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Monitoring of pesticides and heavy metals in cucumber fruits produced from different farming systems

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ABSTRACT

A total of 216 kg of cucumber samples, representing three different types of farming production [e.g., conventional (C), greenhouse (G) and organic (O)], were collected from different locations in Giza governorate (Egypt), and subjected to pesticide residue and heavy metal analyses. Residues of some organochlorine pesticides (OCPs), such as hexachlorobenzene (HCB), heptachlor, aldrin, endrin, dieldrin and o,p′-DDT, as well as organophosphorus pesticides (OPPs), such as chlorpyrifos-methyl, thiometon and phorate were found in a number of samples at concentrations exceeding their MRLs. Lindane was detected in 33.3%, 50.0% and 25.0% of samples from C, G and O cucumber, respectively, without violation. The insecticide methamidophos showed high frequency in the analyzed samples of C, G and O cucumber accounting to 66.7%, 41.7% and 50.0%, respectively, without violation. The majority of the analyzed samples contained detectable concentrations of Zn, Cu, Mn, Fe, Cd, Pb, Cr, Ni and Co. Only, Pb and Cd were found in a number of samples at concentrations exceeding their MLs. Contamination among the three types of cucumber either by pesticides or heavy metals varied from a season to another. Generally, the greenhouse cucumber contained the highest value of total pesticide residues (1.016 mg kg^{-1}), followed by organic (0.442 mg kg^{-1}) and then conventional (0.415 mg kg^{-1}) cucumbers. Heavy metal contamination in the three cucumber types accounted to 4.968, 5.350 and 6.248 mg kg^{-1}, respectively. The study shed light to the problem of multi toxicants in a food commodity such as cucumber; a common element in the daily human diet.

1. Introduction

Food safety is a major public concern worldwide and food consumption has been identified as the major pathway for human exposure to certain environmental contaminants, accounting for >90% of intake compared to inhalation or dermal routes of exposure (Fries, 1995). About 30% of human cancers are caused by low exposure to initiating carcinogenic contaminants in the diet (Tricker and Preussmann, 1990). During the last decades, the increasing demand of food safety has stimulated research regarding the risk associated with consumption of foods contaminated by pesticides, heavy metals and/or toxins (D'Mello, 2003).

Chemophobia is the most common reason for the public to choose organic food on the assumption that such food is free of synthetic pesticides. Organic farms distinguish from all other forms of farming by a rejection of soluble minerals as fertilizers and synthetic pesticides in favor of natural ones (Trewavas, 2004). Subsequently, this has resulted in increasing demand for organic produce of different varieties of vegetables, fruits, milk products and cereals in many parts of the world. Organically-farmed vegetables, such as cucumber, tomato, potato, carrot and others, are being marketed in the Egyptian local markets for about a decade. Vegetables produced under greenhouse conditions are known in Egypt several decades ago. Thus, the Egyptian local markets contain such kinds of vegetables in addition to those long produced from conventional or traditional cultivations under open field conditions.

Food contamination monitoring programs in Egypt have been carried out over several years by many investigators. Most of monitoring programs directed to vegetables and fruits were performed by the Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food, Ministry of Agriculture, Egypt (e.g., Dogheim et al., 1996a,b, 1999, 2001, 2002, 2004). To the best of our knowledge, the type of farming production for vegetables/fruits included in the previously carried out investigations was not taking into consideration. A single paper on chemical contaminants in Egyptian organically-farmed vegetables was published by Salim (2006). According to Dogheim et al. (2004), monitoring of contaminants contributes to improving food safety, warn of actual and potential food scares, and facilitate evaluation of possible health

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Table 1
Detected pesticide residues ($mgkg^{-1}$; fresh wt) in cucumber fruits from conventional, greenhouse and organic farming.

Month	Detected pesticide	Conventional farming				Greenhouse farming				Organic farming			
		S1	S2	S3	Mean ± SD	S1	S2	S3	Mean ± SD	S1	S2	S3	Mean ± SD
June 06	Heptachlor + its epoxide	nd	nd	nd	–	0.422*	0.399*	0.253*	0.358* ± 0.092	nd	nd	nd	–
	Dieldrin	nd	nd	nd	–	nd	nd	nd	–	0.022*	0.019	0.025*	0.022* ± 0.003
	p,p-DDD	nd	nd	nd	–	nd	nd	nd	–	0.005	0.043	0.065	0.038 ± 0.030
July 06	HCB	nd	nd	nd	–	0.242*	0.262*	0.137*	0.214* ± 0.067	0.117*	0.120*	0.950*	0.396* ± 0.480
	Heptachlor + its epoxide	0.050*	0.040*	0.061*	0.050* ± 0.010	nd	nd	nd	–	nd	nd	nd	–
	p,p-DDD	0.003	0.004	0.005	0.004 ± 0.001	nd	nd	nd	–	nd	nd	nd	–
	Methamidophos	0.102	0.067	0.025	0.065 ± 0.038	0.236	0.279	0.375	0.297 ± 0.071	0.182	0.152	0.014	0.116 ± 0.089
	Phorate	nd	nd	nd	–	0.035	0.026	0.043	0.035 ± 0.008	0.047	0.022	0.078	0.049 ± 0.028
	Thiometon	nd	nd	nd	–	nd	nd	nd	–	0.352*	0.185	0.224*	0.254* ± 0.087
	Chlorpyrifos-me	nd	nd	nd	–	0.037*	0.042*	0.022	0.034* ± 0.010	nd	nd	nd	–
	Pirimiphos-me	nd	nd	nd	–	0.310	0.018	0.056	0.128 ± 0.159	nd	nd	nd	–
	Malathion	nd	nd	nd	–	0.400	0.050	0.082	0.177 ± 0.193	nd	nd	nd	–
August 06	HCB	nd	nd	nd	–	0.398*	0.238*	0.330*	0.322* ± 0.080	0.552*	0.334*	0.427*	0.438* ± 0.109
	Lindane	0.103	0.102	0.095	0.100 ± 0.004	0.450	0.152	0.067	0.223 ± 0.201	0.018	0.035	0.025	0.026 ± 0.008
	Heptachlor + its epoxide	0.360*	0.285*	0.195*	0.280* ± 0.083	0.109*	0.125*	0.095*	0.110* ± 0.015	0.053*	0.011	0.205*	0.090* ± 0.102
	Aldrin	0.344*	0.283*	0.405*	0.344* ± 0.061	0.006	0.008	0.120*	0.045* ± 0.065	0.070*	0.080*	0.030*	0.060* ± 0.026
	Dieldrin	0.002	0.005	0.001	0.003 ± 0.002	0.001	0.002	0.007	0.003 ± 0.003	nd	nd	nd	–
	p,p-DDD	nd	nd	nd	–	1.093	1.150	0.950	1.064 ± 0.103	nd	nd	nd	–
	o,p-DDT	0.755*	0.880*	0.252*	0.629* ± 0.332	nd	nd	nd	–	nd	nd	nd	–
	Methamidophos	0.126	0.115	0.085	0.109 ± 0.021	0.103	0.135	0.164	0.134 ± 0.031	0.116	0.256	0.385	0.252 ± 0.135
	Phorate	nd	nd	nd	–	0.285	0.432*	0.399*	0.372* ± 0.077	nd	nd	nd	–
	Thiometon	nd	nd	nd	–	nd	nd	nd	–	0.116	0.125	0.108	0.116 ± 0.009
September 06	HCB	1.610*	0.985*	1.598*	1.398* ± 0.374	nd	nd	nd	–	0.578*	0.723*	0.352*	0.551* ± 0.187
	Lindane	0.193	0.253	0.213	0.220 ± 0.030	0.035	0.040	0.030	0.035 ± 0.005	nd	nd	nd	–
	Heptachlor + its epoxide	nd	nd	nd	–	1.566*	1.880*	1.720*	1.722* ± 0.157	nd	nd	nd	–
	Endrin	nd	nd	nd	–	0.104*	0.102*	0.088*	0.098* ± 0.009	nd	nd	nd	–
	Methamidophos	0.015	0.025	0.080	0.040 ± 0.035	0.105	0.095	0.111	0.104 ± 0.008	nd	nd	nd	–
	Phorate	nd	nd	nd	–	0.782*	0.904*	1.052*	0.913* ± 0.135	nd	nd	nd	–
	Chlorpyrifos-me	nd	nd	nd	–	0.022	0.016	0.031*	0.023 ± 0.008	0.021	0.020	0.018	0.020 ± 0.002
	Pirimiphos-me	nd	nd	nd	–	0.045	0.063	0.082	0.063 ± 0.018	0.184	0.220	0.125	0.176 ± 0.048
October 06	HCB	nd	nd	nd	–	0.065*	0.082*	0.120*	0.089* ± 0.028	0.150*	0.110*	0.065*	0.108* ± 0.043
	Lindane	0.005	0.022	0.003	0.010 ± 0.010	0.051	0.088	0.078	0.072 ± 0.019	nd	nd	nd	–
	Dieldrin	nd	nd	nd	–	1.101*	1.125*	1.270*	1.165* ± 0.091	nd	nd	nd	–
	p,p-DDD	0.020	0.016	0.020	0.019 ± 0.002	nd	nd	nd	–	nd	nd	nd	–
	p,p-DDT	0.007	0.005	0.032	0.015 ± 0.015	nd	nd	nd	–	nd	nd	nd	–
	Methamidophos	0.224	0.185	0.230	0.213 ± 0.024	0.241	0.871	0.099	0.404 ± 0.411	0.093	0.522	0.031	0.215 ± 0.267
	Phorate	nd	nd	nd	–	nd	nd	nd	–	0.030	0.030	0.052	0.037 ± 0.013
	Pirimiphos-me	nd	nd	nd	–	nd	nd	nd	–	0.045	0.062	0.026	0.044 ± 0.018
	Malathion	nd	nd	nd	–	nd	nd	nd	–	0.032	0.066	0.025	0.041 ± 0.022
	Fenthion	nd	nd	nd	–	nd	nd	nd	–	0.102	0.074	0.032	0.069 ± 0.035
November 06	HCB	nd	nd	nd	–	2.224*	1.305*	0.955*	1.495* ± 0.655	nd	nd	nd	–
	Lindane	nd	nd	nd	–	0.212	0.223	0.188	0.208 ± 0.018	nd	nd	nd	–
	Aldrin	0.003	0.005	0.002	0.003 ± 0.002	nd	nd	nd	–	nd	nd	nd	–
	Dieldrin	0.040*	0.005	0.002	0.016 ± 0.021	nd	nd	nd	–	nd	nd	nd	–
	p,p-DDT	0.002	0.006	0.002	0.003 ± 0.002	nd	nd	nd	–	nd	nd	nd	–
	Methamidophos	0.007	0.012	0.004	0.008 ± 0.004	0.062	0.058	0.041	0.054 ± 0.011	0.019	0.010	0.018	0.016 ± 0.005
	Thiometon	0.062	0.040	0.120	0.074 ± 0.041	0.051	0.030	0.023	0.035 ± 0.015	0.052	0.060	0.062	0.058 ± 0.005
	Chlorpyrifos-me	nd	nd	nd	–	0.032*	0.011	0.006	0.016 ± 0.014	0.012	0.001	0.021	0.011 ± 0.010
	Pirimiphos-me	0.012	0.018	0.007	0.012 ± 0.006	nd	nd	nd	–	nd	nd	nd	–
	Profenofos	nd	nd	nd	–	nd	nd	nd	–	0.252*	0.019	0.015	0.095* ± 0.136

December 06	HCB	nd	nd	nd	–	1.030*	0.954*	0.885*	0.956* ± 0.073	nd	nd	nd	–
	Lindane	0.134	0.155	0.122	0.137 ± 0.017	0.056	0.082	0.108	0.082 ± 0.026	0.77	0.052	0.085	0.302 ± 0.405
	Endrin	nd	nd	nd	–	nd	nd	nd	–	0.012*	0.132*	0.017*	0.054* ± 0.068
	o,p-DDD	0.004	0.004	0.005	0.004 ± 0.001	nd	nd	nd	–	0.025	0.015	0.012	0.017 ± 0.007
	p,p-DDT	nd	nd	nd	–	nd	nd	nd	–	0.006	0.055	0.041	0.034 ± 0.025
	Methamidophos	0.028	0.036	0.075	0.046 ± 0.025	nd	nd	nd	–	0.035	0.007	0.052	0.031 ± 0.023
	Phorate	nd	nd	nd	–	nd	nd	nd	–	0.347*	0.257	0.301	0.302 ± 0.045
	Chlorpyrifos-me	nd	nd	nd	–	1.055*	0.855*	0.074*	0.661* ± 0.518	0.020	0.031*	0.027	0.026 ± 0.006
January 07	Lindane	nd	nd	nd	–	nd	nd	nd	–	0.055	0.054	0.079	0.063 ± 0.014
	Methamidophos	0.045	0.038	0.035	0.039 ± 0.005	nd	nd	nd	–	0.355	0.220	0.270	0.282 ± 0.068
February 07	nd												
March 07	Methamidophos	0.075	0.082	0.053	0.070 ± 0.015	nd	nd	nd	–	nd	nd	nd	–
	Malathion	1.253*	0.928*	1.021*	1.067* ± 0.167	nd	nd	nd	–	nd	nd	nd	–
April 07	Lindane	nd	nd	nd	–	0.038	0.044	0.062	0.048 ± 0.012	nd	nd	nd	–
	p,p-DDD	nd	nd	nd	–	0.005	0.013	0.011	0.010 ± 0.004	nd	nd	nd	–
May 07	HCB	nd	nd	nd	–	nd	nd	nd	–	0.025*	0.016*	0.008	0.016* ± 0.008
	Dieldrin	nd	nd	nd	–	0.152*	0.134*	0.854*	0.380* ± 0.411	nd	nd	nd	–
	p,p-DDD	nd	nd	nd	–	nd	nd	nd	–	0.060	0.065	0.053	0.059 ± 0.006
	o,p-DDT	nd	nd	nd	–	nd	nd	nd	–	0.123	0.099	0.075	0.099 ± 0.024
	Pirimiphos-me	nd	nd	nd	–	nd	nd	nd	–	0.531	0.401	0.205	0.379 ± 0.164

S1, S2 and S3 are samples collected from different locations and each value is an average of three determinations.
* Values designated by asterisks are higher than the Codex-MRLs for the respective pesticide (see MRLs in Table 2).

hazards by providing information on levels of environmental pollution in the country. Furthermore, it may be convenient to compare levels of contaminants in commodities produced under different farming systems. Therefore, the present study aims at providing data on pesticides and heavy metals in cucumber fruits designated, according to the system of their production, as conventional (C), greenhouse (G), and organic (O) cultivations.

2. Materials and methods

2.1. Samples collection and preparation

A total of 18 kg of cucumber fruits were monthly collected from different local markets and locations in Giza Governorate, Egypt. These represented 6 kg from each of conventionally-farmed cucumber (C); greenhouse-farmed cucumber (G); and organically-farmed cucumber (O). The G and O were collected from three large supermarkets (namely: Hyper One, Carrefour & Metro). From each supermarket, a sample of 2 kg (in 1 kg packs, of identified source) either for G or O was purchased. The C cucumber samples were collected from small shops and peddlers in rural areas. This sampling system was performed throughout one complete year (June 2006–May 2007); giving rise to a sum of 216 kg for the all cucumber types. Each sample unit (2 kg) was chopped into small pieces, mixed, minimized by quartering to 500 g and then a-3 × 100 g subsamples were taken for pesticide analyses in addition to 3 × 20 g subsamples for heavy metals determinations. The resulted subsamples, in addition to the remainder fruit pieces, were kept at −20 °C until utilized.

2.2. Analysis of pesticide residues

2.2.1. Extraction and clean-up

The Official Analytical Methods of Analysis (AOAC, 1995) was followed. Triplicate sub samples (100 g, each) were homogenized with 200 mL portions of acetonitrile for 2 min in a waring blender at high speed then filtered. The aqueous filtrate was shacked vigorously with 100 mL petroleum ether (40/60) for 1–2 min in a separatory funnel. Ten milliliters of saturated NaCl solution and 600 mL distilled water were added to the same separatory funnel and shacked again for 30–45 s. The aqueous layer was discarded while the organic one was collected after washing with water. About 15 g of anhydrous Na_2SO_4 were added to the organic solvent layer, shaked vigorously and transferred directly to a column chromatography containing 20 g activated Florisil and 2 g anhydrous Na_2SO_4 on the upper Florisil layer. The column pre-washed with 40–50 mL petroleum ether followed by adding the petroleum ether extract. The column, respectively, eluted with 3 × 200 mL of 6%, 15% and 50% diethyl ether/petroleum ether solutions. The combined eluates were concentrated under vacuum to a definite volume (ca. 5 mL).

2.2.2. Gas chromatographic determination

The detection and quantification of pesticide residues in the samples were performed on a Hewlett-Packard GC model 5890A equipped with ^{63}N electron capture detector (ECD) and a flame ionization detector (FID). An HP-101 (methyl silicon fluid) capillary column (30 m × 0.25 mm, 0.25-μm film thickness) was used. The chromatograms were integrated with an HP-3392A integrator. The applied temperature programming was as follows: initial temperature, 80 °C; hold for 2 min; increased to 160 °C at 3 °C min^{-1}; hold 2 min; increase to 220 °C at 5 °C min^{-1}; hold 20 min. Injector and detector temperatures were 220 °C and 300 °C, respectively. The flow rates of nitrogen, hydrogen and air were adjusted at 10 psi, 30–35 mL min^{-1} and 300–350 mL min^{-1}, respectively.

Table 2
Numbers and percentages of contaminated and violated samples of different types of cucumber fruits collected from the Egyptian local markets during 2006/2007 with respect to detected pesticides in the analyzed samples.[a]

Pesticide	Contaminated samples with each pesticide						MRL (mg/kg)[b]	Violative samples					
	Conventional cucumber		Greenhouse cucumber		Organic cucumber			Conventional cucumber		Greenhouse cucumber		Organic cucumber	
	n	%	*n*	%	*n*	%		*n*	%	*n*	%	*n*	%
HCB	3	8.3	15	41.7	15	41.7	0.01	3	8.3	15	41.7	14	38.9
Lindane	12	33.3	18	50.0	9	25.0	2.00	0	0.0	0	0.0	0	0.0
Heptachlor	6	16.7	9	25.0	6	16.7	0.03	6	16.7	6	16.7	2	5.6
Aldrin	6	16.7	3	8.3	3	8.3	0.02	3	8.3	1	2.8	3	8.3
Dieldrin	6	16.7	9	25.0	3	8.3	0.02	1	2.8	6	16.7	2	5.6
Endrin	nd	–	3	8.3	3	8.3	0.005[c]	0	0.0	3	8.3	3	8.3
o,p-DDD	3	8.3	nd	–	3	8.3	na	–	–	–	–	–	–
p,p-DDD	6	16.7	6	16.7	6	16.7	na	–	–	–	–	–	–
o,p-DDT	3	8.3	nd	–	3	8.3	0.20	3	8.3	0	0.0	0	0.0
p,p-DDT	6	16.7	nd	–	3	8.3	0.20	0	0.0	0	0.0	0	0.0
Chlorpyrifos-me	nd	–	12	33.3	9	25.0	0.03	0	0.0	7	19.4	1	2.8
Fenthion	nd	–	nd	–	3	8.3	3.00	0	0.0	0	0.0	0	0.0
Malathion	3	8.3	3	8.3	3	8.3	0.50	3	8.3	0	0.0	0	0.0
Methamidophos	24	66.7	15	41.7	18	50.0	1.00	0	0.0	0	0.0	0	0.0
Phorate	nd	–	9	25.0	9	25.0	0.30	0	0.0	5	13.9	1	2.8
Pirimiphos-me	3	8.3	6	16.7	9	25.0	2.00	0	0.0	0	0.0	0	0.0
Profenophos	nd	–	nd	–	3	8.3	0.05	0	0.0	0	0.0	1	2.8
Thiometon	3	8.3	3	8.3	9	25.0	0.20	0	0.0	0	0.0	2	5.6

nd: not detected; na: not available.
[a] Total number of analyzed samples for each type of cucumber = 36.
[b] Maximum Residue Limits (MRLs) refer to Codex (2006a) for cucumber.
[c] MRL refers to Codex (1994) for vegetables.

Injected volume of analyzed samples equaled 1 μL and quantification based on peak areas given.

2.2.3. Quality assurance procedure

The Codex quality assurance criteria (Codex, 1993) were followed to determine the performance of the multiresidue method. Recoveries and limits of quantification (LOQ) were determined on samples at spiking levels 0.01–0.05 mg kg^{-1} from the pesticide mixture standard. The average recoveries ranged between 76% and 102%, and quantification limits between 0.003 and 0.043 mg kg^{-1}. The results of analyses were not corrected for recoveries.

Blank samples were fortified with the pesticide mixture and analyzed as a normal sample with each set of samples. The results were recorded on control charts. Repeated analysis of old samples was regularly carried out to control reproducibility.

2.3. Analysis of heavy metals

Determination of heavy metals in cucumber fruits was performed according to the method of AOAC (1995).

2.3.1. Digestion

Samples in triplicates were homogenized separately and 20 g of the fresh homogenate was transferred into a crucible and oven dried at 105 °C for 24 h. Few drops of concentrated nitric acid were added to the dried samples and ashed in a muffle furnace at 500–550 °C for 4 h. The ash was left to cool and then decomposed using concentrated nitric acid (10 mL). The ash suspension was filtered into a 25 mL volumetric flask and the solution was completed to the mark using deionized water.

2.3.2. Measurement

Prepared samples were measured on a Perkin–Elmer model 2380 atomic absorption spectrophotometer (AAS) with flame atomization (air–acetylene), equipped with a 10 cm burner and a deuterium lamp for background correction. Maximum absorbance was obtained by adjusting the cathode lamps at specific slit widths and definite wave lengths as follows:

Slit width = 0.2 nm for Fe, Mn, Co and Ni; and 0.7 nm for Cu, Zn, Pb, Cd, and Cr. Wave lengths were, respectively: 248.3, 279.5, 240.7, 232.0, 324.8, 213.9, 283.3, 228.8 and 357.9 nm.

The calibration curves were prepared from standards by dissolving appropriate amounts of the metal salts in purified nitric acid, diluting with deionized water and storing as stock solutions in a quartz flask. Fresh working solutions were obtained by serial dilution of stock solutions.

2.3.3. Quality assurance procedure

The recovery and reproducibility of the method was tested continuously by fortified clean samples with each of the metals at concentration levels ranged between 0.03 and 0.05 mg kg^{-1} and processed as previously described. The performance of the AAS was frequently tested by measuring the characteristic mass. The average recoveries ranged between 88% and 95%. Blank Samples were analyzed with every set of samples and the detection limits (i.e., the concentration produces an absorbance signal three times the magnitude of the baseline noise (Beaty and Kerber, 1993) were estimated for each measured metal. For the analyzed metals, the detection limits ranged 0.002–0.04 mg kg^{-1}. The results of analyses were not corrected for recoveries and expressed on fresh weight bases.

2.4. Chemicals

2.4.1. Conventional chemicals and solvents

These included: acetonitrile, petroleum ether, diethyl ether (Pestiscan chromatography grade or similar quality), anhydrous sodium sulphate, sodium chloride, Florisil 60-100 US mesh (BDH chemicals), and nitric acid (68%, super pure free from Pb; Merck Dorset, England).

2.4.2. Pesticides and heavy metals reference standards

A mixture of organochlorine (OC) pesticide standards containing HCB, lindane, heptachlor, aldrin, dieldrin, endrin, o,p′-DDD, p,p′-DDD, o,p′-DDT, and p,p′-DDT was purchased from Chemical Service, Inc. (West Chester, PA). Standards of Organophosphorus

(OP) pesticides (malathion, chlorpyrifos, chlorpyrifos-methyl, pirimiphos-methyl, phorate, thiometon, fenthion, diazinon, profenofos and methamidophos) were kindly provided from the Central Laboratory of Pesticide Residues and Heavy metals Analysis in Foods, Ministry of Agriculture, Cairo, Egypt.

Metals stock standards of Cd, Cu, Cr, Co, Ni, Fe, Pb, Mn and Zn were obtained from Merck, Darmstadt, Germany (Merck's ampoules; 1000 mg).

3. Results and discussion

Most of the organochlorine pesticides (OCPs) have been banned since decades in different parts of the world including Egypt, but their residues still appear as pollutants in food as well as in the environment. Their occurrence and long-range transport at local, regional and global scales has been recently explored (Harner et al., 2006). Frequent detection of these compounds in different environmental compartments could provide information about to what extend the threats posed by these xenobiotics may exist.

The data shown in Table 1 reveal occurrence of some OCPs in cucumber fruits at levels exceeding maximum residue limits (MRLs) for some of them. HCB, lindane, heptachlor, aldrin, dieldrin, endrin and some DDT metabolites were detected in the different types of cucumber samples (i.e., C, G and O). These results disagree with Dogheim et al. (1999, 2001, 2002) who reported undetectable concentration levels of OCP residues in cucumber, but other commodities contained some DDTs only (Dogheim et al., 1999). Recently, all the aforementioned OCPs were found in some organically-farmed vegetables (e.g., green onion, root beet, potatoes) from Egyptian farms, although at concentrations below tolerance levels (Salim, 2006). Also, the occurrence of these long persistent group of compounds in vegetables from other countries has been reported either in traditionally-farmed vegetables (Zawiyah et al., 2007) or organically-farmed ones (Zohair et al., 2006). Hydrophobic OCP uptake by different vegetable crops including cucumber, potatoes, carrots, tomatoes, leeks, cabbages, spinaches and others had been widely reported in the literature (e.g., Lichtenstein, 1959; Mattina et al., 2000; Zohair et al., 2006; Salim, 2006). In these studies, crops were grown in soils treated with the insecticides up to five and 20 years earlier. Vegetables grown in conventional or organic soils have shown to accumulate OCPs efficiently with residue levels 4- to 45-fold greater than those in soils (Gonzalez et al., 2005). In addition to plant uptake, the occurrence of OCPs may refer to atmospheric deposition of these volatile and semi-volatile compounds on the cultivated crops (Gonzalez et al., 2003; Trewavas, 2004).

Pesticides (e.g., methamidophos, phorate, fenthion, pirimiphos-methyl, chlorpyrifos-methyl, malathion, thiometon) were also detected in measurable concentration levels. Percent of contaminated samples differed among the three cucumber types. For example, contamination with HCB accounted to 8.3% in C cucumber and reached 41.7% in each of G and O cucumber (Table 2). Compared with the MRLs established by Codex (2006a), the HCB-violated samples accounted to 41.7% and 38.9% of G and O, corresponding to 8.3% of C cucumber samples. This may indicate illegal use of this compound. The highest contamination frequencies occurred with the OP pesticide methamidophos recording 66.7%, 41.7% and 50.0%, of the samples analyzed from C, G and O cucumber, respectively, but at levels below the MRLs (Table 2). Such finding coincides with the results of Dogheim et al. (2004) who reported that the most analyzed samples of vegetables and fruits contained methamidophos, although at levels below the MRLs. They referred methamidophos contamination to spray drifts from neighboring crops such as cotton. Also, in Brazilian monitoring programs in selected vegetables and fruits, methamidophos was ranked the second after chlorpyrifos among the most ten frequently detected pesticides (Caldas et al., 2006). Concentration levels of profenofos found in O cucumber samples in the present study (0.095 mg kg^{-1}) were much higher than those previously reported by Abbassy (2001) in cucumber (0.017 mg kg^{-1}). Contamination with lindane accounted to 33.3%, 50.0% and 25.0% with no violation in the three types of cucumber. Conventional cucumber samples (C) showed undetectable levels of phorate, while 25.0% of either G or O cucumber samples showed contamination levels which exceeded the MRL (0.30 mg kg^{-1}) in 13.9% and 2.8% of the analyzed samples, respectively (Table 2).

In Dogheim et al. (2002), cucumber fruits were found to contain a number of pesticides including chlorpyrifos at a mean concentration of 0.06 mg kg^{-1}, while chlorpyrifos-methyl was not detectable. In recent years, application of chlorpyrifos-methyl (Reldan®) replaced chlorpyrifos (Dursban®) on vegetable crops owing to its lower acute toxicity. This may interpret occurrence of chlorpyrifos-methyl in many of the analyzed samples in the present study (Table 1). Supporting our findings in this respect, the occurrence of this insecticide was found to be common in most leafy vegetables and aromatic plants analyzed by Dogheim et al. (2004). On the other hand, pirimiphos-methyl was reported in cucumber as a mean of 0.07 mg kg^{-1} (Dogheim et al., 2001). Concentration levels more or less than this value were obtained in the present study (Table 1).

The data presented in Table 1 were computed to estimate the seasonal variations of total pesticide residues in cucumber fruits produced under different farming systems as shown in Table 3. In C and G cucumber, the samples of fall season (September–November) followed by those of summer (June–August) contained the highest pesticide residue levels. The lowest contamination level occurred in winter (December–February) for C, and in spring (March–May) for G cucumber samples. In descending order, the general means of total pesticide residues in different seasons for the organically-farmed cucumber were: 0.619 ppm (summer), 0.485 ppm (winter), 0.480 ppm (fall), 0.184 ppm (spring). In general, contamination of C cucumber (in most seasons) and G cucumber (in all seasons) with OCP residues was higher than those of OPP residues. In O cucumber, the opposite trend was found; where contamination levels with OPPs were higher than those of OCPs in the concerned seasons except summer (Table 3). Variation of pesticide residues in vegetables grown in different seasons is well documented. For instance, low temperature, short day length and rains in winter season were reported as factors causing decline of pesticide residues in vegetables grown in winter than those in other

Table 3
Seasonal variation of pesticide residue concentrations in cucumber fruit samples produced under different farming systems.

Type of cucumber	Season	Residues (mg kg^{-1})		
		OCPs	OPPs	∑OCPs + OPPs
Conventional	Summer	0.473	0.058	0.531
	Fall	0.561	0.116	0.677
	Winter	0.047	0.028	0.075
	Spring	0.0	0.379	0.379
Greenhouse	Summer	0.780	0.392	1.172
	Fall	1.628	0.537	2.165
	Winter	0.362	0.220	0.582
	Spring	0.146	0.0	0.146
Organic	Summer	0.357	0.262	0.619
	Fall	0.219	0.261	0.480
	Winter	0.156	0.329	0.485
	Spring	0.058	0.126	0.184

Each value is a general mean for results of 12 months; calculated from the data of Table 1.
OCPs: Organochlorine pesticides; OPPs: Organophosphorus pesticides.

Table 4
Mean heavy metals concentration (mg kg^{-1}; fresh wt) in cucumber fruit samples from conventional farming.

Metal	June 2006	July 2006	August 2006	September 2006	October 2006	November 2006	December 2006	January 2007	February 2007	March 2007	April 2007	May 2007
Zn	1.348 ± 0.637	1.947 ± 0.556	2.560 ± 0.276	1.536 ± 0.599	0.053 ± 0.002	1.270 ± 0.631	1.482 ± 0.711	1.380 ± 0.480	1.544 ± 0.752	1.072 ± 0.198	0.704 ± 0.186	1.475 ± 0.496
Cu	0.520 ± 0.167	1.514 ± 0.289	0.689 ± 0.049	0.541 ± 0.072	0.264 ± 0.063	0.294 ± 0.174	0.411 ± 0.101	0.657 ± 0.317	0.455 ± 0.259	0.266 ± 0.134	0.407 ± 0.201	0.284 ± 0.098
Mn	0.837 ± 0.257	0.326 ± 0.025	0.247 ± 0.009	0.305 ± 0.170	0.112 ± 0.002	0.230 ± 0.133	0.252 ± 0.135	0.382 ± 0.271	0.304 ± 0.129	0.110 ± 0.032	0.380 ± 0.177	0.289 ± 0.134
Fe	4.011 ± 0.807	4.683 ± 0.931	2.192 ± 0.482	2.017 ± 0.545	0.100 ± 0.019	3.067 ± 1.053	2.041 ± 0.625	1.950 ± 0.516	1.833 ± 0.236	1.767 ± 0.552	6.607 ± 4.384	7.811 ± 2.321
Cd	0.099* ± 0.001	0.028 ± 0.016	0.040 ± 0.010	0.054* ± 0.035	0.051* ± 0.008	0.018 ± 0.015	0.027 ± 0.002	0.039 ± 0.036	0.076* ± 0.021	0.384* ± 0.641	nd	0.043 ± 0.009
Cr	nd	0.044 ± 0.043	0.024 ± 0.034	2.086 ± 0.533	nd	1.049 ± 0.911	1.680 ± 0.685	0.004 ± 0.002	0.154 ± 0.017	0.003 ± 0.001	0.155 ± 0.010	nd
Pb	0.135* ± 0.016	0.364* ± 0.088	0.649* ± 0.034	0.112* ± 0.011	0.090 ± 0.012	0.261* ± 0.166	0.096 ± 0.022	0.124* ± 0.116	0.283* ± 0.115	0.293* ± 0.092	0.295* ± 0.097	0.445* ± 0.502
Ni	0.021 ± 0.003	0.036 ± 0.063	0.108 ± 0.009	nd	nd	nd	nd	nd	nd	0.096 ± 0.020	0.096 ± 0.009	nd
Co	0.040 ± 0.008	0.026 ± 0.011	0.028 ± 0.006	0.051 ± 0.039	nd	0.007 ± 0.004	0.039 ± 0.024	0.002 ± 0.001	0.033 ± 0.009	0.039 ± 0.019	nd	0.023 ± 0.021
Total	7.011	8.968	6.537	6.702	0.670	6.196	6.028	4.538	4.682	4.030	8.644	10.370

Each value is a mean ± SD for the results of monthly collected samples from three different locations.
n = 36 samples for each element/year. nd = not detected.
Values are compared with the MLs established by Codex (2006b) for Cd (0.05 mg kg^{-1}) and Pb (0.10 mg kg^{-1}) in fruiting vegetables and cucurbits; Codex (1998) for Cu (10.0 mg kg^{-1}) in fruits and vegetables; and EOS (1993) for Fe (15.0 mg kg^{-1}) and Zn (5.0 mg kg^{-1}) in bulb and juice of vegetables and fruits. MLs for the other measured metals (e.g., Mn, Cr, Ni and Co) are not available. Values in the table designated by asterisks exceed the MLs for the respective metal.

Table 5
Mean heavy metals concentration (mg kg^{-1}; fresh wt) in cucumber fruit samples from greenhouse farming.

Metal	June 2006	July 2006	August 2006	September 2006	October 2006	November 2006	December 2006	January 2007	February 2007	March 2007	April 2007	May 2007
Zn	0.442 ± 0.067	1.859 ± 0.488	2.813 ± 0.854	1.042 ± 0.181	0.073 ± 0.023	1.125 ± 0.117	1.014 ± 0.174	1.739 ± 0.502	0.853 ± 0.119	3.614 ± 0.752	1.362 ± 0.090	0.915 ± 0.120
Cu	0.257 ± 0.007	0.778 ± 0.083	0.742 ± 0.234	0.271 ± 0.041	0.297 ± 0.191	0.190 ± 0.043	0.230 ± 0.024	0.569 ± 0.094	0.182 ± 0.058	0.437 ± 0.262	0.453 ± 0.123	0.507 ± 0.062
Mn	0.310 ± 0.048	0.326 ± 0.068	0.483 ± 0.291	0.265 ± 0.171	0.200 ± 0.094	0.194 ± 0.022	0.266 ± 0.062	0.234 ± 0.072	0.319 ± 0.005	0.454 ± 0.262	0.383 ± 0.047	0.300 ±0.077
Fe	2.987 ± 0.384	1.763 ± 0.152	1.958 ± 0.719	3.388 ± 0.286	0.113 ± 0.004	2.546 ± 0.279	3.162 ± 0.330	3.154 ± 0.763	2.929 ± 0.364	3.004 ± 1.008	0.364 ± 0.054	0.096 ± 0.014
Cd	0.030 ± 0.003	0.046 ± 0.029	0.056* ± 0.022	0.036 ± 0.006	0.026 ± 0.006	0.026 ± 0.013	0.025 ± 0.004	0.011 ± 0.002	0.029 ± 0.007	0.016 ± 0.005	0.048 ± 0.004	0.040 ± 0.003
Cr	0.727 ± 0.067	0.060 ± 0.056	0.068 ± 0.030	1.324 ± 0.911	0.014 ± 0.006	0.479 ± 0.113	1.054 ± 0.425	nd	0.565 ± 0.099	0.004 ± 0.001	nd	nd
Pb	nd	0.327* ± 0.140	0.287* ± 0.112	0.602* ± 0.275	0.072 ± 0.036	0.336* ± 0.182	0.592* ± 0.252	0.080 ± 0.007	0.268* ± 0.099	0.298* ± 0.090	0.153* ± 0.009	0.325* ± 0.046
Ni	0.031 ± 0.004	0.015 ± 0.026	nd	0.028 ± 0.010	nd	0.045 ± 0.007	0.019 ± 0.005	nd	nd	0.111 ± 0.020	nd	0.021 ± 0.007
Co	0.028 ± 0.013	0.030 ± 0.014	0.055 ± 0.057	0.033 ± 0.006	nd	0.048 ± 0.040	0.032 ± 0.006	0.028 ± 0.005	0.029 ± 0.002	0.055 ± 0.060	nd	0.023 ± 0.008
Total	4.812	5.204	6.462	6.988	0.795	4.989	6.394	5.815	5.174	7.993	2.763	2.227

Each value is a mean ± SD for the results of monthly collected samples from three different locations.
n = 36 samples for each element/year. nd = not detected.
Values are compared with the MLs established by Codex (2006b) for Cd (0.05 mg kg^{-1}) and Pb (0.10 mg kg^{-1}) in fruiting vegetables and cucurbits; Codex (1998) for Cu (10.0 mg kg^{-1}) in fruits and vegetables; and EOS (1993) for Fe (15.0 mg kg^{-1}) and Zn (5.0 mg kg^{-1}) in bulb and juice of vegetables and fruits. MLs for the other measured metals (e.g., Mn, Cr, Ni and Co) are not available. Values in the table designated by asterisks exceed the MLs for the respective metal.

Table 6
Mean heavy metals concentration (mg kg^{-1}; fresh wt) in cucumber fruit samples from organic farming.

Metal	June 2006	July 2006	August 2006	September 2006	October 2006	November 2006	December 2006	January 2007	February 2007	March 2007	April 2007	May 2007
Zn	0.476 ± 0.066	2.562 ± 0.136	1.818 ± 0.981	1.026 ± 0.214	0.185 ± 0.052	0.946 ± 0.041	1.029 ± 0.183	1.028 ± 0.157	1.102 ± 0.117	1.850 ± 0.366	4.077 ± 0.680	1.568 ± 0.455
Cu	0.241 ± 0.034	0.718 ± 0.102	0.545 ± 0.250	0.303 ± 0.094	0.362 ± 0.094	0.225 ± 0.044	0.155 ± 0.005	0.292 ± 0.135	0.222 ± 0.012	0.363 ± 0.047	0.372 ± 0.035	0.294 ± 0.106
Mn	2.150 ± 0.062	0.281 ± 0.051	0.538 ± 0.156	0.411 ± 0.043	0.205 ± 0.038	0.118 ± 0.048	0.356 ± 0.045	0.251 ± 0.105	0.126 ± 0.009	0.167 ± 0.097	0.839 ± 0.074	0.322 ± 0.068
Fe	1.650 ± 0.333	1.746 ± 0.300	2.260 ± 0.344	3.778 ± 0.751	0.081 ± 0.019	2.032 ± 0.521	3.534 ± 0.946	1.662 ± 0.855	1.895 ± 0.331	3.458 ± 0.511	0.846 ± 0.047	4.002 ± 0.506
Cd	0.028 ± 0.003	0.061* ± 0.037	0.095* ± 0.082	0.062* ± 0.044	0.075* ± 0.001	0.018 ± 0.005	0.030 ± 0.007	0.031 ± 0.020	0.034 ± 0.003	0.018 ± 0.007	0.101* ± 0.003	0.021 ± 0.010
Cr	0.514 ± 0.017	0.001 ± 0.002	0.050 ± 0.010	1.848 ± 0.276	0.057 ± 0.006	nd	1.750 ± 0.319	0.004* ± 0.001	nd	0.012* ± 0.014	0.153 ± 0.004	0.379* ± 0.008
Pb	0.014 ± 0.003	0.330* ± 0.115	0.364* ± 0.068	0.342* ± 0.043	0.062 ± 0.029	0.616* ± 0.522	0.309* ± 0.047	0.136* ± 0.011	0.887* ± 0.174	0.281* ± 0.083	nd	0.161* ± 0.020
Ni	0.025 ± 0.004	0.084 ± 0.021	nd	nd	nd	nd	nd	0.071 ± 0.029	0.029 ± 0.006	0.168 ± 0.018	nd	nd
Co	0.022 ± 0.003	0.068 ± 0.027	0.013 ± 0.001	0.035 ± 0.014	nd	0.239 ± 0.068	0.022 ± 0.014	0.040 ± 0.009	0.028 ± 0.008	0.056 ± 0.024	nd	0.024 ± 0.010
Total	5.120	5.851	5.683	7.769	1.027	4.194	7.185	3.515	4.323	6.373	6.388	6.771

Each value is a mean ± SD for the results of monthly collected samples from three different locations. n = 36 samples for each element/year. nd = not detected.
Values are compared with the MLs established by Codex (2006b) for Cd (0.05 mg kg^{-1}) and Pb (0.10 mg kg^{-1}) in fruiting vegetables and cucurbits; Codex (1998) for Cu (10.0 mg kg^{-1}) in fruits and vegetables; and EOS (1993) for Fe (15.0 mg kg^{-1}) and Zn (5.0 mg kg^{-1}) in bulb and juice of vegetables and fruits. MLs for the other measured metals (e.g., Mn, Cr, Ni and Co) are not available. Values in the table designated by asterisks exceed the MLs for the respective metal.

seasons (Bhanti and Taneja, 2005, 2007). The prevalence of pests and diseases in different seasons and subsequent demand of their control may reflect on contamination levels of pesticides in the sprayed crops.

Regarding contamination of cucumber fruits by heavy metals, the data demonstrating mean concentration levels of nine heavy metals in the different types of cucumber samples are presented in Tables 4–7. The values for the monthly collected samples are recorded and compared with the maximum levels (MLs) established by Codex (1998, 2006b) and the Egyptian Organization for Standardization and Quality Control (EOS, 1993). Lead (Pb) and cadmium (Cd) were the only metals showing concentration levels exceeding the permissible MLs (0.10 and 0.05 mg kg^{-1}, respectively; Codex, 2006b) in some samples of the three types of cucumber. Among the mean values of 12 months, 10 ones entitled to C cucumber contained Pb at levels higher than its ML, and the highest value (0.649 mg kg^{-1}) was found in samples of August (Table 4). In the same cucumber type, Cd was violated in samples belongs to 5 months, and the highest value (0.384 mg kg^{-1}) was reached in samples of March. Over a complete year, concentration levels of Cu, for example, in C cucumber, ranged between 0.053 mg kg^{-1} in October and 2.650 mg kg^{-1} in August. Some monthly collected samples contained undetectable concentrations of Ni, Co and Cr (Table 4). As total heavy metal concentration in C cucumber, samples of May recorded the highest contamination level (10.370 mg kg^{-1}), while that of October recorded the lowest level (0.670 mg kg^{-1}).

By a similar manner, occurrence of heavy metals in the other two types of cucumber (G and O) could be demonstrated in light of the results shown in Tables 5 and 6. Pb and Cd were respectively violated in 9 and 1 of the monthly 12 samples of G cucumber, and the samples of June contained undetectable Pb concentration levels. The total contamination level ranged between 0.795 mg kg^{-1} in October and 7.993 mg kg^{-1} in March (Table 5). For O cucumber (Table 6), undetectable Pb level was recorded for the samples of April, but samples belongs to 9 months contained levels of Pb exceeding the MLs. On the other hand, Cd was violated in five monthly samples and reached 0.101 mg kg^{-1} in the April samples. The total contamination level ranged between 1.027 mg kg^{-1} in October and 7.769 mg kg^{-1} in September (Table 6).

The pattern of contamination of cucumber by heavy metals in different seasons could be demonstrated in terms of general means of total metal contents in each season, and also the percentage of each metal in these total metal contents as shown in Table 7. The order of heavy metals contamination by seasons in C cucumber (Table 7) was: summer (7.705 mg kg^{-1}) > spring (7.681 mg kg^{-1}) > winter (5.083 mg kg^{-1}) > fall (4.523 mg kg^{-1}). Pb constituted 4.97%, 4.48%, 3.30% and 3.41% in the total contamination levels of the above mentioned seasons, respectively. Cd constituted 1.85% of the total metals concentration estimated for spring samples. Samples of the fall season contained the highest percentage of Cr (23.1%), while those of summer contained the lowest value (0.29%; Table 7).

In a similar manner, the pattern of heavy metal contamination in the other two types of cucumber could be elucidated. Samples of G cucumber (Table 7) belongs to winter season contained the highest levels of heavy metals (5.794 mg kg^{-1}) while those of fall season showed the lowest value (4.257 mg kg^{-1}). However, Pb constituted 5.41% of the total metals found in winter corresponding to 7.91% in fall season. Cd, Mn and Cr, as %, showed similar trends (Table 7).

In case of O cucumber (Table 7), the metal contamination by different seasons showed the following order: spring (6.511 mg kg^{-1}) > summer (5.551 mg kg^{-1}) > winter (5.008 mg kg^{-1}) > fall (4.330 mg kg^{-1}). Samples of winter constituted the highest percentage of Pb (8.87%) and the lowest percentage of Cd (0.63%). The

Table 7
Seasonal variation of heavy metal concentrations in cucumber fruit samples produced under different farming systems.

Element	Summer		Fall		Winter		Spring	
	mg kg^{-1}	%[b]	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%
Conventional								
Zn	1.952	25.33	0.953	21.07	1.496	28.90	1.048	14.11
Cu	0.908	11.78	0.366	8.10	0.805	9.99	0.319	4.15
Mn	0.470	6.10	0.216	4.77	0.313	6.15	0.260	3.38
Fe	3.629	47.09	1.728	38.21	1.941	38.19	5.395	70.24
Cd	0.056	0.72	0.041	0.91	0.047	0.93	0.142	1.85
Cr	0.023	0.29	1.045	23.10	0.613	12.05	0.053	0.69
Pb	0.383	4.97	0.154	3.41	0.168	3.30	0.344	4.48
Others[a]	0.340	3.72	0.020	0.43	0.024	0.49	0.084	1.10
Total	7.705	100.00	4.523	100.00	5.083	100.00	7.681	100.00
Greenhouse								
Zn	1.705	31.03	0.746	17.53	1.202	20.75	1.964	45.37
Cu	0.592	10.78	0.253	5.94	0.327	5.64	0.466	10.76
Mn	0.373	6.79	0.220	5.16	0.273	4.71	0.379	8.76
Fe	2.236	40.71	2.016	47.35	3.082	53.19	1.155	26.68
Cd	0.044	0.80	0.029	0.69	0.022	0.37	0.035	0.80
Cr	0.285	5.19	0.606	14.23	0.540	9.31	0.001	0.02
Pb	0.205	3.73	0.337	7.91	0.313	5.41	0.259	5.98
Others[a]	0.053	0.97	0.050	1.19	0.035	0.62	0.069	1.63
Total	5.493	100.00	4.257	100.00	5.794	100.00	4.328	100.00
Organic								
Zn	1.619	29.16	0.719	16.61	1.053	21.03	2.498	38.37
Cu	0.501	9.03	0.297	6.85	0.223	4.45	0.343	5.27
Mn	0.990	17.83	0.245	5.65	0.244	4.88	0.443	6.80
Fe	1.885	34.00	1.964	45.35	2.364	47.20	2.769	42.52
Cd	0.061	1.10	0.052	1.19	0.032	0.63	0.047	0.72
Cr	0.188	3.39	0.635	14.67	0.585	11.67	0.181	2.78
Pb	0.236	4.25	0.340	7.85	0.444	8.87	0.147	2.26
Others[a]	0.071	1.23	0.078	1.83	0.063	1.27	0.083	1.28
Total	5.551	100.00	4.330	100.00	5.008	100.00	6.511	100.00

The data refer to Tables. 4–6.
[a] Others mean Ni and Co.
[b] % of each metal concentration in the total concentration of all metals.

highest percentage value for Zn (38.37%) was found in spring samples and that for Cr (14.67%) in the samples of fall season.

It has been long recognized that heavy metals are among the major contaminants of food supply and may be considered as the most important problem to our environment (Zaidi et al., 2005). Heavy metal contamination may be occurred due to irrigation with contaminated water, the addition of fertilizers and metal-based pesticides, industrial emissions, transportation, harvesting process, storage and/or sale. It is well known that plants take up metals by absorbing them from contaminated soils as well as from deposits on parts of the plants exposed to the air from polluted environments (Sharma et al., 2008).

In agreement with the findings of the present study, many investigators (e.g., Soliman et al., 1997; Dogheim et al., 2004;), have reported occurrence of Pb in different kinds of vegetables at concentration levels exceeding its MLs. The same was also reported for some Egyptian organically-farmed vegetables (Salim, 2006). Other metals (e.g., Cd, Cu, Zn, Fe) were reported below their respective MLs by the above mentioned investigators. They compared Cd concentration at 0.10 mg kg^{-1} level which is higher than the MLs used in the present investigation (0.05 mg kg^{-1}; Codex, 2006b). Supporting our finding regarding violation of Cd in some of the analyzed cucumbers, the results reported by Peris et al. (2007) who found that Cd (and Pb) were higher than their tolerance limits in horticultural crops taken from some agricultural fields in Castellón, Spain, as a representative area of the European Mediterranean region. The other metals they measured (e.g., Cu, Zn, Mn, Fe, Cr, Ni, Co) were found lower than their tolerance limits, and heavy metal contents in leafy crops were generally higher than in inflorescence crops except for Zn (Peris et al., 2007).

In cucumber fruit samples collected from Alexandria (Egypt) markets, concentration levels of Pb, Cd, Cu and Zn were 0.19 (0.10–0.33), 0.15 (0.09–0.25), 5.69 (4.11–8.34) and 19.9 (16.2–26.9) mg kg^{-1} dry wt; as mean and range values, respectively (Radwan and Salama, 2006). At estimated moisture content in cucumber fruits equaled (64%), our results in Tables 4–6 could be modulated on dry weight basis. As general mean values, concentration levels of Pb, Cd, Cu and Zn in C cucumber will equal: 0.73, 0.20, 1.47 and 3.81 mg kg^{-1} dry wt, respectively. For G cucumber: 0.78, 0.09, 1.15 and 3.92 mg kg^{-1}; and for O cucumber: 0.82, 0.13, 0.96 and 4.12 mg kg^{-1} dry wt, respectively, for the concerned metals. This means that contamination levels of cucumber fruits in the present study were very higher for Pb and very lower for Cu and Zn, generally. The calculated values for Cd in the different types of cucumber (0.20, 0.09 and 0.13 mg kg^{-1} dry wt) lie within its range reported by the above mentioned authors. Differences in such cases can be referred to many factors, such as time, location and duration of sampling.

To compare between the different types of cucumber with respect to total concentration of pesticide residues and heavy metals, all the results obtained were computed to yield general means for summation of contaminants over 12 months. Contamination in greenhouse cucumber with pesticide residues recorded the highest value (1.016 mg kg^{-1}), followed by organic (0.442 mg kg^{-1}) and conventional (0.415 mg kg^{-1}) cucumbers. Also, the G cucumber contained the highest level of either OC or OP pesticide residues

(0.729 and 0.287 mg kg^{-1}, respectively). In C cucumber, OC and OP pesticide residues were 0.270 and 0.145 mg kg^{-1}, respectively, compared to 0.197 and 0.245 mg kg^{-1} in O cucumber. Heavy metal contamination in the 3 cucumber types accounted to 6.248, 5.350 and 4.968 mg kg^{-1} in C, O and G cucumbers, respectively. These results coincide with those in the literature regarding occurrence of contaminants (e.g., pesticides and heavy metals) in the organically-farmed crops (Gonzalez et al., 2003, 2005; Trewavas, 2004; Salim, 2006; Zohair et al., 2006); even though at levels below the allowed by Codex Alimentarius. The greenhouse condition may favor spread of plant pathogenic diseases and insect pests that acquire excessive use of organic pesticides, which in turn be protected from rapid degradation by direct sunlight. This may interpret the high contamination level of pesticides in this type of farming compared with that in open field conditions. In traditional farming, excessive quantities of organic fertilizers are usually used and may be considered the major source of heavy metal contamination (Dach and Starmans, 2005).

4. Conclusion

Monitoring programs of pesticide residues and heavy metals in vegetables and fruits have shown that presence of these toxicants in the majority of analyzed samples occur at concentrations below the established tolerance levels. Moreover, the commodity in question may contain several compounds of these toxicants. Several investigators (e.g., Tricker and Preussmann, 1990; Zaidi et al., 2005; Bhanti and Taneja, 2005, 2007; Peris et al., 2007; Sharma et al., 2008) have reported that residues of OCPs, OPPs and certain heavy metals in foods at levels currently regarded as safe adversely affect human health. On the other side, exposure to multi toxicants of different degrees of potency, and having either similar or dissimilar mode of action, is a toxicological complex issue (Caldas et al., 2006). Assessment of the potential health hazard of chemical mixtures is a difficult and challenging toxicological problem, and is a subject of major current concern to both the scientific and regulatory communities. In general, all the methods assume additive for the individual effects, although synergism and antagonism among the compounds cannot be ruled out (Mumtaz, 1995). Cucumber samples subjected to analyses in the present investigation showed to contain a "cocktail" of toxicants, even in the organically-farmed fruits. The latter type is sold at 3–5-fold prices of the other types of cucumber. Therefore, a cost/benefit analysis has to be taken into consideration in order to make balance between price and safety. On the other hand, safety of multi toxicants in a food commodity is better to be derived from experimental toxicological assessments; a matter which will be handled in future study. Because of the cocktail of pesticides potentially present in cucumbers grown under different conditions, we cannot state which are safer, but regardless thorough washing of all cucumbers and peeling of the skin are methods for reducing pesticide exposure.

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