Study Of The Chemical Pollution Of The Fish And Water Of The Drainage Ponds Of The 10th Ramadan City

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ABSTRACT

The drainage and oxidizing ponds of 10th Ramadan city, Egypt which carry its industrial and sewage effluents were used by unknown persons for fish implantation. The present study was conducted for evaluation the degree of the risk of this fish upon the public health. Forty water and Nile Tilapia (*Oreochromis niloticus*) fish samples (20 for each) were collected from 10th Ramadan city ponds during spring 2009 for detection and determination of 11 Polychlorinated biphenyls (PCBs) congeners [PCB 28(2,4,4´), PCB44 (2,2´,3,5´), PCB52 (2,2´,5,5´), PCB70 (2,3´,4´,5), PCB101 (2,2´,4,5,5´), PCB105 (2,3,3´,4,4´), PCB 118 (2,3´,4,4´,5), PCB138 (2,2´,3,4,4´,5), PCB152 (2,2´,3,5,6,6´), PCB180 (2,2´,3,4,4´,5,5´) and PCB192 (2,3,3´,4,5,5´,6)] and seven heavy metal residues (lead, cadmium, arsenic, manganese zinc, copper and iron) in the mentioned water and fish samples.

The obtained results revealed that the levels of the estimated PCBs and heavy metals recorded high expected concentrations; PCBs residues exceeded the permissible limits in some samples, while; the examined heavy metals were above the permissible limits in all the examined samples. The public health importance of the contaminated compounds was discussed.

INTRODUCTION

10th Ramadan city was located in Sharkia Governorate at north east of Cairo. It is one of the largest industrial cities in Egypt, and contained different plants in the various industrial activities and consequently, it had a large number of populations. Thus, this city produced large quantity of both industrial drain and sewage effluents. These effluents collected in large drainage and oxidation ponds located near this city. Some unknown peoples for illegal exploiting the wide distance of the drainage ponds, implanted different types of fish especially tilapia fish. Axiomatically, if these fishes arrive to the markets, the consumers exposed to serious unlimited health hazardous. In spite of governmental authorities exerted extreme efforts to prohibit this fish from marketing, the risk still exist if the fish still in these ponds. This problem get great attention of the Egyptian media during spring 2009.

In the present study, we succeed to arrive to the drainage ponds of 10th Ramadan city and collected fish and water samples for assessment of polychlorinated biphenyls (PCBs) and heavy metal residues which are the most expected pollutants from both industrial and sewage effluents in the collected samples

Polychlorinated biphenyls (PCBs) belong to a broad family of man-made organic chemicals. PCBs were domestically manufactured from 1929 until their manufacture was banned in 1979. They consist of 209 compounds. have a range of toxicity and vary in consistency from thin, light-colored liquids to yellow or black waxy solids. Furthermore, these compounds are long persistence in the environment and enrichment in food chain *(1)*. Due to their non-flammability, chemical stability, high boiling point, and electrical insulating properties. PCBs were used in hundreds of industrial and commercial applications including electrical, heat transfer, and hydraulic equipment; as plasticizers in paints, plastics, and rubber products; in pigments, dyes, and carbonless copy paper; and many other industrial applications *(2)*. Today PCBs can still be released into the environment from poorly maintained hazardous waste sites that contain PCBs, improper dumping of PCB wastes; leaks or releases from electrical transformers containing PCBs; and disposal of PCB-containing consumer products into municipal or other landfills not designed to handle hazardous waste. PCBs may also be released into the environment by the burning of some wastes in municipal and industrial incinerators *(2)*

Heavy metals are natural components of the Earth's crust. They can not be degraded or destroyed and had low rate of elimination from the consumer body *(3)*. They enter the human and animal bodies via food, drinking water and air. Some heavy metals as copper, iron, manganese and zinc are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. On the other hand, other heavy metals as cadmium, lead and arsenic are non essential for human and animal bodies. Thus, their existence means occurrence of pollution.

Many previous Egyptian studies detected considerable levels of PCBs and heavy metals in fish tissues and water *(4-6)*. Therefore, assessment of these chemical pollutants in water and fish in drainage ponds of 10th Ramadan city is suitable for evaluation of degree of contamination the examined ponds.

MATERIAL AND METHODS

Forty water and Nile Tilapia (*Oreochromis niloticus*) fish samples (20 for each) were collected from 10th Ramadan city ponds during spring 2009 for detection and determination of 11 Polychlorinated biphenyls (PCBs) congeners [PCB 28(2,4,4′), PCB44 (2,2′,3,5), PCB52 (2,2′,5,5′), PCB70 (2,3′,4′,5), PCB101 (2,2′,4,5,5′), PCB105 (2,3,3′,4,4′), PCB 118 (2,3′,4,4′,5), PCB138 (2,2′,3,4,4′,5), PCB152 (2,2′,3,5,6,6′), PCB180 (2,2′,3,4,4′,5,5′) and PCB192 (2,3,3′,4,5,5′,6)] and seven heavy metal residues (lead, cadmium, arsenic, manganese zinc, copper and iron) in the mentioned water and fish samples.

I. Collection of samples

A. Collection of water samples

Twenty water samples were collected from different locations of drainage ponds. Amount of each sample was 2 liter, one liter used for PCBs detection and the other one used for heavy metal estimation. The water samples were identified and kept in refrigerator till the analysis was carried out.

B. Collection of fish samples

Twenty tilapia fish samples were taken and each one placed in polyethylene bags. The samples were identified and kept frozen till the analysis was carried out.

II. Analysis of the samples for detection of the chemical pollutants

A. Preparation and extraction of samples for detection of PCBs

1. Extraction and preparation of water samples

One liter of each examined water samples was transferred into 2 liter separatory funnel. Then 10 ml of saturated sodium chloride solution was added to the sample and extracted three times using 60 ml. of 15% methylen chloride in hexane. The combined extract were dried through anhydrous sodium sulphate layer and collected in 500 ml flask, the flask was then evaporated using rotary evaporator at 40°C. until dryness *(7)*.

The clean up of the water samples was conducted *(8)*.

2. Extraction and preparation and of fish samples

Exactly 20 gm of the each examined fish tissue samples were homogenized with 20 gm of anhydrous sodium sulfate with tissue homogenizer till have a fine homogenate. The homogenate was extracted with 100 ml of n-hexane: acetone (2:1). Extraction was carried out using orbital shaker for 2 hours, and then the extract was filtered through anhydrous sodium sulphate and evaporated till dryness at 40°C *(9)*.

Partitioning technique performed to remove the dissolved fat from the extract ***(10)***.

3. Clean up of fish samples

Sample extracts applied to chromatography column in 2-3 ml of hexane and eluted successively with hexane florisil (60/100 mesh) activated at 250 °C for 12-15 hours, placed in a desiccator until cool, deactivated with 0.5% H_2O, stored in a sealed container in a desiccator overnight, and then used within 72h. Columns were rinsed with 100 ml hexane collecting eluant in beaker. Stop the flow before the top of solvent reaches the top of sodium sulfate. The eluant into discarded waste container. Samples extracts were applied to the column in 2-3 hexane, elute the column with 60ml hexane, to elute the polychlorinated biphenyls (PCBs) collecting eluant in the 100 ml flask and reduce to 0.5ml *(5)*.

4.Preparation of blank solution

The same volumes of solvents (n-hexane-methylen chloride) used for water extraction or (hexane – acetone) used for tissue extraction and sodium sulfate anhydrous were subjected to the same extraction, partitioning and clean up procedures as mentioned in the examined samples to detect any possible traces of the studies PCBs in the solvents or distilled water.

5.Gas chromatographic analysis

At Pesticide Residue Department, Central Pesticide Laboratory, Hewlett Packard GC Model 6890 equipped with Ni^{63} – electron capture detector. GC conditions: HP- 5MS capillary column (30m length X 0.32mm internal diameter (i.d..), X 0.25μm film thickness), carrier gas: N_2 at a flow rate of 4 ml/min; injector and detector temperatures were 230°C and 300°C respectively. The initial column temperature was initial oven temperature, 180°C for 2 min, raised at 3 °C/min. and then held at 220°C for 1 min., then raised at 9°C /min. to 280°C and then held to 2 minutes, until a total time of 30 minutes had elapsed, DB-17 (J & scientific) capillary column (30m length X 0.32mm initial diameter (i.d.) X25 μm film thickness). Operating temperature were: column temperature was programmed 160°C to 230°C at a rate of 3°C /min. to 260°C at a rate 10°C then hold 10 minutes. Injector temperature were 280°C and detector temperature was 300°C with nitrogen carrier gas flow at 4 ml./ min was used to confirm the detected PCBs.

The PCBs residue components were identified by comparing their retention times with those of the standards quantified by extrapolation of corresponding sample peak areas with those from standard curves prepared for each PCB standard. Small variations in retention times and response factors of each compound during the experiments were corrected by obtaining fresh chromatograms of the standard mixture after every nine injections. Standard solutions of concentrations ranging from 0.01 to 0.04 ppm were prepared for each PCB standard and 1μl was injected into the GC. Peak areas of standard solutions were plotted against their concentrations. A line of best fit was drawn through the point and the limits of detection were taken at 5 times the detector noise level.

5. Determination of percentage rate of recovery

The reliability of analytical method was examined by fortifying the tested samples with known quantities of tested PCBs following the same procedures of extraction, partitioning, clean up and analysis. The percentage rate of recovery of PCBs varied from 84.65% to 99.98% for PCB28 and PCB138 respectively.

B.Preparation and extraction of samples for detection of heavy metals

1.Preparation of water samples for detection of heavy metals

One liter of each examined water samples was filtered through 0.45 μm Watman membrane filter and acidified by addition of 3 ml of aqueous solution of nitric acid (1:1) per liter of water. All samples were stored at 4°C until analysis *(11)*.

2. Preparation of fish samples for detection of heavy metals

Preparation and digestion of samples

The examined samples were prepared according to the described method *(12)*. One gram of each examined fish samples was transferred to a clean screw capped glass bottle and digested with 10 ml of digesting solution (nitric acid/ perchloric acid 4:1). Initial digestion was conducted for 4 hours at room temperature, followed by heating at 40-45°C for one hour in water bath, then temperature raised to 75°C until the end of digestion. After cooling at room temperature, the digest was dilute to 20ml. with deionized water and filtered through 0.45µm Whatman filter paper. The filtrate was kept in refrigerator till analysis was carried out.

Preparation of blank solution

Ten ml. solution of nitric/ perchloric acid (4:1) were put in a screw capped glass bottle and exposed to the same digestion, dilution and filtration procedures as previously described in preparation of fish samples to detect any traces of studied metals in acids or deionized water.

3.Quantitative determination of the examined metal residues

Quantitative determination of lead, cadmium, arsenic, manganese, zinc, copper and iron residues were conducted using Jhermo Jarrell Ash Atomic Absorption Spectrophotometer, in Central Pesticide Laboratory. The concentrations of metal (ppm) in the examined water samples were reading directly from the digital scale reading. Meanwhile, tissue samples were calculated according the following equation:

Concentration of metal in samples= AXB÷W, where A= metal concentration (ppm) in the prepared samples from the digital scale reading of Atomic Absorption Spectrophotometer, B= the final volume of the prepared samples, W= weigh of samples in gram.

Statistical analysis

Statistical analysis of data was conducted using "Statistic for animal and veterinary science *(13)*.

RESULTS AND DISCUSSION

Table 1. Concentrations (ppb) of polychlorinated biphenyls (PCBs) in the examined water and fish samples (n = 20 for each).

PCBs congeners	Water			Fish		
	Min.	Max.	Mean ±S.E.*	Min.	Max.	Mean ±S.E.
PCB44	0.1	5.8	0.835 ±0.4	0.30	500	120.185 ±42.025
PCB105	0.2	5.6	0.935 ±0.387	0.1	1700	65.03 ±59.78
PCB118	0.5	10.1	1.132 ±0.547	0.5	2550	371.832 ±148.85
PCB138	0.1	6.4	0.88 ±0.388	0.25	2900	237.755±158.64
PCB180	0.1	3.4	0.351 ± 0.192	22	1500	87.355 ±74.96
PCB192	ND**	ND	ND	1.5	95	11.2 ±5.792
Total PCBs	0.15	12.7	3.878 ±1.041	0.35	4335	887.357 ±318.04

*: Non detected PCB was considered zero for mean calculation.
**ND= Not detected.

The results recorded in Table 1 indicates that the mean values of PCB44, PCB105, PCB118, PCB138, PCB180 and total PCBs in the examined water samples were 0.835 ±0.4, 0.935 ±0.387, 1.132 ±0.547, 0.88 ±0.388, 0.351 ± 0.192 and 3.878 ±1.041 ppb respectively, these levels were obviously higher than those recorded in Venice Lagoon, Italy (0.003- 0.018 ppb) *(21)*, Mississippi River, USA (0.02- 0.16 ppb) *(22)* and in water reservoir in China (0.0008- 0.324 ppb) *(23)*. Furthermore, another study in Italy *(24)* detected PCBs in Venice Lagoon water, in very low levels (0.0004- 0.002 ppb) in compared with our figures.

Table 2. Frequency distribution of polychlorinated biphenyls (PCBs) residues in the examined water and fish samples (n = 20 for each).

PCBs Congeners	Water						Fish					
	N.D.		Within P.L.*		Over P.L.		N.D.		Within P.L.**		Over P.L.	
	No	%	No	%	No	%	No.	%	No	%	No	%
PCB44	15	75	1	5	4	20	10	50	10	50	0.0	0.0
PCB105	13	65	1	5	6	30	11	55	9	45	0.0	0.0
PCB118	13	65	1	5	6	30	7	35	12	60	1	5
PCB138	13	65	2	10	5	25	8	40	11	55	1	5
PCB180	12	60	5	25	3	15	16	80	4	20	0.0	0.0
PCB192	20	100	0.0	0.0	0.0	0.0	14	70	6	30	0.0	0.0
Total PCBs	4	20	5	25	11	55	1	5	15	75	4	20

*P.L.: Permissible limit of total PCBs in water is 0.5 ppb ***(14)***
P.L.: Permissible limit of total PCBs in fish is 2000 ppb *(15)***

Table 2 showed that 4(20%), 6(30%), 6(30%), 5(25%) and 3(15%) of the examined water samples had PCB44, PCB105, PCB118, PCB138 and PCB180 in the levels exceeded the permissible limit (0.5 ppb) ***(14)***. Moreover, the total PCBs were exceeded the recommended permissible limit in 11 (55%) samples out of the examined water samples.

Regarding the fish tissues, Table 1 showed that the mean levels of PCB44, PCB105, PCB118, PCB138, PCB180, PCB192 and total PCBs in the examined fish muscles were 120.185 ±42.025, 65.03 ±59.78, 371.832 ±148.85, 237.755±158.64, 87.355 ±74.96, 11.2 ±5.792 and 887.357 ±318.04 ppb respectively. The obtained results recorded very higher levels of total PCBs residues than those previously detected in Red sea fish in Egypt (8.37 – 66.44 ppb) ***(5)***. Furthermore, foreigner studies in Brazil ***(26)***, Italy ***(27)***, Netherlands ***(28)*** and China ***(29)*** calculated obviously lower PCBs residues in fish tissue samples compared with those recorded in the current investigation.

Table 2 revealed that both PCB118 and PCB138 were detected in levels exceeded the recommended permissible limit (2000 ppb) ***(15)*** in one fish sample (5%), while; the total PCBs exceeded the recommended permissible limit in 4 (20%) out of 20 examined fish samples.

PCB28, PCB52, PCB70, PCB101, PCB152 were not detected in all the examined water and fish samples, while; PCB192 could not be detected in all the examined water samples.

Regarding the heavy metal residues in the examined samples, Table 3 showed that the mean levels of lead, cadmium, arsenic, manganese, zinc, copper and iron in the examined pond's water samples were 7.77 ±0.530, 2.013 ±0.236, 1.51 ±0.067, 3.179 ±0.112, 17.55 ±0.446, 9.613 ±0.362 and 381.64 ±17.02 ppm respectively. These levels were clearly higher than those obtained in surface water in Egypt ***(4,30,31)***. Moreover, another foreigner studies recorded drastically lower heavy metal residues in surface water than our estimations, a study in Malaysia recorded that the mean levels of zinc, copper, manganese, cadmium and lead residues in surface water were 0.02, 3.02, 0.44, 0.01 and 1.58 ppm respectively ***(321)***, while; another study in Philippines detect arsenic residues with the mean levels 0.001 ppm in surface water ***(33)***. Furthermore, arsenic residues were detected in surface water·In Pakistan in high anxiety levels (0.06- 0.1 ppm) which were 6-10 times higher than the permissible limit, these disquieting levels were lower than those in the present study ***(34)***.

Table 3. Concentrations (ppm) of heavy metal residues in the examined water and fish samples (n = 20 for each).

Heavy Metal	Water			Fish		
	Min.	Max.	Mean ±S.E	Min.	Max.	Mean ±S.E
Lead	1.1	10.4	7.77 ±0.530	180	347.5	278.25 ±11.639
Cadmium	0.95	4.5	2.013 ±0.236	0.55	7.2	3.535 ±0.640
Arsenic	0.85	1.93	1.51 ±0.067	41.7	255	108.18 ±16.256
Manganese	2.1	3.9	3.179 ±0.112	66	205	125.16 ±9.561
Zinc	14.26	21.0	17.55 ±0.446	527	955	732.55 ±27.867
Copper	7.5	12.7	9.613 ±0.362	217.5	436.6	318.05 ± 15.449
Iron	260.4	495.3	381.64 ±17.02	1255	9560	4396.78 ±632.9

Table 4. Frequency distribution of Heavy metal residues in the examined water and fish samples (n = 20 for each).

Elements	Water					Fish				
	PL* (ppm)	Within permissible limits		Over permissible limits		Permissible limits (ppm)	Within permissible		Over permissible limits	
		No.	%	No	%		No	%	No	%
Lead	0.015	0.0	0.0	20	100	0. 5 [17]	0.0	0.0	20	100
						0.1 [18]	0.0	0.0	20	100
Cadmium	0.005	0.0	0.0	20	100	0.05 [17]	0.0	0.0	20	100
						0.1 [18]	0.0	0.0	20	100
Arsenic	0.01	0.0	0.0	20	100	1.0 [19]	0.0	0.0	20	100
Manganese	0.05	0.0	0.0	20	100	5.4 [20]	0.0	0.0	20	100
Zinc	5.00	0.0	0.0	20	100	150 [20]	0.0	0.0	20	100
Copper	1.3	0.0	0.0	20	100	10 [20]	0.0	0.0	20	100
Iron	0.3	0.0	0.0	20	100	30 [21]	0.0	0.0	20	100

*P.L.: Permissible limit of total PCBs in water is 0.5 ppb *(16)*

Table 4 showed that all the examined water samples contained the tested heavy metals in the limits extremely exceeded the recommended permissible limits.

Concerning the heavy metal residues in the examined fish muscle samples, Table 3 revealed that the mean levels of lead, cadmium, arsenic, manganese, zinc, copper and iron were 278.25 ±11.639, 3.535 ±0.640, 108.18 ±16.256, 125.16 ±9.561, 732.55 ±27.867, 318.05 ± 15.449 and 4396.78 ±632.9 ppm respectively. These levels are clearly higher than those recorded in the previous Egyptian studies *(4,6,31,)*. Also, a study in USA, recorded heavy metal residues in lower levels than those in the present study in canned fish *(35)*. Moreover, the recent foreigner study in China *(36)* detected 2.13, 0.17, 0.35, 19.1 and 0.52 ppm of arsenic, cadmium, copper, zinc and lead residues respectively in fresh water fish which were obviously lower than those in our study, in Pakistan, arsenic and iron residues recorded 2.3 and 1517 ppm in fish tissues respectively *(34)*. Furthermore, another study in Malaysia *(32)* estimated manganese (16-20ppm), zinc (37-43 ppm), copper (11.5- 12 ppm), cadmium (0.2- 0.9 ppm) and lead (0.9- 1 ppm) in fish tissues which were lower than our figures.

As the obtained results of the water samples, Table 4 showed that all the estimated heavy metals exceeded the permissible limits in all the examined fish muscle samples.

From the public health point of view, PCBs have significant ecological and human health effect as cancer, neurotoxicity, reproductive and developmental toxicity, liver damage, skin irritation and endocrine disruption *(16)*, furthermore, immune system suppression *(37)*. Concerning heavy metals, lead toxicity inhibits the biosynthesis of heme *(38)*, thus chronic lead poisoning characterized by anemia; also, muscular pain and also neuropathy of both central and peripheral nervous system *(39)*. Moreover, chronic lead exposure leads to chromosomal aberration *(40)*. Cadmium toxicity may be manifested by renal dysfunction *(41)*, hypertension *(42)* and hepatic injury *(43)*. The International Agency for Research on Cancer *(44)* classified cadmium and cadmium compound as class 1 human carcinogens. On the other hand, arsenic toxicity causes skin lesion (known as melanosis) in some skin of the palms and feet *(45)*, renal failure, cancer in skin, kidney and liver, and internal bleeding *(46)*. Chronic exposure to copper caused vomiting, epigastric pain, diarrhea and jaundice *(47)*. Although, zinc toxicity from excessive ingestion is uncommon, gastrointestinal distress and diarrhea have been reported following ingestion of polluted food by zinc *(48)*. Manganism (manganese toxicity) leads to decrease mental capability in children and cause symptoms identical to Parknson ´s disease in adults *(49)*. Moreover, although iron poisoning is seldom, the symptoms of its toxicity are hemorrhagic gastroenteritis associated with diarrhea and vomiting *(50)*.

From aforementioned results, it could be concluded that the levels of both PCBs and heavy metal residues in the examined samples were obviously very high comparing with those recorded in all the available previous studies. All the examined samples had the heavy metals residues above the permissible limits. On the other hand, although; the PCBs residues were within the permissible limits in 45% of water and 80% of fish. These results are expected because the examined water and fish samples were collected from polluted ponds used for the industrial and sewage drainage effluents of 10th Ramadan city. Although the examined water was not prepared for fish production, the aim of the current study is to throw the light upon the degree of the dangerous of the examined fish on the consumer health.

CONCLUSION AND RECOMMENDATIONS

1- The drainage ponds of 10th Ramadan city must be remained under continuous Governmental censorship to prevent fish production.

2- Continuous monitoring of the hazardous residues in fish samples from the markets.

3- Good treatment of the industrial and sewage water effluents reduces the risk of the environmental pollution.

4- Replacing the drainage ponds in the future by another safety method to get rid of the polluted effluents.

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الملخص العربي

دراسة التلوث الكيميائي لأسماك و مياه برك الصرف لمدينة العاشر من رمضان

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أجريت هذه الدراسة لتقييم درجة التلوث في أسماك و مياه برك الصرف و الأكسدة لمدينة العاشر من رمضان و هذه البرك تستخدم للتخلص من مياه الصرف الصناعي و الصحي للمدينة و التي تعد واحدة من أكبر المدن الصناعية في مصر، و قد قام بعض الأشخاص المجهولين بوضع صغار أسماك في مياه البرك بغية استغلال مساحتها الكبيرة غير عابئين بما تشكله تلك الأسماك من خطورة بالغة علي الصحة العامة.

تم تجميع ٤٠ عينة (٢٠ عينة مياه و ٢٠ عينة أسماك بلطي) تم إعداد العينات لقياس البولي كلورينيتد بيفينيل و المعادن الثقيلة و تم قياس العينات و قد أسفرت الدراسة عن النتائج التالية.

وجدت مركبات البولي كلورينيتد بيفينيل في أغلب العينات و بتركيزات أعلي من المسموح بها في ٥٥% من عينات المياه و ٢٠% من عينات الأسماك. أما المعادن الثقيلة فقد وجدت و بتركيزات أعلي من الحدود المسموح بها في كل العينات المختبرة (الماء و الأسماك) و بلا استثناء.

من هذه الدراسة نستخلص أن أسماك برك الصرف و الأكسدة لمدينة العاشر من رمضان تحمل بين طياتها خطورة شديدة علي الصحة العامة للمستهلك إذا وصلت للأسواق و تم تداولها، و قد تمت مناقشة الأهمية الصحية للملوثات التي تم الكشف عنها في الدراسة الحالية.