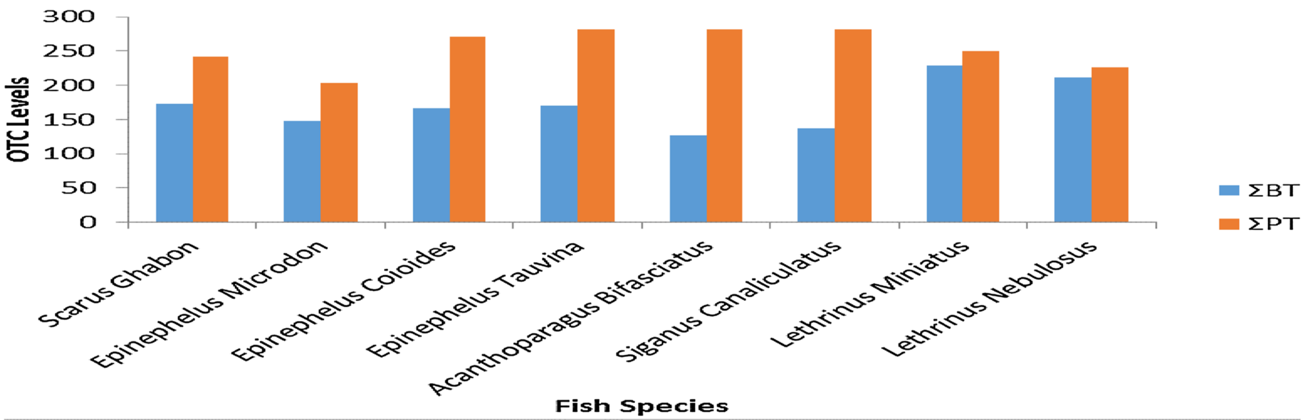

Fig. 1 Cummulative levels of BTs and PTs in eight fish species

Table 3 Estimated daily intake (EDI) values for eight fish species

Specie	Common name	ΣOTC	Consumption (g/day)	Estimated daily intake (ng/kg bw/day)
Scarus ghabon	Bluebarred parrot fish	414.1	1.5	9.56
Epinephelus microdon	Grouper	351.5	2	10.8
Epinephelus coioides	Orange spotted grouper	437.3	1.3	8.7
Epinephelus tauvina	Greasy grouper	452.6	0.85	5.9
Acanthoparagus bifasciatus	Doublebar bream	408.1	0.9	5.6
Siganus canaliculatus	Rabbit fish	418.6	1.5	9.6
Lethrinus miniatus	Emperors	477.6	0.95	6.9
Lethrinus nebulosus	Spangled emperor	438	1.2	8.1

Table 4 Concentrations of OTCs (ng/g dry weight) in the muscles of different fish from different parts of the world

TBT	DBT	MBT	TPT	DPT	MPT	ΣBTs	ΣPTs	Species/ref.	Sampling site
17	3	<3	<5	<3	–	20	–	Bream (Ruedel et al. 2007)	Rhine Bimmen, 2003
29.6	5.1	3.1	<0.3	n.d.	n.d.	37.8		Sardine (Santos et al. 2009)	Market North Portugal
76	2.3	–	151	14	–	79.3	–	Perch (Rantakokko et al. 2010)	Sipoo, Baltic Sea
16.50 ± 5.5	78.65 ± 8.5	70.25 ± 5.5	50.25 ± 2	17.10 ± 1	6.05 ± 0.2	75.75 ± 81	52.25 ± 3	Croaker (Jadhav et al. 2011)	Karwar, India
129.7	77.9	141.5	477.3	380.5	172.3	349.1	1030	Narrow barred (Lee et al. 2005)	Taiwan

detection limit, whereas others contained OTCs up to several hundred ng/g (Table 4). This variation in the OTC levels can be attributed to species specific differences such as accumulation and metabolism ability. Differences in habitat contamination also play a role in accumulation. In conclusion, levels of OTCs in muscle tissue of the fish in Saudi market during this study are in the lower range as compared to reports for the same fish group from other parts of the world.

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