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SEASONAL RESIDUE LEVELS OF CERTAIN PESTICIDES IN EL-MANZALA LAKE, EGYPT

By

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ABSTRACT

Seasonal levels of certain pesticide residues were evaluated in water samples collected from El-Manzala lake. The determination was carried out using multi residue method of gas liquid chromatography. The investigated pesticides included insecticides (organochlorine and pyrethroids), herbicides and fungicides. This survey was performed in April, August and December 1998. Thirteen organochlorine insecticides were detected at different tested monthly intervals. The majority of these compounds showed their highest residue levels in December. *o,p*-DDT, α-HCH, γ-HCH and hexachlorobenzene showed similar residue level of 0.1 µg/L. Also each of *p,p*-DDE and heptachlor-epoxide showed 0.16 µg/L. However, the residue levels were found to be 0.18, 0.14 and 0.12 µg/L for *p,p*-DDD dieldrin and endrin respectively. Four compounds namely β-HCH, *p,p*-DDT, Δ-HCH and dicofol showed the highest concentrations in August with residue levels of 0.07, 0.08, 0.32 and 0.5 µg/L for these compounds respectively. The highest levels of detected pyrethroids were also observed in December. With residue levels of 0.88, 0.86, 0.42 and 0.34 µg/L for deltamethrin, cypermethrin, permethrin and fenvalerate respectively. Similar trend of results was observed for the detected herbicides and fungicides since these compounds revealed the highest residue levels in December. Such

residue levels of detected herbicides were 0.48, 0.38 and 0.23 µg/L for atrazine, trifluralin and simazine respectively, whereas the fungicide residues were 0.56, 0.42, 0.54, 0.5, 0.5, 0.56 and 0.32 µg/L for chlorothalonil, dichlorfluanide, imazalil, iprodione, procymidone, triadimefon and vinelozolin respectively.

INTRODUCTION

El-Manzala lake is the largest among the four Nile delta lakes. The lake area is about 905 square kilometers, 77.3% of which is open water and the remainder are marshes and islands. The lake is located on the southwest border of Port Said city. The lake is connected to Mediterranean Sea in the north through El-Gamil channel. The entry of Baher-El-Bakar, Ramsis, El-Sero and Hadous drains into the lake has resulted in high levels of pesticidal pollutants, which resulted from the agriculture and sanitary drainage. Therefore it is of a great importance to monitor residue levels of different persistent pesticides.

Organochlorine pesticides have received considerable attention in the last decade since studies have shown extreme persistence of these pollutants in the world-wide environment and accumulation in human and animal tissues (Tanabe *et al.*. 1983; Jensen 1983; Kutz *et al.*, 1991; Burgar *et al.*, 1995 ; Ahmed *et al.*, 1998; El-Zoghbi *et al.*, 1999 and Ismail *et al.*, 2000). The use of multi residue method for determination of 48 pesticides (20 organophosphorus, 7 organochlorine, 14 organonitrogen and 7 pyrethroids) by gas chromatography according to the method of Nakamura *et al.*,1994. Our objective in this study is to pursue detection of pesticide residues in water of El-Manzala lake. These pesticides are used in controlling agricultural pests and vector-borne diseases in public health such as some aquatic snails and mosquito larvae in addition to some recommended herbicides and fungicides.

MATERIALS AND METHODS

Water samples:

Five stations were chosen for regular sampling to determine pesticide residues in the drain water of El-Manzala lake. The water samples were taken by immersing glass jars each of two and half liter capacity at three level from surface, subsurface water and water near the bottom at various locations. The water samples of each location were then mixed and transferred in dark place under cooling condition (4°C) to the laboratory of ministry of agriculture (Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food).

Physico-chemical properties of water samples:

Some physico-chemical tests were carried out according to the standard methods of AOAC (1995).

PH value:

The pH values of water samples were determined by using pH-meter. The means of pH values were 8.0, 7.8 and 8.0 for April, August and December samples of 1998 respectively.

Biological oxygen demand:

The amount of dissolved oxygen in water that will be consumed is a function of the organic matter content, such criteria is a mirror of its decomposition by micro-organisms. High BOD means low water quality and probably the development of anaerobic water. It usually results when water have received organic wastes. The determination of BOD values were carried out to investigate the oxygen quantity that is required by bacteria to oxidize organic substances such as pesticides, sewage or industrial wastes in water. The recorded BOD values were 72 ±2.1, 91± 1.3 and 86 ±1.8 mg/L during April, August and December 1998, respectively.

Determination of pesticide residues in water:

The methods of sampling, extraction, clean up, isolation, identification and quantification of pesticide residues by using gas chromatographic multi residues determination were achieved according to AOAC official methods of analysis (1995).

Extraction and clean up

Water samples, each of 500 ml were placed in separatory funnel and mixed with 75 ml of dichloromethane and 150 ml/L hexane mixture. Each sample was extracted three times and shaken vigorously (manually) for at least 3 min every time (sufficient shaking / extraction time was very important for the quantitative recovery of several pesticides) and allowed to settle and phases to separate. After the extraction, the organic fractions were combined and evaporated to near dryness. Residues were quantitatively transferred on top of a glass column (22 cm x 1.5 cm i.d), packed with silica gel (6 cm) and topped with anhydrous sodium sulphate (1 cm). The column was eluted with dichloromethane and the elute was evaporated to near dryness. Residues were then dissolved in 1 ml acetone and kept in glass vials for analysis.

Gas chromatography and quantitation

GC Gas chromatography model 5890 series II was used under a moderate flow rate of nitrogen (60 ml/min) as a carrier Gas. The residue was treated with acetone-dichloromethane-petrolium ether. Capillary column PAS-1701 (E.C.D. tested 1701 silicone) was used. The concentrated extract was added on top of column by auto Injector. Separation condition and quantitation were conducted according to the method reported by Valerio *et al.* (1990).

RESULTS AND DISCUSSION

The multi residue procedure was a significant advancement in residue analysis. It provided a simple and rapid analysis for the more

significant pesticides being usual right now. However, pesticide usage patterns have been changed. Pesticides that were once heavily used have been replaced by more potent compounds (Scaroni *et al.* 1994; Nakamura *et al.* 1994; Millet *et al.* 1996 and Fenandez *et al.* 1996).

Residues of organochlorine pesticides:

Results of Table (1) showed residues of thirteen organochlorine insecticides among detected insecticides in April, August and December 1998. These insecticides include *p,p*-DDD, *p,p*-DDE, *o,p*-DDT, *p,p*-DDT, dicofol, dialdrin, endrin, α-HCH, β-HCH, Δ-HCH, γ-HCH (lindane), heptachloro-epoxide and hexachlorobenzen. The most striking observation is the fact that four compounds among the detected organochlorine insecticides reached their maximum levels in August 1998. The monitored levels of these compounds were 0.08,0.5, 0.07 and 0.32 µg/L for *p,p*-DDT, dicofol, β-HCH and Δ-HCH respectively. Also, the elevation in the levels of γ-HCH (lindane) and α-HCH was time-dependent all over the experimental period. γ-HCH showed levels of 0.04, 0.07 and 0.1 µg/L in April, August and December respectively. Moreover, certain other insecticides were increased and showed similar residue levels in August and December. These compounds were heptachloro-epoxide (0.16 µg/L) and hexachlorobenzen (0.1 µg/L) in August and December whereas the level in April was 0.06 and 0.03 µg/L for heptachloro-epoxide and hexachlorobenzene respectively. These criteria are mainly attributed to the agricultural drainage water entering El-Manzala lake via different drains with relatively high residues of organochlorine insecticides. These observations refer to the extensive use of these highly persistent insecticides for long period in agriculture pest control. Also, El-Manzala lake water is slightly alkaline with pH of 7.4 to 8.2. Such alkaline medium enhances the dehyderochlorination of *p,p*-DDT into *p,p*-DDE. In this context, the present results showed high residue level of *p,p*-DDE (0.16 µg/L) compared with *p,p*-DDT (0.014 µg/L) in December. The results of organochlorine residues are in agreement with those of Abo-Elamaym *et al.* (1971) who found that the

levels of lindane, heptachloro, *p,p*-DDE and *o,p*-DDT ranging from 0.1 to 0.95 ppb in the water of El-Mahmoudia canal and Mariut lake. However, when comparing the present results with those of Ismail *et al.* (1995) regarding organochlorine residues in the bitter lakes; It was amazing to note that the detected concentrations of certain organochlorines residues in El-Manzala lake ranged from 10 to 100-fold of those detected in the bitter lakes. Also the number of organochlorine compounds detected in El-Manzala lake was higher than those of the bitter lake.

Table (1): Residues of organochlorine insecticides detected in different months of water sampling (µg/L)*

Herbicides	Residues of herbicides in different months		
	April	August	December
	PH BOD	PH BOD	PH BOD
	8.2 73±20	7.4 91±10	8.1 86±10
Dicofol	0.08±0.023	0.5±0.015	0.4±0.012
p,p-DDD	0.04±0.012	0.026±0.013	0.18±0.011
p,p-DDE	0.06±0.021	0.012±0.022	0.16±0.013
γHCH(lindan)	0.04±0.013	0.05±0.012	0.1±0.019
heptachloro-epoxid	0.06±0.017	0.16±0.013	0.16±0.015
hexachlorobenzen	0.03±0.013	0.1±0.011	0.1±0.009
o,p-DDT	0.04±0.011	0.016±0.012	0.1±0.017
p,p-DDT	0.06±0.0004	0.08±0.016	0.014±0.015
Dieldrin	0.06±0.012	0.04±0.011	0.14±0.016
Endrin	0.06±0.013	0.04±0.012	0.12±0.014
α-HCH	0.04±0.011	0.07±0.021	0.1±0.012
β-HCH	0.06±0.015	0.07±0.022	0.06±0.018
Δ-HCH	0.04±0.012	0.32±0.021	0.08±0.013

n.d. = not detected * Means of five stations±SD

b-Residues of pyrethroides:

Results in Table 2 showed the average levels of detected pyrethroide insecticides in drain water of El-Manzala lake in April, August and December 1998. Four pyrethroide insecticides were detected in this study which included cypermethrin, deltamethrin, fenvalerate and permethrin. The results of pyrethroide residues are in agreement with those of Mao. *et al.* (1993) who found that the levels of tralomethrin, deltamethrin, and decamethrinic acid was validated at low nanograms per liter (part per trillion) in water samples. The highest levels of detected pyrethroides were recorded in December. Levels of cypermethrin and deltamethrin showed elevation with time-dependent. These two pyrethroids showed similar levels 0.88 and 0.86 µg/L in December and identical level in August. The presence of deltamethrin and cypermethrin with such high levels than other detected pyrethroids is due to the use of these compounds at least three times in the season in controlling the cotton leaf and ball worms which are sprayed with these compounds repeatedly.

Table (2): Residues of Pyrethroide insecticides detected in different months of water sampling (µg/L)*

Herbicides	Residues of herbicides in different months					
	April		August		December	
	PH	BOD	PH	BOD	PH	BOD
	8.2	73±20	7.4	91±10	8.1	86±10
Cypermethrin	0.14±0.01		0.6±0.16		0.86±0.13	
Deltamethrin	0.24±0.02		0.6±0.12		0.88±0.14	
Fenvalerate	0.12±0.03		nd		0.34±0.12	
Permethrin	0.2±0.01		0.08±0.01		0.42±0.13	

n.d. = not detected * Means of five stations±SD

c-Residues of herbicides:

Results in Table 3 showed the individual variations of each detected herbicide in water samples which collected in April, August and December 1998. Three herbicides were detected in this study including atrazine, semazine and trifluralin. The highest levels of these herbicides were detected in December. These residues were 0.48, 0.23 and 0.38 µg/L for atrazine, semazine and trifluralin respectively. Atrazine was the only herbicide to show time-dependent in its detected level during that season. Also, atrazine showed the highest residues in all months of sampling. The detected residues of atrazine were 0.22, 0.3 and 0.48 µg/L in April, August and December respectively. Simazine which used for the control of corn weeds was detected in the level of 0.16 and 0.23 µg/L in April and December respectively. Also, trifluralin was detected in April (0.08 µg/L) and December (0.38 µg/L). The results of herbicide residues are in agreement with those of Valerio *et al.* (1990) who found that the levels of triazines and other herbicides in water samples was ranged from 0.2 to 1.0 µg/L.

Table (3): Residues of herbicides detected in different months of water sampling (µg/L)*

Herbicides	Residues of herbicides in different months					
	April		August		December	
	PH	BOD	PH	BOD	PH	BOD
	8.2	73±20	7.4	91±10	8.1	86±10
Atrazine	0.22±0.12		0.3±0.13		0.48±0.13	
Simazine	0.16±0.03		n.d.		0.23±0.01	
Trifluralin	0.08±0.02		n.d.		0.38±0.12	

n.d. = not detected * Means of five stations±SD

Table (4): Residues of fungicides detected in different months of water sampling (µg/L)*

Herbicides	Residues of herbicides in different months					
	April		August		December	
	PH	BOD	PH	BOD	PH	BOD
	8.2	73±20	7.4	91±10	8.1	86±10
Chlorothalonil	0.08±0.01		0.18±0.01		0.56±0.07	
Dichlofluanide	0.16±0.02		n.d.		0.24±0.09	
Imazalil	0.1±0.03		n.d.		0.54±0.09	
Iprodione	0.16±0.02		n.d.		0.5±0.01	
Procymidone	0.26±0.02		n.d.		0.5±0.06	
Triamidefon	0.06±0.02		n.d.		0.56±0.02	
Vinclozolin	0.1±0.04		n.d.		0.32±0.04	

n.d. = not detected * Means of five stations±SD

d-Residues of fungicides:

Results in Table 4 elucidated the average residue levels of each detected fungicides at different stations in April, August and December 1998. These fungicides were chlorothalonil, dichlorofluanide, imazalil, iprodione, procymidone, triadimefon and vinclozolin. The results clearly showed that although residues of fungicides were detected in April, they were disappeared in August expect chlorothalonil, which showed time-dependent in increasing its detected level all over the tested period. The levels of chlorothalonil, were 0.08, 0.18 and 0.56 µg/L in April, August and December respectively. The observed disappearance of other fungicides in August could be due to the relatively high decomposition of such fungicides which used in April. However, chlorothalonil is considered more highly persistent in water reported Valerio *et al.* (1990). The results revealed detection of different pesticides with different residue levels in tested drains and El-Manzala lake. The application of some of those pesticides such as organochlorine pesticides was curtailed in early 1970s. The detection of these organoclorine pesticides is due to

their highly resistance to the environmental factors (biological, chemical and physical factors). Also, this study showed detection of some presently recommended pesticides such as pyrethroide insecticides in controlling agricultural pests and vector-born diseases in public health such as some aquatic snails and mosquito larvae. Moreover, some recommended herbicides and fungicides were detected. The principal hazards of pesticides residues in water could result in large number of aquatic invertebrates and fish may be killed. Also, such residues of pesticides may be taken up into tissues of aquatic organisms and enter the biological food chain. Moreover chronic or long-term side effects may occur to animals or human being who drink the water or eat the fish containing such residues (Robson and Barrett 1977). Most herbicides and fungicides are endangering the water as well because of toxicity causing for instance struma, methemoglobinemia , gastroenteritis, lesions of liver and kidney, mutagenic effects or at least misflauars Wolfgang (1979).

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الملخص العربي

مستويات متبقيات بعض المبيدات في بحيرة المنزلة – مصر

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في هذا البحث تم تقدير مستويات بعض المبيدات في عينات مياه أخذت من بحيرة المنزلة وذلك باستخدام جهاز الفصل الكروماتوجرافي (GLC) . وشملت المبيدات التي فحصت مبيدات حشرية (الكلور ونية العضوية – البيروثرويد) ومبيدات حشائش ومبيدات فطرية . وتم إنجاز هذا الحصر في أبريل وأغسطس وديسمبر ١٩٩٨ . أوضحت النتائج وجود عدد ١٣ مبيد حشري كلوريني عضوي في فترات التقدير المختلفة ، كما أوضحت النتائج أن غالبية هذه المركبات أظهرت اعلي مستويات لها في شهر ديسمبر . كما أظهرت المركبات hexachlorbenzene, γ-HCH, α-HCH, *o-p*-DDT نفس المستوي (٠,١ ميكروجرام/لتر) ، ايضا كان مستوي كلا من heptachlor-epoxide, *p-p*-DDE متساويا (٠,١٦ ميكروجرام/لتر)، إلا أن مستوي كلا من endrin, dieldrin, p-p-DDD كان ٠,١٨ ، ٠,١٤ ، ٠,١٢ ميكروجرام/لتر علي الترتيب .

وفي شهر اغسطس أظهرت المركبات dicofol, β-, Δ-HCH, p-p-DDT HCH اعلي تركيز لها حيث كان مستوي المتبقي لهذه المركبات ٠,٠٧ ، ٠,٠٨ ، ٠,٣٢ ، ٠,٥ ميكروجرام/لتر علي التوالي. كما لوحظ ان اعلي مستوي للبيروثرويد كان في شهر ديسمبر وكان مستوي المتبقي للمركبات fenvalerate, permathrin, cypermethrin, deltamethrin هو علي التوالي ٠,٨٨ ، ٠,٨٦ ، ٠,٤٢ ، ٠,٣٤ ميكروجرام/لتر .

كما لوحظ أن نفس اتجاه النتائج لمبيدات الحشائش والمبيدات الفطرية حيث كان اعلي مستوي لها في شهر ديسمبر .

وكان مستوي مبيدات الحشائش simazine, trifluralin, atrazine هو علي التوالي ٠,٤٨ ، ٠,٣٨ ، ٠,٢٣ ميكروجرام/لتر بينما كان مستوي المبيدات الفطرية

imazalil, iprodione, procymidone, ,chlorothalonil, dichlorfluanide triadimefon, vinelozolin هي على التوالي ٠,٥٦ ، ٠,٤٢ ، ٠,٥٤ ، ٠.٥ ، ٠,٥، ٠,٥٦ ، ٠,٣٢ ميكروجرام/لتر .