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RESIDUES OF ORGANOCHLORINES AND TRACE HEAVY MEATLS IN FISH

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ABSTRACT

The contamination of the aquatic environment and the marine organisms with trace elements and the other contaminants have been of considerable interest. The present study is related to monitoring of trace elements (cadmium (Cd), lead (Pb) and mercury (Hg) and organochlorine pesticides as well as polychlorinated biphenyls (PCB) concentrations in fish tissues of different species collected from different Egyptian governorates. A total of seventy one samples of different fish species were subjected to heavy metals analysis for mercury, cadmium, and lead investigation. However, only thirty five samples were analyzed for eighteen chlorinated pesticides and seven polychlorinated biphenyl (PCB) congeners. In heavy metals analysis, the results showed that only 12.7% of the samples were free from any detectable amount of Cd. However, 87.3% of the total number of fish samples analyzed was contaminated with Cd element, of which 7 % exceeded the maximum limits established for Cd by EU (2007) and EOS (2009). The concentration levels ranged from 0.005 to 0.091 mg/kg and the violated samples were Barbony, Denise, saraghieus, Morgan and Sopeet. Data showed that 91.3% of all tested samples were contaminated with mercury. The concentration levels varied from 0.03 to 1.4 mg/kg. Also, data demonstrated that 8.7% of all tested samples had levels of mercury exceeded the established ML's for Hg. Morgan fish recorded the most violated samples (3 samples exceeded ML of Hg), while the lowest were Mousa and Wakar samples. Data showed that lead recorded the lowest contamination percentage (i.e. 77.1%). The concentration range varied from 0.03 to 1.8 mg/kg. Also, results showed that 4.2% of all tested samples containing lead levels exceeded the ML of Pb. The violated samples were Denis, Loot and Wakar. In the residues analysis of pesticide and PCB's, results showed that total contamination of fish by organochlorine pesticides (DDE p,p and DDD p,p) and PCBs were 57% and 37%, respectively. It was noticed that 14.3% from the total of samples analyzed were contaminated with detectable levels (i.e. more than LOQ) of organochlorine pesticide residues, in concentration levels ranged from 0.005 to 0.04 (mg/kg), Results showed that the percentage of the violation was 54.3%. The violated samples were Bory, Bolty, and Karameet. Data showed that the highest contamination percentage with DDEp,p recorded in Bory samples (i.e. 26%), followed by Bolty (i.e. 11.4%) and the lowest in Karameet fish samples (i.e. 8.6%).However, 8.5% from total number of samples were contaminated with DDD p,p less than LOQ (0.05 mg/kg) Also, results showed that all Karameet samples were contaminated with PCBs (28, 52, 101, 118, and 180), in concentration levels less than LOQ. On the other hand 14% of all analyzed Bolty samples were contaminated traces of PCBs (101,118,138,153 and 180). However, 71% of all analyzed Bory fish samples contaminated with detectable levels of PCBs (101,118,138,153 and 180), no exceeding of the levels of detected PCBs above the established MRL's.

Keywords: Heavy metals, Atomic absorption, fish, freshwater, marine

INTRODUCTION

Fish possess antiatherogenic properties, presumably because of their high content of essential omega-3 polyunsaturated fatty acids (ie, eicosapentaenoic acid or docosahexaenoic acid). Several studies demonstrate the benefits of fish consumption in patients with cardiac disease, including a decreased mortality following myocardial infarction Burr ML *et al*., (1989); Rissanen T, *et al*., (2000); Schmidt EB *et al*., 2000; Albert CM *et al*., (2002); Guallar E *et al*., (2002). In addition, regular fish intake is recommended to decrease the risk of coronary artery disease. On the other hand, many studies have illustrated that certain fish contain high levels of environmental toxins, such as mercury, polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides, and related compounds (Guallar E *et al*., (2002); Yamaguchi N *et al*., (2003). Some of these toxins may negate the cardiovascular health advantages of fish meals (Guallar E *et al*., 2002).
Organochlorines have at least 1 aromatic ring and include PCBs, which have 2 aromatic rings. Organochlorines can be divided into pesticide OCs (ie, dichlorodiphenyltrichloroethane [DDT]) and nonpesticide OCs (ie, PCBs). PCBs are unwanted byproducts of a variety of industrial processes and are still found in transformers and capacitors that were manufactured before PCBs were banned in 1977. PCBs persist in the environment because of their resistance to degradation, and they bioconcentrate in fish along the food chain. PCBs and related compounds have adverse dermatologic, reproductive, developmental, endocrine, hepatic, and immunologic effects Mussalo-Rauhamaa H ,(1991) Patterson DG *et al*., (1994); ; Patterson DG *et al*., (1994); Schade G and B Heinzow, (1998) (Nakai K and H. Satoh., (2002); DDT is the best-known OC pesticide. Similar to PCBs, OC pesticides such as DDT are resistant to degradation and accumulate in fish and in the environment. Exposure to OC pesticides may cause neurotoxicity and cardiac and pulmonary dysfunction (Nakai K and H. Satoh, 2002. Because of all risks of these fish contaminants a lot of monitoring studies and risk assessment were done.

Also, the concentrations of heavy metals in aquatic environment and marine organisms have been of considerable interest because of their toxic effects which are important for human beings (Von Schiruding *et al*., 1991; Ipinmoroti *et al*., 1997).

Heavy metals have the tendency to accumulate in various organs of marine organisms, especially fish, which in turn may enter into the human metabolism through consumption causing serious health hazards (Puel *et al*., 1987). Fish are an excellent source of high quality protein, and are low in saturated fat, which makes them a healthy food choice. Because of its nutritional value, fish continue to be available to Egyptian consumers, which advice to limit consumption to avoid exposure to hazardous levels of mercury. Specially, long lived, larger fish that feed on the other fish accumulate the highest levels of methyl mercury and pose the greatest risk to people who eat them. Specially, pregnant women, women of child-bearing age and young children are advised to limit their consumption of fish.

Investigations of metals in fish are an important aspect of environmental pollution control because human activities progressively increase the concentration of heavy metal in the aquatic system. The study of fish muscle tissue is one of the means for investigating the amount of heavy metals reaching man by food chain and has therefore been investigated more than other organs (Nabawi *et al*., 1987)

All around the world a lot of research work have been documented on trace metal concentration in marine and fresh water fishes (Papadopoulon *et. al*., 1980; Romeo, 1987; Tariq *et al*., 1993; Asaolu, 2002).

The present work was undertaken to study the concentration levels of selected trace metals (cadmium (Cd), lead (Pb) and mercury (Hg) and organochlorine pesticides as well as polychlorinated biphenyls (PCBs) concentrations in commercially important fish species in Egypt.

MATERIALS AND METHODS

A total of seventy one samples of different species of the fish samples which collected from nine Egyptian local markets located in nine governorates (Cairo, Qalyobiya, Sharkiya, Ismalia, Damiatta, Minufiya, Alexandria, Tanta, and Port Said). All collected samples were subjected to heavy metals analysis, while only thirty five fish samples were analyzed for 18 chlorinated pesticides and 7 polychlorinated biphenyls (PCBs) congeners.

Table (a): The common, the English, and the scientific name of the fish samples

English name	Scientific name	Common name
Sea Bream	*Pagrus pagrus*	Morgan
Groupers	*Epinephelus spp.*	Wakar
European Sea Bass	*Dicentrarchus labrax*	Karoos
Gilthead Sea Bream	*Sparus auratus*	Denis
Sole	*Solea spp*	Mousa
Nile Tilapia	*Oreochromis niloticus niloticus*	Bolti
Red Mullet	*Parapenaeus spp*	Parpony
Meager	*Argyromus regium*	Loot
Cat fish	*Clarias spp*	Karameet
Flathead Grey Mullot	*Mugil cephalus*	Bory
Cuttel Fish	*Sepia spp*	Sopeet
Eles	*Angulla spp*	Henshaan
White bream	*Sargus sargus*	Sharagiesh

Heavy metals analysis:

Sampling:

One kg of fish samples was prepared according to the published guidelines (*Codex Alimentarius* 1993). The samples were homogenized with electrical bamix (with platinum cutter). The analysis of samples was performed on their arrival to the laboratory or they were stored at -5º.

Chemicals and reagents:

- Deionized water.
- Nitric acid (HNO_3) (GR Pro Analyse , 65%) (Merck)

- Hydrochloric acid (GR, 37%)
- Sulfuric acid (GR, ISO, 96%) (Merck)
- Hydrochloric acid (10 mol/L) (49.1 ml conc. HCl is diluted to 50 ml with deionized water).
- Hydrochloric acid (10%) (270 ml of conc. HCl is diluted to 1L with deinized water).
- 2 mol HNO_3 (130 ml of HNO_3) is diluted to 1L with deionized water used for cleaning the digestion tubes.
- 0.3 % HNO_3 (5 ml conc. nitric acid is diluted to 1L with deionized water)
- Potassium permanganate solution (5%) in deionized water.
- Sodium hydroxide solution (0.1 % w/v).
- Sodium tetrahydroborate (1% w/v) sodium tetrahydroborate is dissolved in 0.1% w/v sodium hydroxide solution. The solution then filtered into plastic vessel.
- N- Hexane (HPLC).
- Reagent of matrix modifier: A mixture of 10 gm of ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and 0.87 gm of magnesium nitrates ($Mg(NO_3)_2.6H_2O$) were dissolved in 500 ml distilled water.
- Metals stock standards of Pb, Cd and Hg (1000) mg/L (Merck):
  For AAS, the intermediate and working solutions of Cd and Pb prepared from stock solution with different concentrations in 0.3 % HNO_3. However, the intermediate and working solutions of Hg prepared from stock solution with different concentrations in 10% HCl,

Apparatus and Equipments:

- Digestor (Techetor 2020)
- Steam water path (temperature range 0-100 ºC).
- Atomic Absorption Spectrometer (Analytical technology, INC, Unicam (AAS 929) equipped with Graphite furnace with auto sampler, flame atomic absorption and continuous flow vapour system (VP90).
- Digestion vessel 100 ml Erlenmeyer flasks with large glass marbles as covers.
- Volumetric flasks (25 and 50 ml).

Digestion:

Cd and Pb analysis:

An analytical methodology used was that described in the thesis of NMKL, (1991), the sample was digested by wet digestion technique, using concentrated nitric acid. The digestion residue dissolved into 0.3% HNO_3. One to three gm of fish sample was transferred to glass digestion tube and 10 ml of conc. HNO_3 added. The solutions were boiled for 72 hours. The nitric acid solution was evaporated almost to dryness and the residue was transferred with 0.3% HNO_3 to 25 ml volumetric flask

Hg analysis:

The method described in (AOAC, 1985) was selected for determination of the total mercury in the samples. The sample was digested by using a mixture of hydrochloric, nitric and sulphuric acids. 1.5 gm of fish sample was transferred into 100 ml Erlenmeyer flask. One ml of 10 M HCl and 5 ml of conc. HNO_3 were added and after five minutes, 5 ml of conc.

H_2SO_4 was added, and then the flask was covered with large glass marble. After 15 min, the flask was placed on the top of stream bath for 2 hour at temperature range from 70^0 C to 80^0 C. After 2 hour the flask was removed from the steam bath. After cooling, 22 ml of deionized water followed by 20 ml n- hexane were added. Then the mixture was shaked till the fats were extracted into n- hexane layer. The hexane layer was retained on wattman filter paper number 4, and then the flask was rinsed with 20 ml deionized water and also filters. The filtrate was transferred to 50 ml volumetric flask and diluted to the mark with deionized water. The reagent blank was prepared analogously to samples beginning from the wet digestion.

Determinations:

Cadmium and lead were determined by Atomic Absorption Spectroscopy (AAS), using deuterium lamp for background correction.

Typical furnace parameter for Pb, Cd in AAS is given in the following table:

Step	Temp. (ºC)	Time (sec)	Ramp (ºC/sec)	Gas flow (ml/min)
Drying	120	40	30(Cd), 10 (Pb)	2
Ashing	800	20	50	2
Atomization	1800	3	0	0
Cleaning	2500	3	0	2
Cooling	20	5	0	2

Mercury was detected by Atomic Absorption Spectrometer continuous vapour system (VP90) at wave length 253.7 nm and flow rate 200 – 300 ml/min of inert argon gas.

Quality control procedure:

All analytical methods and instruments were fully validated as a part of the laboratory quality assurance system and were audited and accredited by the Center of Metrology and Accreditation Finnish Accreditation Services (FINAS) ISO/IEC Guide 25. The criteria of quality assurance described by (Dogheim *et a.l* 2002). The recoveries were between 70-120% and CV less the 20%. Fortification of all samples with the contaminants of interest has been carried out to ensure that the method performed satisfactory for the particular food examined. Analysis of duplicate samples represents precision of analysis. Limits of Quantification of lead, cadmium, and mercury were 0.04, 0.002, and 0.03 (mg/kg), respectively.

Organochlorine Pesticide residues and PCB congeners analysis:

Sampling procedures are according to *Codex Alimentarius* (1993) and were extracted according to Pesticide Analytical Manual, (1994).

Chemicals and reagents:

- Acetonitril (Lab-scan) (HPLC), or similar quality.
- De-ionized Water generated by Milli-Q or similar quality.
- Anhydrous Sodium Sulphate (Riedel-deHane) or similar quality heated overnight at 150 ^oC and transferred to desiccators directly.
- Florsil, particle size 0.150-0.250 mm (60-100 mesh ASTM), for column chromatography. Florsil was activated overnight at 300 ^oC.

Hexane (Lab-scan) (HPLC), or similar quality.

- Petroleum ether (Lab-scan) (Pestiscan), or similar quality.
- Benzene (Lab-scan), or similar quality.
- Ethyl acetate (Lab-scan) (HPLC), or similar quality.
- Acetone(Lab-scan) (HPLC), or similar quality.
- Clean up elute I (Hexane: Benzene: Ethyl Acetate) (180 :19:1).
- Clean up elute II (Ethyl Acetate: Hexane) (30:70).
- Saturated acetonitrile with petroleum ether: Mix a ratio of 1:1 of acetonitrile and petroleum ether in a separatory funnel, shake for 3 minutes, let layers to separate and take lower acetonitrile layer for sample partitioning.
- Sodium Chloride (Riedel-deHaen)(Assay 99.8%),or similar quality.
- Sodium chloride saturated solution: Dissolve sodium chloride in one litre of de-ionized water and continue adding sodium chloride with shaking until precipitation.

Determination :

The organochlorines and PCBs were determined by GC -ECD with the following conditions:

- Two capillary columns with different polarities (HP-PAS-5: 0.32 mm x 0.52 µm x 25 m and DB-1701P: 0.32 mm x 0.25 µm x 25 m).
- N2 constant flow, 1.3 mL/min; inlet temperature, 225°C; injection volume, 1 µl (splitless); initial oven temperature, 90°C, held for 2 min, then a 20°C/min ramp to 150°C followed by a 6°C/min ramp to 270°C (held for 18 min).

RESULTS AND DISCSSION

Heavy Metals Analysis:

The present study includes the concentration levels of Cd, Hg, and Pb, elements in 71 fish samples of different species were collected from different Egyptian governorates. All collected samples were subjected to trace element analysis to investigate Cd, Pb and Hg elements.

In general, data in Table (1) showed that only 12.7% of samples were free from any detectable amount of Cd. However, 87.3% of the total number of fish samples analyzed was contaminated with Cd element. 38.7% of contaminated samples contained levels of Cd less than LOQ (0.005 mg/kg), while 61.3% of samples were contaminated with detectable levels above the LOQ, in concentration levels ranged from 0.005 to 0.091 mg/kg. Data showed that 4.2 %of the total number of sample contained levels of Cd contaminant in conc. exceeded the ML's of Cd established by EU (2007) and EOS (2009). The violated fish samples were Barbony, Denise, Sharagiesh, Morgan and Sopeet.

Sixty nine samples were subjected to mercury analysis; data showed that only 8.7% of all tested samples were free from any mercury, while 91.3% samples were contaminated with mercury.

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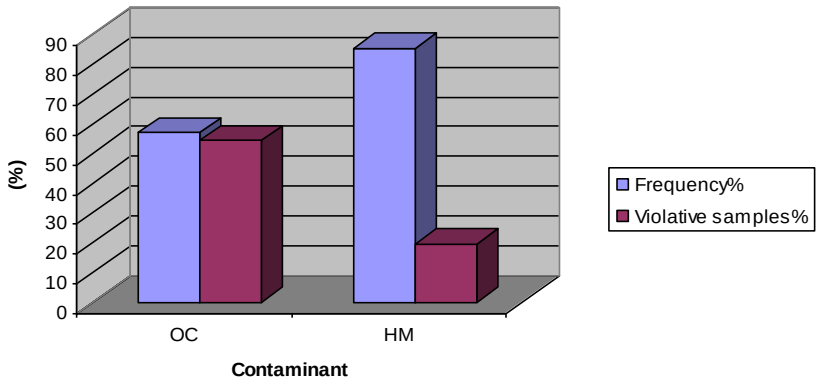
41.3% of the contaminated samples (63 samples) were contaminated with mercury levels less than LOQ of Hg (0.03 mg/kg), while 58.7% of the contaminated samples were contaminated with detectable levels above LOQ of Hg in concentration levels ranged between 0.03 to 1.4 mg/kg. Also, data demonstrated that 8.7% of all tested samples had levels of mercury exceeded the established ML's for Hg. The Morgan recorded the most violated samples (3 samples exceeded ML of Hg), while the lowest were Mousa and Wakar samples.

Lead recorded the lowest contamination percentage (77.1%). Data showed that 22.9% of all samples were free from any detectable levels of Pb. However, 22.2% of all contaminated samples contaminated levels of Pb less than LOQ of Pb (0.03 mg/kg), while 77.8% of all samples analyzed contaminated with Pb in levels above LOQ, in concentration range varied from 0.03 to 1.8 mg/kg. Also, Results showed that 4.3% of all tested samples containing lead levels exceeded the ML of Pb. The violated samples were Denis, Loot and Wakar. Fig (1) showed the total contamination and violation of heavy metals in studied samples.

Fig.(1): frequency % and violation % of heavy metals and onganochlorine pesticides studied fish



The contamination of most of analyzed fish samples with Hg, Cd, and Pb may be derived from anthropogenic activities especially from industrial and agricultural wastes from several drains. Differences on heavy metal concentrations may be determined by the predominant food items on the diet of each species, habitat contamination, and metabolic variation among individuals.

Also, these differences in the concentration of these detected metals (Hg, Cd and Pb) in fish samples can suggest to that degree of particular species picks up the matter from the sediment and water during feeding. It is well known fact that bottom feeders are known to concentrate more metal levels than the surface feeders (Zehra*, et. al,* 2003).

Organochlorine pesticide residues and PCB congener's analysis:

In the present study thirty five samples of different fish species subjected to organochlorine pesticides and PCB analysis.

In general, data in Table (2) and Fig (1) showed the total contamination of fish by organochlorine pesticides (DDE p,p and DDD p,p) and PCBs were 57% and 37%, respectively. It was noticed that 14.3% from the total of samples analyzed were contaminated with detectable levels (i.e. more than LOQ) of organochlorine pesticide residues, in concentration levels ranged from 0.005 to 0.04 (mg/kg), Results showed that the percentage of the violation was 54.3%. The violated samples were Bory, Bolty, and Karameet. Data showed that the highest contamination percentage with DDEp,p recorded in Bory samples (i.e. 26%), followed by Bolty (i.e. 11.4%) and the lowest in Karameet fish samples (i.e. 8.6%).However, 8.5% from total number of samples were contaminated with DDD p,p less than LOQ (0.05 mg/kg). Also, results showed that all Karameet samples were contaminated with PCBs (28, 52, 101, 118, and 180), in concentration levels less than LOQ. On the other hand 14% of all analyzed Bolty samples were contaminated traces of PCBs (101,118,138,153 and 180). However, 71% of all analyzed Bory fish samples contaminated with detectable levels of PCBs (101,118,138,153 and 180), no exceeding of the levels of detected PCBs above the established MRL's.

More commonly, people are chronically exposed to PCBs from the consumption of tainted fish. PCBs are readily absorbed into the body but are only slowly metabolized and excreted. Half-lives range from 1 to 460 days, depending on the level of chlorination. The liver is the primary site of metabolism where hydroxylation and conjugation occur, but metabolism is slow, and most PCBs accumulate in adipose tissue. Chronic effects include dermatologic manifestations, developmental deficits with exposure in utero, disruption of thyroid or female sex hormones, elevation of liver enzymes (overt hepatotoxicity uncommon), decreased immunity, impaired memory and learning in adults and children, and carcinogenesis Jacobson JL and SW. Jacobson, (1996) (Kaiser J., 2000) Moysich KB *et al*., (2002); (Faroon OM *et al*., (2001); Ribas-Fito N *et al* (2001);. Polychlorinated biphenyls are complete carcinogens, acting as initiators and promoters (Faroon OM *et al*., 2001). The most susceptible tissues are liver, biliary tract, and intestines, followed by stomach, lip, and skin. PCBs pass to babies during pregnancy and breast-feeding, and studies illustrate their detrimental effects on the immune system and neurodevelopment (Moysich KB *et al*; (2002), Winneke G *et al*., (2002); Jacobson JL and SW. Jacobson, 1996 and Nakai K and H. Satoh 2002). In a Michigan cohort, 313 women were exposed to PCBs from Lake Michigan fish. Prenatal exposure was associated with decreased IQ and intellectual impairment in children examined from birth to age 11years (Nakai K and H. Satoh 2002). In a North Carolina cohort, 880 pregnant women were selected from the general population. PCB exposure was associated with decreased muscle tone, lower activity levels, hyporeflexia, and lower psychomotor scores in children from birth to 5 years.38 PCBs are present in all categories of food as well as in the environment (Schafer KS and SE. Kegley., 2002). Because of baseline environmental and nutritional exposure, humans have an average of 1.4 ppb of PCBs in their serum Mussalo-Rauhamaa H., (1991);Patterson DG *et al*., (1994), Koopman-Esseboom C *et al*., (1994) (Patterson DG *et al*., (1994); (Longnecker MP *et al*., 1998;).

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Because PCBs concentrate in fatty tissue, the levels can be 300 times higher in adipose tissue Schade G and B. Heinzow, 1998; or breast milk. Studies on the detrimental effects of PCBs prompted regulations on the allowable levels of PCBs in food and warnings about dangerous toxins in fish. The US Food and Drug Administration (FDA) allow 0.1 to 3.0 ppm of PCBs for all foods. Recently, concern about the levels of PCBs in fish has increased. In 1984 the FDA lowered the limit to 2.0 ppm for edible fish (Patterson DG *et al*., 1994).Organochlorine pesticides are the second type of OCs. Pesticide OCs are diphenyl aliphatics previously used to OC pesticides entered the air, water, and soil when they were sprayed on crops and forests. They bound to particles in the water, settled, and deposited in sediment. Organochlorine pesticides remain in sediment for a very long time because of their resistance to degradation (half-lives of months to years), and so they are still taken up by small organisms and fish even today. Similar to PCBs, OC pesticides concentrate over 1000-fold in fish and marine mammals. In the 1990s, DDT and its metabolites were detected in 94% of whole fish samples (Schafer KS and SE. Kegley 2002 and Turusov V *et al*., 2002). Because of their neurotoxic properties, OC pesticides were banned in 1973. DDT is the best-known OC pesticide. It can be absorbed through the respiratory system, gastrointestinal tract, or the skin. DDT and other OC pesticides impair nerve impulse conductions. Exposure to large amounts (ie, grams) of DDT over a short time causes tremors, seizures, sweating, headaches, nausea, vomiting, and dizziness. Chronic toxicity has reproductive, developmental, neurologic, hepatic, and carcinogenic effects. The US Environmental Protection Agency determined that DDT is a probable human carcinogen. In addition, children can be exposed to DDT by eating fish or drinking breast milk contaminated with these compounds. In the United States between 1985 and 1991, the average 8.5- month-old infant consumed 4 times more DDT for each pound of body weight than the average adult. Exposure to DDT during development in children may affect the reproductive and nervous systems.

Conclusion:

- The result from this study suggested that significant differences existed in the element concentrations across different fish species.
- Overall, 87.3% of the total number of all samples analyzed was contaminated with at least one of three investigated elements (Cd, Pb, and Hg).
- Mercury recorded the highest contamination percentage, followed by cadmium and lead.
- The concentration levels of Hg and Pb exceeded the current Maximum Permitted Limits set by EU, however no exceeding of the levels of Cd above the ML
- Most of the violated samples were marine species.
- 57% from total fish samples were contaminated with organochlorine pesticides with violation reached to 54.3|%..
- No violation was found in all contaminated samples with PCBs.

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تقدير بعض العناصر الثقيلة ومتبقيات المبيدات فى بعض أنواع الأسماك المصرية

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المعمل المركزى لتحليل متبقيات المبيدات و العناصر الثقيلة فى الأغذية. مركز البحوث الزراعية- الدقى- وزارة الزراعة- مصر

يعتبر تلوث البيئة المائية و الكائنات البحرية بالعناصر الثقيلة و الملوثات الأخرى من الموضوعات محل الإهتمام لذلك تم التركيز فى هذه الدراسة عل تقصى هذه العناصر و الملوثات (الكادميوم – الرصاص – الزئبق –المبيدات الكلورنية – المركبات عديدة الكلور) فى أنسجة أنواع مختلفة من الأسماك و التى تم جمعها من محافظات مصر المختلفة. تم تحليل 71 عينة أسماك و تقصى عناصر الكادميوم و الرصاص و الزئبق بها بينما تم تحليل 35 عينة وتقصى 18 مبيد من المبيدات الكلورنية و 7 من متجانسات المركبات عديدة الكلور. و قد اظهرت نتائج تحليل العناصر الثقيلة ان 87,3 % من مجمل عينات الأسماك كانت ملوثة بعنصر الكادميوم و شملت على 7% منها متعدية للحدود القصوى المشرعة من الإتحاد الأوروبى لعام 2007 و كذلك تشريعات الهيئة العامة للمواصفات المصرية لعام 2009 . و قد تراوحت مستويات التلوث ما بين 0,005 الى 0,091 مليجرام / كجم و كانت العينات المتعدية من أنواع الاسماك هى الباربونى و الدنيس و الشراغيش و المرجان و السبيط . أظهرت النتائج أن 91,3 % من العينات المختبرة كانت ملوثة بالزئبق منهم 8,7% متعدية للحدود القصوى و تراوحت كمية التلوث ما بين 0,03 الى 1,4 مليجرام / كجم وقد سجل سمك المرجان أعلى عدد من العينات المتعدية للحدود القصوى للزئبق (3 عينات) فى حين أن عينات أسماك موسى و الوقار كانت الأقل تلوثا بالرصاص (77,1%) منهم 4,2 % متعدية للحدود القصوى و تراوحت قيمة التلوث ما بين 0,03 الى 1,8 مليجرام/ كجم و قد كانت الأنواع المتعدية هى أسماك الدنيس و اللوط و الوقار. أظهرت نتائج تحليل متبقيات المبيدات الكلورنية و مركبات عديد الكلور فى عينات الأسماك المجمعة أن 57% من العينات كانت ملوثة بالمبيدات الكلورنية (د.د.إ بارا بارا و د.د.د. بارا بارا) فى حين 37% منها كانت ملوثة بمركبات عديدة الكلور. و قد وجد أيضا أن 14.3 % من العينات الكلية و التى تم تحليلها كانت ملوثة بمبيد د.د.إ بارا بارا و تراوحت قيمته ما بين 0,005 الى 0,04 مليجرام / كجم و كانت كل العينات متعدية للحدود المسموح بها بنسبة54.3% و كان ذلك فى كل عينات الأسماك محل الدراسة (القراميط- البورى- البلطى) و قد سجلت أسماك البورى أعلى نسبة من التلوث (26,%) يليه سمك البلطى (11,4%) ثم أخيرا القراميط (8,6%). ووجد أيضا أن 11,4% من العينات كانت ملوثة بمبيد د.د.د. بارا بارا و لكن قيمتها أقل من أقل كمية يمكن تقديرها من المبيد (0,05 ملجم/ كجم) و أن 14% من العينات الكلية متعدية للحدود القصوى لهذا المبيد (0,002 ملجم/كجم) و قد لوحظ أنه لم يوجد أى تعدى للحدود القصوى لكل أنواع الأسماك محل الدراسة (القراميط- البورى- البلطى) الملوثة بمركبات عديدة الكلور.

قام بتحكيم البحث

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Table (1): Minimum, Maximum, Mean in mg/kg as well as Frequencies, Number and percentages of different types of fish samples, violated samples and the detected metals residues in analyzed samples collected from Egyptian local markets.

Commodity	Total no. of samples analyzed	Analysed metal	Samples no. contaminated with each metal	no of free samples	<LOQ mg/kg	No of samples contained conc. More than LOQ	Conc. Range (mg/kg)	ML's (mg/kg)		Violative samples	
								ESO	EU	No.	%
Karameet	**3**	**Cd**	1	2	1	-	<LOQ	0.1	0.05	-	-
		Pb	3	-	1	2	(0.05-0.16)	1	0.3	-	-
		Hg	3	-	3	-	<LOQ	0.5	0.5	-	-
Barbony	**3**	**Cd**	3	-	-	3	(0.009 - 0.08)	0.1	0.05	1	33.3
		Pb	3	-	1	2	(0.036 – 0.12)	1	0.3	-	-
		Hg	3	-	-	3	(0.038 – 0.1)	0.5	0.5	-	-
Bory	**10**	**Cd**	10	-	5	5	(0.005 – 0.011)	0.1	0.05	-	-
		Pb	9	1	2	7	(0.03-0.13)	1	0.3	-	-
		Hg	9	1	9	-	<LOQ	0.5	0.5	-	-
Denis	**8**	**Cd**	8	-	4	4	(0.006 – 0.09)	0.1	0.05	1	12.5
		Pb	4	4	1	3	(0.03-1.8)	1	0.3	1	12.5
		Hg	6	2	-	6	(0.035 – 0.3)	0.5	0.5	-	-
Henshaan	**1**	**Cd**	-	1	-	-	-	0.1	0.05	-	-
		Pb	1	-	1	-	-	1	0.3	-	-
		Hg	1	-	-	1	0.034	0.5	0.5	-	-
Karafes	**3**	**Cd**	3	-	-	3	(0.006 – 0.01)	0.1	0.05	-	-
		Pb	2	1	-	2	(0.03 - 0.2)	1	0.3	-	-
		Hg	3	-	-	3	(0.11 – 1.4)	0.5	0.5	1	33.3
Karoos	**5**	Cd	5	1	3	1	0.006	0.1	0.05	-	-
		Pb	4	1	1	3	(0.05 – 0.08)	1	0.3	-	-
		Hg	5	-	-	5	(0.04 - 0.22)	0.5	0.5	-	-
Litrene*	**1**	Cd	1	-	1	-	-	0.1	0.05	-	-
		Pb	-	1	-	1	0.03	1	0.3	-	-
		Hg	1	-	-	-	-	0.5	0.5	-	-
Loot	**5**	Cd	3	2	3	-	-	0.1	0.05	-	-
		Pb	5	1	1	3	0.03 – 1.4	1	0.3	1	20
		Hg	5	-	2	3	0.04 – 0.06	0.5	0.5	-	-
Morgan	**7**	Cd	7	-	2	5	(0.006 – 0.018)	0.1	0.05	-	-
		Pb	6	1	-	-	(0.04 – 0.26)	1	0.3	-	-
		Hg	6	1	-	6	(0.15 – 1.3)	0.5	0.5	3	42.9
Mousa	**4**	Cd	2	2	-	2	(0.007 – 0.014)	0.1	0.05	-	-
		Pb	4	-	1	3	(0.04 – 0.26)	1	0.3	-	-
		Hg	4	-	1	3	(0.15 – 1.3)	0.5	0.5	1	25
Mermara	**4**	Cd	3	-	1	2	(0.008 – 0.027)	0.1	0.05	-	-
		Pb	2	1	-	2	(0.034 – 0.04)	1	0.3	-	-
		Hg	3	-	-	3	(0.033 – 0.035)	0.5	0.5	-	-
Sharagies	**3**	Cd	3	-	-	3	(0.014 0.06)	0.1	0.05	1	33.3
		Pb	2	1	1	1	0.07	1	0.3	-	-
		Hg	2	1	2	-	-	0.5	0.5	-	-
Morgan	**1**	Cd	1	-	-	1	0.06	0.1	0.05	1	100
		Pb	1	-	1	-	-	1	0.3	-	-
		Hg	1	1	-	-	-	0.5	0.5	-	-

Table (1): continued

Commodity	Total no. of samples analyzed	Analysed metal	Samples no. contaminated with each metal	no of free samples	<LOQ mg/kg	No of samples contained conc. More than LOQ	Conc. Range (mg/kg)	ML's (mg/kg)	Violative samples	Commodity	Total no. of samples analyzed
								ESO	EU	No.	%
Sopeet	2	Cd	2	-	-	2	(0.028 – 0.091)	0.1	0.05	1	50
		Pb	-	2	-	-	-	1	0.3	-	-
		Hg	1	1	-	-	0.03	0.5	0.5	-	-
Sharagiesh	3	Cd	3	-	-	3	0.011 – 0.018	0.1	0.05	-	-
		Pb	3	-	-	3	(0.1 – 0.26)	1	0.3	-	-
		Hg	3	-	-	3	0.005-0.012	0.5	0.5	-	-
Bolty	4	Cd	3	1	1	2	0.005 – 0.012	0.1	0.05	-	-
		Pb	3	1	2	1	0.09	1	0.3	-	-
		Hg	4	-	4	-	**<LOQ**	0.5	0.5	-	-
Wakar	7	Cd	6	1	3	3	0.005 – 0.013	0.1	0.05	-	-
		Pb	5	2	1	4	(0.07 1.1)	1	0.3	1	14.3
		Hg	7	-	5	2	0.073 0.57	0.5	0.5	1	14.3
Morgan	1	Cd	1	-	1	-	-	0.1	0.05	-	-
		Pb	-	1	-	-	-	1	0.3	-	-
		Hg	1	-	-	1	0.34	0.5	0.5	-	-
			No.	%	**No.**	%	**No.**	%	**No.**	%	**No.**	%
Total	71	Cd	62	87.3	9	12.7	24	33.8	38	53.5	5	7.04
	70	Pb	54	77.1	16	22.9	12	17.1	42	60	3	4.2
	69	Hg	63	91.3	6	8.7	26	37.7	37	53.6	6	8.45

The samples was collected from: Gharbiya, Ismailia, Cairo, Minufiya, Sharkiya , Qalyobiya, port Said, Alexandria, Damietta.
LOQ of cd: 0.005mg/kg, pb: 0.03mg/kg, Hg: 0.03mg/kgBold numbers: means that the concentration is less than the limit of quantification (LOQ) of each metal
For statistical calculation: Samples that registered below the detection limit of the test were listed as one half the detection limits.
EOS: Egyptian organization standard
EU: European Union EU (EC 2005)
ND: Not detected

Table (2): Frequency, Frequency%, LOQ, Number and Percentages of different types of fish samples, violated samples and the detected organochlorines and PCBs residues in analyzed samples collected from Egyptian local markets.

Commodity / Marine fish species	Total no. of samples	Analysed compound	Frequency	Frequency (%)	LOQ mg/kg	No of samples contained conc. More than >LOQ	No of samples contained conc. less than <LOQ	MRL's (mg/kg) (EU)	Violative compound		Violative samples	
									No.	%	No.	%
Karameet	3	p,p-DDE	3	8.6	0.01	1	2	0.002	3	43	3	8.6
		PCB 28	1	2.8	0.005	0	1	0.2	0	0	0	0
		PCB 52	1	2.8	0.005	0	1					
		PCB 101	2	5.7	0.005	0	2					
		PCB 118	2	5.7	0.005	0	2					
		PCB 153	1	2.8	0.005	0	1					
		PCB 180	2	5.7	0.005	0	2					
Bolty	20	p,p-DDD	1	2.8	0.05	0	1	0.002	1	14	1	2.9
		p,p-DDE	4	11.4	0.01	1	3	0.002	4	57	4	11.4
		PCB 101	2	2.8	0.005	0	2	0.2	0	0	0	0
		PCB 118	2	2.8	0.005	0	2					
		PCB 138	2	2.8	0.005	0	2					
		PCB 153	2	2.8	0.005	0	2					
		PCB 180	2	2.8	0.005	0	2					
Bory	12	p,p-DDD	3	8.5	0.05	0	3	0.002	1	14	3	8.5
		p,p-DDE	9	25.7	0.01	2	7	0.002	1	14	9	26
		PCB 101	3	8.5	0.005	0	0	0.2	0	0	0	0
		PCB 118	3	8.5	0.005	0	0					
		PCB 138	8	22.8	0.005	0	0					
		PCB 153	7	20.0	0.005	1	0					
		PCB 180	4	11.4	0.005	0	0					

Table (2): Continued

Commodity (Fish)	Total no. of samples analyzed	Analyzed compound	Samples contaminated with each compound		free samples		Samples contained conc. less than LOQ		Samples contained conc. More than LOQ		Violative samples	
			No.	%	No.	%	No.	%	No.	%	No.	%
Total	35	OC	20	57	15	43	15	42.8	5	14.3	19	54.3
		PCBs	13	37	22	62.9	0	0	0	0	0	0

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