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Spinach or Amaranth Contains Highest Residue of Metalaxyl, Fluazifop-P-butyl, Chlorpyrifos, and Lambda-cyhalothrin on Six Leaf Vegetables upon Open Field Application

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ABSTRACT: To select representative leaf vegetables which may contain the highest residue, field experiments of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin on six crops including pakchoi, rape, crown daisy, amaranth, spinach, and lettuce were designed and conducted. In this study, a high-performance liquid chromatograph and electrospray ionization tandem mass spectrometer with multiple reaction monitoring was used to simultaneously determine metalaxyl and fluazifop-P-butyl residue in various samples, and a gas chromatograph with electron capture detector was used to detect chlorpyrifos and lambda-cyhalothrin. The limits of quantification (LOQ) of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin were in the range of 0.001−0.01 mg kg^{-1} for all samples, and the average recoveries of all pesticides ranged from 67.6 to 119.1% at spiked levels of 0.01−0.1 mg kg^{-1}. In supervised field trials, the half-lives of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin were in the range of 1.11−3.79 days, 1.11−2.27 days, 1.13−5.17 days, and 1.77−6.24 days. It was also found that all pesticide residues in spinach and/or amaranth were higher than others after application. It is recommended that spinach or amaranth can be selected as a representative crop of leaf vegetables in studying systemic fungicide, insecticides, and herbicides with similarity as metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin.

KEYWORDS: *metalaxyl, fluazifop-P-butyl, chlorpyrifos, lambda-cyhalothrin, leaf vegetables, representative crop, residues*

INTRODUCTION

Leaf vegetables, especially pakchoi, rape, crown daisy, amaranth, spinach, and lettuce, are widely cultivated in China, while, to control pests and diseases, more than 800 pesticides belonging to over 100 different chemical classes are widely used in agricultural practice worldwide.[1] Now the registration of a pesticide, except field experiments for evaluation of its effect and various toxicological studies, requires extensive field experiments for the evaluation of their residue on different crops and in different places.[2] Classification of crops or products and selection of a represent crop are intended to promote the process.[3] Metalaxyl is a systemic fungicide used to control plant diseases caused by Oomycete fungi. Application may be by foliar or soil incorporation, surface spraying (broadcast or band), drenching, and seed treatment. Due to its broad-spectrum activity, metalaxyl is used worldwide on a variety of fruit and vegetable crops. Its effectiveness results from inhibition of uridine incorporation into RNA and specific inhibition of RNA polymerase-1.[4] Fluazifop-P-butyl is a selective herbicide for control of annual and perennial grasses in many broadleaf crops.[5] Chlorpyrifos is an organophosphorus compound that displays broad-spectrum insecticidal activity against a number of important arthropod pests. So, it is employed in a wide variety of agricultural and specialty pest control scenarios.[6] Lambda-cyhalothrin is a broad-spectrum pyrethroid insecticide used to control a wide range of insect pests in a variety of crops. Application rates in field crops typically range from 0.005 to 0.015 kg (a.i.) ha^{-1}.[7] The four pesticides mentioned above are used in the cultivation of leaf vegetables. The chemical structures of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin are presented in Figure 1.

Gas chromatographic methods were used to determine metalaxyl, chlorpyrifos, and lambda-cyhalothrin in fruits and vegetables.[8,9] However, there is a clear tendency to use liquid chromatographic techniques in the determination of pesticide residues.[10] Fluazifop-P-butyl had been determined by high-performance liquid chromatography (HPLC) with ultraviolet (UV) detector or with mass spectrometer detector (MSD).[11]

The QuEChERS (quick, easy, cheap, effective, rugged, and safe) method was introduced by Anastassuades et al. in 2003.[12] The procedure involved miniaturized extraction with acetonitrile, liquid−liquid partitioning, and a cleanup step which was carried out by mixing the acetonitrile extract with loose sorbents.[13] In the current study, a modified QuEChERS extraction was used in sample pretreatment.[14−16]

The present study was designed to investigate the residue decline of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin in pakchoi, rape, crown daisy, amaranth, spinach, and lettuce according to the registered GAP conditions and select a representative crop among the crop type of leaf vegetables.

MATERIALS AND METHODS

Chemicals and Reagents. Metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin standard materials were provided by Institute for the Control of Agrochemicals, Ministry of Agriculture, China (ICAMA). The chemical structures of four pesticides are presented in Figure 1. Mixed standard solutions were prepared and stored at −20 °C (with concentration of 10 mg L^{-1}). Metalaxyl wettable powder (10%): Yixing Sinon Chemical Co. LTD (Jiangsu, China). Fluazifop-P-butyl miscible oil (15%): Ishihara Taurus Pesticide Co.

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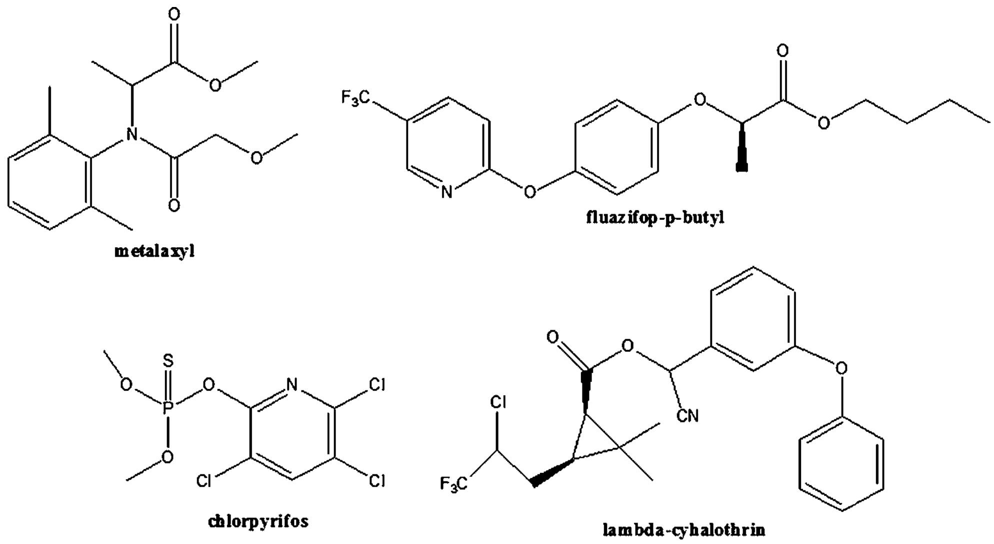

Figure 1. The chemical structures of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin.

Table 1. LC−MS/MS Parameters of Two Pesticides

pesticide	retention time (min)	fragmentor (V)	quantifying ions	qualifying ions	collision energy (V)
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

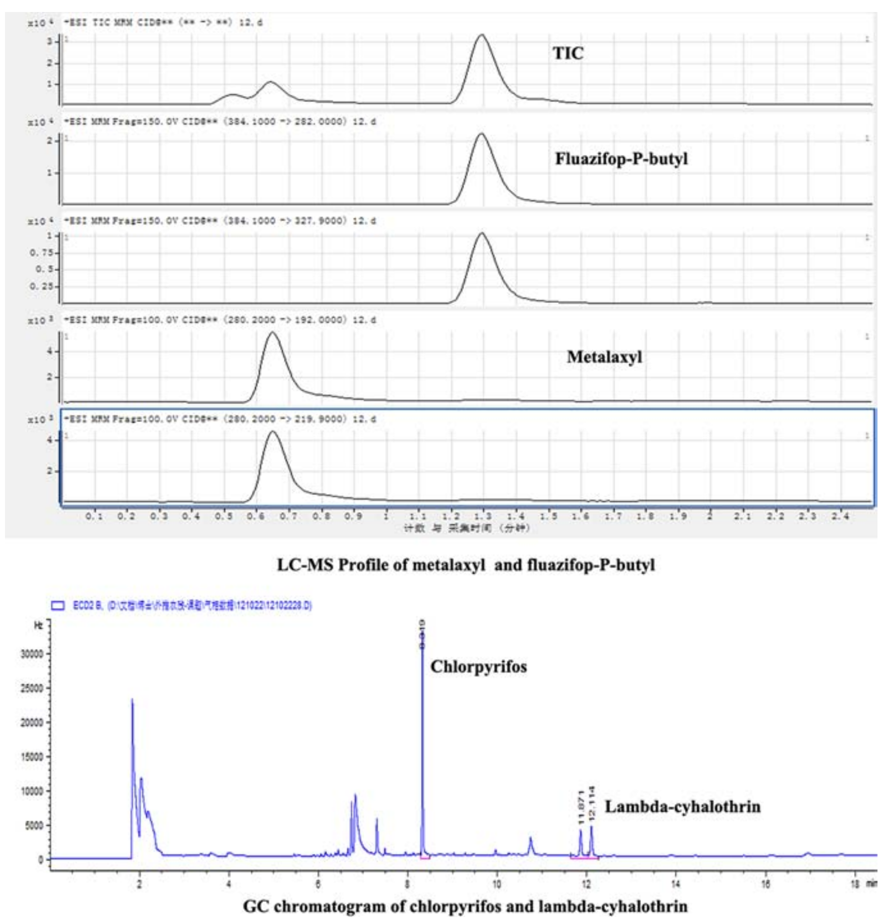

Figure 2. LC−MS profiles of metalaxyl and fluazifop-P-butyl and GC chromatogram of chlorpyrifos and lambda-cyhalothrin.

LTD (Zhejiang, China). Chlorpyrifos miscible oil (480g L^{-1}): Dow AgroSciences LLC. Lambda-cyhalothrin mircoemulsion (5%): Nuopuxin Chemical Co. LTD (Shenzhen, China). Acetonitrile, HPLC-grade: Honeywell Burdick & Jackson (Muskegon, USA). Sodium chloride, analytical grade: Beijing Reagent Company. Primary secondary amine (PSA): Agilent Technologies. Deionized water (18 M cm^{-1}) was prepared by a Milli-Q Pure treatment system (Millipore, USA). Anhydrous magnesium sulfate (Beijing Reagent Company, analytical grade) was heated at 120 °C for 5 h and allowed to cool to room temperature before use.

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

matrix	standard curve equation	R^2	linear range (mg/kg)
	Metalaxyl		
pakchoi	$y = 36{,}109.8x - 1{,}206.8$	0.993	0.01−10
rape	$y = 91{,}183.1x + 701.1$	0.999	0.01−10
crown daisy	$y = 128{,}849.6x + 5{,}875.6$	0.999	0.005−10
amaranth	$y = 101{,}708.7x + 536.2$	0.999	0.01−10
spinach	$y = 124{,}465.8x - 2{,}838.2$	0.995	0.005−10
lettuce	$y = 120{,}857.4x + 1{,}079.7$	0.999	0.01−10
	Fluazifop-P-butyl		
pakchoi	$y = 131{,}631.2x - 2{,}080.8$	0.998	0.001−20
rape	$y = 148{,}417.8x - 4{,}630.4$	0.999	0.002−10
crown daisy	$y = 125{,}911.9x + 78.2$	0.999	0.001−10
amaranth	$y = 128{,}007.2x + 383.2$	0.999	0.002−10
spinach	$y = 135{,}209.6x - 2{,}108.6$	0.998	0.001−10
lettuce	$y = 170{,}106.4x - 5{,}986.1$	0.998	0.002−10
	Chlorpyrifos		
pakchoi	$y = 93{,}482.9x - 311.8$	0.999	0.005−10
rape	$y = 100{,}990.1x + 1{,}148.8$	0.999	0.005−10
crown daisy	$y = 102{,}545.9x - 1{,}659.5$	0.998	0.002−10
amaranth	$y = 112{,}042.4x + 321.0$	0.998	0.005−20
spinach	$y = 113{,}438.5x + 1{,}363.8$	0.999	0.005−20
lettuce	$y = 113{,}023.4x + 387.4$	0.999	0.005−10
	Lambda-cyhalothrin		
pakchoi	$y = 58{,}581.8x - 1{,}841.6$	0.994	0.01−10
rape	$y = 62{,}852.5x - 2{,}832.2$	0.998	0.01−10
crown daisy	$y = 67{,}374.8x - 4{,}245.1$	0.997	0.005−10
amaranth	$y = 53{,}708.9x - 877.9$	0.991	0.01−10
spinach	$y = 71{,}059.6x - 1{,}712.4$	0.997	0.01−10
lettuce	$y = 55{,}026.6x - 181.6$	0.999	0.01−10

Field Experiments and Sampling. The field trials including the dissipation study were designed according to the pesticide label. The supervised field trials were carried out in 2012 between June and August at two sites: Beijing, Hebei Province, China. The area of the experiment plot was 10 m^2 (5 m × 2 m), and each treatment was designed with three replicated plots. A buffer area was maintained between the plots.

The rate of application in dissipation experiments for metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin was 1800, 1050, 1500, and 360 g (a.i.)/ha (double of the recommended dosage) with one time spray. The recommended dosage is the highest dosage in the pesticide label among different companies for the same form of a pesticide. The recommended dosage of a pesticide for six leaf vegetables was the same for the reason that one pesticide was usually used for one category of agriculture products. Metalaxyl and fluazifop-P-butyl were sprayed together, while chlorpyrifos and lambda-cyhalothrin were sprayed at the same time. The vegetable samples were collected in 2 h, 1, 2, 3, 5, 7, 14, 21, and 30 days after spraying of the pesticides. The collected vegetable samples were stored at −20 °C in the freezer.

About 500 g samples were collected randomly from several points from each plot. Vegetable samples were cut into small pieces and then ground with a mechanical slicer. All samples were stored at −20 °C until analyzed.

Extraction and Cleanup of Samples. A modified QuEChERS extraction was used in sample pretreatment. 10 g of previously homogenized samples were taken into a 50 mL Teflon centrifuge tube, 10 mL of acetonitrile was added, and then samples were mixed thoroughly for 1 min with a vortex mixer. After addition of 4 g of anhydrous magnesium sulfate and 1 g of sodium chloride, the samples were vortexed immediately for 1 min and centrifuge extracted for 5 min at 3800 rpm. An aliquot of 1 mL of the upper layer was placed into a 2 mL microcentrifuge

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

		metalaxyl		fluazifop-P-butyl		chlorpyrifos		lambda-cyhalothrin	
matrix	spiked level (mg/kg)	recovery (%)	RSD (%)	recovery (%)	RSD (%)	recovery (%)	RSD (%)	recovery (%)	RSD (%)
pakchoi	0.01	80.9	10.5	92	7.8	88.1	13.9	94.6	13.9
	0.1	100.4	5.4	113.6	1.4	108.9	3.0	110.1	3.0
rape	0.01	90.6	7.4	83	7.2	81.2	8.8	81.2	11.4
	0.1	103.5	3.5	95.9	1.4	88.3	2.8	75.7	10.9
crown daisy	0.01	95.2	12.3	85.3	2.7	108.4	8.7	84.9	8.2
	0.1	114.6	11.5	102.9	9.2	106.8	5.9	98.1	10.4
amaranth	0.01	93.2	3.5	89.2	6.5	98.4	5.9	117.0	11.5
	0.1	92.7	2.1	104.7	2.5	99.0	7.4	91.6	8.7
spinach	0.01	92.5	10.0	93.6	2.7	83.9	1.4	71.2	12.8
	0.1	110.0	8.3	119.1	2.6	108.6	3.5	113.5	3.6
lettuce	0.01	110.8	9.1	94.5	6	104.0	10.5	67.7	10.0
	0.1	95.9	1.1	111.9	3.2	110.7	5.9	112.6	6.0

Table 4. Initial Concentrations of Four Pesticides in Six Leaf Vegetables (mg kg^{-1})

	Shijiazhuang				Beijing			
leaf vegetables	metalaxyl	fluazifop-P-butyl	chlorpyrifos	lambda-cyhalothrin	metalaxyl	fluazifop-P-butyl	chlorpyrifos	lambda-cyhalothrin
pakchoi	15.0	4.93	104.7	2.11	7.53	0.95	12.4	0.47
rape	7.58	2.15	41.0	2.13	3.47	0.53	21.9	0.66
crown daisy	7.55	10.3	47.8	1.69	3.41	4.55	24.0	0.90
amaranth	15.4	5.9	153.0	2.65	7.61	6.77	40.6	0.91
spinach	23.0	23.4	138.2	6.67	8.44	10.1	64.6	1.29
lettuce	8.98	7.53	28.5	1.46	1.93	1.29	49.0	1.16

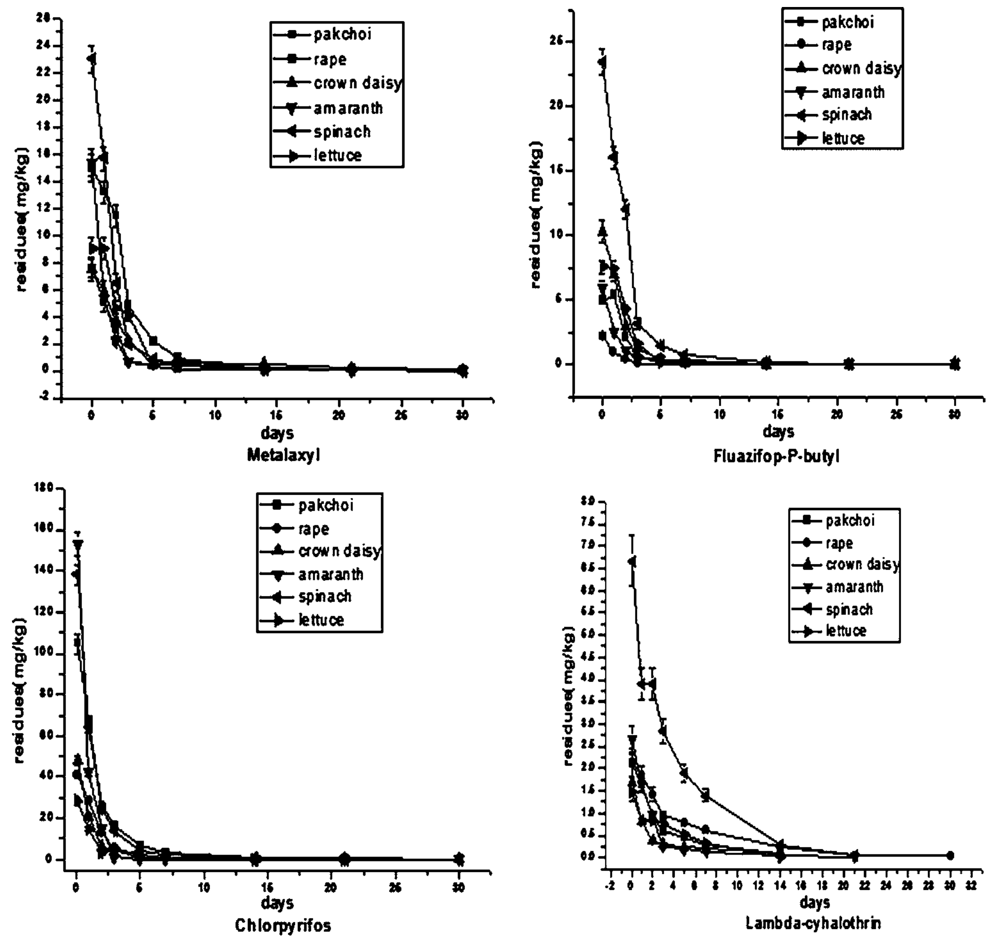

Figure 3. Dissipation curves of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin in six leaf vegetables in Shijiazhuang.

tube containing 30 mg of primary secondary amine (PSA) sorbent and 150 mg of anhydrous magnesium sulfate. The samples were vortexed for 1 min and then centrifuged for 3 min at 10000 rpm. The upper extracts were filtered through a 0.22 μm filter membrane and transferred into an autosampler vial for analysis.

LC−MS/MS Analysis. Determinations of metalaxyl and fluazifop-P-butyl were performed in 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, 8L min^{-1}; nebulizer gas, 35 psi; and capillary voltage, 4000 V. Nitrogen gas served as the nebulizer and collision gas. Agilent MassHunter data acquisition, qualitative analysis, and quantitative analysis software was 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 time of metalaxyl and fluazifop-P-butyl was 0.65 and 1.3 min, respectively. The LC−MS/MS parameters of two pesticides are shown in Table 1. The LC−MS profiles of metalaxyl and fluazifop-P-butyl are presented in Figure 2.

GC Analysis. Chlorpyrifos and lambda-cyhalothrin were analyzed by a gas chromatograph (Agilent GC 6890) with 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). The temperature of the injection port was 280 °C, 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. The injection volume was 1 μL in a splitless mode. Under the conditions described above, the retention time of chlorpyrifos was 8.5 min while lambda-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. GC chromatograms of chlorpyrifos and lambda-cyhalothrin are presented in Figure 2.

RESULTS AND DISCUSSION

Method Validation. Different concentrations of working solutions (0.01, 0.1, 0.5, 1 mg L^{-1}) were prepared by diluting the stock solution in acetonitrile. Quantification was accomplished using the standard curve constructed by plotting analyte concentrations against peak areas. Good linearity was achieved between 0.002 and 20 mg L^{-1}, and the correlation coefficient was in the range of 0.991−0.999. The limits of quantification (LOQ) at a signal-to-noise (S/N) ratio of 10 for the four analytes were in the range of 0.001−0.01 mg kg^{-1} for all samples. All data are presented in Table 2.

The mean recoveries of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin from fortified samples in five replicated experiments were in the range 80.9 −114.6%, 83−119.1%, 81.2−110.7%, and 67.7−117% at two spiked levels (0.01 and 0.1 mg kg^{-1}). The relative standard deviation (RSD) ranged from 1.1% to 13.9%. The recovery and RSD are shown in Table 3.

Initial Concentrations of Four Pesticides. Initial concentrations of four pesticides in six leaf vegetables are presented in Table 4. The results show that the initial concentration of metalaxyl, fluazifop-P-butyl, and lambda-cyhalothrin in spinach was the highest, and the initial concentration of chlorpyrifos in amaranth was higher than the others in Shijiazhuang. The initial

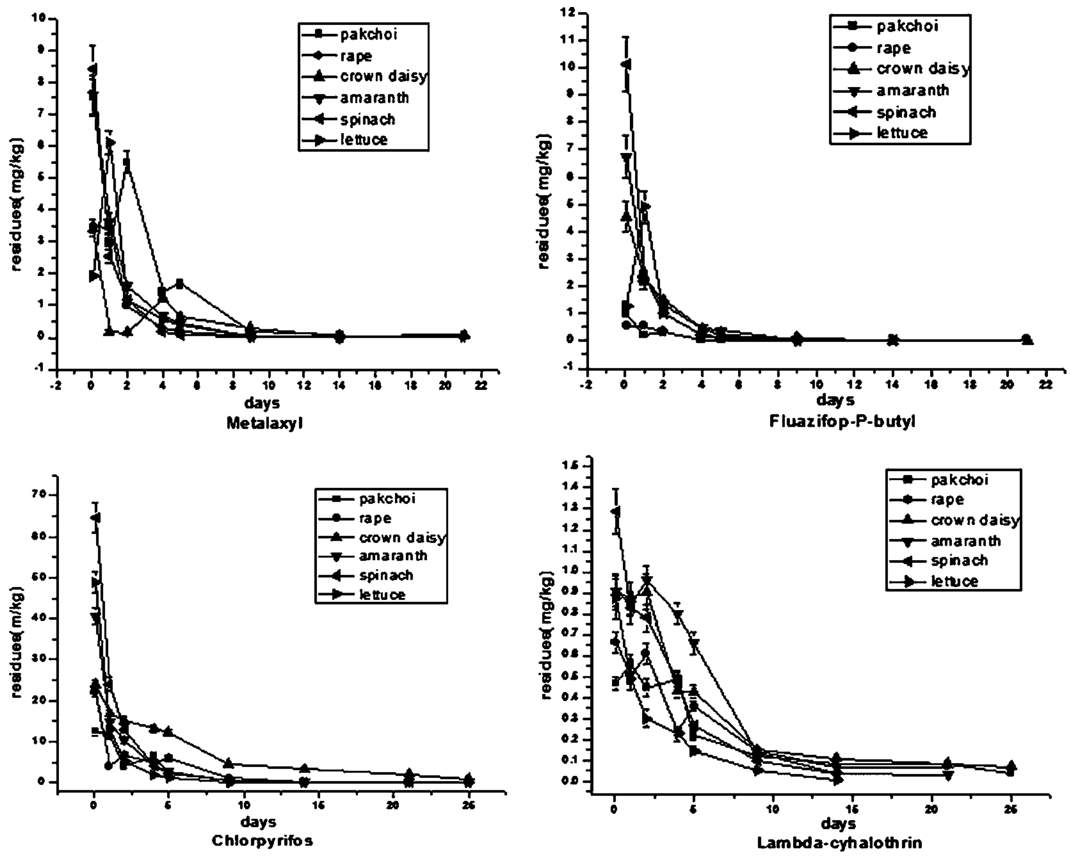

Figure 4. Dissipation curves of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin in six leaf vegetables in Beijing.

concentrations of four pesticides in spinach were the highest in Beijing.

Maximal Concentrations of Four Pesticides. The maximal concentrations of metalaxyl were in agreement with the initial concentrations in the six leaf vegetables except lettuce in Shijiazhuang, and the maximal concentration of metalaxyl reached 23.0 mg kg^{-1}. The maximal concentration of fluazifop-P-butyl in pakchoi was appeared at 1 day after spray and reached 23.4 mg kg^{-1} in spinach. The maximal concentration of chlorpyrifos and lambda-cyhalothrin was 153 mg kg^{-1} in amaranth and 6.67 mg kg^{-1} in spinach. The situation was similar in Beijing; the maximal concentrations of four pesticides were found in spinach.

Residue Dynamics of Four Pesticides. The dissipation curve of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin in six leaf vegetable samples in Shijiazhuang are listed in Figure 3. The dissipation curves of the four pesticides in six leaf vegetable samples in Beijing are listed in Figure 4. The dissipation process follows the first-order kinetic reaction. The degradation rate constant and half-life were calculated using the first-order rate equation $C_t = C_o e^{-kt}$, where C_t represents the concentration of the pesticide residue at time t, C_o represents the maximal concentration after application, and k is the dissipation degradation rate constant ($days^{-1}$). The half-life ($t_{1/2}$) was calculated from the k value for each experiment ($t_{1/2} = \ln 2/k$). $C_t = C_o e^{-kt}$, half-life, and R^2 of residue dissipation are summarized in Table 5.

The half-life of metalaxyl in six leaf vegetables was in the range of 1.11−3.79 days. Half-lives of fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin were in the range of 1.11−2.27 days, 1.13−5.17 days, and 1.77−6.24 days. Dissipation of lambda-cyhalothrin in leaf vegetables was lower than that of the other three pesticides. We noticed that the half-life of analytes in Shijiazhuang was longer than that in Beijng for most vegetables. The half-life of pesticides in six leaf vegetables differed among the two experiment sites in Shijiazhuang and Beijing because of the effect of environment factors like light, heat, moisture, rainy climate, and growth dilution factor.

Conclusions. The method described for residue analysis of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin is suitable for determining residues in six leaf vegetables. Average recoveries for analytes in six leaf vegetables were in the range of 67.6−119.1% at two spiked levels with 0.01 and 0.1 mg kg^{-1}. The relative standard deviation (RSD) ranged from 1.1% to 13.9%. The maximal concentrations of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin in spinach and amaranth were higher than others. The half-life of pesticides in six leaf vegetables differed among the two experiment sites in Shijiazhuang and Beijing because of the effect of environmental factors like light, heat, moisture, rainy climate, and growth dilution factor. We know that the dissipation behavior of pesticides can be influenced by seasons, so, it is essential to study the dissipation behavior of pesticides at different seasons. In our further study, the dissipation behavior of pesticides at different seasons will be involved. It should be noted that in our study the trials were conducted only at two different sites and only four representative pesticides. Spinach or amaranth contains the highest residues of metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin on six leaf vegetables upon open field application in the study. It is recommended that spinach or amaranth may be selected as a representative crop of leaf vegetables in studying systemic fungicide, insecticides, and herbicides with

Table 5. Half-Life and Other Statistical Parameters for Four Pesticides in Six Leaf Vegetables

matrix	locality	metalaxyl regression eq	metalaxyl determination coeff (R^2)	metalaxyl half-life (day^{-1})	fluazifop-P-butyl regression eq	fluazifop-P-butyl determination coeff (R^2)	fluazifop-P-butyl half-life (day^{-1})	chlorpyrifos regression eq	chlorpyrifos determination coeff (R^2)	chlorpyrifos half-life (day^{-1})	lambda-cyhalothrin regression eq	lambda-cyhalothrin determination coeff (R^2)	lambda-cyhalothrin half-life (day^{-1})
pakchoi	Beijing	$C_t = 7.53\ e^{-0.352t}$	0.945	1.97	$C_t = 0.95\ e^{-0.529t}$	0.785	1.31	$C_t = 12.5\ e^{-0.253t}$	0.919	2.74	$C_t = 0.56\ e^{-0.111t}$	0.883	6.24
	Hebei	$C_t = 15.0\ e^{-0.229t}$	0.826	3.03	$C_t = 5.36\ e^{-0.306t}$	0.892	2.27	$C_t = 104.7\ e^{-0.347t}$	0.935	2.00	$C_t = 2.11\ e^{-0.257t}$	0.924	2.70
rape	Beijing	$C_t = 3.47\ e^{-0.625t}$	0.980	1.11	$C_t = 0.53\ e^{-0.378t}$	0.774	1.83	$C_t = 21.9\ e^{-0.320t}$	0.849	2.17	$C_t = 0.66\ e^{-0.131t}$	0.862	5.29
	Hebei	$C_t = 7.58\ e^{-0.425t}$	0.841	1.53	$C_t = 2.15\ e^{-0.499t}$	0.771	1.39	$C_t = 41.0\ e^{-0.483t}$	0.971	1.44	$C_t = 2.13\ e^{-0.179t}$	0.982	3.87
crown daisy	Beijing	$C_t = 3.41\ e^{-0.234t}$	0.787	2.96	$C_t = 4.55\ e^{-0.422t}$	0.914	1.64	$C_t = 24.0\ e^{-0.134t}$	0.960	5.17	$C_t = 0.90\ e^{-0.12t}$	0.881	5.78
	Hebei	$C_t = 7.55\ e^{-0.183t}$	0.701	3.79	$C_t = 10.3\ e^{-0.505t}$	0.925	1.37	$C_t = 47.8\ e^{-0.611t}$	0.849	1.13	$C_t = 1.69\ e^{-0.392t}$	0.649	1.77
amaranth	Beijing	$C_t = 7.61\ e^{-0.582t}$	0.989	1.19	$C_t = 6.77\ e^{-0.622t}$	0.974	1.11	$C_t = 40.6\ e^{-0.382t}$	0.845	1.82	$C_t = 0.96\ e^{-0.183t}$	0.904	3.88
	Hebei	$C_t = 15.4\ e^{-0.804t}$	0.850	0.86	$C_t = 5.90\ e^{-0.433t}$	0.764	1.60	$C_t = 153\ e^{-1.28t}$	0.983	0.54	$C_t = 2.65\ e^{-0.299t}$	0.776	2.32
spinach	Beijing	$C_t = 8.44\ e^{-0.521t}$	0.609	1.33	$C_t = 10.1\ e^{-0.579t}$	0.690	1.20	$C_t = 64.6\ e^{-0.505t}$	0.962	1.37	$C_t = 1.29\ e^{-0.264t}$	0.979	2.63
	Hebei	$C_t = 23.0\ e^{-0.354t}$	0.788	1.96	$C_t = 23.4\ e^{-0.319t}$	0.893	2.17	$C_t = 138\ e^{-0.333t}$	0.784	2.08	$C_t = 6.67\ e^{-0.233t}$	0.992	2.98
lettuce	Beijing	$C_t = 6.13\ e^{-0.613t}$	0.891	1.13	$C_t = 4.91\ e^{-0.601t}$	0.768	1.15	$C_t = 49.0\ e^{-0.406t}$	0.709	1.71	$C_t = 1.16\ e^{-0.357t}$	0.983	1.89
	Hebei	$C_t = 9.04\ e^{-0.427t}$	0.958	1.62	$C_t = 7.53\ e^{-0.551t}$	0.894	1.26	$C_t = 28.5\ e^{-0.390t}$	0.804	1.78	$C_t = 1.46\ e^{-0.266t}$	0.966	2.61

similarity as metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin, which need further validation. The results of dissipation were studied to provide data for metalaxyl, fluazifop-P-butyl, chlorpyrifos, and lambda-cyhalothrin supervised residue trials.

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Notes

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■ REFERENCES

(1) Singh, S. B.; Foster, G. D; Khan, S. U. Determination of thiophanate methyl and carbendazim residues in vegetable samples using microwave-assisted extraction. *J. Chromatogr., A* **2007**, *1148*, 152−157.

(2) Mestres, G.; Mestres, R. Crop Groupings: A Survey of its Possibilities for Deltamethrin Registration. *Arch. Environ. Contam. Toxicol.* **1985**, *14*, 321−324.

(3) Muller, E. Establishment of Maximum Residue Levels for minor uses. *Bull. OEPP/EPPO* **2007**, *37*, 215−218.

(4) Sukul, P.; Spiteller, M. Metalaxyl: persistence, degradation, metabolism, and analytical methods. *Rev. Environ. Contam. Toxicol.* **2000**, *164*, 1−26.

(5) Friesen, G. H.; Wall, D. A. Effect of Application on Efficacy of Fluazifop-P-Butyl in Flax. *Weed Technol.* **1991**, *5*, 504−508.

(6) Racke, K. D. Environmental fate of chlorpyrifos. *Rev. Environ. Contam. Toxicol.* **1993**, *131*, 1−150.

(7) Leistra, M.; Zweers, A. J.; Warinton, J. S.; Crum, S.J. H.; Hand, L. H.; Beltman, W. H. J.; Maund, S. J. Fate of insectide lambda-cyhalothrin in ditch enclosures differing in vegetation density. *Pest Manage. Sci.* **2003**, *60*, 75−84.

(8) Oliva, J.; Navarro, S.; Barba, A.; Navarro, G. Determination of chlorpyrifos, penconazole, fenarimol, vinclozolin and metalaxyl in grapes, must and wine by on-line microextraction and gas chromatography. *J. Chromatogr., A* **1999**, *833*, 43−51.

(9) Seenivasan, S.; Muraleedharan, N. N. Residues of lambda-cyhalothrin in tea. *Food Chem. Toxicol.* **2009**, *47*, 502−505.

(10) Pous, X.; Ruíz, M. J.; Picó, Y.; Font, G. Determination of imidacloprid, metalaxyl, mycolbutanil, propham, and thiabendazole in fruits and vegetables. *Fresenius' J. Anal. Chem.* **2001**, *371*, 182−189.

(11) Wigfield, Y. Y.; Lanouette, M. Supercritical Fluid Extraction of the Fortified Residues of Fluazifop-P-butyl (Fusilade II) and Its Major Metabolite, Fluazifop-P, in Onions. *J. Agric. Food Chem.* **1993**, *41*, 84−88.

(12) Anastassiades, M.; Lehotay, S. J.; Štajnbaher, D.; Schenck, F. J. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residue in produce. *J. AOAC Int.* **2003**, *86*, 412−431.

(13) Zhao, P. Y.; Wang, L.; Luo, J. H.; Li, J. H.; Pan, C. P. Determination of pesticide residues in complex matrices using multi-walled carbon nanotubes as reversed-dispersive solid-phase extraction sorbent. *J. Sep. Sci.* **2012**, *35*, 153−158.

(14) Chen, L.; Li, X. S.; Wang, Z. Q.; Pan, C. P.; Jin, R. C. Residue dynamics of procymidone in leeks and soil in greenhouses by smoke generator application. *Ecotoxicol. Environ. Saf.* **2010**, *73*, 73−33.

(15) Koesukwiwat, U.; Sanguankaew, K.; Leepipatpiboon, N. Rapid determination of phenoxy acid residues in rice by modified QuEChERS extraction and liquid chromatography-tandem mass spectrometry. *Anal. Chim. Acta* **2008**, *626*, 10−20.

(16) Wang, L.; Xu, J.; Zhao, P. Y.; Pan, C. P. Dissipation and residues of fluroxypyr-methyl in rice and environment. *Bull. Environ. Contam. Toxicol.* **2011**, *86*, 449−453.