PCB, PCDD AND PCDF RESIDUES IN SEDIMENTS AND FISH OF THE RIVER NILE IN THE CAIRO REGION, EGYPT

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Introduction

PCBs, PCDDs and PCDFs are halogenated aromatic compounds that have been identified as contaminants in almost all components of the global ecosystem including air, aquatic and marine sediments, fish, wildlife and human adipose tissue, milk and blood[1]. Due to their great chemical stability, their lipid solubility, and their ubiquitous prevalence in environment, organochlorine pesticides, polychlorinated biphenyls (PCBs) constitute what is called Persistent Organic Pollutants (POPs)[2]. Commercial PCB mixtures have been used in a wide variety of applications, including dielectric fluids in capacitors and transformers, heat transfer fluids, hydraulic fluids, lubricating and cutting oils, and as additives in pesticides, paints, copying paper, carbonless copy paper, adhesives, sealants, and plastics[3]. In contrast, PCDD/Fs are industrial by-products that are formed during the production of chlorinated phenols and their derived products, PCBs and other chlorinated organic compounds, as well as during the bleaching of wood and pulp paper[2]. Also incineration is an important source for PCDD/F.

Human chronic exposure to these highly lipophilic and persistent compounds via food chain has led to the accumulation of both parent compounds and their metabolites in lipid rich tissues such as adipose tissues and human breast milk[4]. One of the main sources of these compounds is dietary fish, which accumulate such compounds by direct absorption through the gills, and by ingesting contaminated sediments, insects and smaller fish[5]. Although the use of PCBs in Egypt as well as other countries is banned currently, the past use of these substances in transformers, electrical equipment, ship painting and other industrial was common[6]; furthermore, no available data have been performed on PCDD/Fs in Egypt[7]. The current work aimed to assess PCBs and dioxins in sediment and fish samples along the River Nile near the industrial areas of Greater Cairo.

Material and Methods

Thirty-six sediment samples were collected monthly during a period of one year, from Feb. 2003 to Feb. 2004 from the River Nile in Greater Cairo from three sites, namely Helwan, Rod El-Farag, and Shobra El-Khyma (sites were chosen near suspected sources of agricultural or industrial pollution). Eighteen fish samples "*Oreochromis niloticus*" were fished from four locations along the River Nile as follows: 7 samples from Helwan; 1 sample from Rod El- Farag; 5 samples from Shobra El-Khyma and 5 samples from El- Qanater El-Khayria sites. Fish samples were collected during 2002-2004. All free tissue from different fish samples was pooled into one sample. The pooled fish muscle samples were homogenized and then freeze dried using Dura-Dry Freeze Dryer.

Extraction and clean-up of PCBs and PCDD/Fs was following the method described by Roots[8]. The instrumental analysis was performed with a high-resolution mass spectrometer Finnigan MAT 95S (Thermo Electron GmbH, Bremen, Germany) coupled with an Agilent GC 6890 (Agilent Technologies, Palo Alto, CA, USA) according to[9, 10].

Statistical analysis

All data were subjected to statistical analyses using Statistical Analysis System[11]. The significance of the differences among treatment groups with variable means was determined by Waller-Duncan k-ratio T test[13] using a probability level of $P \leq 0.05$.

Results and Discussions

Polychlorinated biphenyls (PCBs)

PCBs were classified into three categories (indicator PCBs, non-*ortho* and mono-*ortho*): the first category consisted of 6 congeners that are predominantly present in most PCB mixtures and in environmental samples as stated by[13] and they included these 6 congeners: #28, #52, #101, #138, #153 and #180. The second category consisted of the non-*ortho* PCBs: #77, #81, #126, #169, whereas the third category included the mono-*ortho* PCBs: #105, #114, #118, #123, #156, #157, #167 and #189. The results in Table 1 present the concentration levels of the individual PCB congeners in the sediment samples. PCB congeners were observed in 100 % of the investigated sediment samples at the three tested sites, except for PCB #169 which was not detected in only one sample from the Helwan site and one from the Rod El-Farag site; and for PCB #123 which was not detected in five samples, two from Helwan, one from Rod El-Farag, and two from Shobra El-Khyma. The most abundant PCB congeners were found as the indicator PCBs constituting 88.6-90.5 % of the total amount of PCBs at the three sites, however PCB #28 represented 25.9%, 30.8% and 45.4 % of the total amount of the indicator PCB congeners in Helwan, Rod El-Farag and Shobra El-Khyma sites, respectively. These results also indicated that the most abundant PCB congeners of the non-*ortho* and mono-*ortho* PCBs were PCB #77 and #118, comprising up to 78.1% and 54.7 % of the total amount of non-*ortho* and mono-*ortho* PCBs, respectively.

Sediment samples collected from Helwan contained relatively higher concentrations of the investigated PCBs, mean level of congeners analyzed is of 2244 pg/g dry wt., and the lowest concentrations of PCBs were found in Rod El-Farag with mean levels of 1461 pg/g dry wt.. The mean concentration of the sum of PCBs analyzed in Shobra El-Khyma was 2099 pg/g dry wt. The current results indicated that the mean concentrations of total PCB congeners in Helwan and Shobra El-Khyma was significantly higher compared to Rod El-Farag samples, while there was no significant difference between Helwan and Shobra El-Khyma sites. Barakat[6] reported that the median of 99 individual PCB concentrations in 23 sediment samples collected from the Alexandria Harbor, Egypt was 260 ng/g dry wt. In the same way, Fernandez[14] analyzed sediment samples from 13 sites along the Ebro River (Spain), sampled during October 1995, for 13 PCB congeners and reported that the concentrations of total PCBs ranged between 5.28 and 27.9 µg/kg dry wt. The current results clearly indicated that the concentrations of PCBs reported herein were markedly lower than those reported earlier[7,15]. Moreover, Sapozhnikova[15] found higher concentrations (116-304 ng/g dry wt.) of 55 PCB congeners in sediment samples collected in May 2000 and May 2001 from Salton Sea, USA.

Table 1 shows that the indicator PCB congener concentrations were higher than the non-*ortho* and mono-*ortho* PCB concentrations. The indicator PCBs account for ca. 50% of the commercial mixtures of PCB[13]. Moreover, the results of Gardinali[16] supported our findings and suggested that the non-*ortho* PCB congeners are usually present in lower concentrations than other PCB congeners.

Regarding the total PCB concentration levels at the different sites under investigation it clearly indicated that the mean concentration levels of total PCB congeners in Helwan were higher than in the other two sites (Rod El-Farag and Shobra El-Khyma). These results may be due to the presence of a large industrial area in Helwan where the factories discharge their wastes into the River Nile[17]. Beside there are cement factories which use PCBs as dedusting agents and may discharge these wastes into the River Nile. Concentrations at Rod El-Farag site were decreased (Table 1). In this regard, the evaporation, chemical and biological degradation, adsorption on suspended matter and sediments, dilution, and transportation factors may contribute to the observed decline in residue levels[18]. On the other hand, our results indicated that the residue concentrations of total PCBs increased again in Shobra El-Khyma site and this may be due to the electrical power station located there which discharges wastes in the River Nile.

The results for the concentration levels of PCB congeners in fish samples are depicted in Table 2. These results indicated that all PCB congeners investigated were found in all fish samples from the four observed sites, except PCB #169 which was not detected in 3 fish samples collected from Helwan and 4 fish samples collected from El-Qanater. These results were found to be in the same trend as the sediment samples. The most abundant PCB congeners in fish were the indicator PCBs which constituted 83.6-91.6% of the total amount of PCBs in the four sites. The results illustrated that the most abundant PCB congener of the indicator PCBs was PCB #28 which represented 48.1%, 55.4%, 61.1% and 28.0% in Helwan, Shobra El-Khyma, El-Qanater and Rod El-Farag, respectively. However, PCB #77 was the most abundant of the non-*ortho* PCBs, constituting 49.2–89.0% of the total amount of non- *ortho* PCBs. Similarly PCB #118 comprised up to 57.2% of the total amount of mono-*ortho* PCBs. Moreover, our data indicated that there were insignificant differences in total PCBs in fish collected from

Helwan, Shobra El-Khyma and El-Qanater sites, whereas fish collected from the El-Qanater site were found to contain lower concentrations of non-*ortho* and mono-*ortho* PCB congeners compared with the two other sites. In general, the mean concentration levels of total PCB congeners were 817, 853 and 695 pg/g fresh wt. for Helwan, Shobra El-Khyma and El-Qanater sites, respectively, whereas the one fish sample collected from Rod El-Farag site contained the highest PCB concentrations (1377 pg/g fresh wt). The available data showed that different fish species (*Mugil*, *T. nilotica* and C. *Lazero*) in the River Nile and Delta Lakes contained concentrations below the low end of the maximum residue limits (MRL)[19]. Whereas high concentrations of Aroclor 1248 (180-227 ng/g wet wt.) and ∑6 congeners (26-90 ng/g wet wt.) were found in fish samples located at the El-Max and Abu-Quir coast of the Mediterranean Sea[20, 21]. Furthermore, 7 indicator PCB congeners were determined in mussels collected during April 2000 from 11 sites at the Egyptian Red Sea Coast and the reported concentration levels ranged from 6.75 to 66.4 ng/g wet weight, which were 10-53 fold greater than the concentrations of the 7 PCB congeners reported in the current study in the fish samples[22]. These reported concentrations of PCBs in the coastal area of the Mediterranean and Red Sea areas are higher than our finding in the River Nile, which were below the limits set by the US FDA[23] (2 μg/g wet wt.) and fall within the limits set by Egyptian Standards, 1993 (1 μg/g wet wt. for total PCBs in fish).

Table 1: Mean concentrations (pg/g dry wt., Mean ± SD) of PCBs congeners and PCDD/Fs in sediment samples.

	Helwan	RodEl-Farag	Shobra El-Khyma
Sum of indicator PCBs	1987^{a}±384	1306^{a}±190	1900^{a}±419
Sum of non-*ortho* PCBs	26.0^{a}±2.78	16.3^{a}±2.94	26.0^{a}±4.67
Sum of mono-*ortho* PCBs	230^{a}±34.7	139^{b}±22.3	173^{ab}±31.5
Total PCBs	**2244^{a}±606**	**1461^{b}±211**	**2099^{ab}±446**
TEQ*	0.23 – 1.3	0.12 – 0.28	0.08 – 0.51
Sum Tetra- to Octa-chlorodibenzo-p-dioxins	14.5^{a} ± 13.9	82.3^{b} ± 7.89	115^{ab} ± 14.4
Sum Tetra- to Octa-chlorodibenzofurans	630^{a} ± 112	157^{b} ± 18.6	315^{b} ± 65.5
Total **sum PCDD and PCDF (Tetra to Octa)**	**775^{a} ± 123**	**240^{b} ± 25.4**	**430^{b} ± 72.1**
TEQ*	5.7 – 38.1	1.8 – 6.4	1.8 – 11.2

Within each row, means superscript with different letters are significantly different ($p< 0.05$); n= 12 samples
*(Humans, WHO, 1998)

Table 2: Concentrations (Mean ± SD) of PCBs (pg/g fresh wt.) congeners and PCDD/F (pg/g lipid) in Tilapia fish samples

	Helwan (n=7)	Shobra El-Khyma (n=5)	El-Qanater (n=5)	RodEl-Farag (n=1)
Sum of indicator PCBs	683^{a}±89.1	754^{a}±54.5	636^{a}±106	1159
Sum of non-*ortho* PCBs	16.7^{a}±2.45	13.8^{a}±1.68	7.39^{b}±1.34	11.8
Sum of mono-*ortho* PCBs	117^{a}±23.5	84.6^{ab}±18.5	51.1^{b}±8.74	206
Total PCBs	**817^{a}±110**	**853^{a}±54.6**	**695^{a}±113**	**1377**
TEQ*	2.8 – 14.6	1.1-7.5	0.42 – 3.7	14.9
Sum of PCDDs	16.2^{a}± 3.24	12.2^{ab} ± 3.07	6.09^{b} ± 3.32	3.30
Sum of PCDFs	105^{a} ± 16.0	42.8^{b} ± 12.1	21.6^{b} ± 5.05	110
Sum of PCDD/Fs	**121^{a} ± 14.7**	**55.1^{b} ± 10.7**	**27.7^{b} ± 6.57**	**113**
TEQ*	8.0 – 27.1	2.9 - 14.4	2.0 - 7.4	19.5

Within each row, means superscript with different letters are significantly different ($p< 0.05$).
*(Humans, WHO, 1998); n= number of samples

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs)

The concentration levels of total sum PCDD/Fs (tetra to octa) in sediment samples are depicted in Table 1, those for the fish samples in Table 2.

It clearly indicated that the PCDDs:PCDFs ratio showed a pre-dominance of PCDFs in all sediment samples which represented 81.3%, 65.6% and 73.2 % of the total amount of PCDD/Fs at the Helwan, RodEl-Farag and Shobra El-Khyma sites, respectively. The concentration levels of total sum PCDD/Fs (tetra to octa) which were found in Helwan were relatively higher than the other two sites and ranged from 295 to 1806 pg/g dry wt., an

intermediate concentration level was found in Shobra El-Khyma ranging from 114 to 1078 pg/g dry wt. and the lowest concentration level was found in RodEl-Farag ranging from 140 to 423 pg/g dry wt.. These results indicated that the differences in total PCDD/Fs concentrations between the three tested sites were significantly different ($p< 0.05$). Regarding the sum of polychlorinated dibenzofurans (PCDFs) in fish samples, it was found that it constituted 77.2-87.0% of the total sum of PCDD/Fs in all fish samples collected from different sites except the one fish sample collected from RodEl-Farag which was found to be 97.0% of the total concentration of PCDD/Fs (Table 2). The mean concentrations of total sum PCDD/Fs in fish samples were highest in the Helwan samples (121 pg/g lipid) followed by the RodEl-Farag sample (113 pg/g lipid; one sample) followed by the Shobra El-Khyma samples (55.1 pg/g lipid), whereas the El-Qanater sample was found to contain the lowest concentration (27.7 pg/g lipid). In this regard, no measurements had been performed on PCDD/Fs in Egypt until now[7]. The presence of PCDD/Fs in the aquatic environment may be due to some commercial formulations of DDT which once contained toxic impurities including PCDD/Fs[15]. On the other hand, the occurrence of dioxins in the aquatic environment in the River Nile may be due to the extensive use of HCB pesticides which have well known low levels of dioxin-like activity (ca. 0.0001- 0.001 relative to 2,3,7,8- TCDD[24,25]).

Conclusions

The data of the current study revealed that the concentrations of PCBs and dioxins in the aquatic environment in the River Nile, Egypt were markedly lower than those reported previously for the River Nile, the Mediterranean Sea and Red Sea coasts as well as those reported for other aquatic environments allover the world. The data also suggested that there is no risk for humans in consumption of River Nile water and fish regarding the PCBs and PCDD/Fs levels.

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