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Influence of Different Planting Seasons of Six Leaf Vegetables on Residues of Five Pesticides

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ABSTRACT: To investigate the influence of different planting seasons on the dissipation of pesticides, field experiments of thiophanate-methyl, metalaxyl, fluazifop-P-butyl, chlorpyrifos, and λ-cyhalothrin on six crops including pakchoi, rape, crown daisy, amaranth, spinach, and lettuce were designed and conducted. In this study, a high-performance liquid chromatography and electrospray ionization−tandem mass spectrometer with multiple reaction monitoring was used to simultaneously determine thiophanate-methyl and its metabolite carbendazim, metalaxyl, and fluazifop-P-butyl in various samples; gas chromatography with an electron capture detector was used to detect chlorpyrifos and λ-cyhalothrin. The limits of quantitation (LOQs) of these six pesticides were in the range of 0.001−0.01 mg kg^{-1} for all samples, and the average recoveries of all pesticides ranged from 60.1 to 119.1% at 0.01 and 0.1 mg kg^{-1} spiked levels. The relative standard deviation (RSD) ranged from 1.1 to 13.9%. All maximal concentrations of the six pesticides in six leaf vegetables in autumn were higher than in summer in Beijing. For most pesticides half-lives in autumn were longer than in summer. The results showed that the initial concentration, maximal concentration, and half-lives of pesticides were influenced not only by environmental factors such as light, heat, moisture, and rainy climate but also by plant matrices.

KEYWORDS: *pesticide residues, dissipation, plant seasons, leaf vegetables*

INTRODUCTION

Pesticides are widely used in agricultural production and have played a key role in providing reliable products to consumers and farmers.[1−3] Whereas the efficacy of a pesticide is influenced by environmental factors such as light, heat, moisture, rainy climate, and growth dilution factor, it should be noted that the dissipation of pesticides can be influenced by planting seasons, so, the study of the dissipation of pesticides in different planting seasons is essential.

Thiophanate-methyl [1,2-α-(3-methoxycarbonyl)-2-thioureido]-benzene is applied at different growing stages in fruit and vegetable crops to control fungal diseases.[4,5] It is unstable and easily converts to carbendazim (methyl benzimidazol-2-ylcarbamate) in plants. The fungicidal activity of thiophanate-methyl is due to the presence of carbendazim.[6] Metalaxyl is an important phenylamide fungicide with protective and curative action, which is widely used to control diseases caused by air- and soilborne Peronosporales on a wide range of temperate, subtropical, and tropical crops.[7] Its effectiveness results from inhibition of uridine incorporation into RNA and specific inhibition of RNA polymerase-1.[8] Fluazifop-P-butyl is a selective herbicide for the control of annual and perennial grasses in many broadleaf crops.[9] Chlorpyrifos is an organophosphorus (OPPs) insecticide.[10] λ-Cyhalothrin is a broad-spectrum pyrethroid insecticide used to control a wide range of insect pests in a variety of crops. In the literature, application rates of λ-cyhalothrin in field crops typically range from 0.005 to 0.015 kg (ai) ha^{-1}.[11,12] The five pesticides mentioned above are used in the cultivation of leaf vegetables, especially pakchoi, rape, crown daisy, amaranth, spinach, and lettuce. The chemical structures of these pesticides are presented in Figure 1.

In the current study, a modified QuEChERS (quick, easy, cheap, effective, rugged and safe) method was used in sample pretreatment.[13−15] The QuEChERS method was introduced by Anastassiades et al. in 2003.[16] The procedures involved miniaturized extraction with acetonitrile, liquid−liquid partitioning, and a cleanup step, which were carried out by mixing the acetonitrile extract with loose sorbents.[17]

The present study was designed to investigate the influence of different planting seasons on the dissipation of thiophanate-methyl, metalaxyl, fluazifop-P-butyl, chlorpyrifos, and λ-cyhalothrin in pakchoi, rape, crown daisy, amaranth, spinach, and lettuce in Shijiazhuang and Beijing.

MATERIALS AND METHODS

Chemicals and Reagents. Thiophanate-methyl, carbendazim, metalaxyl, fluazifop-P-butyl, chlorpyrifos, and λ-cyhalothrin standard materials were provided by the Institute for the Control of Agrochemicals, Ministry of Agriculture, China (ICAMA). The chemical structures of the pesticides are presented in Figure 1. Mixed standard solutions were prepared and stored at −20 °C (with a concentration of 10 mg L^{-1}): thiophanate-methyl suspending agent (500 g L^{-1}) (Dragon Lantern Chemical Co. Ltd., Jiangsu, China); metalaxyl wettable powder (10%) (Yixing Sinon Chemical Co. Ltd., Jiangsu, China); fluazifop-P-butyl missible oil (15%) (Ishihara Taurus Pesticide Co. Ltd., Zhejiang, China); chlorpyrifos miscible oil (480 g L^{-1}) (Dow AgroSciences LLC); λ-cyhalothrin mircoemulsion (5%) (Nuopuxin Chemical Co. Ltd., Shenzhen, China); acetonitrile, HPLC grade (Honeywell Burdick &

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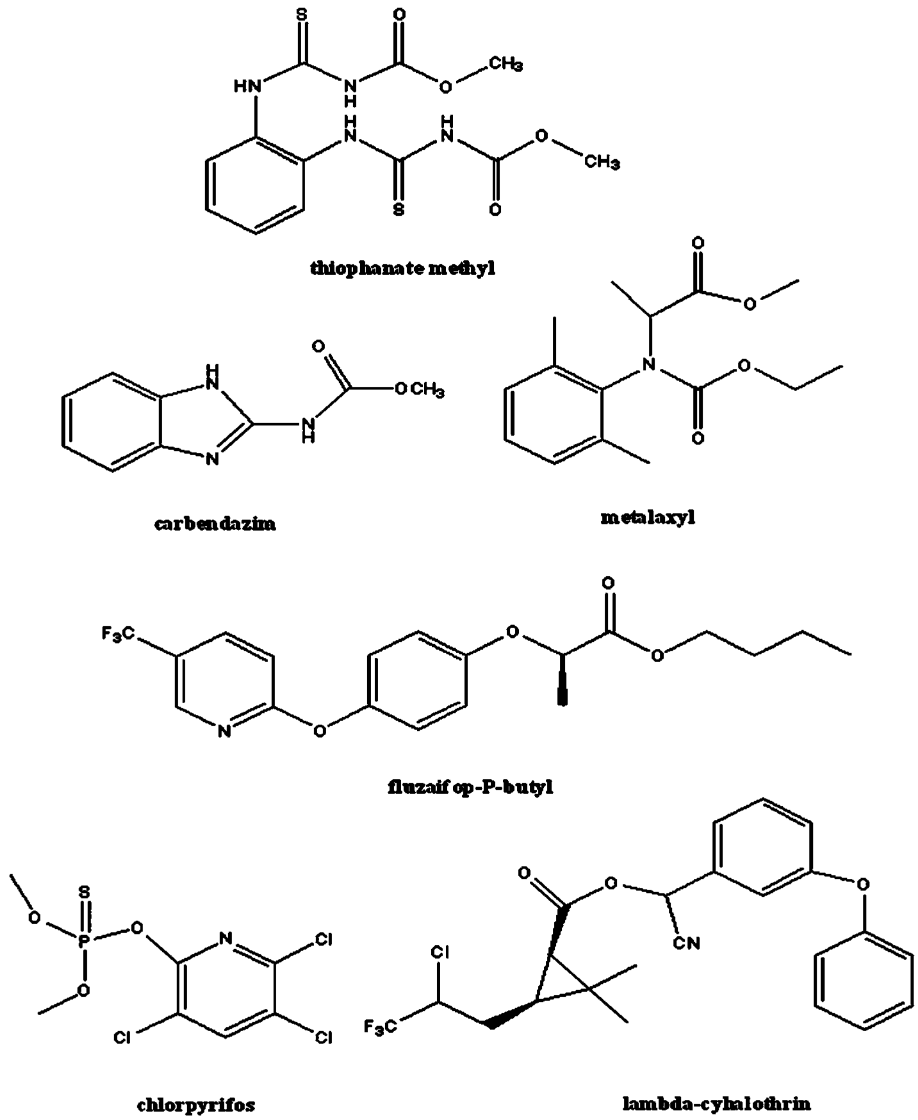

Figure 1. Chemical structures of thiophanate-methyl and its metabolite carbendazim, metalaxyl, fluazifop-P-butyl, chlorpyrifos, and λ-cyhalothrin.

Table 1. Liquid Chromatography−Tandem Mass Spectrometry Parameters of Four Pesticides

pesticide	retention time (min)	fragmentor (V)	quantifying ion pair	qualifying ion pair	collision energy (V)
thiophanate-methyl	0.59	110	343.1/151	343.1/311	20; 5
carbendazim	0.53	90	192/160	190/132	20; 25
metalaxyl	0.65	100	280.2/192	280.2/219.9	15; 11
fluazifop-P-butyl	1.3	150	384.1/282	384.1/327.9	18; 13

Table 2. Standard Curve Equations of Pesticides in Six Leaf Vegetables

pesticide	matrix	standard curve eq	R^2	linear range (mg/kg)
thiophanate-methyl	pakchoi	$y = 7683.6x - 40.7$	0.991	0.01−10
	rape	$y = 5350.5x + 89.7$	0.997	0.01−10
	crown daisy	$y = 8412.7x - 271.4$	0.999	0.01−10
	amaranth	$y = 7397.1x - 273.6$	0.992	0.01−10
	spinach	$y = 7991.0x + 215.4$	0.996	0.005−10
	lettuce	$y = 8434.9x - 197.0$	0.998	0.01−10
carbendazim	pakchoi	$y = 52174.8x + 468.2$	0.999	0.01−10
	rape	$y = 42142.9x + 3853.2$	0.998	0.005−10
	crown daisy	$y = 59931.5x + 195.6$	0.999	0.01−10
	amaranth	$y = 47065.9x + 241.0$	0.999	0.01−10

Table 2. continued

pesticide	matrix	standard curve eq	R^2	linear range (mg/kg)
	spinach	$y = 65178.7x - 288.4$	0.998	0.005−10
	lettuce	$y = 56169.3x - 688.0$	0.998	0.01−10
metalaxyl	pakchoi	$y = 36109.8x - 1206.8$	0.993	0.01−10
	rape	$y = 91183.1x + 701.1$	0.999	0.01−10
	crown daisy	$y = 128849.6x + 5875.6$	0.999	0.005−10
	amaranth	$y = 101708.7x + 536.2$	0.999	0.01−10
	spinach	$y = 124465.8x - 2838.2$	0.995	0.005−10
	lettuce	$y = 120857.4x + 1079.7$	0.999	0.01−10
fluazifop-P-butyl	pakchoi	$y = 131631.2x - 2080.8$	0.998	0.001−20
	rape	$y = 148417.8x - 4630.4$	0.999	0.002−10
	crown daisy	$y = 125911.9x + 78.2$	0.999	0.001−10
	amaranth	$y = 128007.2x + 383.2$	0.999	0.002−10
	spinach	$y = 135209.6x - 2108.6$	0.998	0.001−10
	lettuce	$y = 170106.4x - 5986.1$	0.998	0.002−10
chlorpyrifos	pakchoi	$y = 93482.9x - 311.8$	0.999	0.005−10
	rape	$y = 100990.1x + 1148.8$	0.999	0.005−10
	crown daisy	$y = 102545.9x - 1659.5$	0.998	0.002−10
	amaranth	$y = 112042.4x + 321.0$	0.998	0.005−20
	spinach	$y = 113438.5x + 1363.8$	0.999	0.005−20
	lettuce	$y = 113023.4x + 387.4$	0.999	0.005−10
λ-cyhalothrin	pakchoi	$y = 58581.8x - 1,841.6$	0.994	0.01−10
	rape	$y = 62852.5x - 2832.2$	0.998	0.01−10
	crown daisy	$y = 67374.8x - 4245.1$	0.997	0.005−10
	amaranth	$y = 53708.9x - 877.9$	0.991	0.01−10
	spinach	$y = 71059.6x - 1712.4$	0.997	0.01−10
	lettuce	$y = 55026.6x - 181.6$	0.999	0.01−10

Table 3. Recoveries of Pesticides in Six Leaf Vegetables ($n = 5$)

		thiophanate-methyl		carbendazim		metalaxyl		fluazifop-P-butyl		chlorpyrifos		λ-cyhalothrin	
matrix	spiked level (mg/kg)	recovery (%)	RSD (%)	recovery (%)	RSD (%)	recovery (%)	RSD (%)	recovery (%)	RSD (%)	recovery (%)	RSD (%)	recovery (%)	RSD (%)
pakchoi	0.01	82.2	10.6	84.0	4.9	80.9	10.5	92	7.8	88.1	13.9	94.6	13.9
	0.1	86.9	9.3	86.1	6.6	100.4	5.4	113.6	1.4	108.9	3.0	110.1	3.0
rape	0.01	96.8	9.8	100.9	1.1	90.6	7.4	83	7.2	81.2	8.8	81.2	11.4
	0.1	102.3	1.3	100.6	2.2	103.5	3.5	95.9	1.4	88.3	2.8	75.7	10.9
crown daisy	0.01	99.2	10.6	89.7	8.2	95.2	12.3	85.3	2.7	108.4	8.7	84.9	8.2
	0.1	80.9	3.4	100.5	3.1	114.6	11.5	102.9	9.2	106.8	5.9	98.1	10.4
amaranth	0.01	60.1	5.1	83.1	5.6	93.2	3.5	89.2	6.5	98.4	5.9	117.0	11.5
	0.1	70.2	5.0	72.0	8.0	92.7	2.1	104.7	2.5	99.0	7.4	91.6	8.7
spinach	0.01	76.3	6.8	74.5	9.9	92.5	10.0	93.6	2.7	83.9	1.4	71.2	12.8
	0.1	98.4	8.5	102.1	5.5	110.0	8.3	119.1	2.6	108.6	3.5	113.5	3.6
lettuce	0.01	72.7	6.3	112.6	2.5	110.8	9.1	94.5	6	104.0	10.5	67.7	10.0
	0.1	67.8	2.5	103.8	6.6	95.9	1.1	111.9	3.2	110.7	5.9	112.6	6.0

Jackson, Muskegon, MI, USA); sodium chloride, analytical grade (Beijing Reagent Co.); primary−secondary amine (PSA) (Agilent Technologies). Deionized water (18.2 MΩ cm^{-1}) was prepared by a Milli-Q Pure treatment system (Millipore, Bedford, MA, USA). Anhydrous magnesium sulfate (Beijing Reagent Co., analytical grade) was heated at 120 °C for 5 h and then cooled to room temperature before use.

Field Experiments and Sampling. The field trials including dissipation study were designed according to the pesticide label. The supervised field trials were carried out in summer (between May and July)

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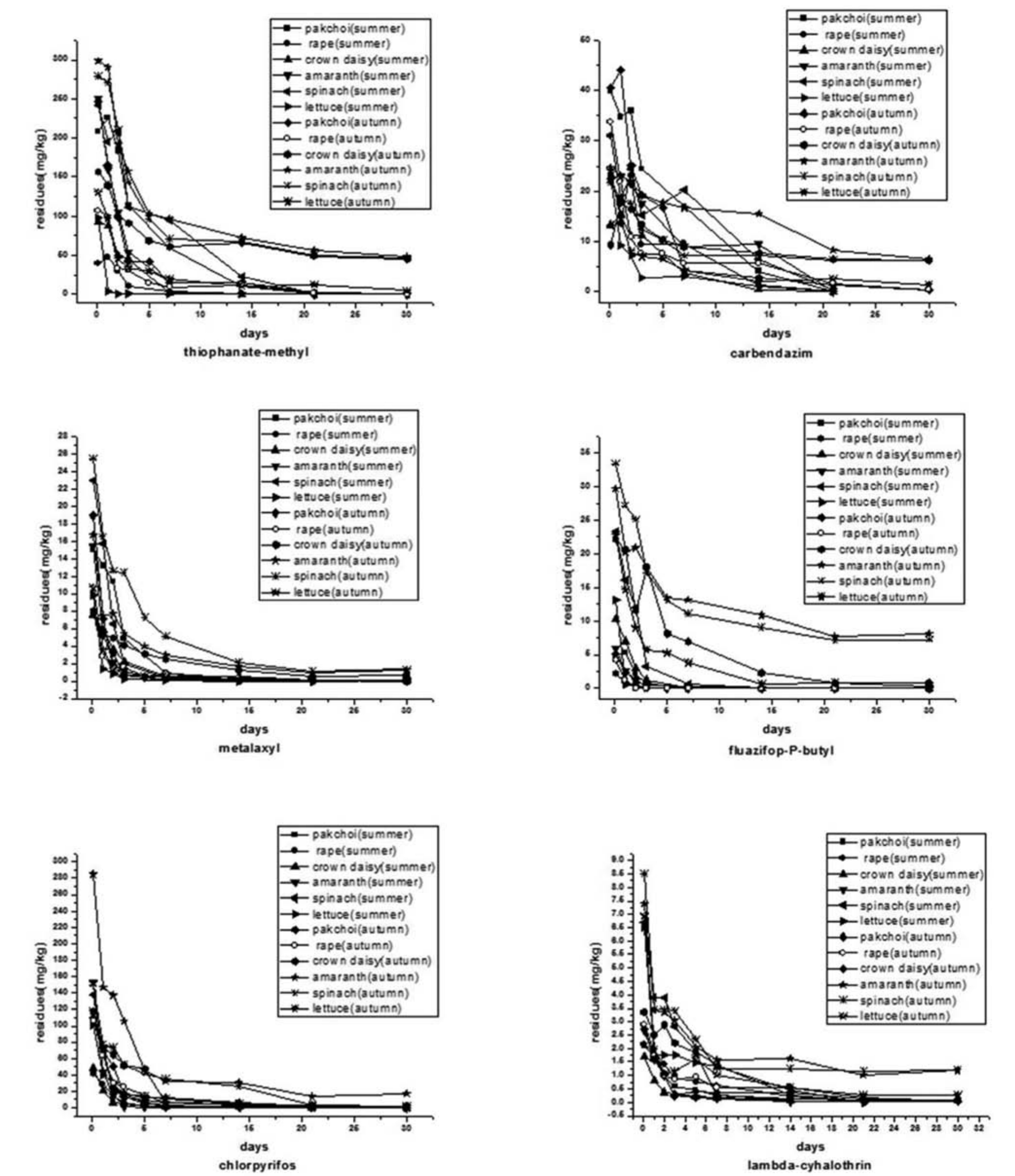

Figure 2. Dissipation curve of thiophanate-methyl, carbendazim, metalaxyl, fluazifop-P-butyl, chlorpyrifos, and λ-cyhalothrin in six leaf vegetable samples in Shijiazhuang.

and autumn (between August and October) of 2012 at two sites in China: Shijiazhuang (Hebei province), located at north latitude 38° 02′ and east longitude 114° 02′; Beijing, located at north latitude 39° 54′ and east longitude 116° 23′. The area of the experimental plot was 10 m^2 (5 m × 2 m), and each treatment was designed with three replicated plots. A buffer area with 2.5 m^2 (5 m × 0.5 m) was maintained between the plots with different vegetables.

In dissipation experiments the dosages of thiophanate-methyl, metalaxyl, fluazifop-P-butyl, chlorpyrifos, and λ-cyhalothrin were 3375, 1800, 1050, 1500, and 360 g (ai) ha^{-1} (double the recommended dosage) with one-time spray. The recommended dosage is the highest on the pesticide labels of the same form among different companies. The dosage of a pesticide used in six leaf vegetables was same. Thiophanate-methyl, metalaxyl, and fluazifop-P-butyl were sprayed together, and

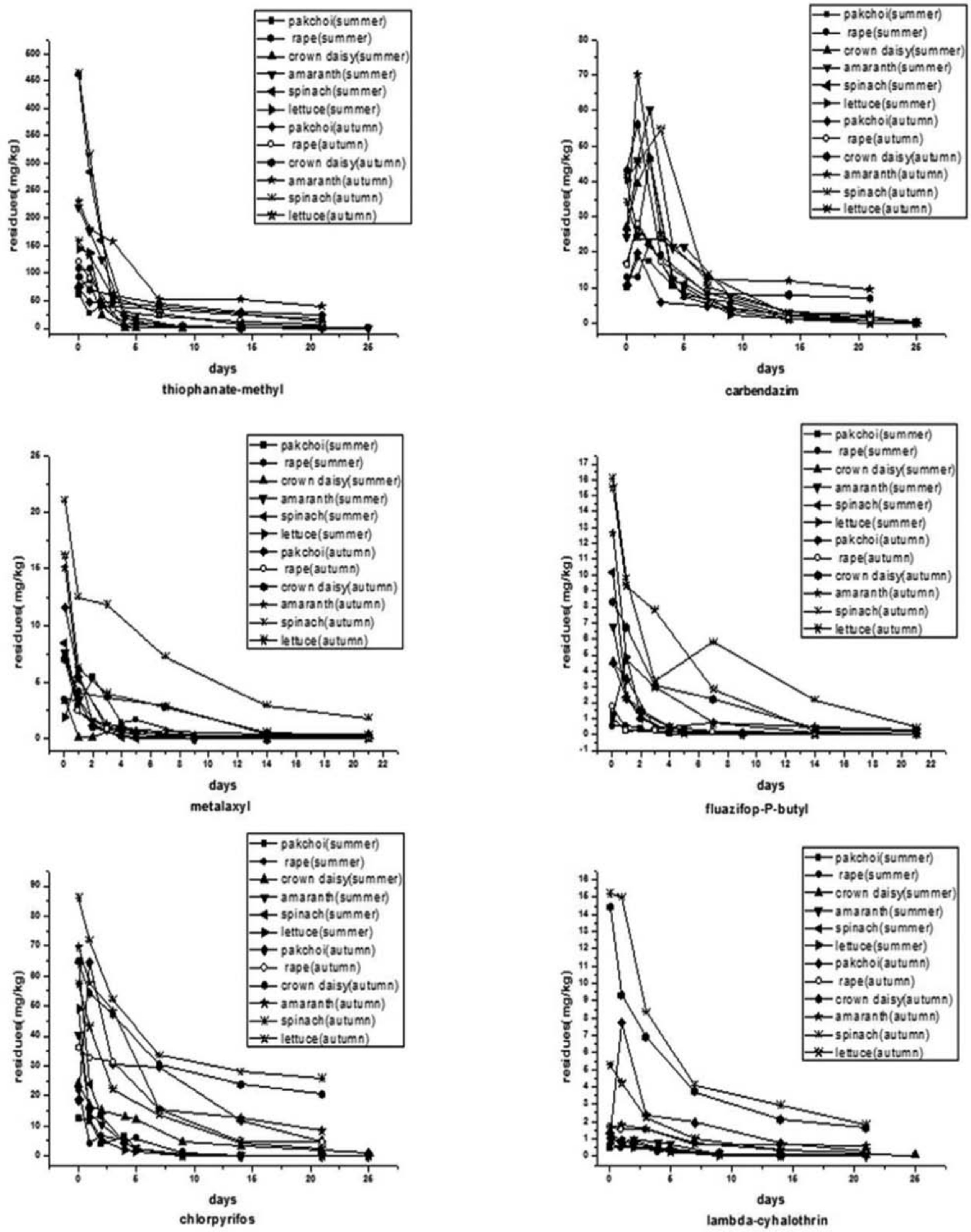

Figure 3. Dissipation curve of thiophanate-methyl, carbendazim, metalaxyl, fluazifop-P-butyl, chlorpyrifos, and λ-cyhalothrin in six leaf vegetable samples in Beijing.

chlorpyrifos and λ-cyhalothrin were sprayed at same time. Blank samples were obtained from a control plot before pesticide applications, which were used for the controls and fortifications. There was only one set of control samples for each vegetable. About 500 g of testing vegetable sample was collected randomly from several points of each plot at 2 h and 1, 2, 3, 5, 7, 14, 21, and 30 days after spraying of the pesticides. Vegetable samples were cut into small pieces and then ground with a homogenizer. All samples were stored at −20 °C until analysis.

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Table 4. Initial Concentrations of Pesticides in Six Leaf Vegetables in Two Planting Seasons (Milligrams per Kilogram)

		Shijiazhuang						Beijing					
leaf vegetable	planting season	thiophanate-methyl	carbendazim	metalaxyl	fluazifop-P-butyl	chlorpyrifos	λ-cyhalothrin	thiophanate-methyl	carbendazim	metalaxyl	fluazifop-P-butyl	chlorpyrifos	λ- cyhalothrin
pakchoi	summer	276.6	45.9	9.1	5.2	91.5	2.1	60.5	18.7	6.7	0.3	9.2	0.5
	autumn	137.6	32.9	13.5	11.6	107.2	2.2	64.0	11.7	4.1	2.9	58.7	3.5
rape	summer	48.0	27.0	1.9	1.8	39.1	1.7	85.4	17.5	4.6	0.5	12.4	0.6
	autumn	72.0	18.3	3.2	4.5	56.7	1.8	79.4	24.5	2.6	0.5	40.5	1.7
crown daisy	summer	124.6	19.4	3.5	10.5	29.5	1.2	72.2	36.7	2.2	3.3	20.2	1.0
	autumn	109.6	13.2	5.4	18.2	64.3	2.4	77.0	34.0	5.8	7.1	58.9	10.2
amaranth	summer	191.1	37.5	3.8	3.5	140.9	2.1	182.1	47.6	6.2	5.2	32.1	1.2
	autumn	204.7	23.5	7.8	20.7	127.8	3.6	178.7	34.4	5.7	5.7	63.1	1.6
spinach	summer	399.3	36.2	17.4	11.0	100.9	5.9	361.8	30.2	7.4	4.8	44.9	1.2
	autumn	227.7	16.7	15.0	22.6	102.3	3.7	346.2	31.3	16.6	11.4	73.8	12.9
lettuce	summer	19.3	16.6	5.9	3.1	65.8	5.0	105.6	41.6	2.0	1.6	27.5	1.2
	autumn	63.0	18.6	7.1	11.6	73.0	2.5	124.4	48.5	9.2	16.4	48.8	4.2

Analytical Method. A modified QuEChERS method was used in sample pretreatment. Ten grams of previously homogenized sample was taken into a 50 mL Teflon centrifuge tube, 10 mL of acetonitrile was added, and sample was mixed thoroughly for 1 min with a vortex mixer. After the addition of 4 g of anhydrous magnesium sulfate and 1 g of sodium chloride, the sample was shaken vigorously for 1 min with a vortex mixer and centrifuged for 5 min at 3800 rpm. After centrifugation, 1 mL of the clarified supernatant was placed into a 2 mL microcentrifuge tube containing 30 mg of PSA sorbent and 150 mg of anhydrous magnesium sulfate. The mixture was shaken vigorously for 1 min and then centrifuged for 3 min at 10000 rpm. The upper extract was filtered through a 0.22 μm filter membrane and transferred into an LC vial for chromatographic analysis.

LC-MS/MS Analysis. Thiophanate-methyl, carbendazim, metalaxyl, and fluazifop-P-butyl were separated by an Agilent 1200 HPLC equipped with a reversed-phase column (ZORBAX SB-C18, 3.5 μm, 2.1 mm × 50 mm, Agilent, USA) at 30 °C. The mobile phase used was acetonitrile/water (containing 0.1% formic acid) (70:30, v/v) with a flow rate of 0.3 mL min^{-1}. The injection volume was 2 μL.

For the mass spectrometric analysis, an Agilent 6410 triple-quadrupole LC-MS system was applied. The ESI source was operated in positive ionization mode, and its parameters were as follows: gas temperature, 350 °C; gas flow, 8 L min^{-1}; nebulizer gas, 35 psi; and capillary voltage, 4000 V. Nitrogen gas served as the nebulizer, and argon gas was used as collision gas. Agilent Mass Hunter Data Acquisition, Qualitative Analysis and Quantitative Analysis software were used for method development and data acquisition. The multiple reaction monitoring (MRM) mode was selected to monitor the precursor-to-product ion transitions. The retention times of thiophanate-methyl, carbendazim, metalaxyl, and fluazifop-P-butyl were 0.59, 0.53, 0.65, and 1.3 min, respectively. LC-MS/MS parameters of these four pesticides are shown in Table 1.

GC Analysis. Chlorpyrifos and λ-cyhalothrin were analyzed by a gas chromatography (Agilent 6890) with an electron capture detector (ECD) equipped with a HP-5 capillary column (30 m length × 0.25 mm i.d. × 0.25 μm film thickness), and nitrogen was used as carrier gas (1.0 mL min^{-1} column flow rate). The temperature of the injection port was 280 °C and the detector temperature, 300 °C. The column temperature was initially at 120 °C for 1 min, raised at 20 °C min^{-1} to 280 °C, and maintained for 10 min. Injection volume was 1 μL in spiltless mode. Under the conditions described above, the retention time of chlorpyrifos was 8.5 min. λ-Cyhalothrin had two peaks with retention times of 12.2 and 12.5 min, respectively, and the sum area of the two peaks was used in quantification.

Statistical Analysis. The degradation rate constant and half-life were calculated using the first-order rate equation $C_t = C_0 e^{-kt}$, where C_t represents the concentration of the pesticide residue at time t, C_0 represents the initial concentration after application, and k is the degradation rate constant (days^{-1}). The half-life ($t_{1/2}$) was calculated from the k value for each experiment ($t_{1/2} = \ln 2/k$).

■ RESULTS AND DISCUSSION

Linearity. Calibration curves were constructed from standard solutions in extracts of six blank matrices, at four different concentrations in the range of 0.01−1.0 mg L^{-1} for all pesticides. Good linearity was found for the pesticides with coefficients of determination (R^2) of >0.99. The limits of quantitantion (LOQs) of pesticides were defined by the ratio of signal/background noise (S/N) 10 in spiked samples. The ratio of S/N of pesticide can be calculated in the soft of Qualitative Analysis. The limits of determination (LODs) of the pesticides were in the range of 0.001−0.01 mg kg^{-1} for all samples. All data are presented in Table 2.

Recovery and Precision of Method. Accuracy and precision of the methods were obtained by spiking 0.01 and 0.1 mg kg^{-1} in six leaf vegetables. Accuracy was evaluated in terms of recovery. The mean recoveries of pesticides from fortified samples in five replicated experiments were in the range

Table 5. Half-Lives (HL) and Other Statistical Parameters (RE, Regression Equation; DE, Determination Coefficient) of Pesticides in Six Leaf Vegetables in Two Planting Seasons

			thiophanate-methyl			carbendazim			metalaxyl			fluazifop-P-butyl			chlorpyrifos			λ-cyhalothrin		
location	matrix	planting season	RE[1]	DE[2] (R^2)	HL[3] (day^{-1})	RE	DE (R^2)	HL (day^{-1})	RE	DE (R^2)	HL (day^{-1})	RE	DE (R^2)	HL (day^{-1})	RE	DE (R^2)	HL (day^{-1})	RE	DE (R^2)	HL (day^{-1})
Shijiazhuang	pakchoi	summer	$C_t = 276.6e^{-0.279t}$	0.928	2.5	$C_t = 45.9e^{-0.197t}$	0.930	3.5	$C_t = 9.1e^{-0.204t}$	0.852	3.4	$C_t = 5.2e^{-0.474t}$	0.879	1.5	$C_t = 91.5e^{-0.500t}$	0.972	1.4	$C_t = 2.1e^{-0.335t}$	0.942	2.1
		autumn	$C_t = 137.6e^{-0.200t}$	0.949	3.5	$C_t = 32.9e^{-0.160t}$	0.950	4.3	$C_t = 13.5e^{-0.820t}$	0.908	0.8	$C_t = 11.6e^{-1.560t}$	0.951	0.4	$C_t = 107.2e^{-0.466t}$	0.914	1.5	$C_t = 2.25e^{-0.437t}$	0.712	1.6
	rape	summer	$C_t = 48.0e^{-0.365t}$	0.975	1.9	$C_t = 27.0e^{-0.206t}$	0.938	3.4	$C_t = 1.9e^{-0.170t}$	0.678	4.1	$C_t = 1.8e^{-0.731t}$	0.892	1.0	$C_t = 39.1e^{-0.537t}$	0.968	1.3	$C_t = 1.7e^{-0.143t}$	0.953	3.7
		autumn	$C_t = 72.0e^{-0.202t}$	0.934	3.4	$C_t = 18.3e^{-0.118t}$	0.904	5.8	$C_t = 3.2e^{-0.189t}$	0.918	3.7	$C_t = 4.5e^{-1.769t}$	0.970	0.4	$C_t = 56.7e^{-0.205t}$	0.950	3.4	$C_t = 1.8e^{-0.120t}$	0.921	5.8
	crown daisy	summer	$C_t = 124.6e^{-0.471t}$	0.970	1.5	$C_t = 19.4e^{-0.258t}$	0.973	2.7	$C_t = 3.5e^{-0.144t}$	0.832	4.8	$C_t = 10.5e^{-0.634t}$	0.978	1.1	$C_t = 29.5e^{-0.512t}$	0.904	1.4	$C_t = 1.2e^{-0.394t}$	0.839	1.8
		autumn	$C_t = 109.6e^{-0.0352t}$	0.705	19.7	$C_t = 13.2e^{-0.0293t}$	0.655	23.7	$C_t = 5.4e^{-0.0891t}$	0.887	7.8	$C_t = 18.2e^{-0.124t}$	0.925	5.6	$C_t = 64.3e^{-0.140t}$	0.797	5.0	$C_t = 2.4e^{-0.147t}$	0.821	4.7
	amaranth	summer	$C_t = 191.1e^{-0.296t}$	0.912	2.3	$C_t = 37.5e^{-0.222t}$	0.888	3.1	$C_t = 3.8e^{-0.230t}$	0.811	3.0	$C_t = 3.5e^{-0.468t}$	0.870	1.5	$C_t = 140.9e^{-1.258t}$	0.983	0.6	$C_t = 2.1e^{-0.448t}$	0.877	1.6
		autumn	$C_t = 204.7e^{-0.0580t}$	0.794	12.0	$C_t = 23.5e^{-0.0435t}$	0.959	15.9	$C_t = 7.8e^{-0.0826t}$	0.792	8.4	$C_t = 20.7e^{-0.0390t}$	0.799	17.8	$C_t = 127.8e^{-0.0881t}$	0.739	7.8	$C_t = 3.6e^{-0.0490t}$	0.663	14.2
	spinach	summer	$C_t = 399.3e^{-0.299t}$	0.957	2.4	$C_t = 36.2e^{-0.218t}$	0.886	3.2	$C_t = 17.4e^{-0.530t}$	0.977	1.2	$C_t = 11.0e^{-0.280t}$	0.931	2.5	$C_t = 100.9e^{-0.564t}$	0.953	1.2	$C_t = 5.9e^{-0.225t}$	0.995	3.1
		autumn	$C_t = 227.7e^{-0.063t}$	0.891	11.0	$C_t = 16.7e^{-0.0564t}$	0.736	12.3	$C_t = 15.0e^{-0.103t}$	0.864	6.7	$C_t = 22.6e^{-0.0487t}$	0.751	14.2	$C_t = 102.3e^{-0.146t}$	0.948	4.8	$C_t = 3.7e^{-0.0511t}$	0.586	13.6
	lettuce	summer	$C_t = 19.3e^{-1.043t}$	0.691	0.7	$C_t = 16.6e^{-0.403t}$	0.812	1.7	$C_t = 5.9e^{-1.222t}$	0.867	0.6	$C_t = 3.1e^{-0.983t}$	0.715	0.7	$C_t = 65.8e^{-0.375t}$	0.884	1.8	$C_t = 5.0e^{-0.279t}$	0.839	2.5
		autumn	$C_t = 63.1e^{-0.0937t}$	0.818	7.4	$C_t = 18.6e^{-0.256t}$	0.796	2.7	$C_t = 7.1e^{-0.588t}$	0.899	1.2	$C_t = 11.6e^{-0.133t}$	0.876	5.2	$C_t = 73.0e^{-0.330t}$	0.757	2.1	$C_t = 2.5e^{-0.108t}$	0.718	6.4
Beijing	pakchoi	summer	$C_t = 60.5e^{-0.491t}$	0.935	1.4	$C_t = 18.7e^{-0.164t}$	0.962	4.2	$C_t = 6.7e^{-0.339t}$	0.947	2.0	$C_t = 0.3e^{-0.265t}$	0.708	2.6	$C_t = 9.2e^{-0.236t}$	0.928	2.9	$C_t = 0.5e^{-0.103t}$	0.894	6.8
		autumn	$C_t = 64.0e^{-0.0754t}$	0.921	9.2	$C_t = 11.7e^{-0.0984t}$	0.838	7.0	$C_t = 4.1e^{-0.144t}$	0.680	4.8	$C_t = 2.9e^{-0.239t}$	0.884	2.9	$C_t = 58.7e^{-0.114t}$	0.894	6.1	$C_t = 3.5e^{-0.110t}$	0.695	6.3
	rape	summer	$C_t = 85.4e^{-0.364t}$	0.899	1.9	$C_t = 17.5e^{-0.163t}$	0.965	4.3	$C_t = 4.6e^{-0.671t}$	0.988	1.0	$C_t = 0.5e^{-0.364t}$	0.775	1.9	$C_t = 12.4e^{-0.278t}$	0.887	2.5	$C_t = 0.6e^{-0.119t}$	0.879	5.8
		autumn	$C_t = 79.4e^{-0.128t}$	0.893	5.4	$C_t = 24.5e^{-0.163t}$	0.962	4.3	$C_t = 2.6e^{-0.157t}$	0.794	4.4	$C_t = 0.5e^{-0.117t}$	0.672	5.9	$C_t = 40.5e^{-0.146t}$	0.980	4.8	$C_t = 1.7e^{-0.105t}$	0.966	6.6
	crown daisy	summer	$C_t = 72.2e^{-0.544t}$	0.796	1.3	$C_t = 36.7e^{-0.212t}$	0.877	3.3	$C_t = 2.2e^{-0.205t}$	0.858	3.4	$C_t = 3.3e^{-0.433t}$	0.927	1.6	$C_t = 20.2e^{-0.124t}$	0.972	5.6	$C_t = 1.0e^{-0.173t}$	0.946	4.0
		autumn	$C_t = 77.0e^{-0.0624t}$	0.943	11.1	$C_t = 34.0e^{-0.0930t}$	0.706	7.4	$C_t = 5.8e^{-0.136t}$	0.921	5.1	$C_t = 7.1e^{-0.184t}$	0.973	3.8	$C_t = 58.9e^{-0.0710t}$	0.936	9.8	$C_t = 10.2e^{-0.0988t}$	0.910	7.0
	amaranth	summer	$C_t = 182.1e^{-0.436t}$	0.922	1.6	$C_t = 47.6e^{-0.186t}$	0.948	3.7	$C_t = 6.2e^{-0.559t}$	0.993	1.2	$C_t = 5.2e^{-0577t}$	0.983	1.2	$C_t = 32.1e^{-0.521t}$	0.995	1.3	$C_t = 1.2e^{-0.198t}$	0.914	3.5
		autumn	$C_t = 178.7e^{-0.0820t}$	0.802	8.4	$C_t = 34.4e^{-0.0703t}$	0.622	9.9	$C_t = 5.7e^{-0.253t}$	0.709	2.7	$C_t = 5.7e^{-0.170t}$	0.848	4.1	$C_t = 63.1e^{-0.130t}$	0.875	5.3	$C_t = 1.6e^{-0.0527t}$	0.752	13.2
	spinach	summer	$C_t = 361.8e^{-0.526t}$	0.975	1.3	$C_t = 30.2e^{-0.239t}$	0.978	2.9	$C_t = 7.4e^{-0.887t}$	0.993	0.8	$C_t = 4.8e^{-0.642t}$	0.931	1.1	$C_t = 44.9e^{-0.569t}$	0.994	1.2	$C_t = 1.2e^{-0.254t}$	0.982	2.7
		autumn	$C_t = 346.2e^{-0.378t}$	0.752	1.8	$C_t = 31.3e^{-0.142t}$	0.940	4.9	$C_t = 16.6e^{-0.111t}$	0.968	6.2	$C_t = 11.4e^{-0.145t}$	0.872	4.8	$C_t = 73.8e^{-0.0791t}$	0.876	8.8	$C_t = 12.9e^{-0.102t}$	0.914	6.8
	lettuce	summer	$C_t = 105.6e^{-0.501t}$	0.935	1.4	$C_t = 41.6e^{-0.266t}$	0.979	2.6	$C_t = 2.0e^{-0.287t}$	0.826	2.4	$C_t = 1.6e^{-0.327t}$	0.776	2.1	$C_t = 27.5e^{-0.614t}$	0.965	1.1	$C_t = 1.3e^{-0.366t}$	0.984	1.9
		autumn	$C_t = 124.4e^{-0.183t}$	0.958	3.8	$C_t = 48.5e^{-0.163t}$	0.902	4.3	$C_t = 9.2e^{-0.173t}$	0.930	4.0	$C_t = 16.4e^{-0.297t}$	0.992	2.3	$C_t = 48.8e^{-0.177t}$	0.974	3.9	$C_t = 4.2e^{-0.159t}$	0.967	4.4

of 60.1−119.1%. Precision was studied as intraday precision and determined by detecting five parallel spiked samples in one day at 0.01 and 0.1 mg kg^{-1} in six leaf vegetables. Precision was expressed by relative standard deviation (RSD). RSDs of pesticides in six leaf vegetables ranged from 1.1 to 13.9%. The recoveries and RSDs are shown in Table 3.

Residue Dynamics of Five Pesticides. The results indicated that on plant surfaces thiophanate-methyl converted to carbendazim very easily. The dissipation curves of thiophanate-methyl, carbendazim, metalaxyl, fluazifop-P-butyl, chlorpyrifos, and λ-cyhalothrin in six leaf vegetable samples in Shijiazhuang and Beijing at two planting seasons are shown in Figures 2 and 3, respectively.

Initial Concentrations of Pesticides. In the first-order rate equation ($C_t = C_0\ e^{-kt}$), C_0 represents the initial concentration after application. The initial concentration was obtained from the matched curve, which was theoretical data and influenced by the residue dynamic. Initial concentrations of pesticides in six leaf vegetables are presented in Table 4. The results showed that the initial concentrations of fluazifop-P-butyl, chlorpyrifos, and λ-cyhalothrin in autumn in six leaf vegetables were higher than those in summer in Beijing. The initial concentrations of thiophanate-methyl, carbendazim, and metalaxyl in autumn were higher than those in summer in half of the six leaf vegetables in Beijing. The initial concentrations of fluazifop-P-butyl in autumn in six leaf vegetables were higher than those in summer in Shijiazhuang. The initial concentrations of metalaxyl in autumn were higher than those in summer in six leaf vegetables except spinach, and the initial concentrations of chlorpyrifos in autumn were higher than those in summer in six leaf vegetables except amaranth in Shijiazhuang. Field experiments over two planting seasons in the same place was conducted by same person, and the spraying technique was the same. Thus, the initial deposit was not influenced by spraying technique, in theory. Therefore, the initial concentration of pesticide was influenced not only by environmental factors such as light, heat, moisture, and rainy climate but also by geographic position and plant matrix.

Half-Lives of Pesticides. The half-lives of thiophanate-methyl in six leaf vegetables in summer were in the range of 0.7−2.5 days and in autumn were in the range of 3.4−19.7 days in Shijiazhuang. Half-lives of carbendazim, metalaxyl, fluazifop-P-butyl, chlorpyrifos, and λ-cyhalothrin in summer were in the range of 1.7−3.5, 0.6−4.8, 0.7−2.5, 0.6−1.8, and 1.6−3.7 days in Shijiazhuang; half-lives of these five pesticides in autumn were in the range of 2.7−23.7, 0.8−8.4, 0.4−17.8, 1.5−7.8, and 1.6−14.2 days. Except for metalaxyl and fluazifop-P-butyl in pakchoi and rape and λ-cyhalothrin in pakchoi, the half-lives of the pesticides in six leaf vegetables in autumn were longer than those in summer in Shijiazhuang. Except for λ-cyhalothrin in pakchoi, the half-lives of the pesticides in six leaf vegetables in autumn were longer than those in summer in Beijing. $C_t = C_0\ e^{-kt}$, half-lives, and R^2 values of residue dissipation are summarized in Table 5.

Maximal Concentrations of Six Pesticides. Maximal concentration was the highest concentration of pesticide after application in vegetables in the field trial. All maximal concentrations of pesticides in six leaf vegetables in autumn were higher than those in summer in Beijing. The situation was the same in Shijiazhuang except for fluazifop-P-butyl in pakchoi. The maximal concentration of thiophanate-methyl in spinach in autumn in Beijing reached as high as 465.3 mg/kg. All data are summarized in Table 6. Like initial concentration, the maximal concentration of pesticide was influenced not only by environmental

Table 6. Maximal Concentrations of Pesticides in Six Leaf Vegetables in Two Planting Seasons (Milligrams per Kilogram)

		Shijiazhuang						Beijing					
leaf vegetable	planting season	thiophanate-methyl	carbendazim	metalaxyl	fluazifop-P-butyl	chlorpyrifos	λ-cyhalothrin	thiophanate-methyl	carbendazim	metalaxyl	fluazifop-P-butyl	chlorpyrifos	λ-cyhalothrin
pakchoi	summer	226.1	39.8	15.0	5.4	104.7	2.1	61.5	18.2	7.5	0.9	12.5	0.6
	autumn	246.8	44.1	18.9	5.2	110.2	2.8	74.6	19.7	11.6	4.5	64.4	7.7
rape	summer	47.7	31.0	7.6	2.2	41.0	2.1	107.1	22.8	3.5	0.5	21.9	0.7
	autumn	107.5	33.7	7.9	4.2	106.2	2.9	120.4	28.0	7.1	1.7	36.1	1.7
crown daisy	summer	92.5	15.3	7.6	10.3	47.8	1.7	88.2	46.7	4.5	3.4	24.0	0.9
	autumn	156.4	17.6	7.9	22.2	117.4	3.4	93.2	56.1	7.0	8.3	64.7	1.9
amaranth	summer	249.7	23.1	15.4	5.9	153.0	2.6	219.9	60.4	6.8	7.6	40.6	1.0
	autumn	298.6	24.7	16.7	29.7	284.9	7.4	230.3	70.0	15.1	12.7	69.5	1.9
spinach	summer	241.9	13.4	23.0	23.4	138.2	6.7	461.0	27.3	10.1	8.4	64.6	1.3
	autumn	278.6	21.7	25.5	33.5	150.2	8.5	465.3	33.9	21.1	16.1	86.0	15.2
lettuce	summer	97.9	22.9	9.8	13.1	100.6	6.5	143.2	46.9	4.9	6.1	49.0	1.2
	autumn	129.9	24.1	10.6	22.8	117.7	6.9	157.8	54.5	16.2	15.5	57.3	5.3

factors such as light, heat, moisture, and rainy climate but also by geographic position and plant matrix.

Conclusions. The method described above is suitable for determination of these pesticides in six leaf vegetables. Average recoveries of pesticides in six leaf vegetables were in the range of 60.1−119.1% at 0.01 and 0.1 mg kg^{-1} spiked levels. RSDs ranged from 1.1 to 13.9%. All maximal concentrations of pesticides in six leaf vegetables in autumn were higher than those in summer in Beijing. The situation was the same in Shijiazhuang except for fluazifop-P-butyl in pakchoi. For most pesticides half-lives in autumn were longer than those in summer. The results showed that the initial concentrations, maximal concentrations, and half-lives of pesticides were influenced not only by environmental factors such as light, heat, moisture, and rainy climate but also by plant matrix. The results of experiments give us advice on rational application of pesticides and some clues about residue violation of some samples produced in autumn. The findings also suggest that further risk assessment evaluations may be necessary from the viewpoint of different season samples.

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