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MONITORING OF PESTICIDE RESIDUES IN DRAINAGE WATER AND FISH SAMPLES COLLECTED FROM DIFFERENT GOVERNORATES, EGYPT

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ABSTRACT

The objective of this study was to monitor pesticide residues in drainge water and fish samples collected from three random locations in four governorates, in Egypt. These governorates are Menofya (Sobk Eldhak village, Quisna), Sharkia (Malames Village, Menia El Kamh), Giza (Bhormos village, Imbaba) and (Moshtohor). Kalyobia The residues of acetamprid were 7.56, 2.02, 8.20 and 4.37ppm; abamectin 6.34, 4.52, 2.63, and 2.28 ppm; chlorphenapyr were ND, ND, 7.45 and ND; clethodim were ND, 4.80, 7.81, and 2.59ppm; residues of dicofol were 7.93, 2.43, ND, 5.11 ppm; glyphosate 2.07, 3.22, 2.61 and 3.41 ppm: oxamyl 6.29, 3.28, 4.43, and 1.46 ppm and pymetrozin 2.77, 5.87, ND, and 4.31 ppm in drainage water taken from Sharkia, Monofya, Kalyobia and Giza Governorates, respectively.

The residue analysis of the fish muscles showed pesticide residues of acetamprid (0.11, ND, 0.17, and 0.08 µg/100g), abamectin (0.15, 0.04, 0.05 and 0.04 µg/100g), chlorphenapyr (ND, ND, 0.14 and, ND µg/100g), clethodim (ND, 0.33, 0.15 and 0.03 µg/100g), dicofol (0.13, ND, ND, and 0.03 µg/100g), glyphosate (ND, 0.06, 0.05, and 0.06 µg/100g), oxamyl (0.12, 0.06, 0.06, and ND µg/100g) and pymetrozin (0.04, 0.01, ND and 0.07 µg/100g) from Sharkia,

Monofya. Kalyobia and Giza governorates. respectively.

Key words *: monitoring , pesticides, residues.*

1. INTRODUCTION

The extensive and unwise use of synthetic pesticides created problems more serious than those for which they were originally applied and resulted in a public anxiety concerning their effects on the environment. The drainage water is always loaded with the residues of chemicals used for pest control. Fish and other aquatic life forms living in drainage water are unable to escape from chemicals once they reached the water and have to submit to their physiological hazards until these xenobiotics are removed from the water by adsorption, sedimentation, leaching, degradation or other mechanisms (Afifi *et al.*, 2002). The present work was directed to monitor pesticide residues in both drainage water and fish muscle samples collected from four different governorates. several publications revealed the existence of pesticide residues mainly organochlorine compounds in various aquatic ecosystems (Hassan *et al.*, 1996; Badawy, 1998; Osfor *et al.*, 1998; and El Kabbany *et al.*, (2002).

2. MATERIALS and METHODS

2.1. Fish & Drainage water

Twenty-five Tilapia *(Oreochormis niloticus)* growing in drainage water were collected from each of the governorates under study.

2.2. Apparatus and Reagents

Liquid-chromatography water model Agilent series 1100-solvent delivery system, quartary pump,chromatograph with UV spectrophotometer detector and C_{18} stainless column (4.6x250mm). Solvent-liquid chromatography grade: (Merk company). Clean up cartridge: Purge C18 cartridge with 5ml acetonitryl/methanol 1:1 and with 4ml acetonitryl followed by 5ml methylene chloride.

2.3. Extraction and clean up of drainage water samples

Drainage water samples collected from different governorates in Egypt during 2003 were extracted and cleaned up for pesticide residues analysis.

50ml water were mixed with 50ml methylene chloride–methanol (1:1). Resulting mixture was drawn through C_{18} cartridge. Stream of air (aireator) and reconstitute residues were eluted with 1ml mobile phase (methanol) and then determined using HPLC analysis according to Mann (1981).

2.4. Extraction and clean up of fish samples

Fish muscles were ground and blended in a waring blender just to pulplike consistency. 200 ml Methanol/ acetone (4/1) were added to 100g blended muscle samples, then the mixture was shaken mechanically using electrical shaker for one hour, and filtered through Buchner funnel. The collected solvent mixtures were evaporated under reduced pressure using rotary evaporator till dryness. The residue was quantitatively transferred into small vials with 5ml methanol. The solvent was then evaporated till dryness and the vials were stored at –15C° until the clean up. Clean up was done on florisil column with 3 mixtures for elution (6, 15, 50% diethyl ether in petroleum ether) as described by AOAC (1990). Residues were dissolved in 1ml methanol and determined using HPLC analysis. The conditions for the determination of pesticide residues in the

Tabe (1): The conditions for the determination of pesticides by high pressure liquid chromatography (HPLC)

Pesticides	Mobile phase	F.R ml/min	Retention time R_t	Detection limit ng.
Abamectin	90 methanol/10acetonitryl	1	4-11	5
Acetampride	80methanol/20acetonitryl	1	2.70	5
Clethodim	60methanol/40acetonitryl	1	3.45	5
Chlorphenapyr	70methanol/30acetonitryl	1	3.11	5
Pymetrozin	40methanol/60acetonitryl	1	2.811	5
Dicofol	15methanol/85acetonitryl	1	2.94	5
Oxamyl	100 methanol	1	3.31	5
Glyphosate	10methanol/90acetonitryl	1	2.59	5

drainage water and fish muscles by HPLC are presented in Table (1).

The Data obtained were analyzed statistically. Means , standard deviations and standard errors were calculated according to Selvin (1996).

3. RESULTS AND DISCUSSION

Data in Table (2) and Fig. (1) indicate the presence of negligible residues of pesticides in drainage water samples from four different governorates in Egypt during 2003. The average of the detected pesticide residues in these governorates were as follows: El-Sharkia drainage water samples contained acetamprid 7.5 ppm, abamectin 6.4ppm, dicofol 7.9 ppm., glyphosate 2.1 ppm, oxamyl 6.3 ppm and pymetrozin 2.8 ppm., while in Menofya drainage water pesticide residues were (2.1, 4.5, 4.8, 2.4, 3.2, 3.3, and 5.9 ppm for acetamprid, abamectin, clethodim, dicofol, glyphsate, oxamyl, and pymetrozin.

The pesticide residues were 8.2ppm for acetamprid, 2.6 ppm for abamectin, 7.5 ppm chlorphenapyre, 7.8 ppm for clethodim, 2.6 ppm for glyphosate and 4.4 ppm for oxamyl, in analyzed drainage water samples from Kalyobia. Pesticides in the drainage water samples collected from Giza Governorate were acetamprid (4.4 ppm), abamectin (2.2ppm), clethodim (2.6 ppm), dicofol (5.1 ppm), glyphosate (3.4 ppm), oxamyl 1.5ppm and pymetrozin (2.6ppm), while the dicofol and clethodim were not found in the samples collected from Kalyobia and Sharkia Governorates, respectively. Chrphenapyre was not detected in drainage water collected from all Governorates except for Kalyobia Governorate. These results indicate that some pesticides were not detected under this condition as aldicarb, carbofuran, cadusafos, diazinone, fenamiphos, fenpyroximate, fentrothion, malathion, methomyl, prothiofos and thiobedndazol in the dranaige water samples collected from Sharkia, Monofya, Kalyobia and Giza Governorates during 2003 in Egypt.

These results are in agreement with those obtained by Hassan *et al.*, (1996) who monitored the pesticide residues in water samples collected from the River Nile. The samples did not contain appreciable amounts of organochlorine residues, and it was concluded that there is no risk to human health. The same trend was found by

Table (2):Pesticide resdues detected in drainage water and *Oreochormis niloticus* Fish muscles samples collected from different governorates during (2003).

Source of samples	SHARKIA		MONOFYA		KALYOBIA		GIZA	
Pesticides	Draings water PPm.	Fish mus µg/100g.	Draings water PPm.	Fish mus. µg/100g.	Draings water PPm	Fish mus. µg/100g.	Draings water PPm.	Fish mus. µg/100g.
Acetamprid	7 5648 + 0 1055	0 1157 + 0.1641	2 0250 ± 0.2826	ND	8 2058 ± 0 1145	0 1725+ 0 1506	4 3789 ± 2 4395	0 0874 ± 0 0730
Aldicarb	ND	ND	ND	ND	ND	ND	ND	ND
Abamectin	6 3414 ± 0 4751	0 1585 ± 0 0380	4 5219 ± 0 3403	0.0906 ± 0 0259	2 6351± 0 1978	0 05037 ±0 0069	2 2882 ± 0 11732	0 0443 ± 0.0189
Carbofuran	ND	ND	ND	ND	ND	ND	ND	ND
Cadusafos	ND	ND	ND	ND	ND	ND	ND	ND
Chlorphenapyre	ND	ND	ND	ND	7 4511 ± 0 1143	0 1490 ±0 0229	ND	ND
Clethodim	ND	ND	1 8076 ± 0 1713	0 3336 ± 0.0225	7.8110 ± 0.1530	0 1548 ±0 0353	2.5944 ± 0 6137	0 0382 ± 0 0977
Diazinon	ND	ND	ND	ND	ND	ND	ND	ND
Dicofol	7.9391± 0 117	0 3333 ± 0 1057	2 4343 ± 0.1352	ND	ND	ND	5 1148 ± 0 1931	0 03714 + 0 0991
Fenamiphos	ND	ND	ND	ND	ND	ND	ND	ND
Fenpyroximate	ND	ND	ND	ND	ND	ND	ND	ND
Fentrothion	ND	ND	ND	ND	ND	ND	ND	ND
Glyphosate	2 0751± 0 4134	ND	2 2243 ± 0.5869	0 0645 + 0 1173	2 6119 + 0 5175	0 05224 ±0.1035	3 4164 ± 0 9695	0 0683 ± 0.1939
Malathion	ND	ND	ND	ND	ND	ND	ND	ND
Methomy	ND	ND	ND	ND	ND	ND	ND	ND
Oxamyl	6 2959 ± 0.7730	0 1260 ± 0 1556	3 280 ± 0.3393	0 00654+0 0667	4 4313 + 2 5312	0 0672 ±0 1519	1 4639 + 0 4592	ND
Prothiofos	ND	ND	ND	ND	ND	ND	ND	ND
Pymetrozin	2 7775 ± 1 1667	0 0409 + 0 1039	5.8710± 2 4749	0 01095±0 1140	ND	ND	4 3150 + 1 1533	0 0750 ± 0 0655
Thiobendazol	ND	ND	ND	ND	ND	ND	ND	ND

Each value represents the mean + STD

ND: Not Detected under the limit of detection 5ng.

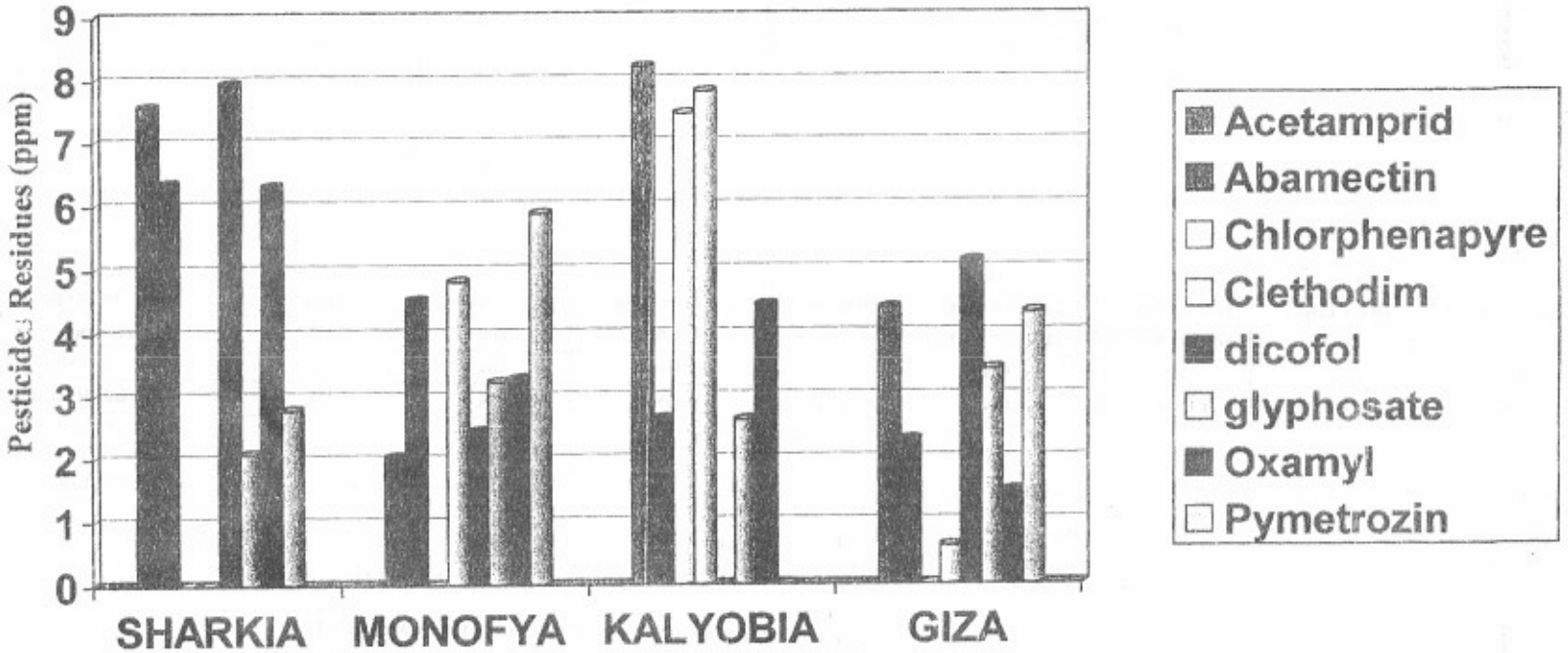

Fig (1) Pesticide residues detected in drainage water samples collected from different governorates during 2003

was found by several investigators, Iwata *et al.*, (1995) who considered the maximum residue level of pesticides in water. It could be mentioned that such levels are available only for drinking water (WHO, 1984), while there is no available data for drainage water.

Accordingly, the high levels in water represented in Table (2), and Fig. (1) should be considered for risk and hazards assessments. Zidan *et al.*, (2002) monitored the pesticide residues in water at Kalyobia Governorate. As for ground water, organochlorine pesticide residues were detected in low concentration in some areas and seasons. Abd El Motaleb and Radwan (2003) identified and determined the pesticide residues in fish harvested from rice field water from Sharkia Governorate. The residue analysis of water and fish tissues revealed abamectin insecticide. On the contrary the fenpyroximate, carbofuran and atrazin were not detected in both water and fish tissues.

3.1. Pesticides residue in fish muscles

Data in Table (2) & Fig. (2) indicate the pesticide residues in the drainage water and the muscles of fish grown in drainage water collected from four governorates in Egypt during 2003. Data concerning the existence of detected pesticides were 0.11, 0.15, 0.13, 0.12 and 0.04 µg/100g fish muscles samples collected from Shrarkia Governorate for acetamprid, abamectin, dicofol, oxamyl and pymetrazin, respectively. The pesticide residues were 0.17, 0.05, 0.14, 0.15, 0.05 and 0.06 µg/100g in the muscles of fish samples collected from Kalyobia Governorate, for acetamprid, abamectin, chlorphenapyre, clethodim, glyphosate and oxamyl, respectively. Data in the same table indicate that in general, fish muscle samples collected from Giza Governorate contain 0.08, 0.04, 0.03, 0.03, 0.06 and 0.07µg/100g of acetampride, abamectin, clethodim, dicofol, glyphosate and pymetrozin, respectively. While the data in the same table show that in general fish muscle samples collected from Menofya Governorate contain 0.09, 0.03, 0.06, 0.006 and 0.01 µg/100g of abamectin clethodim, glyphosate oxamyl and pymetrozin, respectively. The same trend was found by several investigators, (El-Elaimy *et al.*, 1996, Hassan *et al.*, 1996; Badawy 1998; Osfor, *et al.*,

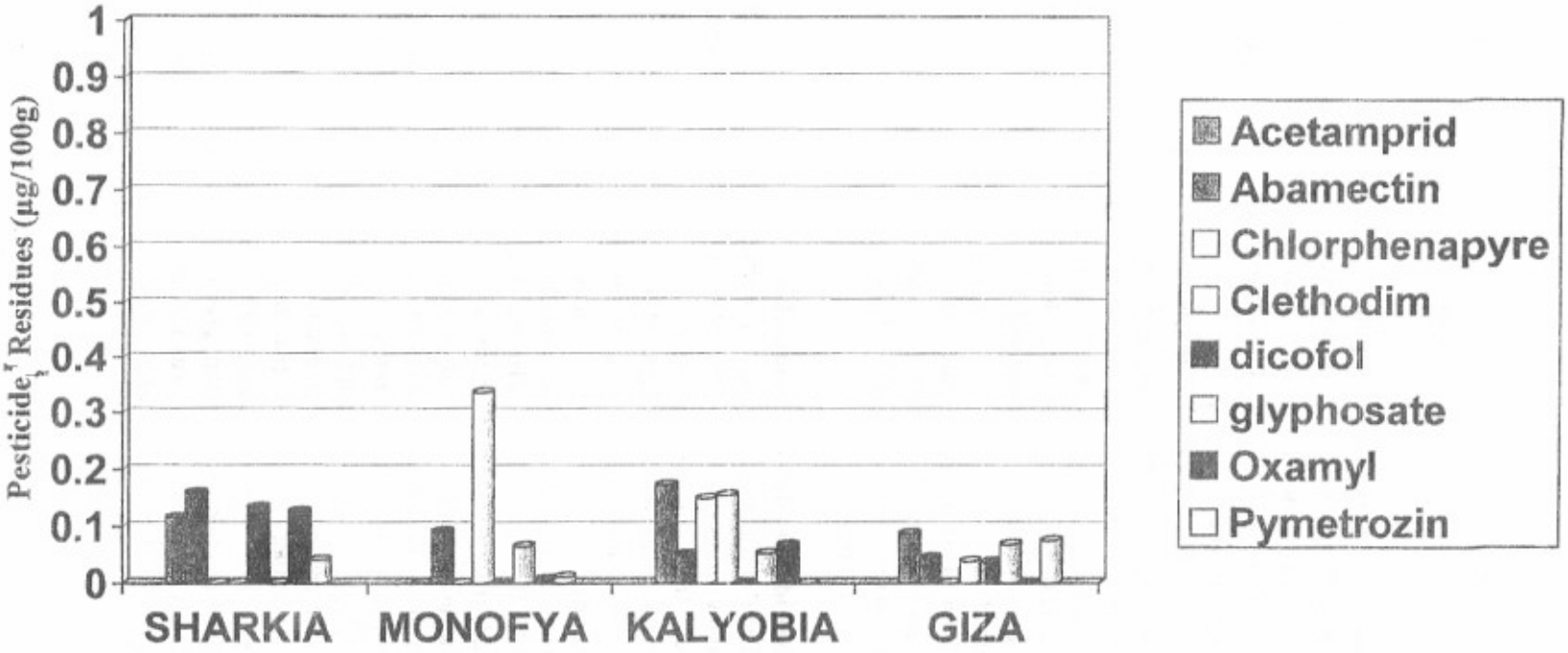

Fig (2) Pesticide residues detected in fish samples collected from drainage water in different governorates during 2003

1998 Afifi *et al.*, 2002 and Abd El Motaleb and Radwan 2003).

In conclusion, the results obtained in the present study suggested that the pesticide residues of acetamprid, abamectin chlorphenaphyre, clethodim, dicofol, glyphosate,oxamyl and pymetrozin lead to sercious effects in fish contaminated with pesticides. There is no available information about the maximum residue level (MRL's) of acetamprid, pymetrozin and clethodium but the maximum residue level (MRL's) of abamectin, chlorphenapyre dicofol, glyphosate and oxamyl were reported in cattle meat by (CAC.1994)as 0.01, 0.7, 3, 1.75,and 0.03 mg/kg body weight, respectively.

The residue concentration of glyphosate, dicofol and chlorphenaphyre in fish muscles collected from different governorates under this study were lower than MRL's. In contrast the residue concentration of oxaml and abamectin in fish muscles collected from the same governorates were higher than MRL's while the MRL's of clethodim, pymetrozin and acetamprid were not reported (CAC. 1994).

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رصد لمتبقيات المبيدات في عينات مياه الصرف وعضلات الأسماك المأخوذة من محافظات مصر المختلفة .

ألفت عبد اللطيف سيد محمد رضوان –ابراهيم السوقى عطا الله

المعمل المركزي للمبيدات – قسم بحوث تحليل المبيدات

ملخص

كان الهدف من الدراسة هو التعرف وتقدير المتبقي من المبيدات في عينات مياه الصرف الزراعي التي تم تجميعها من ثلاثة مواقع مختلفة في أربعة محافظات وهي قرية سبك الضحاك مركز قوسينا محافظة المنوفية مصارف قرية ملامس مركز منيا القمح محافظة الشرقية ومشتهر محافظة القليوبية ومصارف قرية بهرمس مركز امبابة محافظة الجيزة . أظهرت النتائج وجود متبقيات من مبيدات استيامبرايد – ابامكتين – سليثوديوم – ديكوفول – جليفوسات – اوكساميل – بايميتروزين في مياه الصرف المأخوذة من محافظة الشرقية والجيزة . بينما وجد مبيد كلورفينابير بجانب المبيدات السابقة في مصارف محافظة القليوبية .

كما وجدت هذه المبيدات في عضلات الأسماك المأخوذة من هذه المحافظات والتي تم تربيتها في مياه المصارف الزراعية وكانت جميعها قريبة من الحدود المسموح بها ماعدا مبيد سيليثوديم حيث كان أعلي من الحدود المسموح بها وهي ٠,٠٠٣ جزء في المليون .

المجلة العلمية لكلية الزراعة – جامعة القاهرة – المجلد (٥٦) العدد الأول (يناير ٢٠٠٥):١٨٩-٢٠٠.