Annals Agric. Sci., Ain Shams Univ., Cairo, 48(1), 411-426, 2003

SURVEY AND DISTRIBUTION OF PESTICIDES AND METALS IN KARMOUT FISH, *CLARIAS LAZARA* COLLECTED FROM KALUBIA GOVERNORATE, EGYPT

[30]

Zidan, Z.H.[1]; M.I. Abdel-Megeed[1]; G. Gupta[2]; K.A. Mohamed[1]; K.M. Weshahy[1] and A.E. Bayoumi[1]

ABSTRACT

Existence and organ distribution of some pesticide residues and heavy metals in muscle and visceral samples of Karmout fish, *Clarias lazara* collected from different markets locates at Kalubia governorate, Egypt were investigated during the period of April, 1999 to March 2000. Data indicate the detection of different amounts of pesticide residues and heavy metals in fish samples according to the sampling site and season. Fish samples from El-Esmailia and El-Sharkawia markets were found contained the lowest levels of pesticide residues within the 1st five months. The other sites showed different trend of residues as amounts and types. As for residues distribution in fish organ, data indicate that the majority of pesticide residues was detected in the visceral tissues compared with muscles. Most of the analyzed muscles samples were found free of residues or contained low and/or non-detected levels. It is clearly evident to notice that the detected residues in fish tissues were found in amounts almost within the permissible levels. Generally, both of location and season factors played role in this respect. Also, some metals were detected in all samples of fish in a very minute amounts.

Key words: Pesticides, Metals, Survey, Residues, Fish

INTRODUCTION

Organochlorine and polychlorinated biphenyls (PCBs) pesticides 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 micro-organisms and fish led to the build up in the food chain (**Macek and Korn, 1970**). In Egypt, waste waters and agriculture drains containing pesticide residues and/or metals are discharged into the River Nile directly. In addition, despite

1- Department of Plant Protection, Faculty of Agriculture, Ain Shams University, Shoubra El-Kheima, Cairo, Egypt.
2- Department of Agriculture Plant and Soil Science, University of Maryland, Eastern Shore, Princess ANNE, MD, USA.

(Received January 15, 2002)
(Accepted April 8, 2002)

the wide spread use of pesticides in agriculture and metals in industrial areas near Nile river, data on their accumulation in fish exposed to contaminated water are still lacking. In recent years, the use of chlorinated hydrocarbons and some other hazardous compounds has been drastically banned but concern remains about the continuing occurrence of these toxicants in the aquatic ecosystem posing hazards to public health. On the other hand monitoring of chlorinated hydrocarbons, other pesticide residues and/or metals in fish reflects long term exposure since they are degraded slowly **(Lieb *et al* (1974); Zayed *et al* (1994); Abdel Naser *et al* (1996) and Seddek *et al* (1996)**.

The present investigation aimed to throw light on the contamination and body distribution of Karmout fish by pesticides and heavy metals at Kalubia governorate during 1999/2000.

MATERIAL AND METHODS

1. Samples collection and preparation

Fish samples were collected at random from different markets locates at Kalubia governorate during the period from April, 1999 – March, 2000 . Five samples of *Clarias lazara* fish were taken from each market, 500 gram each and transferred to the laboratory for pesticide residues and metals determination. Fish samples were washed with clean tap water to remove mud. The head, tail, fins, and internal organs were removed. Analyses were carried out on muscles tissues and viscera for pesticide residues and muscles only for heavy metals determination.

1. Pesticide residue analysis

1.1. Extraction, Clean-up and GC determination. 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 official methods of analysis **(Anonymous, 1990).**

2.2. Separation and identification of the studied pesticides by GC (Shimadzu, 12-A) analysis equipped with FID and ECD detectors. 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	H_2 1.0 kg/cm^2
Air	0.5 kg/cm
- Attenuation	10 x 5

Fifteen pesticides belonging to different functional groups (fungicides, herbicides 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 lipid chrommatography : 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 tissues samples of *Clarias lazara* 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 the monitored pesticides representing organochlorines (14), organophosphorous (3), pyrethroids (2) and miscellaneous (4), in the muscles and vescera tissues of Karmout fish, *Clarius lazara* which were collected from the main five public markets locates at Kalubia governorate during the four seasons of the year 1999 – 2000 are tabulated as ppb in Tables 2 and 3. Examination of the obtained results indicated the detection of pesticide residues in various amounts and types from the studied sites and during the considered seasons.

1. Existence and distribution of pesticides residues

1.1. Pesticides in fish muscles

Data in Table (2) indicate different pattern of existence and distribution of pesticides residues in the muscles of Karmout according to season, location and pesticide type. As general, most of positive contaminated muscles samples were found containing pesticide residues at ppb levels and within the permissible levels. No clear trend of pesticide distribution was noticed in relation to the studied factors.

Alpha-HCH was detected in great amount (1364 ppb as total) in fish muscles from El-Kanater and distributed as 551.0, 343.0, 405.0 & 65.0 ppb in Spring, Summer, Autumn and Winter, respectively. The product was not found in fish muscles from El-Esmailia and El-Shrkawia sites. It was detected in Kalub El-balad in Winter only (125.0 ppb), while monitored in Shebin El-Kanater samples during Spring and Winetr (145.0 and 63.0 ppb. respectively). Beta-HCH was found in great amount in Kalub El-Balad only in Winter (711.0 ppb), and in El-Kanater during Spring and Summer only (620.5 & 234.0 ppb). It was detected in Shebin El-Kanater in Spring and Winter (177.0 & 69.0 ppb). The product was absent in El-Esmailia samples, while detected in Summer (15.0 ppb) in El-Sharkawia. Delta-HCH was detected in Shebin El-Kanater samples (1984.0 ppb) throughout the studied year except Summer. El-Sharkawia and El-Esmailia came next, showing total residues of 929.0 and 670.0 ppb, respectively. It was detected in Spring only in El-Kanater water (32.5 ppb).

Heptachlor didn't exist in fish muscles from Shebin El-Kanater, while the highest amount as total was found in Kalub El-Balad samples (957.0 ppb) distributed as 226.0, 60.0, 38.0 & 633.0 ppb during Spring, Summer, Autumn and Winter, respectively. A great amount was found during spring in El-Kanater samples (396.5 ppb). Heptachlor-epxide was not found in samples from Kalub El-Balad, while detected in El-Kanater (Spring, 356.0 ppb), El-Esmailia (Summer, 616.0 ppb) and in El-Sharkawia (Autumn, 263.0 ppb). Aldrin was not detected in fish muscles from Shebin El-Kanater, while detected in Spring

Table 2. Detection of some pesticides residues (ppb) in the muscles of *Clarias lazara* fish samples collected from different markets of Kalubia governorate during April (1999) to March (2000).

Market	Season	Detected Pesticides (ppb)													
		α-HCH	β-HCH	Delta-HCH	Hepta-chlor	Aldrin	Hept.-epoxide	*o,p'*-DDE	*Cis*-Chlor-dane	*P,p'*-DDE	Endrin	*o,p'*-DDT	*p,p'*-DDD	*o,p'*-DDD	Aldrin
Shebin El-Kanater	Spring	145	177	1205	ND	ND	ND	ND	ND	ND	ND	ND	ND	92	ND
	Summer	ND	ND	ND	ND	ND	403	155	512	ND	96	832	ND	ND	ND
	Autumn	ND	ND	465	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Winter	63	69	314	ND	ND	ND	ND	ND	ND	906	ND	ND	ND	ND
	Sum.	208	246	1984	-	-	403	155	512	-	1002	832	-	92	-
Kalub El-Balad	Spring	ND	ND	ND	226	162.4	ND	639	ND	ND	ND	ND	ND	ND	ND
	Summer	ND	ND	206	60	ND	ND	349	534	ND	ND	507.5	ND	92	ND
	Autumn	ND	ND	ND	38	ND	ND	292	409	ND	ND	ND	ND	ND	ND
	Winter	125	711	ND	633	282	ND	307	ND	ND	ND	ND	ND	ND	ND
	Sum.	125	711	206	957	444.4		1587	943	-	-	507.5	-	92	-
El-Kanater	Spring	551	620.5	32.5	396.5	839	356	ND	ND	ND	1075	ND	ND	ND	17
	Summer	343	234	ND	13	ND	ND	ND	ND	ND	ND	35	ND	88	54
	Autumn	405	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Winter	65	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Sum.	1364	854.5	32.5	409.5	839	356	-	-	-	1075	35	-	88	71
El-Esmailia	Spring	ND	ND	379	ND	120	ND	459	ND	ND	ND	ND	2981	ND	ND
	Summer	ND	ND	5	ND	103	616	ND	ND	ND	ND	ND	ND	ND	ND
	Autumn	ND	ND	286	128	ND	ND	61	ND	961	ND	ND	ND	ND	ND
	Winter	ND	ND	ND	ND	ND	ND	47	ND	ND	ND	ND	ND	166	ND
	Sum.	-	-	670	128	223	616	567	-	961	-	-	2981	166	-
El-Sharkawia	Spring	ND	ND	414	ND	164	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Summer	ND	15	408	41	ND	ND	ND	ND	ND	23	ND	ND	ND	ND
	Autumn	ND	ND	107	16	706	263	ND	ND	ND	ND	ND	ND	ND	ND
	Winter	ND	ND	ND	49	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Sum.	-	15	929	106	870	263	-	ND	-	23	ND	ND	ND	ND

ND: Not detected under the limit of detection in our laboratory (1 ppb).
Spring date: 21/3-20/9 (4-5-6/1999), Summer date 20/6-21/9 (7-8-9/1999), Autumn date: 21/9-20/12 (10-11-12/1999) and Winter date: 20/12-21/3 (1-2-3/2000).

Table 2. Cont.

Market	Season	Detected Pesticides (ppb)								
		Benefin	Fenitro-thion	Parath-ion	Benalxyl	Fenprop-athrin	Pyrida-ben	Alpha-methrin	Etofen-prox	Profen-ofos
Shebin El-Kanater	Spring	ND	30	72	ND	ND	ND	ND	ND	ND
	Summer	ND	15	ND	101	ND	592	ND	ND	ND
	Autumn	ND	ND	ND	24	ND	17	ND	ND	ND
	Winter	850	ND	ND	ND	39	ND	ND	ND	ND
	Sum.	850	45	72	125	39	609	-	-	-
Kalub El-Balad	Spring	ND	ND	ND	42.5	19	ND	39.5	ND	ND
	Summer	ND	51	19	57	ND	ND	ND	39	ND
	Autumn	ND	578.5	ND	ND	75	ND	ND	ND	516
	Winter	201	83	ND	ND	41	50	ND	ND	ND
	Sum.	201	712.5	19	99.5	135	50	39.5	39	516
El--Kanater	Spring	ND	25	ND	9	ND	ND	ND	ND	15
	Summer	ND	ND	ND	ND	ND	49.5	ND	ND	ND
	Autumn	608	ND	ND	ND	614	576	ND	ND	83
	Winter	ND	45	ND	ND	40	ND	93	ND	ND
	Sum.	608	70	-	9	654	625.5	93	-	98
El--Esmailia	Spring	ND	ND	5	ND	ND	ND	ND	ND	ND
	Summer	ND	9	51	33	ND	ND	44	17	ND
	Autumn	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Winter	ND	ND	18	ND	31	ND	ND	ND	ND
	Sum.	-	9	74	33	31	-	44	17	-
El- Sharkawia	Spring	ND	78	ND	31	ND	ND	ND	ND	ND
	Summer	73	ND	ND	ND	ND	ND	ND	ND	ND
	Autumn	16	ND	ND	ND	114	ND	ND	ND	43
	Winter	ND	124	46	ND	24	ND	ND	ND	ND
	Sum.	89	202	46	31	138	-	-	-	43

ND: Not detected under the limit of detection in our laboratory (1 ppb).
Spring date: 21/3-20/9 (4-5-6/1999), Summer date 20/6-21/9 1(7-8-9/1999), Autumn date: 21/9-20/12 (10-11-12/1999) and Winter date: 20/12-21/3 (1-2-3/2000).

samples at El-Kanater (839.0 ppb). Fish from Kalub El-Balad was containing aldrin residues in Spring (162.4 ppb) and Winter (282.0 ppb). El-Esmailia fish was found contaminated with aldrin during Spring and Summer (120.0 & 103.0 ppb). El-Sharkawia fish was found containing aldrin at 164.0 & 706 ppb during Spring and Autumn, respectively.

O,p'-DDE was not found in El-Sharkawia and El-Kanater fish samples while detected in Summer only (155.0 ppb) in Shebin El-Kanater. Residues were detected in Kalub El-Balad fish ,i.e. 639.0, 349.0, 292.0 & 307.0 ppb in Spring, Summer, Autumn and Winter, respectively. *P,p'*-DDE was detected in fish samples from El-Esmailia during Autumn only (961.0 ppb). *P,p'*-DDD was found in fish samples during summer only at Shebin El-Kanater (832 ppb), Kalub El-Balad (507.5 ppb) and El-Kanater (35.0 ppb). Mirex was detected in El-Esmailia fish only during spring (2981.0 ppb). *O,p'*-DDD was found in fish in summer at Shebin El-Kanater (92 ppb), Kalub El-Balad (92.0 ppb), El-Kanater (88.0 ppb), El-Esmailia (166.0 ppb).

Cis-chlordane was not detected in fish from El-Kanater, El-Esmailia and El-Sharkawia, while detected in Summer only (512.0 ppb) in Shebin El-Kanater. Kalub El-Balad fish was found containing residues at Summer and Autumn only (534.0 and 409.0 ppb, respectively.

Endrin residues were detected in fish from Shebin El-Kanater during Summer and Winter (96.0 & 906.0 ppb), El-Kanater in Spring (1075.0 ppb) and El-Sharkawia (23.0 ppb in Summer). Endrin Keton was detected only in fish muscles from El-Kanater during Spring (17.0 ppb) and Summer (54.0 ppb).

Benefin was found in fish muscle from Shebin El-Kanater at Winter (850 ppb), Kalub El-Balad (Winter, 201.0 ppb), El-Kanater (Autumn, 608.0 ppb), El-Sharkawia (Summer & Autumn, 73.0 & 16.0 ppb).

Fenitrothion was found in the fish muscles from the five selected locations. The highest amount was detected during Autumn in fish from Kalub El-Balad (578.5 ppb) and in Summer and Winter 51.0 and 83.0 ppb, respectively. El-Sharkawia fish muscles were found containing fenitrothion residues during Spring and Winter (78.0 and 124.0 ppb, respectively). Parathion the most toxic and hazardous organophosphorous insecticide was found in fish muscles from Shebin El-Kanater (Spring, 72.0 ppb), Kalub El-Balad (Summer, 19.0 ppb), El-Esmailia (Summer, 51.0 ppb and Winter, 18.0 ppb) and El-Sharkawia (Winter 46.0 ppb). Profenofos residues were detected in fish samples during Autumn at Kalub El-Balad, El-Kanater and El-Sharkawia (516.0, 83.0 and 43.0 ppb, respectively).

In case of Benalaxyl, the total of such compound was detected in high levels especially at Shebin El-Kanater (125.0 ppb) and Kalub El-Balad (99.5 ppb).

The Pyrethroid fenpropathrin was found in Shebin El-Kanater and El-Esmailia fish samples at Winter only (39.0 & 31.0 ppb, respectively. Fenpropathrin residues was also detected in fish from Kalub El-Balad during Spring, Autumn and Winter (19.0, 75.0 and 41.0 ppb), in El-Kanater fish at Autumn and Winter (614.0 & 40.0 ppb) as well as in El-Sharkawia fish samples (114.0 & 24.0 ppb). Two fish samples only were found containing residues of the pyrethroid alpha-methrin, Kalub El-Balad (39.5 ppb, in Spring) and El-Kanater (93.0 ppb, in

Winter) and El-Esmailia (44.0 ppb, in Summer).

Pyridaben was detected in Shebin El-Kanater (Summer, 592 ppb & Autumn, 17 ppb). Fish muscles from El-Kanater was found containing this pesticide during Summer and Autumn (49.5 & 576.0 ppb).

Two samples only of fish were found polluted with Etofenprox at Kalub El-Balad and El-Esmailia in Summer (39.0 & 17.0 ppb).

Reviewing the above mentioned finding, it could be concluded that fish samples collected from Kalubia governorate were found containing pesticide residues in various amounts, and frequencies. Most samples were found free of residues or contained low levels within the permissible levels. Mirex which never used in Egypt before was detected in some samples at some sites. In general, the number of positive contaminated samples was very small and represent negligible percentage among the total samples.

1.2. Pesticides in fish vescera

Data in Table (3) indicate in general, that vesceral tissues of Karmout fish were found containing slightly more pesticide residues compared with that monitored in the muscles of the same fish. The site and season of sampling played role on the existence and distribution of pesticide residues in fish tissues.

Alpha-HCH was detected in fish from all sites, except El-Sharkawia. The highest amount was recorded in El-Esmailia fish during Spring (1955.5 ppb), Kalub El-Balad in Winter (511.0 ppb), El-Kanater in Spring and Summer (511.0 & 433.0 ppb), Shebin El-Kanater in Autumn and Winter (403 & 499 ppb). Beta-HCH was detected in considerable high levels in fish vescera from Shebin El-Kanater in Spring, Summer & Winter (227.0, 651.0 & 998.0 ppb). Fish vescera from Kalub El-Balad was found containing β-HCH at 181 ppb in Winter. El-Kanater site showed the existence of this insecticide during Spring (891.0 ppb) and Winter (12.0 ppb). This compound was found in El-Esmailia fish in Winter only (39.5 ppb and during Spring only in fish from El-Sharkawia (39.0 ppb). Delta-HCH was detected in El-Kanater in Spring and Summer (308.0 & 416.0 ppb), Kalub El-balad in Spring and Autumn (1075.0 & 357.0 ppb), El-Kanater in Autumn and Winter (65.0 & 69.0 ppb), El-Esmailia in Autumn and Winter (875.0 & 89.0 ppb) and El-Sharkawia in Spring and Summer (55.0 & 165.0 ppb, respectively).

Heptachlor was not found in vescera tissues of Karmout fish from Shebin El-Kanater and El-Sharkawia, while detected in Kalub El-Balad in Summer and Winter (130.0 & 193.0 ppb); El-Kanater in all seasons except Summer at very low levels, and in El-Esmailia during Spring and Winter (115.0 and 7.0 ppb, respectively). Heptachlor-epoxide was detected in samples from Kalub El-Balad and El-Kanater during Autmn (52.0 and 472.0 ppb). It was found during spring and Winter in both El-Esmailia (820 & 626 ppb) and El-Sharkawia (334.0 & 774.0 ppb). Shebin El-Kanater revealed the detection of this organochlorine insecticide in fish vescera during Spring and Summer (176 & 16 ppb). Aldrin was detected in El-Sharkawia in all seasons in considerble amount at Spring, Summer, Autumn & Winter (193.0, 65.0, 384.0 & 145.0 ppb, respectively). It was detected in Winter only in fish vescera 363 ppb from Kalub

Table 3. Detection of some pesticides residues (ppb) in the vesceral of *Clarias lazara* fish samples collected from different markets of Kalubia governorate during April (1999) to March (2000).

Market	Season	Detected Pesticides (ppb)												
		α-HCH	β-HCH	Delta-HCH	Hepta-chlor	Aldrin	Hept.-epoxide	*o,p'*-DDE	*Cis*-Chlor-dane	*p,p'*-DDE	Endrin	*o,p'*-DDT	*p,p'*-DDD	*o,p'*-DDD
Shebin El-Kanater	Spring	139	227	ND	ND	164	176	ND	ND	ND	ND	ND	ND	ND
	Summer	ND	651	308	ND	129	16	82	ND	180	ND	ND	ND	ND
	Autumn	403	ND	416	ND	ND	ND	ND	ND	ND	ND	ND	ND	995
	Winter	499	998	ND	ND	255	ND	307	ND	ND	249	ND	ND	ND
	Sum.	1041	1876	724	-	548	192	389	-	180	249	-	-	995
Kalub El-Balad	Spring	ND	26	1075	ND	ND	ND	ND	337	ND	ND	ND	ND	ND
	Summer	ND	ND	ND	130	ND	ND	894	ND	ND	ND	ND	ND	988
	Autumn	ND	ND	357	ND	ND	52	ND	ND	ND	232	ND	ND	76
	Winter	511	181	ND	193	363	ND	194	ND	203.5	ND	ND	ND	ND
	Sum.	511	207	1432	323	363	52	1088	337	203.5	232	-	-	1064
El-Kanater	Spring	511	891	ND	15	87	ND	ND	ND	ND	ND	ND	ND	ND
	Summer	433	ND	ND	ND	ND	ND	ND	ND	ND	ND	29	186	ND
	Autumn	ND	ND	65	22	ND	472	ND	ND	ND	ND	ND	ND	ND
	Winter	ND	12	69	7	1540	ND	ND	ND	ND	ND	727	ND	ND
	Sum.	944	903	134	44	1627	472	-	-	-	-	756	186	-
El-Esmailia	Spring	1955.5	ND	ND	115	721	820	352	ND	ND	ND	ND	ND	ND
	Summer	ND	ND	ND	ND	102	ND	ND	633	366	ND	ND	ND	ND
	Autumn	ND	ND	875	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Winter	129	39.5	89	7	ND	626	ND	ND	320	ND	ND	ND	633
	Sum.	2084.5	39.5	964	122	823	1446	352	633	686	-	-	-	633
El-Sharkawia	Spring	ND	39	55	ND	193	334	ND	ND	ND	831	ND	ND	ND
	Summer	ND	ND	165	ND	65	ND	243	ND	ND	ND	ND	ND	ND
	Autumn	ND	ND	ND	ND	384	ND	ND	ND	ND	ND	ND	ND	ND
	Winter	ND	ND	ND	ND	145	774	140	ND	865	ND	ND	ND	ND
	Sum.	-	39	220	-	787	1108	383	-	865	831	-	-	-

ND: Not detected under the limit of detection in our laboratory (1 ppb).
Spring date: 21/3-20/9 (4-5-6/1999), Summer date 20/6-21/9 (7-8-9/1999), Autumn date: 21/9-20/12 (10-11-12/1999) and Winter date: 20/12-21/3 (1-2-3/2000).

Table 3. Cont.

Market	Season	Detected Pesticides (ppb)								
		Thiram	Benefin	Fenitrothion	Parathion	Benalxyl	Fenpropathrin	Pyridaben	Alphamethrin	Profenofos
Shebin El-Kanater	Spring	22	ND	46	91	21	123	ND	ND	ND
	Summer	37	ND	11	ND	ND	ND	1736	ND	ND
	Autumn	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Winter	ND	1100	ND	19	ND	37.5	ND	ND	ND
	Sum.	59	1100	57	110	21	160.5	1736	-	-
Kalub El-Balad	Spring	ND	ND	93	90	88	ND	ND	ND	ND
	Summer	ND	ND	91	33	ND	ND	ND	ND	ND
	Autumn	ND	ND	ND	ND	ND	ND	44.5	ND	ND
	Winter	ND	ND	433	79	ND	25	ND	ND	ND
	Sum.	-	-	617	202	88	25	44.5	-	-
El-Kanater	Spring	151	ND	ND	72.5	ND	ND	ND	430	ND
	Summer	88	ND	ND	ND	8	ND	11	6	ND
	Autumn	ND	ND	489	ND	ND	ND	ND	ND	ND
	Winter	491	ND	75	ND	ND	26.5	ND	ND	ND
	Sum.	730	-	564	72.5	8	26.5	11	436	-
El-Esmailia	Spring	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Summer	ND	ND	250.5	89	ND	ND	ND	17	326
	Autumn	ND	ND	ND	425	ND	ND	ND	ND	ND
	Winter	ND	22	55	68.5	240	18	30	ND	ND
	Sum.	-	22	305.5	582.5	240	18	30	17	326
El- Sharkawia	Spring	ND	ND	55	91	22.2	ND	ND	ND	ND
	Summer	ND	ND	83	12	42	23	77	ND	710
	Autumn	ND	ND	ND	755	254	171	923	ND	ND
	Winter	ND	145	ND	ND	ND	ND	ND	ND	ND
	Sum.	-	145	138	858	318.2	194	1000	-	710

ND: Not detected under the limit of detection in our laboratory (1 ppb).

Spring date: 21/3-20/9 (4-5-6/1999), Summer date 20/6-21/9 (7-8-9/1999), Autumn date: 21/9-20/12 (10-11-12/1999) and Winter date: 20/12-21/3 (1-2-3/2000).

El-Balad, and Spring & Winter (87.0 & 1540.0 ppb), in Spring & Summer (721.0 & 102.0 ppb) in El-Esmailia. Shebin El-Kanater samples showed the existence of aldrin in all seasons except Autumn. *Cis*-chlodane was detected in fish vescera from Kalub El-Balad during Spring only (337.0 ppb) and El-Esmailia during Summer (633.0 ppb). Endrin was monitored in Shebin El-Kanater in Winter (249 ppb), Kalub El-Balad in Autumn (232.0 ppb), El-Sharkawia in Spring (831.0 ppb), while disappeared from other sites.

O,p'-DDE was found in high level in Shebin El-Kanater in Summer and Winter (82.0 & 307.0 ppb). Kalub El-Balad (894.0 & 194.0 ppb), El-Sharkawia (243.0 & 140 ppb), El-Esmailia (352.0 ppb, Spring), while not detected in site El-Kanater. *P,p'*-DDE was found in Shebin El-Kanater in Summer (180.0 ppb), in Kalub El-Balad in Winter (203.5 ppb), in El-Esmailia in Summer (366.0 ppb) and El-Sharkawia in Winter (865.0 ppb). *O,p'*-DDT was detected only in fish vescera from El-Kanater in Summer (29.0 ppb) and Winter (727.0 ppb). *P,p'*-DDD was found in El-Kanater during Summer only (186.0 ppb). *O,p'*-DDD appeared in Shebin El-Kanater in Autumn (995 ppb), in Kalub El-Balad in Summer (988.0 ppb) and Autumn (76.0 ppb); El-Esmailia in Winter (633.0 ppb), while disappeared from the other sites and seasons.

Thiram was not detected in El-Esmailia, while in Shebin El-Kanater in Spring & Summer the detected amounts were (22.0 & 37.0 ppb), in El-Kanater during the same seasons as (151 & 88 ppb), in addition to Winter (491.0 ppb). Benefin was found in Winter only in three sites Shebin El-Kanater, El-Esmailia and El-Sharkawia at 1100.0, 22.0 and 145.0 ppb, respectively.

Fenitrothion was detected in all tested sites and in some seasons: Shebin El-Kanater in Spring & Summer (46.0 & 11.0 ppb), Kalub El-Balad in Spring, Summer and Winter (93.0, 91.0 & 433.0 ppb, respectively), El-Kanater in Winter and Autumn (489.0 & 75.0 ppb), El-Esmailia during Summer and Winter (250.5 & 55.0 ppb) and El-Sharkawia (55.0 & 83.0 ppb) in Spring and Summer. Parathion was found in fish vescera from all sites, Shebin El-Kanater in Spring and Winter (91.0 & 19.0 ppb), Kalub El-Balad in Spring ,Summer & Winter (90.0, 33.0 & 79.0 ppb), El-Kanater in Spring (72.5 ppb) ; El-Esmailia in Summer, Autumn & Winter (89, 425 & 68.5 ppb) and El-Sharkawia in Spring, Summer & Autumn (91.0, 12.0 & 755.0 ppb). Such finding is quite surprising because parathion was canceled in the country since 1990. In spite of the wide use of profenofos insecticide in pest control programme in Egypt, it was detected in fish vescera from El-Esmailia in Summer (326.0 ppb) and in El-Sharkawia in Summer but in high level (710.0 ppb).

Benalaxyl was detected in Shebin El-Kanater and Kalub El-Balad during Spring only (21.0 & 88.0 ppb), while found in Summer samples only from El-Kanater (8.0 ppb). It was found in Winter samples from El-Esmailia (240.0 ppb), while appeared in Spring, Summer & Autumn in El-Sharkawia at 22.2, 42.0 & 254.0 ppb, respectively.

The pyrethroid fenpropathrin was detected in fish vescera during Winter only from Kalub EL-Balad, El-Kanater and El-Esmailia showing 25.0, 26.5 and 18.0 ppb, respectively. It appeared in samples from Shebin El-Kanater during Spring

and Winter (123.0 & 37.5 ppb) and in El-Sharkawia during Summer and Autumn (23.0 & 171.0 ppb). Alpha-methrin was found in fish vescera samples from El-Kanater during Spring and Summer (430.0 & 6.0 ppb) and in El-Esmailia during Summer only (17.0 ppb), while disappeared from other samples and seasons.

Pyridaben was found in fish vescera from Shebin El-Kanater in Summer (1736 ppb), Kalub El-Balad in Autumn (44.5 ppb), El-Kanater in Summer (11.0 ppb); El-Esmailia in Winter (30.0 ppb) and El-Sharkawia in Summer and Autumn (77.0 & 923.0 ppb, respectively).

As conclusion, data indicate that pesticide residues were existed in more frequency and high amounts in fish vescera compared with fish muscles. Location and season of samples played role in this respect. Accordingly, routine monitoring on pesticide residues in water bodies and fish should be continued to assure safety and quality of these vital resources. It is noticed that the organochlorine insecticides including DDT complex and cyclodiene compounds were dominating the monitored pollutants in water bodies and fish. The existence of pesticides residues in fish tissues was 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).**

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. In addition, it is interesting to detect mirex which was never imported and/or applied in Egypt for agriculture as well as health purposes. Such detection of mirex in the fish muscles may be due to the existence of such compound in the water and reached to the fish according to the fact that such compound derived from the conversion of some long lasting organochlorine pesticides remained from 1960's.

As conclusion, the present monitoring study proved that the contamination of Karmout fish *Clarias lazara* in Kalubia was not serious. The current acceptable daily intake (ADI) adopted by, World Health Organization (WHO) is 0.56 mg, (α, β and Delta – HCH), 0.007 mg (Heptachlor and aldrin), 1.4 mg (DDT), 0.035 mg (chlordane), 0.35 (fenitrothion) and 1.4 mg (fenvalerate) for 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 levels monitored in the present investigation were substantially almost equal with the U.S. Food and Drug Administration guidelines; 5 ppm Σ DDT, 0.3 ppm dieldrin and endrin. However, it was found few exceptions, i.e. aldrin (0.839 & 0.706 ppm) and endrin (0.906 & 1.072 ppm)in the muscles of fish collected from El-Kanater, El Sharkawia, Shebin El-Kanater and El Kanater which were exceeded the mentioned established values (0.3 ppm). The same observation

was recorded by these pesticides in the vesceral of fish which the detected pesticide residues were reached to be 1.540 & 0.721 ppm for aldrin in El-Kanater and El Esmailia and 0.831 ppm for endrin in El-Sharkawia. Taking into consideration the % of positive samples that contained such levels, i.e. 10 %, it could be concluded that that the monitored levels of organochlorines in fish samples from Kalubia are not high enough to cause any hazard and impact on public health.

2. Existence and distribution of metals in fish samples

Data concerning the seasonal distribution of the studied metals, Mn, Cu, Pb, Ni and Co in Karmout fish at five sites locates in Kalubia governorate during the vesical year 1999/2000 are tabulated in Table (4). Examination of the obtained results indicated the detection of very minute amounts of the metals in collected fish samples. The location and time of sampling proved influential in this respect. Cobalt was not detected in most samples with few exceptions at some locations in amounts beyond the detection limits. Shebin El-Kanater fish was free of cobalt. This element was found in Spring samples only at El-Kanater and El-Sharkawia (0.001 & 0.027 ppb). It was detected in Autumn samples at Kalub El-Balad and El-Esmalia (0.034 and 0.034 ppb).

Lead was found in all collected fish samples from Shebin El-Kanater during the four seasons, i.e. 0.016, 0.011, 0.012 and 0.005 ppb at Summer, Winter, Autumn and Spring, respectively. On the contrary, fish from Kalub El-Balad was found free of Pb residues. The same was found with El-Sharkawia fish, where Pb was not detected. This element was found in autumn samples from El-Kanater and El-Esmailia (0.015 and 0.022 ppb), respectively.

It is interesting to notice the detection of Mn, Cu and Ni in all samples of fish collected from the five provinces, but in various amounts at different seasons. Manganese residues were found in considerable amounts, i.e. 0.165, 0.260, 0.182 & 0.187 ppb (Shebin EL-Kanater), 0.305, 0.313, 0.130 & 0.312 ppb (Kalub El-Balad), 0.237, 0.188, 0.237 & 0.379 ppb (El-Kanater), 0.310, 0.165, 0.178 & 0.153 ppb (El-Esmailia) and 0.222, 0.094, 0.277 & 0.134 ppb (El-Sharkawia) during Summer, Winter, Autumn and Spring , respectively. Copper residues were found in all fish samples, but in minute amounts. The existence of traces of metals in fish collected from public markets was reported by many researchers from different locations, i.e. **EPA (1973); Zayed *et al* (1994); Abdel Naser *et al* (1996) and Seddek *et al* (1996).**

In general, the detected metals in abnormal high concentrations in muscles of fish, this may be attributed to the 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.

ACKNOWLEDGMENT

Last but not least I would like to express our thanks and appreciation to Supreme Council of Universities for their continuos help and kind support during the course of the project.

Table 4. Detection of some elements (ppb) in the muscles of *Clarias lazara* fish samples collected from different markets of Kalubia governorate during April (1999) to March (2000).

Station	Season	Metals (ppb)				
		Mn	Cu	Pb	Ni	Co
Shebin El-Kanater	Spring	0.187± 0.17	0.081± 0.07	0.005± 0.01	0.019± 0.01	ND
	Summer	0.165± 0.19	0.038± 0.05	0.016± 0.02	0.032± 0.04	ND
	Autumn	0.182± 0.06	0.006± 0.01	0.012± 0.02	0.020± 0.02	ND
	Winter	0.260± 0.20	0.054± 0.03	0.011± 0.02	0.043± 0.03	ND
	Average/year	0.198	0.045	0.011	0.029	-
Kalub ElBalad	Spring	0.312± 0.26	0.060± 0.03	ND	0.027± 0.04	ND
	Summer	0.305± 0.04	0.097± 0.16	ND	0.049± 0.01	ND
	Autumn	0.130± 0.14	0.044± 0.03	ND	0.025± 0.02	0.034± 0.05
	Winter	0.313± 0.13	0.008± 0.01	ND	0.056± 0.03	0.001± 0.001
	Average/year	0.233	0.052	-	0.039	0.009
El-kanater	Spring	0.379± 0.14	0.047± 0.08	ND	0.029± 0.02	0.001± 0.002
	Summer	0.237± 0.05	0.160± 0.21	ND	0.019± 0.03	ND
	Autumn	0.237± 0.05	0.026± 0.02	0.015± 0.02	0.067± 0.05	ND
	Winter	0.188± 0.11	0.040± 0.05	0.003± 0.01	0.031± 0.05	ND
	Average/year	0.260	0.068	0.005	0.036	0.001
El-Esmailia	Spring	0.153± 0.06	0.095± 0.13	ND	0.032± 0.03	ND
	Summer	0.310± 0.17	0.110± 0.09	0.002± 0.004	0.023± 0.04	ND
	Autumn	0.178± 0.11	0.007± 0.01	0.022± 0.03	0.026± 0.04	0.034± 0.059
	Winter	0.165± 0.20	0.059± 0.05	ND	0.019± 0.01	ND
	Average/year	0.201	0.068	0.006	0.025	0.009
El-Sharkawia	Spring	0.134± 0.06	0.083± 0.07	ND	0.020± 0.018	0.027± 0.04
	Summer	0.222± 0.21	0.121± 0.17	ND	ND	ND
	Autumn	0.277± 0.12	0.083± 0.14	ND	0.041± 0.04	ND
	Winter	0.094± 0.11	0.054± 0.04	ND	0.024± 0.04	ND
	Average/year	0.182	0.085	-	0.021	0.007

ND: Not detected under the limit of detection in our laboratory (1 ppb).
Spring date : 21/3-20/6 (4-5-6/2001), Summer date: 20/6-21/9 (7-8-9/2000), Autumn : 21/9-20/12 (10-11-12/2000) and Winter date: 20/12-21/3 (1-2-3/2001) and

REFERENCES

Abdel-Naser, M.; A.A. Shaaban; M.A. Seham and M.M. Sayed (1996). Levels of some heavy metals in fish caught from river nile at Assiut Governorate, Egypt. ***Assiut Veterinary Medical Journal 34: 68-84.***

Anonymous (1990). Official methods of analysis. Multiresidues method. General methods for organochlorine and organophosphorous pesticides. ***Assoc. Official Anal. Chem. 1: 278-279.***

AOAC (1990). Metals and other elements at trace levels in foods. In: ***Official Methods of Analysis, 15th Edition, pp. 237-273.*** Arlington, Virginia, USA.

Badawy, M.I. (1998). Use and impact of pesticides in Egypt. Int. ***J. Environ. Health Res. 8 (3): 223-239.***

Bjerk, J.E. and E.M. Brevik (1980). Organochlorine compounds in aquatic environment. ***Arch. Environm. Contam. Toxicol. 9: 743-750.***

El-Dib, M.A.; I.A. El-Elaimy; A. Kolb and S.H. Eloma (1996). Activation of *in vivo* metabolism malathion in male *Tilipia nilotica*. ***Bull. Environ. Contam. Toxicol. 57 (4): 667-674.***

Environmental Protection Agency (EPA) (1973). ***Ecological Research Series,*** Water Quality Criteria 1972 Washington D. C., XIX, ***p. 594.***

Hassan, I.M.; M.F. Khallaf, Y.A. Abdel-Daim and M. T. Ibrahim (1996). Organochlorine pesticides residues in water and fish from the river Nile. Proceeding: Sixth conference of Agriculture development research 17-19 December, 1996, Cairo. ***Annals of Agricultural Science, Cairo, (8): 149-161.***

Holladay, S.D.; S.A. Smith; H. El-Habback and T. Cacecci (1996). Influence of chlorpyrifos, an organophosphate insecticide on the immune system of *Nile tilipia*. ***J. Aquatic Animal Health 8 (2): 104-110.***

Lieb, A.J.; D.D. Bills and R.O. Sinnhuber (1974). Accumulation of dietary polychlorinated biphenyls (Aroclor 1254) by rainbow trout (*Salmo gerdineri*). ***J. Agric. Food. Chem. 22: 638–642.***

Leiker, T.J.; C.E. Rostad; C.R. Barnes and W.E. Pereira (1991). A reconnaissance study of halogenated organic compounds in catfish from the lower Mississippi river and its major tributaries. ***Chemosphere. 23 (7): 817-829.***

Macek, K.J. and S. Korn (1970). Significance of the food chain in DDT accumulation by fish. ***J. Fish Res. Board Canada 27: 1496-1498.***

Osfor, M.H.; A.M. El-Wahab and S.A. El-Dessouki (1998). Occurrence of pesticides in fish tissues, water and soil sediment from Manzala lake and river Nile. ***Nahrung, 42 (1): 39-41.***

Seddek, A.L.; D.A. Salem; M.E. Nagwa and Z.M. Zaky (1996). Cadmium, lead, nickle, copper, manganese and flourtine levels in river Nile fish in Assiut Governorate, Egypt. ***Wiener-Tierarztliche Monatsschrift 83(12): 374-377.***

Zayed, M.A.; F.A. Nour Eldien and K.A. Rabie (1994). Comparative study of seasonal variation in metal concentrations in river Nile sediment, fish and water by atomic absorption spectrometry. ***Microchemical J. 49 (1): 27-35.***

مجلة حوليات العلوم الزراعية، كلية الزراعة ، جامعة عين شمس ، القاهرة ، م(٤٨)، ع (١)، ٤١١-٤٢٦، ٢٠٠٣

حصر وتوزيع مبيدات الآفات والمعادن فى عينات من سمك القرموط (*Clarias lazara*) التى تم جمعها من محافظة القليوبية، مصر

[٣٠]

زيدان هندى[١]- محمد إبراهيم عبد المجيد[١]- جيان جوبتا[٢]- خالد عبد العزيز محمد[١]- قدرى محمود وشاحى[١] - علاء الدين بيومى عبد الخالق[١]

١-قسم وقاية النبات – كلية الزراعة – جامعة عين شمس – شبرا الخيمة – القاهرة – مصر

٢- قسم النبات الزراعى وعلوم التربه – جامعة ميريلاند- الولايات المتحده الأمريكيه

يهدف هذا البحث إلى الكشف عن وجود متبقيات المبيدات والمعادن فى كل من الأنسجة العضلية والأحشاء فى عينات سمك القرموط التى تم جمعها من الأسواق المختلفة بمحافظة القليوبية خلال الفترة من أبريل ١٩٩٩ حتى مارس ٢٠٠٠. وقد أظهرت النتائج وجود كميات مختلفة من متبقيات المبيدات والمعادن فى عينات السمك تبعاً للموقع والموسم التى تم جمع العينات منهما.أظهرت عينات السمك من أسواق الإسماعيلية والشرقاوية أقل معدل فى متبقيات المبيدات خلال الخمسة شهور الأولى فى حين أوضحت نتائج المواقع الأخرى إتجاهات مختلفة من نوع وكمية متبقيات المبيدات. أيضاً فقد أشارت النتائج إلى وجود أعلى معدل توزيع للمتبقيات فى الأنسجة الحشوية مقارنة بالعضلات التى يوجد بمعظمها متبقيات بمعدلات فى حدود المسموح بها. وبصفة عامة، وجد أن كل من موقع وموسم الإختبار يلعبان دوراً هاماً فى توزيع متبقيات المبيدات والمعادن (التى أثبتت التحاليل وجود كميات ضئيلة جداً منها) فى أعضاء السمك مجال الإختبار.

تحكيم: ا.د عبد السلام حسين قنصوة

ا.د العيداروس أحمد جمعه