

ASSESSMENT OF SOME HAZARDOUS CONTAMINANTS IN ISMAILIA GOVERNORATE

AHSRAF EL-MARSAFY

*Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in food,
Agricultural Research Centre, Dokki, Egypt.*

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Abstract

The main purpose of the present study is to assess the pesticides and heavy metals contamination in Ismailia governorate that might contribute a risk to human health or environment. The long-term objectives of EFARP* have been defined as strengthening applied agriculture research in Ismailia governorate. This will result in creating productive, sustainable and successful farming systems. This study has contributed to increasing knowledge about the presence of toxic hazardous compounds in the environment of Ismailia governorate as an example of new lands.

Monitoring of organophosphorus, carbamate and synthetic pyrethroids pesticides, which are commonly used in Egypt for pest control, was carried out in addition to persistent organochlorines, which were prohibited several years ago. Heavy metals; lead, cadmium and copper were also included in the monitoring program. One hundred and ten samples (40) plants, (40) soil and (30) water, samples were examined for 63 pesticides. Banana, clover, carrot, dry beans, cowpea, maize, cucumber, strawberry, tomato, potato, mandarin, orange and dill plant samples were collected from Ismailia, Qantara West, Qantara East, Fayed and Kassasin (Ismailia governorate). Irrigation, drainage and drinking water samples were collected from Ismailia governorate. No violations were observed in all analyzed plant samples, while low residues were detected in soil and waater samples.

The data demonstrates the contamination of tomato, potato, and dill samples with profenofos, dimethoate and malathion pesticide residues. Dicofol, chlorothalonil and deltamethrin residues were detected in strawberry, tomato and maize samples.

The HCH isomer was detected in potato samples collected from Qantara west, while 'p, p'-DDE residues were detected in potato samples collected from Fayed.

Dimethoate was the only organophosphorous pesticide residues, while pirimicarb was the only carbamate pesticide residue found in soil samples. However, dicofol, permethrin, triadimefon, tetradifon and DDT complex from the organochlorine and pyrethroid groups were detected in soil samples collected from Ismailia governorate.

Fifty samples of water, soil and plants were examined for copper, lead and cadmium. Copper residues were detected in low concentration. However, lead and cadmium residues varied from being undetectable to very low concentrations.

* EFARP: Egypt-Finland Agricultural Research Project.

INTRODUCTION

Food contamination monitoring is an essential component of ensuring the safety of food supplies and managing health and environment resources, since it provides information on the levels and sources of contaminants in foods, on the amount of contaminants ingested by humans and on contamination levels.

The Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food established through the Quality Control on Agricultural Products (QCAP) Project. A large scale on going monitoring program started in 1995 was designed and implemented by the laboratory, which covers the whole country, Dogheim *et al.* (1988), Dogheim *et al.* (1990) and Dogheim *et al.* (1991). Ismailia is one among twelve other governorates included in program.

In collaboration with EFARP, samples from foods, soil and water were analyzed through the monitoring program. Pesticide residues as well as heavy metals were detected in samples collected from different districts and other sites throughout Ismailia Governorate.

The goal of this study is to assess the situation of contaminants in the implementation area of EFARP. Such work provides useful information for the decision-makers of agricultural and environmental policy of the country.

MATERIALS AND METHODS

Sample collection

Thirty samples of soil thickness (0-30 cm), water (irrigation, drainage and drinking) and plants (banana, clover, carrot, strawberry and Maize) were collected from 10 fields in Ismailia governorate in April 1996 and October 1996. Total number of filed samples is 60.

Twenty samples of soil thickness (0-30 cm) and plants (tomato and cucumber) were collected from 10 green houses in Ismailia governorate in May 1996 and September 1996.

Fifteen samples of soil thickness (0-30 cm), water (irrigation, drainage and drinking) and plants (cowpea, dry beans, potato, mandarin, orange and dill) were collected randomly close to the main roads passing through Ismailia governorate. Sample collection was repeated every 6 months, in June 1996 and December 1996. Total number of samples 30.

Sampling

Two kg from plants, soil and 5 liters of water samples were prepared according to codex guideline FAO/WHO (1993). Around sixty-three compounds were analyzed including organophosphours, nitrogen containing compounds, organochlorines, carbamates and pyrethroids.

Fifty samples of (10) soil, (30) water, and (10) plants were analyzed for lead, cadmium and copper; all samples were prepared according to codex guidelines FAO/WHO (1993).

I. Residue Analysis

Pesticide reference standard

- Organophosphorous and Nitrogen containing Compounds

Atrazine, Bendiocarb, Carbaryl, Chlorpyrifos, Chlorpyrifos-Me, Cyanophos, Diazinon, Dimethoate, Fenitrothion, Fenthion, Malathion, Metalaxyl, Omethoate, Phosalone, Pirmicarb, Pirimiphos ethyl, pirimiphos Methyl, Profenofos, Prothiofos, Pyrazophos, Tolcophos-Methyl, Triazophos.

Organochlorine and pyrethroid Compounds

Bromopropylate, Carbosulfan, Chlorothalonil, Cyfluthrin, Cypermethrin, DDD-p,p', DDE-p', P', DDT-o, p', DDT-p,p', Deltamethrin, Dichlofluanide, Dicofol, Dieldrin, Endrin, Fenvalerate, alpha HCH, Beta HCH, Gamma HCH (lindane), delta HCH, Heptachlor epoxide, Hexachlorobenzene, Iprodione, Permethrine, Procymidone, Propiconazole, Tetradifon, Triadimefon, Triadimenol, Vinclozoline. All standard solution of reference materials is prepared in n.hexane/acetone mixture 9:1.

Equipments

Gas chromatography-HP 5890 equipped with double Electron capture Detector (ECD) with two capillary columns. Injector 225°C, detector 300°C, operating conditions, Nitrogen carrier gas, 2.5 ml/min 75-90 ml/min (Carrier + makeup), column head pressures 82 k.pa.

Gas chromatography-HP 5890 equipped with double Nitrogen phosphorus Detector (NPD), inject 225 °C detector 280°C operating conditions. Hydrogen 3.5±0.1 ml/min, Air 100-200 ml/min, Nitrogen carrier gas 25 ml/min.

Atomic absorption spectrometry. Unicam 929 equipped with GF 90 Furnace, Hollow cathode lamp for Cu, Pb and Cd.

Chromatography Columns

- Pas 5 ECD tested ultra 2 silicon, 25 m x 0.32 mm Film thickness 0.52 μm .
- Pas-1701 ECD tested 1701 silicon 25 m x 0.32 mm, film thickness 0.25 μm .

Temperature programs

Initial temperature 90°C for 2 min ramp (1) 20 °(C/mm) to 150°C, ramp (2) 6° (C/min) to 270°C hold 15 min.

Reagent

Acetone, dichloromethane, n.hexane, petroleum ether, ethanol (Pestiscann). Florisil-PR. Grad (Merk, 60-100 mesh, Anhydrous sodium sulfate (Redeldeltaen), sodium chloride, nitric acid 68%, Ammonium dihydrogen phosphate and Magnesium nitrate.

Multiresidue, Extraction and Clean-Up

According to the Luke method, Association of Official Analytical Chemists AOAC (1995), plant residues were extracted from non-fatty food by blending with acetone or acetone/water. The pesticides were transferred from the aqueous filtrate into the organic phase by shaking with petroleum ether and dichloromethane; after drying, organic phase is concentrated just to dryness and dissolved in hexane/acetone for GC determination. The method allows the determination of 63 pesticide residues from different groups. For water and soil samples, EPA procedure was adopted for analysis of organochlorine and organophosphorus pesticide residues, Dogheim *et al* (1992). Vegetables, fruits, soil and water samples recoveries were always >85% for organochlorines. Recoveries for organophosphorous compounds used for result correction were > 80% in vegetables, fruits and soil samples. Residues in soil samples were expressed per dry matter weight. The detection and confirmation of the presence of residues in all samples depends on the use of chromatography columns of different polarity. Quantitative determination is made using internal standard technique.

II Heavy Metals

Digestion of plant samples occurred according to the VTT method, VTT (1991), while soil samples were analysed according to the EPA method, Doghiem *et al* (1992). Lead, cadmium and copper were analyzed in water and soil samples using the method of the EPA, Saltanpour (1985) and plant samples using the VTT, method VTT (1992).

The average recovery of Cd, Pb and Cu from several different commodities is 85%, 102% and 86%, respectively. For water and soil samples, the recovery ranged from 87% to 110% for Cd, Pb and CU.

"Merk" Copper, Lead and Cadmium stock Standard reference material 1000 mg/L.

III- Quality assurance procedure

The criteria for quality assurance of the codex committee were followed to determine the performance of the Multiresidue method. Recovery percentage, accuracy, limit of determination and coefficient of variation (CV%) was determined for tested compounds using different commodities. The reproducibility expressed as relative standard deviation was less than 20% limit determination in fruits, vegetables and environmental samples was 0.01-0.1 mg/kg. The measurement of uncertainty including random and systematic error (on 95% confidence level) is $<\pm 40\%$. Blank samples were fortified with the pesticide mixture and analyzed as normal samples.

RESULTS AND DISCUSSION

Water Samples

Thirty irrigation, drainage and drinking water samples were examined for residues of 63 pesticides. The data showed that water samples collected from the different sources in the four districts studied lacked from pesticide residues analysed at both sampling dates. In previous studies, Organochlorine pesticide residues were the most prominent group detected in ground water, Nile water and tap water samples for Kafr Elzayat governorate, Dogheim *et al.* (1996). The data revealed relatively higher residue levels of HCH isomers, DDT's, deildrin and heptachlor in samples of ground water, followed by Nile water then tap water. The concentrations detected in the Nile water samples are not in harmony with those obtained for the Ismailia governorate in 1996.

Soil samples

Forty surface soil samples were examined for residues of 63 pesticides. Dimethoate was the only organophosphorous pesticide residue while pirimicarb was the only carbamate pesticide residue found in soil samples collected from Qantara East. The data set in table 1 show that the concentrations detected are almost higher than those in water samples especially for DDT complex in Qantra West, Fayed and Kassasin. This could be due to its higher persistence, strong adsorption on soil particles and low solubility, Dogheim *et al.* (1992).

Dicofol residue was observed in soil samples collected from Ismailia, Qantara west, Qantara East and Kassasin. However, permethrin, Triadimefon and tetradifon residues were observed in Qantara East, tetradifon, DDT complex and Dicofol residues were detected in Kassasin soil samples.

Plant samples

Forty fruit and vegetable samples were examined for 63 pesticides. Table 2 demonstrates the contamination of fruit and vegetable samples with relatively low levels of organochlorine and organophosphorous pesticide residues. Total HCH isomers detected in potato samples collected from Qantara West were 0.22 ppm. However, p, p' DDE residues was detected in potato samples collected from Fayed were 0.03 ppm.

Dicofol, Chlorothalonil and deltamethrin residues were detected in strawberry at 0.63 ppm, in tomato at 0.02 ppm and in maize at 0.19 ppm in samples collected from Qantara East. Dicofol residue was detected in strawberry (2.44 ppm) and mandarin (0.08 ppm) samples collected from Qantara West and Kassasin, respectively. Dimethoate pesticide residue was detected in tomato (0.23 ppm) and orange (0.14 ppm) samples collected from Qantara West and Kassasin.

Profenofos pesticide residue was detected in potato (0.27 ppm) and dill (0.28 ppm) samples collected from Qantara West and Kassasin. Malathion pesticide residue was detected in dill (0.48 ppm) samples collected from Kassasin, however no detectable pesticide residues were observed in different commodities collected from Isamilia.

Heavy metal in water, soil and plant samples

This study demonstrated that lead and cadmium residues levels varied from

being undetectable to very low concentration in water and soil samples collected from Ismailia, Qantara West, Qantara East, Fayed and Kassasin, Table 3 and 4.

Copper residue levels ranged from 0.098 to 0.419 ppm in soil samples collected from Qantara West and Kassasin. However, copper residue levels in water samples was lower than soil samples. Copper residue level ranged between 0.025 (Fayed) and 0.179 (Kassasin) ppm in water samples collected from Ismailia governorate.

No detectable lead residue level was observed in Ismailia plant sample. Otherwise, the lead residue ranged between 0.023 (Qantara East) and 0.206 (Kassasin) ppm, Table 5. In Kassasin tomato sample, lead was higher than the permissible limits established by the Finnish maximum residue levels (MRL's) for lead (0.1 ppm).

Cadmium residue level ranged between 0.001 (Ismailia) and 0.02 (Kassasin) ppm in plant samples, which was lower than the permissible limits established by the Finnish MRL's for cadmium (0.1 ppm).

Copper residue level ranged between 0.449 (Qantara East) and 1.055 (Kassasin) ppm in plant samples, which was lower than the permissible limits established by Finnish MRL's for copper 10 ppm.

CONCLUSION

The data demonstrate that water samples collected from the different sources in the four districts studied lacked the pesticide residues analyzed.

Soil samples showed that very low concentrations DDT complex, dicofol, permethrin, tetradifon and Triademifon. Dimethoate was the only organophosphorus pesticide residue, while pirimcarb was the only carbamate pesticide residue found in soil samples collected from Ismailia governorate. DDE p, p; was the most frequent pesticide found in soil (0.01 ppm).

No violation was detected in any plant samples analyzed. Dicofol was the most frequent pesticide residue mean level (2.44 ppm) maximum level was detected in strawberry samples at 3.68 ppm.

Water, soil and plant samples were examined for copper, lead and cadmium. Copper residues were detected in low concentration, however lead and cadmium residues varied from being undetectable to very low concentration except in Kassasin tomato samples. Lead residues analyzed were higher than the permissible limits established by the Finnish maximum residue levels (MRL's) for lead (0.1 ppm).

Table 1. Pesticide residues in ppm detected in soil samples collected from different sources in Ismailia Governorate during 1996.

Sampling place	Pesticides	No. of samples analyzed	Min	Max	Mean	Frequency
Ismailia	Dicofol	8	0.004	0.004	0.004	1
Qantara West	p,p' - DDE	8	0.007	0.01	0.0085	2
	Dimethoate		1.2	0.995	2	
	Dicofol		0.77	0.77	1	
Qantara East	Permethrin	8	0.31	0.31	0.31	1
	Pirimicarb		0.38	0.38	1	
	Triadimefon		0.11	0.11	1	
	Tetradifon		0.15	0.13	2	
	Dicofol		0.24	0.24	1	
Fayed	p,p' - DDE	8	0.001	0.01	0.01	6
Kassasin	p,p' - DDE	8	0.003	0.98	0.61	3
	Tetradifon		0.02	0.72	0.37	2
	p,p' - DDT		0.0017	0.0017	0.0017	1
	o,p'-DDT		0.0017	0.0017	0.0017	1
	Dicofol		0.0017	0.0017	0.0017	1

Table 2. Pesticide residues in ppm detected in plant samples collected from different sources in Ismailia Governorate during 1996.

Sampling place	Commodity	No. of samples analyzed	Pesticides	Min	Max	Mean	Frequency		
Ismailia	Banana, Clever Carrot, Beans dry, Caw Peas, Maize	6	-	-	-	-	-		
			Qantara West	10	Dithiocarbamates	0.4	0.4	0.4	1
					Dicofol	1.2	3.68	2.44	2
					Dimethoate	0.23	0.23	0.23	1
					Profenofos	0.27	0.27	0.27	1
					alpha HCH	0.13	0.13	0.13	1
Beta HCH	0.05	0.05			0.05	1			
Gamma HCH	0.04	0.04	0.04	1					
Qantara East	Cucumber Strawberry Tomato Maize	10	Dithiocarbamates	0.2	0.2	0.2	1		
			Dicofol	0.07	1.2	0.63	2		
			Chlorothalonil	0.02	0.02	0.02	1		
			Deltamethrin	0.17	0.22	0.19	2		
Fayed	Potato Tomato	7	p.p' - DDE	0.03	0.03	0.03	1		
			Dithiocarbamts	0.23	0.23	0.23	1		
Kassasin	Mandarin Orange Dill Dill	7	Dicofol	0.08	0.08	0.08	1		
			Dimethoate	0.14	0.14	0.14	1		
			Profenofos	0.28	0.28	0.28	1		
			Malathion	0.48	0.48	0.48	1		

Table 3. Lead, cadmium and copper residues in ppm detected in soil samples collected from Ismailia Governorate.

Sampling place	Heavy metal	No. of samples analyzed	Min	Max	Mean	Frequency
Ismailia	Pb	2	0.003	0.003	0.003	1
	Cd		-	-	-	-
	Cu		0.06	0.19	0.125	2
Qantara West	Pb	2	0.004	0.008	0.006	2
	Cd		0.002	0.002	0.002	2
	Cu		0.492	0.904	0.098	2
Qantara East	Pb	2	0.002	0.002	0.002	2
	Cd		0.001	0.001	0.001	1
	Cu		0.16	0.38	0.27	2
Fayed	Pb	2	-	-	-	-
	Cd		-	-	-	-
	Cu		0.175	0.19	0.183	2
Kassasin	Pb	2	-	-	-	-
	Cd		0.001	0.002	0.0015	2
	Cu		0.312	0.526	0.419	2

Table 4. Lead, cadmium and copper residues in ppm detected in water samples collected from different sources in Ismailia Governorate during 1996.

Sampling place	Heavy metal	No. of samples analyzed	Min	Max	Mean	Frequency
Ismailia	Pb	6	-	-	-	-
	Cd		0.01	0.01	0.01	2
	Cu		0.04	0.08	0.056	6
Qantara West	Pb	7	0.001	0.08	0.02	6
	Cd		0.001	0.01	0.005	3
	Cu		0.017	0.07	0.04	7
Qantara East	Pb	5	0.001	0.003	0.0022	4
	Cd		0.001	0.001	0.001	2
	Cu		0.04	0.061	0.051	5
Fayed	Pb	5	-	-	-	-
	Cd		-	-	-	-
	Cu		0.01	0.03	0.025	4
Kassasin	Pb	7	0.002	0.008	0.003	6
	Cd		0.001	0.001	0.001	1
	Cu		0.004	0.928	0.175	7

Table 5. Lead, cadmium and copper residues in ppm detected in plant samples collected from different sources in Ismailia Governorate during 1996.

Sampling place	Commodity	No. of samples analyzed	Heavy metal	Min	Max	Mean	Frequency
Ismailia	Cucumber	2	Pb	-	-	-	-
			Cd	0.001	0.001	0.001	1
			Cu	0.08	0.69	0.715	2
Qantara West	Cucumber	2	Pb	0.149	0.11	0.129	2
			Cd	0.014	0.009	0.011	2
			Cu	0.04	0.78	0.91	2
Qantara East	Tomato	2	Pb	0.44	0.074	0.023	1
			Cd	0.002	0.01	0.0015	2
			Cu	0.803	0.69	0.449	2
Fayed	Cucumber	2	Pb	0.074	0.002	0.074	2
			Cd	0.015	0.001	0.0125	2
			Cu	1.084	0.095	0.887	2
Kassasin	Tomato	2	Pb	0.3	0.113	0.206	2
			Cd	0.02	0.02	0.02	1
			Cu	0.98	1.13	1.055	2

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تقدير بعض الملوثات الخطرة في محافظة الاسماعيلية

أشرف محمود المرصفي

المعمل المركزي للمبيدات - مركز البحوث الزراعية - الدقى - الجيزة.

تهدف هذه الدراسة القيام بعملية مسح لتبقيات المبيدات سواء فوسفورية، كلورينية، كرباماتية، بايرثرويد وكذلك العناصر الثقيلة (نحاس، رصاص، كاديوم) في مناطق محافظة الاسماعيلية (الاسماعيلية - القنطرة غرب - القنطرة شرق - فايد - القصاصين) حيث تم تجميع عدد ١١ عينة ممتثلة في ٤٠ عينة نبات، ٤٠ عينة تربة وكذلك ٣٠ عينة مياه (شرب - صرف - ري) على مدار عام ١٩٩٦.

أظهرت نتائج الدراسة بخلو جميع عينات المياه التي جرى أخذها من كافة المناطق بمحافظة الاسماعيلية من متبقيات المبيدات. أما في حالة عينات التربة فقد وجدت تركيزات منخفضة من متبقيات المبيدات الكلورونية كالدايكوفول والبرميثرين وتترايديفون وتراي اديميفون ومجموع مركبات الـ د.د.ت، بينما كان مركب الدايمثوات هو المبيد الفوسفورى الوحيد الذى وجد في العينات التى جرى تحليلها، أما في حالة المبيدات الكرباماتية فقد كان مبيد الـ بريمكارب هو أيضا المبيد الوحيد الذى وجد في العينات. ومن الملاحظ أن مبيد p,p' DDE هو أكثر المبيدات وجوداً على مستوى عينات التربة جميعاً.

أظهرت نتائج اختبار عينات الحاصليل بعدم وجود أى تعدى للحدود القصوى على مستوى جميع المبيدات المختبرة وكان مبيد الدايكوفول هو أكثر المبيدات وجوداً بتركيز متوسط (٢,٤٤ جزء في المليون)، بينما كان أكبر تركيز لهذا المبيد موجودا بعينات الفراولة بمقدار ٣,٦٨ جزء في المليون.

تم اختبار ٥٠ عينة (٣٠ مياه، ١٠ نبات، ١٠ تربة) وذلك لتقدير مستوى الرصاص - النحاس - الكاديوم في محافظة الاسماعيلية وأظهرت نتائج التحليل وجود كميات قليلة من عنصر النحاس، بينما كان مستوى كل من عنصرى الرصاص والكاديوم يتراوح ما بين خلو هذه العينات الى وجود تركيزات قليلة جدا على مستوى جميع المناطق بمحافظة الاسماعيلية ما عدا في عينات الطماطم التى أخذت من القصاصين فقد تعدى عنصر الرصاص الحد المسوح به وذلك طبقاً للحدود القصوى الفنلندية لهذا العنصر الختير.