

Degradable Residues Characterization and possible MRL setting for Albendazole, Flusilazole and Imazalil in Tobacco Leaves

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Abstract:

A modified QuEChERS method combined HPLC-MS/MS was developed for three fungicides (albendazole, flusilazole and imazalil), which are used for the control of tobacco leaf spot diseases. The method and the detection data could be applied for the study of residue characteristics of the fungicides under field conditions, and the results could provide references for the establishment of MRLs. The sensitivity, accuracy and reproducibility meet the method requirements for pesticide residue analysis. The half-life of 3 fungicides in fresh tobacco leaf were 5.4-16.1, 4.3-7.7 and 4.4-6.9 days. When the fungicide was applied at the recommended maximum dose and 1.5 fold dose, the pesticide residues in cured tobacco leaves were 0.33-1.33, <0.05-1.05, and 0.76-2.00 mg/kg with a PHI of 14 days. Based on these results and principles for MRL setting for food/feed, the possible MRLs in tobacco for albendazole, flusilazole, and imazalil could be set as 2, 2, and 5 mg/kg, respectively.

Keywords: Tobacco; Fungicide for leaf spot diseases; Pesticide residues; Dissipation; MRL

1. Introduction

As an important economic crop in China, tobacco inevitably needs to use pesticides to control various pests and diseases. In recent years, more and more pesticides have been applied to tobacco planting. Albendazole, flusilazole and imazalil are new fungicides for controlling leaf spot diseases of tobacco with good effects. A series of GAP field experiment were carried out and a detection method of the fungicides in tobacco was developed, and the data could contribute to the development of relevant limit

3.2 Dissipation of 3 fungicide residues in fresh tobacco leaves

The original deposition residue of albendazole, flusilazole and imazalil in tobacco leaves were 0.57-2.40, 0.78-3.46, 1.49-4.81 mg/kg. The theoretical half-lives of 3 fungicide in fresh leaves were 5.4-16.1 d, 4.3-7.7 d, 4.4-6.9 d, respectively. The difference of deposition and half-life of the fungicide were related to the recommended dosage, the climate of the field site, etc.

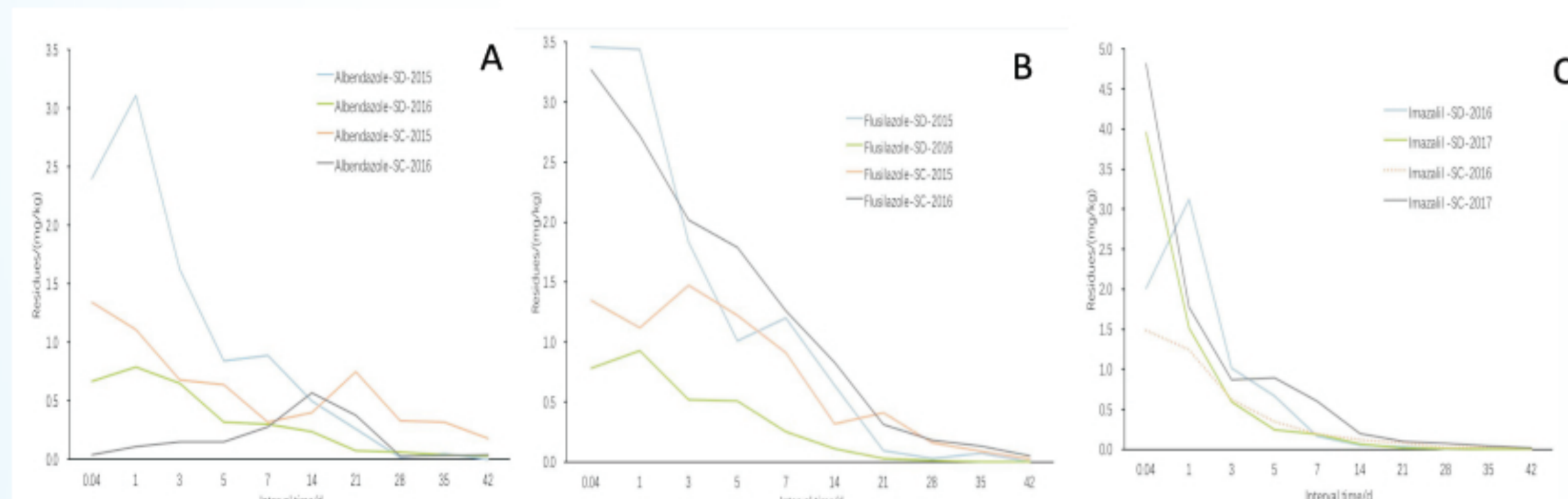


Fig. 1. Dissipation of albendazole, flusilazole and imazalil in fresh tobacco leaves (A. Albendazole; B. Flusilazole; C. Imazalil)

3.4 Effects of different factors on pesticide residues in tobacco leaves

The results of variance analysis of three pesticides are shown in Table 3. The residues of flusilazole and imazalil in tobacco leaves were mainly affected by the interval, and the residue of albendazole in tobacco leaves was mainly affected by the dosage.

Table 3. Influence of single factor and compound factor on pesticide residue

Factor	Albendazole		Flusilazole		Imazalil	
	F	P	F	P	F	P
dosage	16.456	<0.001	6.767	0.011	9.648	0.003
interval	2.312	0.107	14.740	<0.001	38.704	<0.001
dose × interval	1.893	0.031	1.137	0.345	0.990	0.494

* When $P < 0.05$, the factor is significant; The higher of F, the more significant of the factor.

2. Materials and methods

The field experiments including dynamic degradation residue and final residue of different intervals for different doses were carried out in Qingdao, Shandong and Liangshan, Sichuan during two years in accordance with the "Guideline on Pesticide Residue Trials" issued by the Ministry of Agriculture (NY/T 788-2004). In the dynamic degradation residue field experiment, 3 fungicides was sprayed at 1.5 fold of the higher recommended dosage during tobacco maturity, and the fresh tobacco leaf sample was collected randomly from each plot at 2 hour, 1, 3, 5, 7, 14, 21, 28, 35 and 42 days after application. The fungicide was sprayed three times every 7 days at recommended dosage and 1.5 folds, respectively. About 200 pieces of tobacco leaves were collected, 7, 14 and 21 days after the last application. The detection method of 3 fungicides in tobacco was developed by acetonitrile extraction, dispersive solid phase extraction, and HPLC-MS/MS detection.

3. Results

3.1 Method validation

In the range of 0.001~5 mg/kg, the peak area of 3 fungicides was in good linear relation with the mass concentration. The minimum detectable concentration (LOQ) was 0.01, 0.02 and 0.05 mg/kg in fresh tobacco leaves and cured tobacco leaves, respectively. The method meets the requirements of pesticide residue detection and has good reliability.

Table 1. The LODs, coefficient, recoveries and RSDs of albendazole, flusilazole and imazalil

Fungicide	Material	Linear range (mg/L)	Correlation coefficient	LOD (g)	LOQ (mg/kg)	Concentration (mg/kg)	Recoveries (%)	RSD (%)
albendazole	fresh leaf	0.001-5.0	0.9980	5.0x10 ⁻¹¹	0.02	0.02-2	93.9-99.4	1.2-2.7
	cured leaf							
flusilazole	fresh leaf	0.01-5.0	0.9999	1.2x10 ⁻¹¹	0.01	0.01-2	81.5-103	2.9-7.8
	cured leaf							
imazalil	fresh leaf	0.001-5.0	0.9999	1.0x10 ⁻¹¹	0.01	0.01-5	83.7-92.5	2.8-8.8
	cured leaf							

3.3 Residue and risk assessment in cured tobacco leaves

7 days after the last application, the pesticide residues in tobacco leaf of albendazole, flusilazole and imazalil were 0.14-3.03, 0.21-2.92, 0.98-3.48 mg/kg. And 14 days later, the pesticide residues degraded to a lower level of 0.33-1.33 mg/kg, < 0.05-1.05 mg/kg, 0.76-2.00 mg/kg; 21 days later, the pesticide residues in tobacco leaf remained at a fairly low level.

Table 2. The residue of albendazole, flusilazole and imazalil in cured tobacco leaves

Fungicide	Application dose (g a.i./hm ²)	Interval(d)	Pesticide residue (mg/kg)			
			Shandong		Sichuan	
			1 st year	2 nd year	1 st year	2 nd year
albendazole	90	7	0.92±0.06	0.30±0.14	1.30±0.09	1.75±0.15
		14	1.17±0.18	0.42±0.08	1.07±0.04	0.84±0.04
		21	0.93±0.02	0.23±0.07	0.75±0.02	0.97±0.15
	135	7	1.54±0.08	1.05±0.36	3.00±0.04	1.84±0.13
		14	1.07±0.07	1.06±0.13	1.05±0.15	1.17±0.06
		21	0.73±0.05	0.55±0.18	1.80±0.05	1.19±0.06
flusilazole	135	7	0.62±0.24	0.21±0.01	0.34±0.09	1.45±0.06
		14	0.36±0.17	0.36±0.01	0.17±0.06	0.72±0.05
		21	<0.050	0.41±0.01	0.29±0.01	0.43±0.08
	202.5	7	1.33±0.12	0.57±0.16	1.50±0.96	2.70±0.28
		14	0.56±0.01	0.45±0.01	0.64±0.21	1.00±0.04
		21	<0.050	0.48±0.05	0.41±0.11	0.38±0.04
imazalil	300	7	0.98±0.004	1.06±0.01	2.77±0.13	2.86±0.01
		14	1.03±0.03	0.76±0.02	1.77±0.07	1.34±0.02
		21	0.38±0.01	0.46±0.02	1.09±0.02	0.75±0.02
	450	7	2.32±0.11	2.35±0.03	3.18±0.02	3.48±0.04
		14	2.29±0.04	1.29±0.02	2.00±0.01	1.69±0.01
		21	1.20±0.02	0.62±0.02	1.27±0.04	0.85±0.02

4. Discussion and conclusion

Neither in MRL of China nor in GRL of CORESTA, there is no MRL data for tobacco about 3 fungicides. The MRL of other fungicide with the similar chemical structure and the same control object, such as carbendazim or penconazole, is 2 mg/kg. The ADIs of albendazole, flusilazole and imazalil are 0.05, 0.007, 0.03 mg/kg. In the National Food Safety Standard, the MRLs of albendazole, flusilazole and imazalil of most food are 0.1-0.2 mg/kg(temporary), 0.2 mg/kg, 2-5 mg/kg. According to the ADI, the GAP data in tobacco, and the MRL in other food, and the dietary intake ratio, the possible MRLs in tobacco for albendazole, flusilazole, and imazalil, are 2, 2, and 5 mg/kg, with a PHI of 14 days.

*References (abbreviated)