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Multi-Residue Determination of Pesticides in Vegetables on Dalian Market by Gas Chromatograph, 2009-10

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Abstract

This paper presents results from surveillance of pesticide multi-residues in vegetables carried out in 2009-10. 420 samples of 10 different types of fresh vegetables were analyzed for their pesticide multi-residue contents using gas chromatograph and NY/T 761-2008 pesticide multi-residue screen methods. The residues exceeded MRLs of forbidden pesticides found were: carbofuran 0.110 mg/kg (kidney bean) and methamidophos 0.037 mg/kg (celery) in January 2009, methamidophos 0.037 mg/kg (tomato) in May 2009, aldicarb 0.013 mg/kg (kidney bean) in September 2009, omethoate 2.200 mg/kg (celery) in November 2009, carbofuran 0.052 mg/kg (green pepper) in April 2010, parathion 0.056 mg/kg (celery) and carbofuran 0.030 mg/kg (celery) in July 2010. Also, chlorpyrifos used as unforbidden pesticide was most frequently found above MRL, rape (0.820 mg/kg) and celery (0.365 mg/kg) in January 2009, celery (0.330 mg/kg) in May 2009, lettuce (0.298 mg/kg) in September 2009, rape (0.910 mg/kg) in April 2010 and lettuce (0.230 mg/kg) in July 2010. In addition, cypermethrin used as unforbidden pesticide was found above MRL only once in rape (1.270 mg/kg) in May 2009 and none of unforbidden pesticides above MRL was found in November 2009 and January 2010. Most of the samples (96%) were up to the national standard.

Keywords: Multi-residue; Determination; Pesticides; Vegetables; Gas chromatograph

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Introduction

Nowadays, a growing demand for safe and nutritional agricultural products requires more green vegetables grown without the usage of pesticides [1-7]. Over 800 pesticides belonging to over 100 different chemical classes are extensively used to protect crops before and after harvest from infestation by pests and plant diseases in agriculture all over the world [1,2]. Although pesticides play an important role in increasing production and ensuring quality in agricultural practice, residues will evaporate into the air, flow into the rivers, settle in the soil, pollute the productions and transfer to the human bodies, which will cause potential harm to the human being and pose a major threat to biodiversity [3]. Therefore, the issue of produce security, environmental pollution and human health that caused by the usage of pesticides are seriously concerned worldwide.

Since the 21st century, numerous researches on the effects of pesticide multi-residue to quality and security of agricultural products have been carried up successively [5]. The Southeastern Poland monitoring programme for 2004-05 covered 747 samples of 39 different types of fresh fruits and vegetables which were analyzed for pesticide multi-residue contents, and there were 27 samples (3.6%) residues exceeded national MRLs [8]. A total of 4404 samples of fruits and vegetables (34% of Danish origin and 66% from other countries) were analyzed for pesticide multi-residue contents (2000-01), and approximately 89 pesticides were detected which were more frequently found in fruit (60%) than in vegetables (18%) [6]. The present study reports the results from Dalian market (2009-10) of an on-going vegetable monitoring programme conducted by Liaoning Province Agriculture Academic Sciences, is aimed at ensuring that consumers are not exposed to unacceptable pesticide multi-residue levels.

Materials and Methods

Samples collection

The seasons and producing areas are influencing factors of pesticide types and pesticide multi-residue. The sampling plan was performed on the basis of guideline on sampling for pesticide multi-residue analysis (NY/T 789-2004). We did the random sampling of 60 samples each time and the number was difference for each type of vegetables. A total of 420 samples of 10 different types of vegetables (kidney bean, Chinese cabbage, eggplant, tomato, celery, lettuce, rape, cucumber, cabbage and green pepper) were taken from wholesale markets, hypermarkets and farmer's markets in January, May, September and November of 2009 and in January, April and July of 2010, respectively **(Table 1).** After sampling, the unwashed and unpeeled samples were immediately homogenate processing with a waring blender and freezing at -18°C to determine and analyse.

Pesticide selection

In accordance with Regulations of the People's Republic of China on the Control of Agricultural Chemicals and Varieties of Forbidden and Restricted Pesticide, 27 kinds of pesticide were detected in vegetables of Dalian market including organophosphorus pesticides (methamidophos, omethoate, parathion, parathion-methyl, dichlorvos, chlorpyrifos, sumithion, phosmet, phorate, monocrotophos, malathion and fenthion), organochlorine and pyrethroid pesticides (triadimefon, cypermethrin, fenvalerate, fenpropathrin, cyfluthrin, cyhalothrin, deltamethrin, bifenthrin and chlorothalonil) and carbamate pesticides (metalaxyl, pirimicarb, carbaryl, aldicarb, carbofuran and methomyl). A total of 8 kinds of forbidden pesticide (methamidophos, omethoate, parathion, parathion-methyl, phorate, monocrotophos, aldicarb, carbofuran) were specially detected.

Extraction

The samples (25 g) were accurately weighed into a 100 ml polypropylene centrifuge tube and extracted with 50 ml acetonitrile, a high-speed homogenate machine was used to blend at 20000 rpm for 2 min. Then, the mixture was filtered through a piece of filter paper and the combined filtrate (about 40-50 ml) was collected into a 100 ml measuring cylinder containing 5-7 g NaCl. The measuring cylinder was sealed up with a plug and oscillated tempestuously for 1 min. After that, left it to stand for 30 min at room temperature to make acetonitrile phase and water phase stratification. A total of 10 ml acetonitrile were sucked up to a 150 ml beaker which was kept in a water bath at 80°C ventilating with nitrogen or air slowly for evaporating to nearly dryness.

Purification

The methods of purification are different among organophosphorus pesticides, organochlorine and pyrethroid pesticides and carbamate pesticides. The specific content and operation methods are brief introduced as follows.

Organophosphorus pesticides: Acetone (2 ml) was added into the above residue and the beaker was covered with aluminium foil for purifying. The ready solution was transfered to a 15 ml scale centrifugal tube absolutely and acetone (about 3 ml) was used to wash the beaker for three times. The total volume collected was adjusted to exactly 5 ml and blended with a whirlpool mixer. The samples were filtrated with filter membrane (0.22 μm) before determination.

Organochlorine and pyrethroid pesticides: An aliquot of 10 ml n-hexane was added and the beaker was covered with aluminium foil for subsequent use. The Florisil PR column was eluted beforehand and conditioning using 5 ml mixed solution of acetone and n-hexane (mass fraction 10:90) and 5 ml n-hexane successively. When the dissolvent reached to the surface of column adsorption layer, the above sample was immediately poured into Florisil PR column and recovered with a 15 ml scale centrifugal tube. The beaker was washed twice with 5 ml mixed solution of acetone and n-hexane (mass fraction 10:90), then the effluent solution went through Florisil PR column again. The scale centrifugal tube containing the whole leacheate was laid in a pressure blowing concentrator at 50°C for evaporating to less than 5 ml and scaled to 5 ml with n-hexane. After that the mixed solution was blended with a whirlpool mixer. The samples were filtrated with filter membrane (0.22 μm) before determination.

Carbamate pesticedes: Mixed solution (2 ml) of methyl alcohol and dichloromethane in a ratio of 1:99 (mass fraction) was added and the beaker was covered with aluminium foil. The

Table 1 Number of random sampling in 2009-10.

Commodity	Number						
	January, 2009	May, 2009	September, 2009	November, 2009	January, 2010	April, 2010	July, 2010	Total
Kidney bean	8	8	8	7	7	6	8	52
Chinese cabbage	0	0	0	6	0	0	0	6
Tomato	7	7	8	6	8	6	1	43
Cucumber	8	7	8	10	8	6	6	53
Cabbage	8	8	6	9	8	7	8	54
Eggplant	7	8	8	6	7	6	3	45
Celery	7	6	8	5	6	6	11	49
Green pepper	0	0	0	0	0	7	4	11
Lettuce	8	8	7	6	8	9	9	55
Rape	7	8	7	5	8	7	10	52
Total	60	60	60	60	60	60	60	420

amino column was eluted in advance and conditioning using 4 ml mixed solution of methyl alcohol and dichloromethane (mass fraction 1:99). The above sample was rapidly added into the amino column as the dissolvent reached to the surface of column adsorption layer. The eluent was gathered with a 15 ml centrifuge tube and 2 ml mixed solution of methyl alcohol and dichloromethane (mass fraction 1:99) was used to wash the beaker twice, then the eluent went through the amino column and combined. The total solution collected was evaporated to dryness in a pressure blowing concentrator at 50°C under a nitrogen stream. Afterwards, the residue was accurately scaled to 2.5 ml with methyl alcohol and mixed with a whirlpool mixer for detecting.

Analytical methods

By the method of NY/T 761-2008 pesticide multi-residue screen methods for determination of organophosphorus pesticides, organochlorine pesticides, pyrethroid pesticides and carbamate pesticedes in vegetables and fruits, the samples were evaluated with Agilent 6890N gas chromatograph (with detectors of FPD, ECD and NPD). The chromatographic columns and SPE were from Agilen and the reagents used in the tests were all analytical reagents completely. Each sample determined twice parallelly, taking the means as the report results.

Organophosphorus pesticides: A gas chromatograph system (Agilent 6890N, Palo Alto, USA) equipped with an autosampler was used to analyse the residue of organophosphorus pesticides. The gas chromatograph separation was performed using a 50% poly phenyl dimethyl siloxane column (DB-17, 30 m × 0.53 mm × 1.0 μm) (A) and a 100% poly dimethyl siloxane column (HP-1, 30 m × 0.53 mm × 1.5 μm) (B) with the injector temperature of 220°C and the detector temperature of 250°C. The temperature of the column was programmed as follows: 150°C (2 min); 8°C/min to 250°C (12 min). Helium (≥ 99.999%) was used as a carrier gas at a flow of 10 ml/min, hydrogen (≥ 99.999%) was used as a burning gas at a flow of 75 ml/min and the air was used as an aided gas at a flow of 100 ml/min. The sample was divided into two parts and injected by a double autosampler at the same time. The standard solution of 1 ml was injected for comparing. The peak area of sample from column A was compared with the peak area of standard solution for quantitative analysis. If the retention time of the sample from the double columns and standard solution differ with in ± 0.05 min, the unknown component could be concluded.

Organochlorine and pyrethroid pesticides: The gas chromatograph separation was performed using a 100% poly dimethyl siloxane column (HP-1, 30 m × 0.25 mm × 0.25 μm) (A) and a 50% poly phenyl dimethyl siloxane column (DB-17, 30 m × 0.25 mm × 0.25 μm) (B) with the injector temperature of 200°C and the detector temperature of 320°C. The temperature of the column was programmed as follows: 150°C (2 min); 6°C/min to 270°C (8 min, 23 min for deltamethrin). Helium (≥ 99.999%) was used as a carrier gas at a flow of 1 ml/min and an aided gas at a flow of 60 ml/min. The quantitative and qualitative analytical methods were the same as those of organophosphorus pesticides.

Carbamate pesticides: Analytical column (C8, 4.6 mm × 25 cm × 5 μm or C18, 4.6 mm × 25 cm × 5 μm) was used for determination of carbamate pesticides with the column temperature of 42°C and fluorescence detector wavelength of 330 nm and 465 nm. The post-column derivatization condition were as follows: 0.05 mol/L NaOH, flow rate of 0.3 ml/min, OPA reagent flow rate of 0.3 ml/min, hydrolysis temperature of 100°C and derivative temperature of room temperature. The retention time of 20 μl standard solution and sample were injected for qualitative analysis, however the peak area for qualitative analysis.

Quality assurance procedures

A gas chromatograph method using an external standard was developed for quantitative analysis (each sample for twice) and double columns for qualitative analysis. The test results were reliable when the standardized recovery reached to 70%-130%, whereas if the results out of rang, it needed to retest.

Results and Discussion

Maximum residue limits (MRLs) are defined as the highest concentrations of pesticide multi-residues (mg/kg). However, MRLs are not safety limits, and exposure to residues in excess of an MRL does not automatically imply a hazard to health [8]. Details of pesticide multi-residue (mg/kg) detected in 2009-10 were provided in **Tables 2-8**. A total of 420 samples of 10 different types of vegetables were analyzed for their pesticide multi-residue contents.

The samples were analysed for approximately 27 pesticides using gas chromatograph and NY/T 761-2008 pesticide multi-residue screen methods. As seen in **Tables 2-8**, 8 detections of 5 kinds of forbidden pesticides were detected in various vegetables, carbofuran 0.110 mg/kg (kidney bean) and methamidophos 0.037 mg/kg (celery) in January 2009, methamidophos 0.037 mg/kg (tomato) in May 2009, aldicarb 0.013 mg/kg (kidney bean) in September 2009, omethoate 2.200 mg/kg (celery) in November 2009, carbofuran 0.052 mg/kg (green pepper) in April 2010, parathion 0.056 mg/kg (celery) and carbofuran 0.030 mg/kg (celery) in July 2010, none of forbidden pesticides was found in January 2010.

In addition, with regard to unforbidden pesticides, chlorpyrifos was most frequently found above MRL during the 7 sample survey, rape (0.820 mg/kg) and celery (0.365 mg/kg) in January 2009, celery (0.330 mg/kg) in May 2009, lettuce (0.298 mg/kg) in September 2009, rape (0.910 mg/kg) in April 2010, lettuce (0.230 mg/kg) in July 2010. Also, cypermethrin was found above MRL only once in rape (1.270 mg/kg) in May 2009 and none of unforbidden pesticides exceeding MRL was found in November 2009 and January 2010. In most cases pesticide residues occurred on levels well below MRLs.

Table 9 shows the qualifying rates of random sampling for all vegetables in 2009-10. Results of the surveys presented in table 9 indicate that the average qualifying rate values (97%) of samples in 2010 were higher than the results (94%) in 2009. The qualifying rates of cucumber, cabbage and eggplant were all up to 100% during 2009-10. There was a great deal of improvement in the qualifying rates of celery in 2010 (94%) versus 2009 (67%). Also,

Table 2 Pesticide multi-residue in vegetables analyzed in January, 2009.

Commodity	Pesticide	Detected number	Mean (mg/kg)	Max (mg/kg)	MRL (mg/kg)
Kidney bean	Chlorpyrifos	1	0.034	0.034	1
	Chlorothalonil	2	0.013	0.021	5
	Carbofuran	1	0.110	0.110	0
Tomato	Bifenthrin	2	0.004	0.005	0.5
	Triadimefon	1	0.072	0.072	0.1
Cucumber	Chlorothalonil	1	0.018	0.018	5
Cabbage	Metalaxyl	1	0.144	0.144	0.5
Eggplant	Chlorpyrifos	2	0.063	0.098	0.5
	Cypermethrin	2	0.015	0.017	0.5
	Bifenthrin	1	0.003	0.003	0.5
	Chlorothalonil	2	0.009	0.017	5
Celery	Methamidophos	1	0.037	0.037	0
	Chlorpyrifos	3	0.365	0.540	0.05
	Fenpropathrin	1	0.200	0.200	0.5
	Chlorothalonil	3	1.126	1.940	5
	Carbaryl	1	0.790	0.790	2
	Methomyl	1	0.025	0.025	2
Lettuce	Chlorpyrifos	1	0.098	0.098	0.1
	Cyhalothrin	2	0.014	0.015	0.2
	Chlorothalonil	1	0.002	0.002	5
Rape	Chlorpyrifos	1	0.820	0.820	0.1
	Cypermethrin	1	0.060	0.060	0.5
	Fenpropathrin	1	0.011	0.011	0.5
	Cyhalothrin	1	0.003	0.003	0.2
	Chlorothalonil	1	0.002	0.002	5

Table 3 Pesticide multi-residue in vegetables analyzed in May, 2009.

Commodity	Pesticide	Detected number	Mean (mg/kg)	Max (mg/kg)	MRL (mg/kg)
Kidney bean	Fenvalerate	1	0.042	0.042	0.2
	Cyfluthrin	1	0.012	0.012	0.1
Tomato	Methamidophos	1	0.037	0.037	0
	Chlorpyrifos	1	0.045	0.045	0.5
	Cyfluthrin	1	0.034	0.034	0.1
Cucumber	Chlorothalonil	1	0.005	0.004	5
Cabbage	Triadimefon	2	0.006	0.006	0.05
Eggplant	Chlorothalonil	1	0.004	0.003	5
	Methomyl	1	0.024	0.024	2
Celery	Chlorpyrifos	1	0.330	0.330	0.05
	Cypermethrin	1	0.240	0.240	2
	Triadimefon	1	0.011	0.011	0.1
	Chlorothalonil	2	0.094	0.130	5
	Metalaxyl	1	0.020	0.020	0.5
Lettuce	Chlorpyrifos	1	0.027	0.027	0.1
	Cypermethrin	1	0.078	0.078	2
	Fenvalerate	3	0.132	0.350	0.5
	Triadimefon	1	0.004	0.004	0.1
	Chlorothalonil	1	0.003	0.002	5
	Methomyl	1	0.027	0.027	2
Rape	Chlorpyrifos	1	0.024	0.024	0.1
	Cypermethrin	4	0.378	1.270	0.5
	Chlorothalonil	1	0.006	0.006	5
	Methomyl	1	0.026	0.026	2

Table 4 Pesticide multi-residue in vegetables analyzed in September, 2009.

Commodity	Pesticide	Detected number	Mean (mg/kg)	Max (mg/kg)	MRL (mg/kg)
Kidney bean	Chlorothalonil	1	0.002	0.002	5
	Aldicarb	1	0.013	0.013	0
Tomato	Carbaryl	2	0.049	0.080	2
Cucumber	Metalaxyl	2	0.020	0.020	0.5
Cabbage	Triadimefon	1	0.005	0.005	0.05
	Carbaryl	1	0.024	0.024	2
	Methomyl	1	0.038	0.038	2
Eggplant	Bifenthrin	1	0.006	0.006	0.5
Celery	Triadimefon	1	0.013	0.013	0.1
	Carbaryl	4	0.021	0.032	2
	Methomyl	1	0.072	0.072	2
Lettuce	Chlorpyrifos	4	0.298	0.540	0.1
	Chlorothalonil	4	0.305	0.930	5
	Methomyl	2	0.032	0.044	2
Rape	Triadimefon	3	0.003	0.004	0.1
	Chlorothalonil	1	0.010	0.009	5
	Methomyl	1	0.023	0.023	2

Table 5 Pesticide multi-residue in vegetables analyzed in November, 2009.

Commodity	Pesticide	Detected number	Mean (mg/kg)	Max (mg/kg)	MRL (mg/kg)
Kidney bean	Chlorothalonil	1	0.002	0.001	5
	Carbaryl	1	0.016	0.016	2
	Methomyl	1	0.017	0.017	2
Chinese cabbage	Chlorothalonil	1	0.001	0.001	5
Tomato	Chlorothalonil	1	0.011	0.011	5
Cucumber	Chlorothalonil	2	0.004	0.004	5
Cabbage	Cypermethrin	3	0.058	0.078	2
	Methomyl	1	0.032	0.032	2
Eggplant	Chlorothalonil	1	0.010	0.009	5
Celery	Omethoate	1	2.200	2.200	0
	Chlorpyrifos	4	0.068	0.180	0.05
	Chlorothalonil	1	0.780	0.780	5
	Methomyl	2	0.017	0.018	2
Lettuce	Cypermethrin	3	0.018	0.038	2

Table 6 Pesticide multi-residue in vegetables analyzed in January, 2010.

Commodity	Pesticide	Detected number	Mean (mg/kg)	Max (mg/kg)	MRL (mg/kg)
Kidney bean	Cyhalothrin	1	0.022	0.022	0.1
Tomato	Chlorothalonil	1	0.081	0.081	5
Eggplant	Chlorpyrifos	1	0.030	0.030	0.5
	Chlorothalonil	1	0.021	0.021	5
Celery	Chlorpyrifos	1	0.260	0.260	1
	Malathion	1	0.099	0.099	1

the qualifying rates of kidney bean and tomato reached to 100% in 2010, the results all meet the standards comparing with 2009 (kidney bean 94%, tomato 96%). However, lettuce (93%-96%) and rape (93%-95%) had a little effect on the qualifying rates from 2009-10. Chinese cabbage (100%) and green pepper (86%, 100%) were sampled only in November 2009 and April and July 2010, respectively.

Table 10 presents the distribution for all commodities from 2009-10 pesticide multi-residue monitoring programme. A total of 20 of all samples (5%) had multi-residues above the MRLs. Multi-residues below the MRLs were found in 145 (35%) samples. Multi-residues of pesticides for which there were no MRL were found in 255 (61%) samples. Pesticide multi-residues were more frequently found in celeries (10 and 20%, respectively) on Dalian market in 2009-10. To compare results of other vegetables, pesticide multi-residues were found in approximately 9% of green peppers, 6% of rapes, 5% of lettuces, 4% of kidney beans and 2% of tomatoes, respectively.

Table 7 Pesticide multi-residue in vegetables analyzed in April, 2010.

Commodity	Pesticide	Detected number	Mean (mg/kg)	Max (mg/kg)	MRL (mg/kg)
Cucumber	Chlorothalonil	1	0.071	0.071	5
Eggplant	Chlorpyrifos	1	0.022	0.022	0.5
Celery	Chlorpyrifos	1	0.048	0.048	0.05
Green pepper	Chlorpyrifos	4	0.190	0.240	1
	Cypermethrin	2	0.036	0.043	0.5
	Chlorothalonil	1	0.018	0.018	5
	Carbofuran	1	0.052	0.052	0
Lettuce	Chlorpyrifos	2	0.036	0.037	0.1
	Chlorothalonil	3	0.004	0.007	5
Rape	Chlorpyrifos	1	0.910	0.910	0.1

Table 8 Pesticide multi-residue in vegetables analyzed in July, 2010.

Commodity	Pesticide	Detected number	Mean (mg/kg)	Max (mg/kg)	MRL (mg/kg)
Eggplant	Chlorothalonil	1	0.050	0.050	5
	Cypermethrin	1	0.110	0.110	0.5
Celery	Parathion	1	0.056	0.056	0
	Chlorothalonil	1	1.530	1.530	5
	Carbofuran	1	0.030	0.030	0
	Triadimefon	2	0.011	0.012	0.1
	Chlorpyrifos	2	0.031	0.036	0.05
Green pepper	Cyhalothrin	1	0.010	0.010	0.2
Lettuce	Triadimefon	2	0.039	0.066	0.1
	Chlorothalonil	2	2.425	4.840	5
	Cypermethrin	3	0.076	0.140	2
	Chlorpyrifos	1	0.230	0.230	0.1
	Cypermethrin	1	0.054	0.054	2
Rape	Chlorothalonil	1	0.025	0.025	5
	Cyhalothrin	1	0.099	0.099	0.2
	Deltamethrin	1	0.340	0.340	0.5

Table 9 Qualifying rate of random sampling in 2009-10.

Commodity	Qualifying rate (%)						
	January, 2009	May, 2009	September, 2009	November, 2009	January, 2010	April, 2010	July, 2010
Kidney bean	88	100	88	100	100	100	100
Chinese cabbage	-	-	-	100	-	-	-
Tomato	100	86	100	100	100	100	100
Cucumber	100	100	100	100	100	100	100
Cabbage	100	100	100	100	100	100	100
Eggplant	100	100	100	100	100	100	100
Celery	43	83	100	40	100	100	82
Green pepper	-	-	-	-	-	86	100
Lettuce	100	100	71	100	100	100	89
Rape	86	88	100	100	100	86	100
Total	90	95	95	95	100	97	95

In view of the total number of pesticides each time comparing the results of frequency of multi-residues **(Figure 1),** the frequency of multi-residues decreased from 74 to 40% during 2009-10 in overall samples. In detail, Chinese cabbage, eggplant, celery and rape had little fluctuation between the results from 2009-10. A decreasing number of pesticide multi-residues for kidney bean, tomato, cucumber and cabbage were showed from 2009 to 2010. However, there was not a great deal of improvement in frequency of pesticide multi-residues in 2010 versus 2009 for green pepper and lettuce.

Table 10 Distribution of samples from 2009-10 pesticide multi-residue monitoring programme.

Commodity	Samples analysed	Samples with residues above the MRL	Samples with residues below the MRL	Samples without detected residues
Kidney bean	52	2 (4%)[a]	10 (19%)	40 (77%)
Chinese cabbage	6	0 (0%)	1 (17%)	5 (83%)
Tomato	43	1 (2%)	9 (21%)	33 (77%)
Cucumber	53	0 (0%)	7 (13%)	46 (87%)
Cabbage	54	0 (0%)	10 (19%)	44 (81%)
Eggplant	45	0 (0%)	16 (36%)	29 (64%)
Celery	49	10 (20%)	30 (61%)	9 (18%)
Green pepper	11	1 (9%)	8 (73%)	2 (18%)
Lettuce	55	3 (5%)	36 (65%)	16 (29%)
Rape	52	3 (6%)	18 (35%)	31 (60%)
All samples	420	20 (5%)	145 (35%)	255 (61%)

[a]Number of samples. Values in parentheses are the percent of samples.

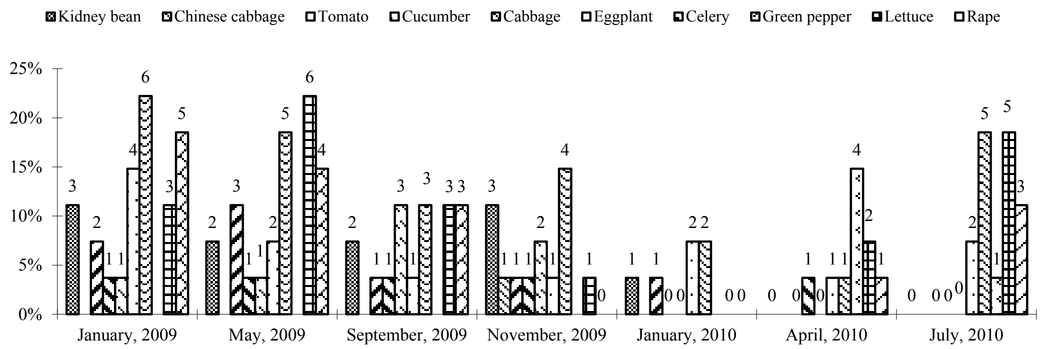

Figure 1 Frequency of multi-residues in vegetables in 2009-10.

Conclusions

The monitoring programme for 2009 and 2010 on Dalian market covered 420 samples of 10 different vegetables. The samples were analysed for 27 pesticides of which 7 (carbofuran, methamidophos, aldicarb, omethoate, carbofuran, chlorpyrifos and cypermethrin) were detected in the samples. Pesticides were easier to keep on celery, rape, lettuce and kidney bean than the other vegetables. Comparatively speaking, owing to more plant diseases and insect pests in summer, the qualifying rates of samples in winter are higher than in summer. Though the period of the survey is only 2 years, the overall situation of vegetables is of high quality and has little fluctuation per year.

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