LEVELS OF PCDD/Fs IN IMPORTED FISH IN EGYPT

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Introduction

Fish and fisheries products are known to be a significant source of dietary exposure to a number of environmental contaminants including dioxins. A programe for inspection and monitoring dioxins in food and feed from animal origin had been started in Egypt since 1999. A total number of 295 from fish were collected during 2007 were studied. The collected samples represented the common consumed fish in Egypt. All samples are subjected for polychlorinated dibenzo-*p*-dioxin (PCDDs) and polychlorinated dibenzofuran (PCDFs) residue analysis. The method of analysis was accredited by the Finnish Accreditation Services (FINAS) since 2001according to the ISO/IEC 17025:2005 under code (DXN, T219). The results demonstrated that the concentration of dioxins in all imported fish not exceeded the maximum level proposed by the Egyptian organization for standardization (4pg/g fresh weight). Herring samples showed the highest contamination level ranged between (0.21–3.6 pg I-TEQ/g fresh weights). Whereas, the squid showed the lowest level ranged between (0.3–0.6 pg I-TEQ/g fresh weight). PCDDs/Fs profile was studied in all samples in order to detect the pattern of the dioxins congeners in different fish species. The most contributed isomer to the total PCDD/Fs was 2,3,7,8 TCDF In Herring, Horse mackerel and Salmon. Whereas 1,2,3,7,8-PeCDF the most contributed isomer for sardine silver smelt. This study high lighted the level of dioxins in imported fish which considerably contribute to the total daily intake of PCDD/PCDFs of the Egyptian population. Moreover, the results of this study will be very useful for comparing the PCDD/Fs pattern with other locally produced fish to detect the source of dioxins in aqua media. On the other hand the results of this study will be also useful for conducting a national total diet studies TDS for dioxins in Egyptian food.

Materials and Methods

Sampling. procedure follows the European Commission regulation[1] (EC) No 1883/2006 which lays down the official sampling methods. Only the fish edible parts with its skin were analyzed as it is commonly eaten. The analytical method based on EPA1613 with in-house modifications[2]. All samples are subjected for homogenization prior to the extraction.

Extraction. 10 g are subjected for extraction using Soxhlet after mixing the homogenized sample with anhydrous sodium sulfate, ^{13}C-labelled internal standards compounds was spiked, dichloromethane: hexane (1:1) were used for extraction, samples were extracted for 18-24 hours. The extract was evaporated to dryness, and the lipid content was determined.

Clean- up column chromatography steps using silica gel, alumina and active carbon were used based on the method described in reference[2].
HRGC/HRMS analyses were conducted using HP 6890 plus gas chromatograph coupled to a Micromass Autospec Ultima mass spectrometer operating in EI mode at 35 eV and with a resolution of 10.000 (5% valley). Sample injections were performed in the splitless mode on DB5 MS column (60 m, 0.25 mm id, 0.1 µm film thickness). The oven program temperature was 190 ^{o}C (hold for 1 min. increased at 15 ^{o}C /min. to 220 ^{o}C and increase at 3 ^{o}C / min to 270 ^{o}C then held for 3 min.). Helium at a flow rate 0.8 ml/min was used as a carrier gas. Injector temperature was 225 ^{o}C; 1 ul of the sample was injected using splitless mode.
Quantitative determination of PCDDs/PCDFs was performed by an isotope dilution method using relative response factors previously obtained from five standard solutions. The TEQ concentrations were calculated using the WHO-TEFs (1998). The result values are presented in pg WHO-TEQ/g fresh weight (fw). It was assumed that non-detected isomer concentrations were equal to the limits of determination. For each run the samples were prepared including a method blank and quality control samples are performed.

Results and Discussion
Table (1) shows the summary of the results obtained from the analysis of total 295 fish samples collected from different Egyptian ports during 2007. It has been shown that the continuous monitoring of the PCDDs and PCDFs content of fish coming from other countries for local consumption is an indispensable process.
The results provide simultaneous determination of PCDDs and PCDFs in fish. The contamination levels were calculated as I-TEQ (Toxic equivalent) values by multiplying with corresponding WHO-TEF (Toxic Equivalency factor) for each congener. The results demonstrated that the concentration of dioxins in all imported fish not exceeded the maximum level proposed by the Egyptian organization for standardization. Herring samples showed the highest contamination level ranged between (0.21–3.6 pg I-TEQ/g fresh weights) see table (1). The 2,3,7,8 TCDF was the most contributed isomer to the total TCDD/Fs followed by OCDF then 1,2,3,7,8 PeCDF as shown in Fig (2). Whereas, the squid showed the lowest level ranged between (0.3–0.6 pg I-TEQ/g fresh weight). Same pattern also observed for the Horse Mackerel samples which are agreed that most of both types of fish had been fished from the same source. On the other hand 1,2,3,7,8-PeCDF the most contributed isomer in sardine and silver smelt. For the others types of fish profiles see (Fig 3,4 and 5).
This study high lighted the level of dioxins in imported fish which considerably contribute to the total daily intake of PCDD/PCDFs of the Egyptian population. Moreover, the results of this study will be very useful for comparing the PCDD/Fs pattern with other locally produced fish to detect the source of dioxins in aqua media. On the other hand the results of this study will be also useful for conducting a national total diet studies TDS for dioxins in Egyptian food.

Acknowledgments
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Reference

1. European Commission (2006). Commission Regulation No 1883/2006/EC laying down the sampling methods and the methods of analysis for the official control of dioxins and the determination of dioxin-like PCBs in foodstuffs. *Official Journal of the European Union* L 364/32.
2. US EPA Method 1613: Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, 1994, Revision B, EPA 821-B-94-005

Tables and Figures

Table (1) Summary for PCDD/Fs results

Types tested	No of samples	∑ PCDDs/Fs (pgTEQ/g fresh weight)	
		Mean	Concentration Range
Herring	64	1.29	0.21-3.6
Horse Mackerel	120	0.93775	0.21-2.75
Red Mullet	27	0.975556	0.08-2.61
Salmon	46	1.022826	0.15-2.84
Sardine	8	0.8475	0.14-2.32
Silver Smelt	25	0.938	0.21-2.11
Squid	5	0.334	0.1-0.68

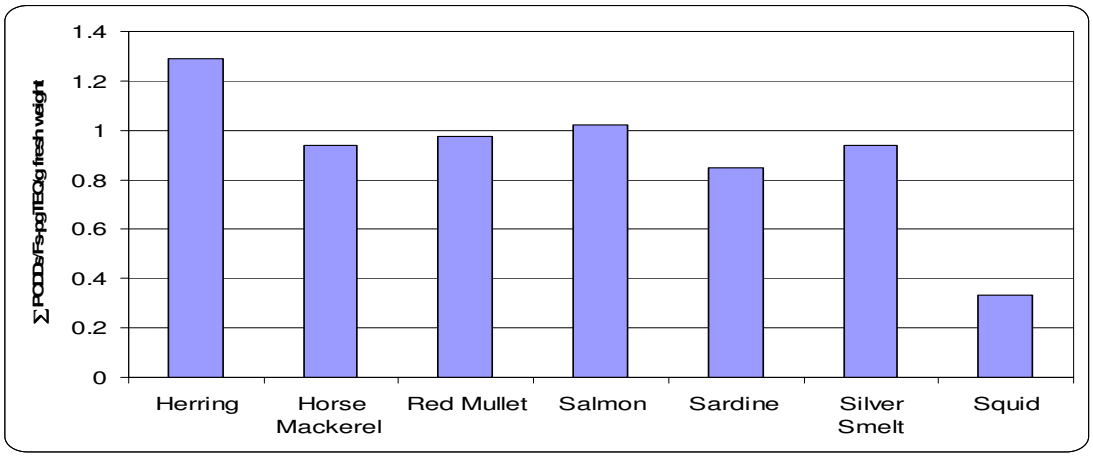

Figure (1) Sum of PCDD/Fs pg-TEQ/g fresh weight

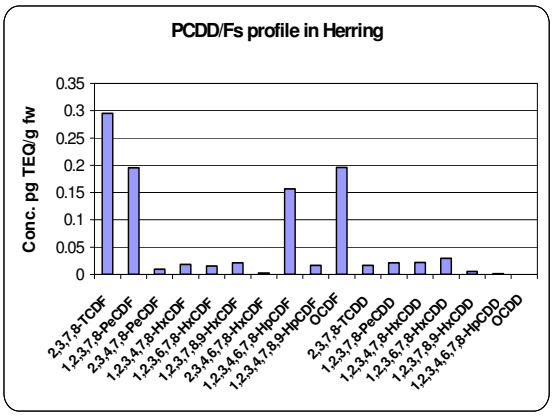

Figure (2) PCDD/Fs pattern in Herring fish

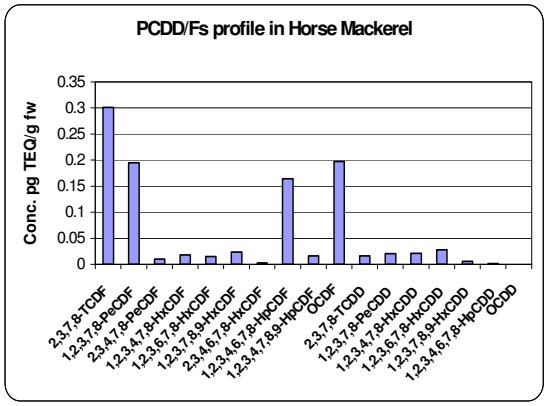

Figure (3) PCDD/Fs pattern in Horse Mackerel

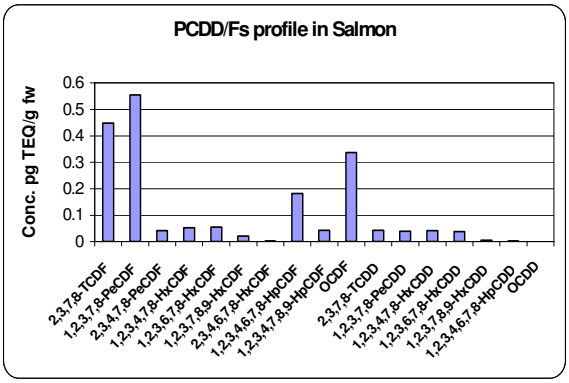

Figure (4) PCDD/Fs pattern in Salmon fish

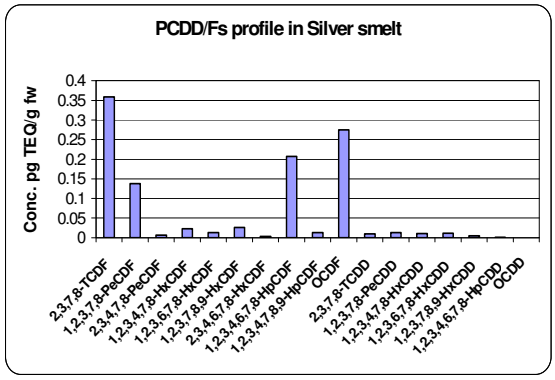

Figure (5) PCDD/Fs pattern in Sliver smelt fish