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EXISTENCE AND DISTRIBUTION OF CERTAIN PESTICIDE RESIDUES AND METALS IN *BAGRUS BAYAD* FISH FROM PUBLIC MARKETS OF KALUBIA GOVERNORATE, EGYPT

[31]

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ABSTRACT

The existence and distribution of certain pesticide residues and metals in the muscles and vescera of *Bagrus bayad* fish collected from the three main public markets locates at Kalubia governorate, Egypt during the four seasons of the year 2000–2001 were determined. Data indicated that the number of detected pesticides were varied from muscles to vescera, season to season and from location to the other. A different trend was recorded between muscles and vescera contamination. It seemed difficult to interpretate clear trend/pattern of pesticides residues in both muscles and/or vescera of fish samples in relation to season and location factors. In general, the detected amounts of pesticides were below the maximum residue limits with few exceptions. The obtained results indicate the existence of some metals in the muscles of the collected fish samples. The detected elements were Mn, Cu, Pb, Ni and Co. Both of Co and Pb were only detected in the samples collected at autumn, whereas the other metals were detected in all the other seasons and/or locations. Manganese was found in the highest amounts in the analyzed fish samples.

Key words: Contamination, *Bagrus bayad*, Fish, Pesticides residues, Metals

INTRODUCTION

In Egypt, waste waters and agriculture drains containing pesticide residues are discharged into the river directly. In addition, despite the wide spread use of pesticides in agriculture, data on their accumulation in fish exposed to contaminated water are still lacking. Organochlorine pesticides and polychlorinated biphenyls (PCBs) are world wide distributed organic pollutants. Such compounds are characterized by high stability and may lead to marked changes in the aquatic ecosystem (**Bjerk and Brevik, 1980**). Uptake and accumulation of these pesticide residues by microorganisms and fish

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led to the build up in the food chain (**Macek and Korn, 1970**).

In recent years, the use of chlorinated hydrocarbons and some other hazardous compounds has been drastically banned but concern remains about the continuing existence of these toxicant s in the aquatic ecosystem posing hazards to public health. On the other hand monitoring of chlorinated hydrocarbons and other pesticide residues in fish reflects long term exposure since they degraded slowly, if at all (**Lieb *et al* 1974 and Leiker *et al* 1991**). In addition, monitoring of metals, in fish reflects long term exposure since they accumulate inside the fish organs (**Zayed *et al* 1994; Abdel Naser *et al* 1996 and Seddek *et al* 1996**).

The present investigation has been undertaken to monitor and clarify the existence and distribution pattern of some chlorinated pesticides residues and metals in fish samples collected from different public markets at Kalubia governorate, Egypt during 2000/2001 seasons.

MATERIAL AND METHODS

1. Samples collection and preparation

Fish samples were collected at random from different markets locates at Kalubia governorate during the period Sepember, 2000 – August, 2001. Five samples of *Bagrus bayad* fish were taken from each market, 500 gram each and transferred to the laboratory for pesticide residues and metals analysis. Fish samples were washed with clean tap water to remove mud. The head, tail, fins, and internal organs were removed. Analysis were carried out on muscle tissues and vescera for determination of pesticide residues and muscles only for heavy metals determination.

2. Pesticide residue analysis

Extraction of pesticides residues was carried out using acetonitrile - petroleum ether partitioning. Clean up was done on florisil column with three mixtures for elution (6, 15, 50 % diethyl ether in petroleum ether) as described by the **Anonymous (1990)**.

GC (Shimadzu, 12-A) analysis equipped with FID and ECD detectors was used for separation and identification of the studied pesticides. The separated data of the studied pesticides are tabulated in Table (1) and the operating conditions for the GC were as follow:

Sixteen organochlorine insecticides were separated on GC column packed with 2% Dexile on sumikasorb.

- Temperature
  Oven temp. prog. 180-250°C (2°C/min)
  Inj./Det.Temp. 250°C
Gas pressure :
  Carrier gas N_2 1.5 kg/cm^2
  Burner gas H_2 1.0 kg/cm^2
  Air 0.5 kg/ cm^2
Attenuation : 10 x 5

Fifteen pesticides belongs to different functional groups (fungicides, herbicides, acaricides and insecticides) were also separated on GC column packed with 3 % silicon OV-101 on chromosorb Q.

Temperature:
Oven temp. prog. : 180-250°C (2 °C /min).

Inj/Det. Temp. 250 °C.

Table 1. Separation of certain pesticides on gas liquid chromatography GLC.

Compound	Rt.	Area/10000	The weight (µg)	Separation factor (R)
α-HCH	4.942	9.3	0.495	2.55
β-HCH	6.455	9.5	0.521	2.66
Delta-HCH	7.648	12.7	0.717	1.79
Heptachlor	8.427	33.2	1.43	1.12
Aldrin	10.433	21.5	0.686	2.45
Heptachlor-epoxide	12.82	12.1	0.498	2.89
o.p'-DDE	14.87	36.2	0.873	2.59
cis-Chlordane	15.69	6.7	0.323	0.95
p,p'-DDE	17.575	46.3	1.069	2.59
o,p'-DDD	18.485	35.3	0.868	1.11
Endrin	19.282	32.8	2.028	1.08
o.p'-DDT	20.633	34.7	0.887	1.65
p.p'-DDD	22.1	111.7	2.648	1.4
p.p'-DDT	24.545	19.4	0.496	0.98
Mirex	28.903	34.8	1.931	5.58
Endrin-keton	29.918	18.7	0.569	1.04
Thiram	2.513	12.86	1.82	2.14
Benefin	2.898	16.26	0.42	1.03
Fenitrothion	5.677	22.60	3.0	6.35
Parathion	6.32	13.98	0.27	1.84
Profenofos	8.975	17.32	2.58	4.39
Benalaxyl	11.287	25.29	0.83	4.0
Fenpropathrin	13.892	26.77	0.73	4.12
Pyridaben	15.955	16.55	1.17	3.88
Alpha-methrin	17.335	26.89	0.83	2.30
Etofenprox	21.0	13.27	2.17	3.72
S-fenvalerate	24.7	47.98	1.83	1.68

* Rt. = Retention time in minutes

3. Metals Analysis

Muscle tissue samples of *Bagrus bayad* fish were taken after preparation for trace metals analysis of Mn, Cr, Co, Pb and Ni by using Atomic Absorption Flame Emission Spectrophotometer (Shimadzu, AA-6200) **(AOAC, 1990)**.

RESULTS AND DISCUSSION

Data concerning the existence and distribution of detected pesticides (ppb) in the muscles and vescera of *Bagrus bayad* fish samples collected from the three main public markets locates at Kalubia governorate during the four seasons are tabulated in Tables (2 and 3). Data on the detected metals, in fish muscles are tabulated in Table (4).

1- Pesticides residues in fish muscles

Data in Table (2) indicate that pesticide residues increased in number and amount in the muscles of fish collected from Benha market followed by that of Benha, Kalub El-Balad and Shebin El-Kanater with mean values of 19.4, 14.56 and 12.68 ppb, respectively. This may be due to the existence of much more industrial factories, large agriculture areas, unconditional sanitation and many sources of contamination in this city. As for seasonal distribution, data in the same table indicate that, in general, fish samples collected in Spring were found containing more amounts and numbers of pesticides. This was pronounced with the three studied sites. As for Benha site, two pesticides were found during the four seasons, the 1st was parathion which was banned since 1985, but monitored in amounts of 88.66, 25.00, 55.00 and 21.00 ppb, at Autumn, Winter, Spring and Summer, respectively. The second compound was the pyrethroid fenpropathrin which is widely and illegally used for controlling insects and spider mites during Summer. It was detected in amounts of 11.00, 72.06, 19.90 and 75.00 ppb at the same seasons, respectively. Thiram, benefin, benolaxyl, S-fenvalerate and *p,p'*-DDD were not detected in any of the analyzed samples. *p,p'*-DDT, *o,p'*-DDD, *o,p'*-DDE and profenofos were found in Autumn samples only, i.e. 27.80, 13.00, 68.55 and 61.00 ppb, respectively. S-fenvalerate and endrin were found in spring samples, reached 89.10, and 90.10 ppb, respectively. *Cis*-chlordane was found in summer (76.00 ppb). It is interesting to notice the less contamination by organochlorine insecticides compared with the other pesticides with different functional groups. The same trend of results was noticed with Kalub El-Balad fish samples. The numbers of pesticides detected in muscles were 5/22, 7/22, 9/22 and 6/22 during Autumn, Winter, Spring and Summer, respectively. The total pesticides amounts reached 162.05, 391.30, 461.55 and 266.15 ppb at the same seasons, respectively. Autumn samples showed the existence of fenpropathrin, β-HCH, aldrin, *o,p'*-DDT and *p,p'*-DDD, reached 62.00, 13.80, 35.50, 19.00 and 31.75 ppb, respectively.

In Kalub El-Balad, two organochlorines were detected in Winter fish samples only, i.e. β-HCH and heptachlor (43.00 and 53.50 ppb). Also, two pyrethroids were found in muscles, namely fenpropathrin and alpha-methrin (20.50 and 51.10 ppb). Two organophosphorus were

Table 2. Detection of some pesticide residues (ppb) in the muscles of *Bagrus bayad* fish samples collected from different markets of Kalubia governorate during September (2000) to August (2001).

Pesticides	Shebin El-Kanater				Kalub El-Balad				Banha			
	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer
Alpha-HCH	31.00±9.0	ND	39.10 ± 0.0	ND	ND	ND	80.00± 0.0	ND	91.00 ± 0.0	ND	53.0 ± 0.0	ND
β-HCH	30.50±8.58	34.10±24.0	ND	ND	13.80± 4.4	43.00± 0.0	ND	ND	ND	58.00 ± 0.0	18.80 ± 0.0	ND
Heptachlor	ND	ND	ND	ND	ND	53.50 ± 0.0	ND	ND	ND	44.10 + 0.0	74.50 ± 0.0	ND
Aldrin	ND	ND	ND	ND	35.50± 0.0	ND	93.10 ± 0.0	23.00 ± 0.0	48.00 ± 0.0	ND	35.50 ± 0.0	19.20 ± 0.0
Hept-epoxide	ND	34.00 ± 0.0	ND	ND	ND	ND	81.00 ± 0.0	ND	ND	11.20 + 0.0	108.00±0.0	ND
o,p'-DDE	80.00±36.0	20.10 + 0.0	ND	ND	ND	ND	ND	ND	68.55±29.5	ND	ND	ND
cis-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	76.00± 0.0
p,p'-DDE	ND	ND	ND	ND	ND	ND	ND	83.00 + 0.0	ND	41.40 + 0.0	ND	58.00± 0.0
o,p'-DDD	ND	ND	ND	ND	ND	ND	21.10 ± 6.0	35.00 ± 0.0	13.00 ± 0.0	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	90.10 ± 0.0	ND
o,p'-DDT	ND	91.80 ± 0.0	ND	ND	19.00± 0.0	ND	ND	ND	ND	ND	43.80±22.2	ND
p,p'-DDD	6.00 ± 0.0	ND	35.10 ± 0.0	151.00±0.0	31.75±14.7	ND	ND	ND	ND	ND	ND	ND
p,p'-DDT	ND	ND	ND	ND	ND	ND	ND	ND	27.80 ± 5.2	ND	ND	ND

Data represents mean of 6 samples ± Std. Dev., ND: Not detected under limits of detection (1 ppb) Other pesticides that not detected at all in the collected samples: Etofenprox, Delta HCH, Mirex and Endrin-keton. Autumn: 21/9-20/12 (10-11-12/2000), Winter: 20/12-21/3 (1-2-3/2001) Spring: 21/3-20/6 (4-5-6/2001) and Summer 20/6-21/9 (7-8-9/2001).

Table 2. Cont.

Pesticides	Shebin El-Kanater				Kalub El-Balad				Banha			
	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer
Thiram	ND	ND	ND	3.00 ± 0.0	ND	ND	ND	76.00 ± 0.0	ND	ND	ND	ND
Benefin	ND	ND	64.50 ± 0.0	ND	ND	83.00 ± 0.0	64.50 ± 0.0	ND	ND	ND	ND	ND
Fenitrothion	ND	34.63±17.8	27.85 ± 5.8	ND	ND	49.10 ± 0.0	26.50 ± 0.0	46.15 ± 28.8	ND	105.00±0.0	33.40 ± 20.6	71.00 ± 0.0
Parathion	ND	ND	47.40 ± 28.2	ND	ND	91.10 ± 0.0	30.80 ± 0.0	ND	66 ± 37.1	25.00 ± 0.0	55.00 ± 0.0	21.00 ± 0.0
Profenofos	26.00 ± 0.0	ND	ND	ND	ND	ND	ND	ND	61.0 ± 3.0	ND	ND	ND
Benolaxyl	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fenpropathrin	ND	56.00±38.0	198.00 ± 0.0	ND	62.00 ± 15.0	20.50 ± 0.0	43.90 ± 0.0	3.00 ± 0.0	11.0 ± 0.0	72.00±38.8	19.90 ± 2.1	75.00 ± 0.0
Alphamethrin	ND	ND	ND	ND	ND	51.10 ± 0.0	20.65±10.2	ND	ND	ND	ND	ND
S-fenvalerate	ND	105.40±0.0	ND	ND	ND	ND	ND	ND	ND	ND	89.10 ± 0.0	ND

Data represents mean of 6 samples ± Std. Dev., ND: Not detected under limits of detection (1 ppb). Other pesticides that not detected at all in the collected samples: Etofenprox, Delta-HCH, Mirex and Endrin-keton. Autumn: 21/9-20/12 (10-11-12/2000), Winter: 20/12-21/3 (1-2-3/2001), Spring: 21/3-20/6 (4-5-6/2001) and Summer 20/6-21/9 (7-8-9/2001).

Table 3. Detection of some pesticide residues (ppb) in the vesceral of *Bagrus bayad* fish samples collected from different markets of Kalubia governorate during September (2000) to August (2001).

Pesticides	Shebin El-Kanater				Kalub El-Balad				Banha			
	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer
Alpha-HCH	227.33±182.4	ND	ND	ND	ND	ND	52.00±0.1	ND	13.00±0.0	ND	ND	ND
β-HCH	215.00±0.0	ND	ND	63.50±10.5	ND	ND	ND	23.00±0.0	ND	ND	39.00±0.0	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin	ND	ND	84.10±0.0	81.00±0.0	135.50±18.5	ND	40.10±0.0	43.00±0.0	28.00±0.0	ND	ND	ND
Hept-epoxide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
o,p'-DDE	ND	26.80±0.0	32.00±0.0	64.00±0.0	ND	ND	ND	ND	112.50±56.5	45.60±0.0	ND	ND
cis-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p'-DDE	ND	ND	ND	105.00±0.0	ND	ND	91.00±0.0	ND	ND	ND	ND	ND
o,p'-DDD	81.00±0.0	ND	46.00±0.0	ND	ND	ND	ND	ND	ND	12.50±0.0	83.00±0.0	27.10±0.0
Endrin	ND	ND	ND	ND	ND	ND	ND	87.00±0.0	ND	ND	ND	ND
o,p'-DDT	ND	14.80±0.0	ND	ND	ND	ND	71.00±0.0	ND	ND	ND	44.00±0.0	32.00± 0.0
p,p'-DDD	ND	70.30±0.0	ND	ND	ND	ND	ND	ND	ND	16.40±0.0	ND	ND
p,p'-DDT	34.10±0.0	ND	ND	ND	ND	ND	ND	ND	515.00±0.0	ND	ND	3.00 ± 0.0

Data represents mean of 6 samples ± Std. Dev., ND: Not detected under limits of detection (1 ppb). Other pesticides that not detected at all in the collected samples: Etofenprox, Delta-HCH, Mirex and Endrin-keton. Autumn: 21/9-20/12 (10-11-12/2000), Winter: 20/12-21/3 (1-2-3/2001), Spring: 21/3-20/6 (4-5-6/2001) and Summer 20/6-21/9 (7-8-9/2001).

Table 3. Cont.

Pesticides	Shebin El-Kanater				Kalub El-Balad				Banha			
	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer
Thiram	63.75±40.4	ND	ND	ND	18.00 ± 0.0	62.60 ± 0.0	ND	ND	ND	ND	ND	ND
Benefin	ND	45.00 ± 0.0	53.00 ± 0.0	ND	ND	17.00 ± 0.0	39.70 ± 0.0	ND	ND	108.00± 0.0	ND	ND
Fenitrothion	ND	76.15±18.2	52.00 ± 0.0	41.5 ± 28.5	48.50±26.5	ND	ND	ND	233.00±208.0	45.10 ± 1.9	81.00 ± 0.0	ND
Parathion	ND	ND	ND	11.00 ± 0.0	ND	46.35 ± 9.6	ND	28.00 ± 0.0	ND	15.30 ± 0.0	ND	3.00 ± 0.0
Profenofos	ND	9.00 ± 0.0	ND	ND	28.00 ± 0.0	ND	ND	ND	121.50±109.5	ND	ND	24.00 ± 0.0
Benolaxyl	ND	ND	ND	8.00 ± 0.0	ND	ND	ND	ND	ND	ND	ND	ND
Fenpropathrin	31.85±7.2	13.70 ± 5.4	53.50 ±42.2	26.00 ± 0.0	ND	ND	39.05 ±13.9	51.00 ± 0.0	154.50 ± 86.5	86.00 ± 0.0	95.50±54.3	23.00 ± 0.0
Alpha methrin	ND	ND	16.15±10.1	ND	ND	ND	ND	ND	ND	ND	9.00 ± 0.0	26.00 ± 0.0
S-fenvalerate	ND	16.500±0.0	78.10 ± 0.0	ND	ND	ND	8.00 ± 0.0	ND	ND	ND	ND	ND

Data represents mean of 6 samples ± Std. Dev., ND: Not detected under limits of detection (1 ppb). Other pesticides that not detected at all in the collected samples: Etofenprox, Delta-HCH, Mirex and Endrin-keton. Autumn: 21/9-20/12 (10-11-12/2000), Winter: 20/12-21/3 (1-2-3/2001), Spring: 21/3-20/6 (4-5-6/2001) and Summer 20/6-21/9 (7-8-9/2001).

detected in Winter fish samples: fenitrothion and parathion (49.10 and 91.10 ppb) in addition to the fungicide benefin (83.00 ppb). Spring samples were found contained the greatest numbers and amounts (9/22). Detected pesticides includes benefin, fenitrothion, parathion, fenpropathrin, alpha-methrin, α-HCH, aldrin, heptachlor-epoxide and *o,p'*-DDD. Their concentrations were 64.00, 26.50, 30.80, 43.90, 20.65, 80.00, 93.10, 81.00 and 21.10 ppb, respectively. Six pesticides were detected in summer samples, i.e. thiram, fenitrothion, fenpropathrin, aldrin, *p,p'*-DDE and *o,p'*-DDD. Their amounts were of 76.00, 46.15, 3.00, 23.00, 83.00 and 35.00 ppb, respectively.

As for Shebin El-Kanater site, data in Table (2) indicate contamination of fish by less numbers of pesticides than the other two sites, reaching, 5/22, 7/22, 6/22 and 2/22 during Autumn, Winter, Spring and Summer, respectively. The mean values of pesticide residues being 34.70, 73.72, 68.66 and 77.00 ppb in positive samples only. Thiram and *p,p'*-DDD were the only pesticides found in summer samples (3.00 & 151.00 ppb). Fenitrothion and fenpropathrin were detected in Winter and Spring, with mean values of 34.63 & 27.85 ppb (fenitrothion) and 56.00 & 198.00 ppb (fenpropathrin). Three pesticides were detected in spring samples only, namely, benefin (64.50 ppb), α-HCH (47.40 ppb). Two organophosphorus compounds were found in spring samples, i.e. fenitrothion and parathion (27.85 & 47.40 ppb). Fenpropathrin was the only pyrethroid detected in fish muscles in spring (198.00 ppb). Our findings are in agreement with that obtained by **El-Dib *et al* (1996); Hassan *et al* (1996); Holladay *et al* (1996); Badawy (1998) and Osfor *et al* (1998).**

2- Pesticides residues in fish vescera

Data in Table (3) indiacte different trend of total pesticide residues in vescera of *Bagrus bayad* compared with muscles. Fish from Shebin El-Kanater was contained the highest number and amount of pesticides contrary to the finding in muscles, i.e. 1740.13 and 1115.48 ppb, respectively. The numbers of compounds reached 30/88 and 20/88 in vescera and muscles, respectively. The corresponding values in Benha fish were 26/88 & 935.85 ppb, while Kalub El-Balad fish revealed 19/88 & 928.8 ppb compared with 32/88 & 1707.07 ppb (Benha) and 27/88 & 1281.05 (Kalub El-Balad) in vescera and muscles, respectively. Also, the numbers of pesticides detected were varied from season to season and from location to the other. It reached 6/22, 7/22, 6/22 & 7/22 (Benha), 4/22, 3/22, 7/22 & 5/22 (Kalub El-Balad) and 6/22, 8/22, 8/22 & 8/22 (Shebin El-Kanater) during Autumn, Winter, Spring and Summer, respectively. This indicate the high content of pesticides in vescera of fish collected during Spring and Summer, while the least contamination occurred during Autumn. The corresponding total amounts of pesticides detected reached 117.75, 328.50, 351.50 & 138.00 ppb (Benha), 230.00, 125.95, 340.85 & 232.00 ppb (Kalub El-Balad), 653.03, 272.25, 414.85 & 400.00 ppb (Shebin El-Kanater) at the same seasons, respectively.

Considering pesticides amount-season relationship, it could be noticed that certain compounds were detected in high amounts than the others. At Benha site, autumn samples of fish were found contained fenitrothion, profenofos, fenpropathrin and *o,p'*-DDE, with concentra-

tion of 233.00, 121.50, 154.00 & 112.50 ppb, respectively. Winter samples contained benefin, fenitrothion, fenpropathrin and *o,p'*-DDE, being 108.00, 45.10, 86.00 and 45.60 ppb, respectively. Seven compounds were detected in summer, but in lower amounts (3.00 – 32.00 ppb), while six products were found in Spring, five of them were existed in high amounts, i.e. fenitrothion, fenpropathrin, *o,p'*-DDD and *o,p'*-DDT (81.00, 95.50, 83.00 & 44.00 ppb, respectively).

Samples from Kalub El-Balad showed different trend of pesticide residues, where fenitrothion and aldrin were found in Autumn samples at high amounts reached 48.50 & 135.50 ppb, respectively, while thiram and profenofos were found in low concentrations (18.00 & 28.00 ppb). Three pesticides thiram, benefin and parathion only were detected in vescera of fish collected at winter, with concentrations of 62.60, 17.00 & 46.35 ppb, respectively. Among the seven pesticides detected in samples collected during Spring, benefin, fenpropathrin, α-HCH, aldrin, *p,p'*-DDE and *o,p'*-DDT were detected in high levels, 39.70, 39.05, 52.00, 40.00, 91.00 and 71.00 ppb, respectively. Fenpropathrin, aldrin and endrin were found in vescera of fish collected in Summer with concentrations of 51.00, 43.00 & 87.00 ppb, respectively.

As for Shebin El-Kanater, data in Table (3) indicate the detection of same numbers of pesticides (8/22) in the samples collected during Winter, Spring and Summer, while less number was found in Autumn (6/22). The corresponding amounts of total residues reached 272.25, 414.85, 400.00 and 653.03 ppb, in the same seasons, respectively. The compounds which were found in great amounts were thiram, α-HCH, β-HCH & *o,p'*-DDD (Autumn 63.75, 227.33, 215.00, 81.00 ppb), benefin, fenitrothion, *p,p'*-DDD (Winter 45.00, 76.15, 70.30 ppb), benefin, fenitrothion, fenpropathrin, S-fenvalerate, aldrin and *o,p'*-DDD (Spring, 53.00, 52.00, 53.50, 78.10, 81.10 & 46.00 ppb) and fenitrothion, β-HCH, aldrin, *o,p*-DDE and *p,p'*-DDE (Summer, 41.50, 63.50, 81.00, 64.00 & 105.00 ppb), respectively.

Reviewing the above mentioned results, it could be concluded the difficulty to interpretate clear trend/pattern of pesticide residues in muscles and/or vescera of fish samples in relation to season and location factors. In general, the detected amounts of pesticides were found below the maximum residue limits with few exceptions.

In the four seasons, the total pesticide residues in both muscles and vescera reached 2855.61, 2209.85 and 2642.92 ppb in the fish collected from Shebin El-Kanater, Kalub El-Balad and Benha, respectively. Such amounts were seasonally distributed as 826.53, 648.28, 826.80 and 554.00 ppb (Shebin El-Kanater), 529.10, 288.00, 732.15 and 498.15 ppb (Kalub El-Balad) and 526.76, 685.26, 972.60 and 458.20 ppb (Benha) at autumn, winter, spring and summer, respectively. Since the compound may be found in muscle, while absent in vescera, the calculation of percent distribution ratio between the two portions of the body seems unreliable.

The existence of pesticide residues in fish tissues found in this study was in agreement with those reported by several investigators, *i.e.* **Leiker *et al* (1991); El-Dib *et al* (1996); Hassan *et al* (1996); Holladay *et al* (1996); Badawy (1998) and Osfor *et al* (1998).**

In conclusion, the present monitoring study proved that the contamination of

Bayad fish *Bagrus bayad* in Kalubia was not serious. The current acceptable daily intake (ADI) values were adopted by, 0.56 mg for α, β and Delta – HCH, 0.007 mg for heptachlor and aldrin, 1.4 mg for DDT, 0.035 mg for chlordane, 0.35 for fenitrothion and 1.4 mg for fenvalerate/70 kg human adult. In the USA, the recommended levels in fish for the protection of piscivores are that total DDT should not exceed 1 mg Kg^{-1} and that of aldrin, dieldrin, endrin, chlordane, lindane, toxaphene and endosulfan should not exceed 0.1 mg kg^{-1} net weight of whole fish either singly or in combination **(EPA, 1973)**. The chlorinated hydrocarbon level monitored in the present investigation were substantially far below the U.S. Food and Drug administration guidelines; 5 ppm Σ DDT, 0.3 ppm dieldrin and endrin. Taking these levels as a guide, it could be concluded that the monitored levels of organochlorines in fish samples from Kalubia are not high enough to cause any hazard and impact on public health.

However, the existence of the detected pesticide residues may be explained by the extensive use of pesticides of various groups, especially insecticides and fungicides in various seasons which highly affecting the water quality and thus reach to the fish muscles and vescera according to their lipophilic nature which make them penetrate and accumulate in the selected organs of the studied fish.

3- Distribution of metals in the muscles

Data in Table (4) indicate the occurrence of different pattern of metals distribution in the three studied sites and seasons. Cobalt and lead were detected in muscles of bayad fish collected during Autumn from Kalub-El-Balad only (0.10 ppb).

The other sites and seasons were found free of cobalt residues or contained in amounts below the level of detection. The other three metals were found in all sites and seasons, but in different amounts. Nickel was found in high amounts during Summer (Shebin El-Kanater) and Winter (Kalub El-Balad and Benha). Their concentration values were 0.06, 0.04 and 0.04 ppb, respectively. Copper was found in the highest amount during autumn and spring at the three tested sites, i.e. 0.04 & 0.04 ppb (Shebin El-Kanater), 0.05 & 0.07ppb (Kalub El-Balad) and 0.06 & 0.07 ppb (Benha) in muscles of fish collected during autumn and spring, respectively.

It is interesting to notice the detection of considerably high amounts of manganese than the other elements. The highest values were recorded during Spring (0.29 ppb), Winter (0.46 ppb) and Summer (0.23 ppb) in samples from Shebin El-Kanater, Kalub El-Balad and Benha, respectively. The other seasons showed slightly less amounts, i.e. 0.25, 0.19 & 0.21 ppb during Summer, Winter and Autumn of Shebin El-Kanater, respectively. Kalub El-Balad samples showed 0.18, 0.29, 0.46 & 0.14 ppb during Summer, Autumn, Winter and Spring, respectively. Benha samples showed 0.23, 0.11, 0.14 & 0.15 ppb from Summer, Winter, Autumn and Spring, respectively. The contamination of fish by high amounts of metals was reported by several investigators, i.e, **Zayed *et al* (1994); Abdel Naser *et al* (1996) and Seddek *et al* (1996).**

As for the detected metals in abnormal high concentrations in muscles of fish, this may be attributed to the

Table 4. Detection of some elements (ppb) in the muscles of *Bagrus bayad* fish samples collected from different markets of Kalubia governorate during September (2000) to August (2001).

Station	Season	Metals (ppb)				
		Mn	Cu	Pb	Ni	Co
Shebin El-Kanater	Autumn	0.21±0.11	0.04±0.05	ND	0.01 +0.01	ND
	Winter	0.19±0.14	0.22±0.30	ND	0.02±0.01	ND
	Spring	0.29±0.19	0.04±0.03	ND	0.01±0.01	ND
	Summer	0.25±0.13	0.03±0.03	ND	0.06±0.03	ND
	Average/year	0.235	0.0825	-	0.025	-
Kalub ElBalad	Autumn	0.29±0.09	0.05±0.04	0.01+0.01	0.02±0.02	0.01±0.02
	Winter	0.46±0.05	0.02±0.01	ND	0.06±0.06	ND
	Spring	0.14±0.05	0.07±0.04	ND	0.02±0.02	ND
	Summer	0.18±0.06	0.03±0.04	ND	0.04±0.04	ND
	Average/year	0.2675	0.0425	0.0025	0.035	0.0025
Banha	Autumn	0.14±0.05	0.06±0.04	ND	0.03±0.03	ND
	Winter	0.11±0.10	0.03±0.02	ND	0.04±0.05	ND
	Spring	0.15±0.12	0.07±0.01	ND	0.01±0.02	ND
	Summer	0.23±0.15	0.05±0.01	ND	0.01±0.01	ND
	Average/year	0.1575	0.0525	-	0.0225	-

ND; Not Detected., Autumn : 21/9-20/12 (10-11-12/2000). Winter: 20/12-21/3 (1-2-3/2001), Spring : 21/3-20/6 (4-5-6/2001) and Summer date: 20/6-21/9 (7-8

aggregate amounts of these metals from different sources, i.e. pesticides, fertilizers and waste water from different industries which make them to be exist in the water resources and reach to the fish organs.

In general, such amounts of metals detected in fish muscles in our study were less than that reported by the **Standard for Organic Food and Farming, (1997)**.

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مجلة حوليات العلوم الزراعية، كلية الزراعة ، جامعة عين شمس ، القاهرة ، م(٤٨)، ع (١)، ٤٢٧-٤٤٠، ٢٠٠٣

تواجد وتوزيع بعض متبقيات المبيدات والمعادن فى سمك البياض (*Bagrus bayad*) من أسواق محافظة القليوبية – مصر

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يهدف هذا البحث إلى دراسة تواجد وتوزيع وتقدير متبقيات المبيدات والمعادن فى عضلات وأحشاء سمك البياض فى عينات تم جمعها من ثلاثة أسواق رئيسية شعبية فى محافظة القليوبية بمصر خلال فترة أربعة مواسم عام ٢٠٠٠-٢٠٠١. وقد أشارت النتائج إلى أن متبقيات المبيدات التى تم الكشف عنها تختلف فى عددها وكميتها وذلك فيما بين العضلات والأحشاء وذلك حسب الموسم والموقع الذى تم جمع العينات منه. فقد أظهرت النتائج بصفة عامة إلى زيادة كمية متبقيات المبيدات فى الأحشاء عن العضلات. من ناحية أخرى، فقد تبين من النتائج المتحصل عليها صعوبة تحديد إتجاه معين فى العلاقة بين متبقيات المبيدات فى الأحشاء والعضلات فى عينات السمك وبين عوامل الموسم وموقع جمع العينات. كذلك، فقد أشارت النتائج إلى أن الكميات المقدرة من متبقيات المبيدات كانت أقل من حدود المتبقيات المسموح بها مع وجود بعض الإستثناءات. إضافة إلى ذلك، فقد أظهرت النتائج إلى وجود بعض متبقيات المعادن فى عضلات عينات السمك. وقد سجل وجود عنصرى الكوبلت والرصاص فى العينات التى تم تجميعها فى موسم الخريف بينما تم الكشف عن متبقيات المعادن الأخرى فى كل المواسم والمواقع المختبرة. وقد تبين من ذلك، أن المنجنيز كان من أكثر المعادن تواجداً فى عينات السمك المختبرة.

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