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Pesticide Residues in Selected Vegetables and Fruits in Alexandria City, Egypt, 1997–1998

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Pesticides use in agriculture is necessary in the production of food. Indeed, they are used widely to control crop pests. Recently, in Egypt, the use of high persistent organochlorine pesticides was curtailed since 1970s. A low persistence organophosphate, carbamate, synthetic pyrθthroid and other pesticides that have currently been used against pests of most vegetable and fruit crops had replaced them. This usage results in the presence of pesticide residues in our plant-based food.

During the last decade, several survey studies on the food contamination with pesticides were reported [e.g., survey on the postharvest-applied agrochemicals in fruits and vegetables in Greece; Papadopoulou (1991), the study on pesticide residues in vegetables in Japan; Yoshida, et al. (1992), a total diet study on many kinds of vegetables and fruits and other food items in Belgium; Dejonckheere, et al. (1996 a) and in Canada; Neidert and Saschenbrecker (1996). In USA, monitoring of pesticides in pears, tomatoes, apples and rice; Roy et al. (1995 and 1997). In Egypt, monitoring of pesticides in some vegetables and fruits; Dogheim, et al. (1996 a and b)].

It is well known that no monitoring study can determine all pesticides in all food items. That would be economically unrealistic and practically impossible. So, the objective of the present survey was to determine the residues of certain groups of pesticides in common vegetables and fruits in the Egyptian diet. Assessment of culinary treatments for removal or reducing of pesticide residues from prepared ready-to-eat vegetables and fruits was also evaluated. The obtained data from this study would help in assessing the risk of human exposure to pesticides and in implementation of the good agricultural practices recommended for agricultural fields.

MATERIALS AND METHODS

Seventy eight samples of four kinds of vegetables (tomato, eggplant, cucumber, Potato) and forty four samples of three kinds of fruits (apple, grape, orange) as major representatives of plant-based food were collected from different retail food

markets of Alexandria city during the period from June 1997 to August 1998. The sampling frequency and number were mainly dependent on the harvesting period among the seasons.

Vegetable and fruit samples (approximately 400 g each) were chopped to small portions to obtain an easily mixed material. The portions of each sample were divided into 4 representative sub-samples (100 g each). Two of these sub-samples were extracted for determination of pesticide residues. When no residue (lower than the method detection limit) was detected in the raw sub-samples, no further analysis was performed based on the method of Dejonckheere et al. (1996 b). On the other hand, samples with detectable residues, another 2 sub-samples were subjected to culinary processes as a manner typical of everyday housekeeping. These processes include washing of tomato, eggplant, cucumber, apple and grape under a flowing stream of tap water, and peeling followed by tap water washing of potato and orange. Then, the processed sub-samples were analyzed for pesticide residues determination.

Solvents and other reagents used (acetone, benzene, ethyl acetate, methylene chloride, n-hexane, florisil 60-100 mesh (pre-treated as in the method of Kadenczki et al. (1992)), sodium hydroxide, stannous chloride, carbon disulfide, cupric acetate monohydrate, hydrochloric acid, ethanol, diethanol amine) were analytical reagent grade. The analytical standards of the tested pesticides were kindly provided by Dr. JP Villeneuve IAEA, Monaco. The selected analytical standards are: (a)- Chlorinated hydrocarbon insecticides: Aldrin, dieldrin, endrin, HCB, lindane, p, p`-DDD, p, p`-DDE, p, p`-DDT. (b)- Halogenated pyrθthroids: Cypermethrin, fenvalertae, lambda-cyhalothrin. (c)- Nitrogen containing halogenated fungicides: Captafol, captan, chlorothalonil, folpet, metalaxyl, vinclozolin. (d)- Organophosphorus insecticides: Azinphos-ethyl, azinphos-methyl, chlorpyrifos, chlorthion, coumaphos, diazinon, dichlorvos, dimethoate, ethion, fenitrothion, fenthion, leptophos, malathion, methidathion, methyl-chlorpyrifos, methyl-parathion, monocrotofos, parathion, profenofos, sulfotep, tetrachlorvinphos, triazophos.

A simple multi-residue method according to Kadenczki, et al. (1992) was applied to extract several pesticides (chlorinated hydrocarbon, organophosphate and halogenated pyrθthroid insecticides and nitrogen containing halogenated fungicides) from vegetables and fruits. The principle of this method is based on having a homogeneous sample pulp adsorbed on the surface of activated florisil to obtain a free-flowing powder, which is extracted in a glass column with methylene chloride-acetone (9+1, v/v). The gas chromatograph (GC) used was HP-5890 Series II equipped with the following: (1)- Electron capture detector (ECD) for detection of halogenated pesticides. (2)- Nitrogen phosphorus detector (NPD) for detection of organophosphorus insecticides and nitrogen-containing fungicides. (3)- Megabore column; HP-608 methyl phenyl polysiloxane (30 m x 0.53 mm i.d x 0.5 um film thickness). (4)- GC test column; HP-1 cross-linked methyl silicone (5 m x 0.53 mm i.d x 2.65 um film thickness) was used to confirm the detected pesticides. (5)- Split/splitless injection mode (0.8 min. hold) at 220°C, helium was

used as a carrier gas at a flow rate of 2.5 ml/min. The oven and ECD parameters were as follows: Oven temperature; initial; 80°C (1 min. hold), 1st ramp: 30°C/min. to 170°C (0.0 min. hold), 2nd ramp: 10°C/min. to 300°C, final temperature; 300°C (10 min. hold). Detector parameters were: Temperature; 300°C, makeup gas; nitrogen; 35 ml/min., anode purge gas; nitrogen; 4 ml/min. flow rate. The oven and NPD parameters were as follows: Oven temperature; initial; 80°C (1min. hold), 1st ramp: 25°C/min. to 190°C (0.0 min. hold), 2nd ramp: 2°C/min to 225°C (0.0 min. hold), 3rd ramp: 5°C/min. to 280°C, final temperature; 280°C (20 min. hold). Detector parameters were: Temperature; 225°C, gases: Hydrogen, air, and helium (makeup gas) at flow rates; 4, 100 and 30 ml/min., respectively.

A single-pesticide method to determine dithiocarbamate fungicides (e.g., mancozeb, maneb, zineb, thiram) in vegetable and fruit samples was used according to the method of Keppel (1969). The principle of this method is based on the conversion of dithiocarbamates to carbon disulfide (CS_2) by using a decomposition-absorption apparatus as in the method of Cullen (1964). The evolved CS_2 that was trapped by the color reagent (cupric acetate monohydrate and diethanol amine) was measured colorimetrically at wavelength 435 nm using UV/VIS- Spectrophotometer (Pye Unicam SP 8-100). The dithiocarbamate concentration was calculated as zineb as the following equation: ug zineb = ug CS_2 x 1.81.

Quality control for the analysis of pesticide residues in vegetables and fruits consisted of the following: (1)- Analysis of blank samples. (2)- Analysis of the samples in duplicate. (3)- Determination of the method detection limits for the analyzed pesticides using samples with no pesticide residues (the methods detection limits obtained ranged from <0.2 to <1.0 ppb for the GC detection of the pesticides tested, and <20.0 ppb for the colorimetric measurement of dithiocarbamates). (4)- Estimation of the extraction procedure efficiency using samples spiked with 100 to 500 ng range of the pesticide standards (except in the case of dithiocarbamates determination, CS_2 was used at 50 ug for sample spiking). The obtained recovery of the analyzed pesticides and CS_2 ranged between 76 and 95%.

RESULTS AND DISCUSSION

Table 1 shows that cypermethrin, dimethoate, profenofos insecticides and dithiocarbamate fungicides (as zineb) were detected in 20, 13.3, 33.3 and 73.3% of the total raw samples of tomato with the mean levels of 8.3, 12.6, 20.8 and 75.0 ppb, respectively. The detected levels of profenofos were reduced to 7.3 ppb in 40% of the total washed tomato samples, while cypermethrin, dimethoate and dithiocarbamate residues were not detected. Dithiocarbamate, profenofos and triazophos pesticides were detected in 80, 50 and 60% of the total unwashed eggplant samples with the mean levels of 160, 23.4 and 15.0 ppb while these levels were reduced to 48.3, 4.1 and 6.2 ppb in 25, 20 and 16.7% of the total

Table 1. Pesticide residue levels (ppb) in vegetable samples collected from Alexandria retail markets, 1997 - 1998.

Detected pesticides	Mean		Maximum		Minimum		No. of samples with residue		Frequency (%)	
	A	B	A	B	A	B	A	B	A	B
Tomato (n = 30)										
Cypermethrin	8.3	n.d	19.1	n.d	2.4	n.d	6	0	20	0
Dimethoate	12.6	n.d	22.5	n.d	5.0	n.d	4	0	13.3	0
Dithiocarbamates	75.0	n.d	113.4	n.d	24.1	n.d	22	0	73.3	0
Profenofos	20.8	7.3	41.8	15.1	7.7	2.3	10	4	33.3	40
Eggplant (n = 10)										
Dithiocarbamates	160.0	48.3	287.0	70.6	80.0	26.0	8	2	80	25
Profenofos	23.4	4.1	36.0	4.1	6.7	4.1	5	1	50	20
Triazophos	15.0	6.2	27.5	6.2	8.8	6.2	6	1	60	16.7
Cucumber (n = 20)										
Dimethoate	18.0	n.d	33.1	n.d	10.1	n.d	4	0	20	0
Dithiocarbamates	434.0	35.4	871.0	35.4	116 .0	35.4	16	1	80	6.3
Profenofos	16.8	4.5	25.0	7.4	9.5	1.6	6	2	30	33.3
Potato (n = 18)										
Fenitrothion	28.0	6.0	42.4	8.6	13.3	3.4	9	2	50	22.2
Malathion	21.2	9.4	36.0	16.4	5.0	2.3	7	2	38.9	28.6

A : Unprocessed vegetables.
B : Processed vegetables.
n : Number of the raw samples analyzed.
n.d: Not detected (the minimum detection limits for organophosphorus, pyrθthroid and dithiocarbamate pesticides analyzed were <0.2, <1.0 and <20.0 ppb, respectively).

washed samples, respectively. As shown in tomato, dithiocarbamate residues were also found at high levels than the other detected pesticides in the unwashed eggplant samples. Dimethoate and profenofos insecticides were detected in 20 and 30% of the total raw cucumber samples analyzed with the mean levels of 18.0 and 16.8 ppb, respectively. The residue levels of profenofos were reduced to 4.5 ppb in 33.3% of the total washed samples, while no residues of dimethoate were detected. Dithiocarbamates were the most frequently detected residues in 80% of the total unwashed cucumber samples with the mean levels of 434.0 ppb. On the other side, only 35.4 ppb of dithiocarbamates was the mean level detected in 6.3% of the total washed cucumber samples. In general, the unprocessed vegetables of tomato, eggplant and cucumber were contaminated with dithiocarbamates at high levels and frequencies than those of organophosphates. Fenitrothion and malathion insecticides were detected in 50 and 38.9% of the total unprocessed potato samples with the mean concentrations of 28.0 and 21.2 ppb, respectively. These levels were reduced to 6.0 and 9.4 ppb in 22.2 and 28.6% of the total peeled and washed tubers, respectively. No chlorinated hydrocarbon insecticides or nitrogen containing halogenated fungicides were detected in all the vegetable samples analyzed.

Table 2 shows the frequent presence of dimethoate, malathion and profenofos insecticides and dithiocarbamate fungicides in 25, 33.3, 33.3 and 50% of the total unwashed apple samples with the mean levels of 7.8, 7.0, 9.8 and 28.1 ppb, respectively. Malathion and profenofos residues were detected in 25 and 50% of the total washed apple samples with the mean levels of 1.9 and 2.7 ppb, respectively. Dimethoate and dithiocarbamate residues were reduced to below their minimum detection limits in all the washed apple samples. Cypermethrin, dimethoate, malathion and profenofos insecticides and dithiocarbamate fungicides were detected at frequencies; 30, 40, 50, 70 and 50% of the total unwashed grape samples with the mean levels of 15.7, 18.2, 8.6, 13.4 and 37.5 ppb, respectively. The detected levels of dimethoate, malathion, profenofos and dithiocarbamate residues were reduced to 2.9, 3.0, 5.3 and 23.7 ppb in 50, 20 28.6 and 30% of the total washed grape samples, respectively. Cypermethrin and dithiocarbamate residues were reduced to below their minimum detection limits in all the washed grape samples. Dimethoate, dithiocarbamate and malathion pesticides were detected in 16.7, 33.3 and 16.7% of the total unpeeled and unwashed orange samples with the mean levels of 4.6, 29.8 and 3.5 ppb, respectively, while these levels were reduced to lower than the method detection limits in all the processed orange fruits. As shown in the case of vegetables, none of chlorinated hydrocarbon insecticides were detected in all the fruit samples analyzed, probably because of their prohibition from agricultural use in Egypt, especially on vegetable and fruit crops. Also, no nitrogen containing halogenated fungicides were detected. This might be attributed to the limited application of these fungicides on vegetables and fruits in the north regions of Egypt.

The maximum residue limits (MRLs) established by the codex committee on pesticide residues (FAO/WHO) in 1992 and the Belgian MRLs cited by Dejonckheere et al. (1996 a) reported that the detected pesticide MRLs in

Table 2. Pesticide residue levels (ppb) in fruit samples collected from Alexandria retail markets, 1997 - 1998.

Detected pesticides	Mean		Maximum		Minimum		No. of samples with residue		Frequency (%)	
	A	B	A	B	A	B	A	B	A	B
Apple (n = 12)										
Dimethoate	7.8	n.d	14.7	n.d	3.1	n.d	3	0	25	0
Dithiocarbamates	28.1	n.d	37.2	n.d	21.3	n.d	6	0	50	0
Malathion	7.0	1.9	10.5	1.9	2.9	1.9	4	1	33.3	25
Profenofos	9.8	2.7	15.6	4.0	3.5	1.4	4	2	33.3	50
Grape (n = 20)										
Cypermethrin	15.7	n.d	30.1	n.d	4.1	n.d	6	0	30	0
Dimethoate	18.2	2.9	31.8	4.7	7.8	1.8	8	4	40	50
Dithiocarbamates	37.5	23.7	55.5	26.0	24.3	21.6	10	3	50	30
Malathion	8.6	3.0	11.4	4.6	4.0	1.4	10	2	50	20
Profenofos	13.4	5.3	24.7	10.7	5.3	2.2	14	4	70	28.6
Orange (n = 12)										
Dimethoate	4.6	n.d	7.7	n.d	1.5	n.d	2	0	16.7	0
Dithiocarbamates	29.8	n.d	34.3	n.d	23.0	n.d	4	0	33.3	0
Malathion	3.5	n.d	5.8	n.d	1.2	n.d	2	0	16.7	0

A : Unprocessed fruits.
B : Processed fruits.
n : Number of the raw samples analyzed.
n.d: Not detected (the minimum detection limits for organophosphorus, pyrθthroid and dithiocarbamate pesticides analyzed were <0.2, <1.0 and <20.0 ppb, respectively).

vegetables and fruits were generally ranged between 0.05 and 4.0 ppm. In the present study, the detected pesticide MRLs were not violated in any of the vegetable and fruit samples analyzed. The mean levels of the detected pesticides in the unprocessed samples ranged from 3.5 ppb for malathion to 434.0 ppb for dithiocarbamates which were reached to their maximum value (871 ppb) detected on and/or in cucumber, but also not violated the Belgian MRL (2 ppm). Despite the dithiocarbamate fungicides had the greatest detectable levels compared with the other compounds detected, it were more easily eliminated by washing and/or peeling of the tested vegetables and fruits. This finding is especially true for dislodge-able surface deposits of the contact pesticides (e.g., dithiocarbamate fungicides) compared with the systemic compounds such as many of organophosphorus insecticides. Fortunately, in almost all cases, a large part of pesticide residues in fresh vegetables and fruits was removed by simple culinary treatments. Moreover, further culinary processes may remove more of the remaining pesticides. The obtained results in the present study are generally in agreement with the other studies on the evaluation of several culinary treatments for reducing or removal of pesticide residues from vegetables and fruits [e.g., Tantawy et al. (1975 and 1979), Dejonckheere, et al. (1996 b)].

As a general trend, the present study shows that the detected pesticides on and/or in vegetables and fruits were at lower levels than those detected in the previous studies reported [e.g., Yoshida, et al. (1992), Dejonckheere, et al. (1996 a), Dogheim, et al. (1996 a and b)]. Also, none of chlorinated hydrocarbon insecticides were detected in the present study. This finding has to confirm that these insecticides were prohibited from their direct application in agricultural practices on vegetable and fruit crops in Egypt.

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