Research Article

Multiresidue Analysis of 86 Pesticides Using Gas Chromatography Mass Spectrometry: II-Nonleafy Vegetables

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Received 20 June 2012; Revised 18 July 2012; Accepted 19 July 2012

Academic Editor: Michele Del Carlo

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A total of 1057 samples of fresh vegetables from import and domestic production were analyzed (cold pepper, egg plant, carrot, cucumber, potato, hot pepper, cultivation tomato, squash, beans, okra, onions, cauliflower, and green house tomato). The aim of this study was to investigate pesticide residues in market foods in Riyadh, which have been collected from Riyadh Development Company (Al-Tamer Vegetables Market). Pesticide residues were determined by gas chromatography with mass selective detector (GC-MSD). A multiresidue method was developed and described for simultaneous determination of 86 pesticides commonly used in crop protection. This method used to determine 86 pesticide residues with a broad range of physicochemical properties in fresh vegetables related to organophosphorus (OPP), organochlorines (OCP), pyrethroids, and carbamates mainly used in agriculture. Sample extract was cleaned up by using AOAC method. Pesticide residues above the maximum residue limits (MRL) were detected in 15.89% of the total samples (168 from 1057 samples), but 83.90% of the total samples (887 from 1057 samples) has no residues or contained pesticide residues at or below MRL. The detected and most frequently found pesticide residues were permethrin (45 times) and endosulfan (34 times) followed by deltamethrin (27 times). The findings of this study pointed to the following recommendations: the need for a monitoring program for pesticide residues in imported food crops.

1. Introduction

Fresh vegetables are an important part of a healthy diet as they are a significant source of vitamins and minerals. However, fresh vegetables can also be a source of noxious toxic substances—pesticides. Vegetables are traded worldwide and the list of pesticides that might have been applied in their agricultural production is usually not known [1–3].

Pesticides constitute a very important group of chemical compounds that have to be controlled due to their high toxicity and their widespread use in agricultural practice for field and postharvest protection. The presence of pesticide residues in food is a direct result of pesticide use on crops. Over 1000 compounds may be applied to agricultural crops in order to control undesirable moulds, insects, and weeds [4]. The pesticide residues causing food contamination have become increasingly frequent in recent years raising question

about their human health and economic consequences [5]. Widespread contamination of water, air, and soil by chemicals and industrial pollutants means that the crops that we grow and the animals we use for food are often exposed to toxic substances [6].

The levels of pesticide residues in foodstuffs are generally legislated so as to minimize the exposure of the consumer to harmful or unnecessary intakes of pesticides, to ensure the proper use of pesticides in terms of granted authorization and registration (application rates and preharvested intervals), and to permit the free circulation of pesticide-treated products, as long as they comply with the fixed maximum residue limits (MRLs). MRL for pesticide residues represents the maximum concentration of that residue (expressed in mg/kg) that is legally permitted in specific food items. The establishment of MRL is based on good agricultural practice

data on food derived from commodities. MRLs are not toxicological limits, but they must be toxicologically acceptable. Exceeded MRLs are strong indicators of violations of good agricultural practices [7–9].

A multiresidue method is described for determination of 86 pesticides commonly used in crop protection. Good sensitivity and selectivity of the method are obtained with limits of quantification 0.01 mg/kg in almost all cases. The method was applied very satisfactorily to routine analysis as a complement to traditional GC-MS method and finally, limit of detection was also 10–20 times lower than maximum residue levels (MRL) established by codex alimentarius commission. More than 500 samples from leafy vegetables have been collected from vegetables market (Riyadh Development Company) in Riyadh. Pesticide residues were detected in 24.69% of the total samples (140 from 567 samples) and pesticides concentration was higher than MRL in 104 samples [10].

The objective of this study was to investigate the presence of pesticide residues in nonleafy vegetables in food market in Saudi Arabia. Samples were collected from the central market located in Riyadh (Al-Tamer Vegetables Market), during two years, that is, 2007–2008. Collected data are to be used as a reference point for future monitoring and taking preventive measures to minimize human health risks.

2. Materials and Method

2.1. Reagents and Equipments. All pesticide standards were obtained from (Riedel de Haen and Supelco). We prepared 1 mg/mL stock solution of each by dissolving 20 mg of the pure analytical standard in 20 mL of acetone. A single composite standard solution was prepared by diluting with acetone according to limit of detection (LOD). All standard solutions were stored in glass-stoppered flasks at 4°C. Mixed compound calibration solutions were prepared in acetone and they were used as spiking solution. Solvents (residue analysis grade) used were acetone, acetonitrile, petroleum ether, and other reagents such as sodium chloride and anhydrous sodium sulphate; florisil 60–100 mesh for residue analysis was also purchased from (Fluka). The florisil (activated magnesium silicate used as adsorbent) and anhydrous sodium sulphate were activated at 100°C over night and stored in 500 mL glass flask with glass stoppers and stored in oven at 100°C. The equipments used included a high-speed blender with a stainless steel jar (waring, USA), a shaking separation final (GFL, Germany), a rotary evaporator, R 215 and cooler circulator chiller B-740 (Buchi, Switzerland), Buchner funnel and chromatographic tubes with Teflon stopcocks and coarse fritted glass (Agilent, USA), and syringes (Hamilton Bonadus AG, Switzerland). All glassware were rinsed thoroughly using soap and deionization water, then washed with acetone and dried in oven (100–130°C) over night

2.2. Samples Collection. This study was conducted during two years from January 2007 to December 2008. More than 500 nonleafy vegetable samples (cold pepper, egg plant, carrot, cucumber, potato, hot pepper, cultivation tomato, squash, beans, okra, onions, cauliflower, and green house tomato)

have been collected from Al-Tamer Vegetables Market in Riyadh, Saudi Arabia. Samples were put in sterile polythene bags and transported to the laboratory where they were analyzed immediately or stored at 4°C until analysis within 24 h.

2.3. Sample Preparation, Extraction, and Partitioning. The chopped samples of raw nonleafy vegetable (120 g) were placed in a stainless steel jar 1L and extracted with 200 mL of acetonitrile and 10 g celite, the blender was vigorously homogenized into high speed for 2 min, and the mixture was filtrated by using Buchner funnel fitted with shark-skin filter paper into 500 mL suction flask (Buchi, Switzerland). An aliquot of organic was transferred to 1L separator funnel and added 100 mL of petroleum ether (PE) and the mixture was vigorously shaken for 1–2 min and then was added 100 ml saturated solution of NaCl and 600 water. The mixture was vigorously mixed and the separator funnel was allowed to be held at horizontal position for few minutes. The aqueous layer was discarded and the solvent layer was washed with twice time 100 mL portions of distilled water and the washed layer was transferred into 100 mL beaker and washed with 15 g of anhydrous sodium sulphate. Finally, the extract was concentrated to 5 mL volume and transferred directly to florisil column ($n = 3$).

2.4. Minimum Detection Limit (MDL). To determine the maximum residue limits (MRL), retention time (Rt), limit of quantification (LOQ), ion target, qualifier ions m/z by scan mode, and perform the GC-MS quantification (Table 1) by using a four-point calibration curve plotting peak area versus mg l^{-1} concentration of 86 pesticides using the dilution levels ranged from 0.0001 to 5.00 mg l^{-1} .

2.5. Florisil Column Cleanup. Florisil column cleanup was conducted according to the AOAC [11]. The column was peppered containing about 12 cm activated florisil topped with 1 cm anhydrous sodium sulphate, and column was washed by 40 mL petroleum ether (PE) and was added extract concentrated to 5 mL and was allowed to pass through the column. The walls of the tube were rinsed additional small portions of petroleum ether and elute at 5 mL/min with 200 mL 6% eluting solvent (diethyl ether in petroleum ether) (PE), and then 200 mL 15% and finally 200 ml 50% eluting solvent (diethyl ether in PE) at 5 mL/min.

2.6. Chromatographic Instrumentation and Quantification. Gas chromatograph-mass spectrometer (Agilent model 6890N) gas chromatograph coupled with (model 5975B) quadrupole mass spectrometer with a GC column HP-5MS 5% phenyl and 95% methyl siloxane, 30 m $\times$ 0.25 mm id $\times$ 0.25 μm film thickness. GC operating conditions: splitless injection, injector temperature 250°C, helium carrier gas (99.9999 purity) at flow rate 0.9 mL/min with column head pressure 7.4 psi, oven temperature from 70°C (2 min hold), then raised to 130°C at the rate (25°C/min) afterwards raised to 220°C at (2°C/min) and then raised to 280°C at (10°C/min) and eventually (4.6 min hold). The sample (1 μL) was injected in split less modes. The MS system was

TABLE 1: Parameter of retention time, LOQ, target, and qualifier ions m/z by scan mode.

Number	Compounds	Retention time min	LOQ	Target ion m/z	Qualifier ions m/z	
					Q_1	Q_2
1	Dichlorvos	7.211	0.02	109	185	79
2	Propamocarb	9.849	0.04	58	71	129
3	Mevinphos	10.828	0.09	127	192	109
4	Chloroneb	13.015	0.01	191	193	206
5	Methomyl	14.837	0.10	105	88	57
6	Propachlor	16.350	0.02	120	77	176
7	Propoxur	16.440	0.03	110	152	81
8	Ethoprophos	17.183	0.05	157	97	139
9	Bendiocarb	18.808	0.01	151	126	166
10	Sulfotep	19.350	0.01	322	202	97
11	Alfa-BHC	19.449	0.02	183	181	219
12	Hexachlorobenzene	19.949	0.05	284	249	142
13	Dichloran	20.412	0.03	176	206	124
14	Dimethoate	20.694	0.02	87	93	125
15	Simazine	21.240	0.01	201	186	173.2
16	Carbofuran	21.517	0.01	164	149	123
17	Lindane	21.953	0.01	219	181	111
18	Fonofos	22.837	0.06	109	137	246
19	Delta-BHC	23.934	0.05	181	219	111
20	Diazinon	24.181	0.03	179	137	152
21	Iprobenfos	25.472	0.04	91	204	122
22	Pirimicarb	26.194	0.05	166	72	238
23	Dichlofenthion	26.869	0.01	279	223	162
24	Phosphamidon I	27.074	0.03	127	72	264
25	Phosphamidon II	27.105	0.05	127	72	264
26	Chlorpyrifos-Me	27.530	0.03	286	125	288
27	Vinclozolin	27.643	0.02	212	285	187
28	Carbaryl	27.846	0.03	144	115	116
29	Alachlor	28.292	0.04	160	188	146
30	Ronnal	28.738	0.02	285	287	125
31	Metalaxyl	28.894	0.05	206	146	192.2
32	Fenitrothion	30.004	0.07	277	125	109
33	Linuron	30.118	0.04	61	187	124
34	Aldrin	30.417	0.02	66	263	91
35	Thiobencarb	30.794	0.08	100	72	125
36	Malathion	31.310	0.03	127	173	99
37	Fenthion	31.679	0.03	278	125	109
38	Pirimiphos-ethyl	34.279	0.05	318	333	304
39	Captan	34.791	0.06	79	151	114
40	Chlorfenvinphos	35.549	0.02	267	323	269
41	Chlordane-trans	35.990	0.04	373	375	237
42	Alfa-endosulfan	36.919	0.09	239	237	195
43	Nanchlor-trans	37.168	0.01	409	100	237
44	Chlordane-cis	37.311	0.05	375	373	377
45	Disulfoton sulfone	37.670	0.03	213	153	97
46	Dieldrin	39.172	0.02	79	265	81
47	P,P-DDE	39.688	0.01	246	318	248
48	O,P-DDD	40.321	0.01	235	237	165
49	Endrin	40.920	0.02	263	265	281
50	Beta-endosulfan	41.820	0.03	207	239	195

TABLE 1: Continued.

Number	Compounds	Retention time min	LOQ	Target ion m/z	Qualifier ions m/z	
					Q_1	Q_2
51	Chlorobenzilate	42.683	0.04	251	139	253
52	P,P-DDD	43.234	0.01	235	237	165
53	Benodanil	43.773	0.03	231	323	203
54	Ethion	44.131	0.01	231	97	153
55	Carbophenothion	45.558	0.04	157	121	125
56	Resmethrin I	48.965	0.03	123	171	143
57	Resmethrin II	49.532	0.03	123	171	143
58	Hexabromobenzene	49.772	0.04	551	554	549
59	Phosmet	50.300	0.03	160	161	77
60	EPN	50.726	0.04	157	169	185
61	Dicofol	50.955	0.02	139	111	251
62	Fenoxycarb	51.040	0.07	255	186	116
63	Tetramethrin II	51.322	0.02	164	123	81
64	Tetradifon	52.029	0.05	159	111	229
65	Mirex	52.460	0.01	272	274	270
66	Furathiocarb	52.620	0.04	163	57	164
67	Amitraz	53.373	0.03	132	121	147
68	Lambda-cyhalothrin	53.770	0.05	181	197	208
69	Azenophos-ethyl	53.882	0.03	132	160	77
70	Allethrin I	54.515	0.04	123	181	81
71	Allethrin II	54.523	0.04	123	181	81
72	Allethrin III	54.590	0.04	123	181	81
73	Permethrin I	54.891	0.02	183	163	165
74	Permethrin II	55.111	0.02	183	163	165
75	Coumaphos	55.165	0.02	263	226	109
76	Cyfluthrin III	55.855	0.05	163	165	226
77	Cyfluthrin I	55.997	0.04	163	165	226
78	Cyfluthrin IV	56.103	0.04	163	165	226
79	Cyfluthrin II	56.162	0.04	163	165	226
80	Cypermethrin II	56.284	0.03	163	165	181
81	Cypermethrin IV	56.424	0.03	163	165	181
82	Cypermethrin I	56.522	0.03	163	165	181
83	Cypermethrin III	56.575	0.03	163	165	181
84	Fenvalerate I	57.454	0.05	125	167	281
85	Fenvalerate II	57.716	0.03	125	167	281
86	Deltamethrin	58.440	0.02	253	181	281

routinely set in selective ion monitoring (SIM) mode and each compound was quantitated based on peak area using one target and one or two qualifier ion. Mass spectrometer parameter was set as follows: electron impact ionization mode with 70 eV electron energy and scan mass range 100–400 at 0.62 sec/cycle. Ion source temperature 230°C, MS quad temperature 150°C, EM voltage 1450, and solvent delay 4 in.

3. Results and Discussion

A multiresidue procedure was carried out to monitor the pesticide residues in a wide range of the most common consumed non leafy vegetables samples collected during two years, that is, 2007-2008. The analyzed samples composed of thirteen species of non leafy vegetables, that is, hot pepper, bell pepper, onions, potato, cucumber, okra, bean, carrot, cultivation tomato, green house tomato, squash, egg plant,

and cauliflower. A wide range of pesticide residues were detected and quantified in the analyzed samples during the two years of this study. In 2007, it was detected the residues of 31 pesticides while in 2008 it was detected the residues of 28 pesticides.

3.1. Pesticide Residues in Nonleafy Vegetables during the Year of 2007. Data in Table (2) shows the amounts of the detected pesticide residues in non leafy vegetable samples from different farms and locations collected from Al-tamer vegetables market in Riyadh, Saudi Arabia during the year of 2007. According to the detected pesticides, it is clear that there are a wide range of compounds which included insecticides (31 compounds), herbicides (four compounds, that is, linuron, simazine, alachlor, and aldrin), and fungicides (one compound, that is, tetradifon). The detected insecticide residues which represent the majority of the detected compounds, it was found that such insecticides could be classified chemically into their major four chemical groups, that is, organochlorines, organophosphorus, pyrethroids, and carbamates. The detected organochlorines substances were six insecticides, that is, chloroneb, lindane, endosulfan, dicloran, mirex, and P,P-DDD while the organophosphorus insecticides included nine agents, that is, chlorpyrifos, dimethoate, malathion, mevinphos, disulfoton, phosmet, ethoprophos, diazinon and iprobenfos. As for pyrethroids, it was detected of seven compounds included permethrin, deltamethrin, cypermethrin, λ -cyhalothrin, cyfluthrin, fenvalerate, and resmethrin. For carbamates, only three compounds were detected, that is, carbaryl, bendiocarb, and thiobencarb. The mentioned pesticides were detected in thirteen non leafy vegetables, included hot pepper, cold pepper, onions, potato, cucumber, okra, bean, carrot, and cultivation tomato, green house tomato, squash, egg plant, cauliflower.

According to the detected pesticides in and/or on the non leafy vegetables (Table 2) involved in this study, it was observed that total numbers of the detected compounds were found in cold pepper followed by cucumber, hot pepper, potato, okra, bean, carrot, squash, egg plant, cultivation tomato, green house tomato, onions, and cauliflower. The total number of the detected compounds in such leafy vegetables in this study was 10, 9, 8, 8, 8, 8, 7, 7, 5, 4, 3, and 1 compound, respectively.

The data tabulated in Table 2 also showed the detected amounts of pesticide residues in non leafy vegetables could be ranked in descending order as follows: cold pepper, egg plant, carrot, cucumber, potato, hot pepper, cultivation tomato, squash, bean, okra, onions, cauliflower, and green house tomato which represent the lower non leafy vegetable contained pesticide residues. In terms of figures, the sum of the detected pesticide residues in such non leafy vegetables were 1.507, 0.457, 0.302, 0.296, 0.293, 0.264, 0.239, 0.186, 0.163, 0.089, 0.0654, 0.062, and 0.05 ppm, respectively. From such ranking, it was observed that cold pepper, egg plant, and carrot were the most contaminated non leafy vegetables.

The frequency of the detected pesticide residues was calculated in the analyzed non leafy vegetables, it was found that the most frequent compounds was permethrin followed by deltamethrin and linden, endosulfan, chlordane, linuron,

dimethoate, phosmet, and carbaryl. In terms of figures, the frequencies for these pesticides were 11, 8, 6, 5, 5, 5, 4, and 4, respectively. The other detected compounds were frequented from three to one time. From the presented results it could conclude that cold pepper, egg plant, and carrot were the most contaminated non leafy vegetables, and the pyrethroids are the most frequented pesticides during the year of 2007.

3.2. Pesticide Residues in Leafy Vegetables during 2008. In the agriculture season of 2008, data represented the detected amounts of pesticide residues in non leafy vegetables collected during the season of 2008 are listed in Table 3. According to the detected amounts and/or compounds, it was observed that the pattern of the detected pesticide residues in the collected non leafy vegetable samples were slightly differed from those presented in 2007 season. For example, in 2008 season, it was found the chloroneb, lindane, endosulfan, dicloran, and P,P-DDD as organochlorine compound, diazinon, phosphamidon, sulfotep, dimethoate, and mevinphos as organophosphorus, cypermethrin, deltamethrin, cyfluthrin, permethrin, resmethrin, tetramethrin, lambda cyhalothrin, and fenvalerate as pyrethroids. Also, it was detected propoxur, carbofuran, propamocarb, and bendiocarb as carbamates insecticides. As for fungicides, it found benomyl, tetradifon, and chlorobenzilate. As for the detected amounts, it is clear that cypermethrin represented the highest amounts of the detected residues which ranged between 0.086 and 0.762 ppm while the other detected concentrations were ranged between 0.077 and 0.0003 ppm. Overall, the pesticide residues which were found in this study were approximately similar to other studies [12–14].

In addition, based on the number of detected residues, in non leafy samples, could be ranked in descending order as follow cucumber, cold pepper, potato, onions, okra, green house tomato, egg plant, bean, squash, hot pepper, cultivation tomato, cauliflower, and carrot. The detected number of compound residues was 12.0, 9.0, 9.0, 8.0, 7.0, 7.0, 7.0, 6.0, 6.0, 5.0, 4.0, 4.0, and 3.0, respectively. As for the detected amounts of the mentioned pesticides, the ranking of non leafy samples becomes different to be egg plant is the most contaminated leafy samples followed by green house tomato < cold pepper < okra < cucumber < onions < cauliflower < carrot < potato < bean < squash < hot pepper < cultivation tomato. In terms of figures, the total detected amounts are 1.041, 0.849, 0.833, 0.694, 0.485, 0.344, 0.308, 0.298, 0.298, 0.216, 0.193, 0.183, and 0.057 ppm, for the mentioned leafy samples, respectively. In case of the frequencies of pesticide residues between the collected vegetables samples, it was observed that cypermethrin was the most frequented compound followed by endosulfan followed by dicloran and chlorobenzilate in which their frequencies were 7.0, 6.0, 5.0, and 5.0, respectively. The other detected compounds were frequented from four to one time. However, the presented data of 2008 season clearly shows that egg plant samples were the most contaminated non leafy vegetables followed by cold pepper, okra, and cucumber while hot pepper and cultivation tomato were the lowest contaminated vegetable samples. Data was mentioned previously partially in agreement with [15, 16].

Pesticide	Hot pepper	Cold pepper	Onions	Potato	Cucumber	Okra	Bean	Carrot	Tomato out	Tomato in	Squash	Egg plant	Cauliflower	Freq.
Chloroneb														3.00
Lindane	0.009					0.002	0.006	0.039		0.03		0.006		6.00
Endosulfan	0.119	0.063	0.041	0.004		0.046					0.002			5.00
Dicloran		0.006												1.00
Mirex		0.007												1.00
Chlordane	0.002	0.012			0.017		0.005					0.014		5.00
PP-DDD					0.003	0.001								2.00
Chlorpyrifos							0.002				0.003			2.00
Diazinon	0.039	0.142												2.00
Dimethoate	0.007	0.013		0.034	0.012									4.00
Phosmet	0.022													1.00
Mevinphos						0.008		0.0012						2.00
Malathion							0.0029							1.00
Disulfoton														1.00
Iprobenfos	0.006				0.017						0.002	0.011		3.00
Ethoprophos									0.005					1.00
Deltamethrin		0.025		0.01	0.165		0.036				0.153	0.228	0.062	8.00
Cyfluthrin	0.06	1.022								0.0014				2.00
Permethrin		0.086	0.0014	0.129	0.059	0.102	0.106	0.174	0.212	0.008	0.022	0.0623		11.00
Resmethrin					0.012				0.007	0.01				3.00
Cypermethrin								0.058						1.00
Lambda-cyhalothrin						0.001								1.00
Fenvalerate		0.131	0.023	0.087								0.036		3.00
Carbaryl								0.0012	0.009		0.0022	0.1		4.00
Bendiocarb								0.005						1.00
Thiobencarb							0.001							1.00
Endrin						0.025								1.00
Linuron				0.009	0.004	0.006	0.004	0.003						5.00
Simazine				0.007										1.00
Alachlor				0.013							0.002			2.00
Aldrin								0.021						1.00
Number DC	8.00	10.00	3.00	8.00	9.00	8.00	8.00	8.00	5.00	4.00	7.00	7.00	1.00	
Total detected	0.264	1.507	0.0654	0.293	0.296	0.089	0.163	0.302	0.239	0.05	0.186	0.457	0.062	

TABLE 3: Detected pesticide residues in nonleafy vegetable samples collected from Al-Tamer Vegetables Market in the year of 2008.

Pesticide	Hot Pepper	Cold Pepper	Onions	Potato	Cucumber	Okra	Bean	Carrot	Tomato out	Tomato in	Squash	Egg Plant	Cauliflower	Freq.
Chloroneb			0.004			0.018								2.00
Lindane			0.0085			0.002								2.00
Endosulfan	0.018				0.117	0.076				0.0395		0.158	0.088	6.00
Dicloran	0.0265	0.087	0.104		0.003			0.041						5.00
P,P-DDD		0.038		0.027										2.00
Diazinon					0.033	0.1								2.00
Phosphamidon					0.004									1.00
Sulfotep						0.07								1.00
Dimethoate										0.012	0.015	0.051	0.01	4.00
Mevinphos														1.00
Malathion					0.054									1.00
Deltamethrin	0.015	0.031	0.047	0.077		0.005								4.00
Cyfluthrin	0.11	0.105	0.116									0.574		4.00
Permethrin		0.095	0.005		0.085							0.057		4.00
Resmethrin				0.15		0.25			0.011	0.004				4.00
Tetramethrin					0.001									1.00
Cypermethrin		0.466			0.138	0.278	0.086			0.762		0.178	0.206	7.00
Lambda-cyhalothrin				0.0003	0.002									2.00
Fenvalerate						0.065		0.237			0.077			3.00
Bendcarb										0.002	0.066			2.00
Propoxur			0.05	0.001			0.001							3.00
Carbofuran				0.005	0.0014						0.002	0.011		3.00
Propamocarb	0.013				0.034		0.014	0.02	0.04	0.026				7.00
Amitraz				0.0135						0.004				2.00
Metalaxyl		0.002	0.011	0.006					0.004					4.00
Tetradifon		0.002							0.002					2.00
Chlorobenzilate		0.007		0.018	0.013		0.008					0.012		5.00
Benomyl											0.002			1.00
Number DC	5.00	9.00	8.00	9.00	12.00	7.00	6.00	3.00	4.00	7.00	6.00	7.00	4.00	
Total detected	0.183	0.833	0.344	0.298	0.485	0.694	0.216	0.298	0.057	0.849	0.193	1.041	0.308	

TABLE 4: Average of the percentage of nonleafy vegetable samples contained pesticide residues exceeds the MRL values during the four mainly seasons during the two years of 2007-2008.

Season	Year	Selected samples												Mean %	
		Cooled Pepper	Hot Pepper	Onion	Potato	Cucumber	Okra	Beans	Carrot	Tomato out	Tomato in	Squash	Egg plant		Cauliflower
Winter	2007	0.00	33.33	0.00	16.67	50.00	100.00	20.00	33.33	100.00	25.00	33.33	0.00	0.00	31.67
Spring		60.00	20.00	0.00	33.33	60.00	21.50	42.86	25.00	33.33	28.57	37.50	0.00	0.00	27.85
Summer		20.00	16.67	0.00	20.00	29.41	23.08	28.57	10.00	0.00	8.33	8.33	14.29	0.00	13.74
Autumn		11.11	7.69	0.00	9.09	0.00	18.18	15.38	12.50	14.29	8.33	0.00	17.65	0.00	8.79
Mean percentage		22.78	19.42	0.00	19.77	34.85	40.69	26.70	20.21	36.91	17.56	19.79	7.99	0.00	
Winter	2008	13.33	21.05	11.11	16.67	5.00	100.00	0.00	10.00	0.00	30.00	10.00	9.09	14.29	18.50
Spring		0.00	0.00	16.67	16.67	22.22	40.00	20.00	25.00	0.00	5.00	28.57	25.00	100.00	23.01
Summer		50.00	40.00	0.00	8.33	50.00	50.00	25.00	0.00	100.00	0.00	50.00	14.29	0.00	29.82
Autumn		25.00	28.57	12.50	20.00	7.69	20.00	28.57	0.00	0.00	33.33	28.57	10.00	25.00	18.40
Mean percentage		23.75	7.64	22.50	13.33	13.57	17.05	29.17	14.58	8.75	16.67	19.17	27.98	14.58	

The detected amounts of pesticide residues during the two mentioned seasons, that is, 2007/2008, were compared with that MRL values; it could calculate the average of percentage of non leafy vegetable samples contained amounts of residues exceeds the MRL values as listed in Table 4. From such data, it is clear that the majority of the analyzed vegetable samples collected in 2007 contained exhibited higher values than those of 2008 except five non leafy vegetables, that is, cold pepper, onions, beans, egg plant, and cauliflower which were higher in their values than those of 2007. In addition, when the analyzed samples distributed between the four mainly seasons of each year, that is, winter, spring, summer, and autumn (based on the analyzed date), neither correlation nor trend could be observed between the pesticide residues content and the mentioned season. The selected plant foods will not give a for adverse biological effects to take place providing the residues of pesticides are controlled to be kept to a minimum. Pesticides residue monitoring programs should then be implemented to assure the minimum allowable residue levels in plant foods, especially with regards to permethrin, endosulfan, and deltamethrin [17].

The results of the detected amounts of pesticide residues in the selected vegetable, it is therefore clear that patterns of pesticide use are crop dependent: the predominant use of pesticides in vegetables is mainly to control a wide range of pests. In addition, the obtained results clearly indicate the actual situation of the misuse of insecticides which may affect in turn at long period the consumers health, and the most reasonable explanation for the highly detected pesticide residues in cold pepper, egg plant, and carrot may be due to the intensive use of insecticides and the highly deposited amount of the applied compounds on the broad leaves of such vegetables. Overall, insecticides found in this study were similar to those found in other studies [12, 13, 18–21].

4. Conclusion

However, the detected amounts of the mentioned insecticides in these important non leafy vegetables make the necessary to continue the pesticide residue monitoring programs which must be implemented to assure the minimum allowable residue levels in plant foods. With the LLC and GCMS multiresidue method, the optimum conditions were met to extract and determined 86 pesticides in more than 1057 vegetable samples less time and low detection limit (0.001 ppm). The samples no residues and contained pesticide residues at or below MRL were detected in 83.90%. Meanwhile, the detected pesticides concentration had exceeded the MRL in 15.89% of the total tested samples.

Acknowledgment

This project was supported by King Saud University, Deanship of Scientific Research and College of Food and Agriculture Sciences Research Center.

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