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Dissipation and Evaluation of Hexaflumuron Residues in Chinese Cabbage Grown in Open Fields

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The dissipation and residue behavior of hexaflumuron in Chinese cabbage (*Brassica pekinensis*) under different treatments were investigated at two main cabbage-growing areas in China. The dissipation rates of hexaflumuron in cabbages and soils fit a first-order decay process very well. The dissipation times for 50% of the hexaflumuron in cabbage and soil were 3.37 and 3.01 days from Hunan province and 5.58 and 3.68 days in Tianjin, respectively, when Chinese cabbage was treated with 180 g of active ingredient (ai)/ha. Hexaflumuron residual times in cabbage and soil were influenced strongly by the application rate and frequency. The application regimen of hexaflumuron in the cabbage field, a rate of 120 g of ai/ha with two applications at a 7 day interval and a 21 day preharvest interval, was recommended from the point of view of ensuring food safety. The residual levels of hexaflumuron in cabbages were lower than the standards of the "Positive List System for Agricultural Chemical Residues in Foods" based on the recommended application regimen.

KEYWORDS: Hexaflumuron; Chinese cabbage; soil; residue behavior; preharvest interval (PHI); food safety

INTRODUCTION

Hexaflumuron {IUPAC name, [1-(3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenyl)-3-(2,6-difluorobenzoyl) urea]} is a new benzoylphenylurea insect growth regulator (IGR) (*1*, *2*) with a novel mode of action to inhibit chitin synthesis in the cuticle of immature insects (*3*, *4*). Over the past years, the usage of hexaflumuron has increased rapidly in agricultural practice for the control of a wide range of leaf-eating insects and their larvae in vegetables, fruits, etc. (*4*–*6*). Market introduction of hexaflumuron to China was initiated in 1998, and since then it has been used extensively in Chinese agricultural production (*7*, *8*). According to the insecticidal effect, the labeled application rate from the producer of hexaflumuron in agricultural fields is 120 g of active ingredient (ai)/ha.

Chinese cabbage (*Brassica pekinensis*) is a principal leafy vegetable for people in many countries every day. It has recently been grown in other Asian and Western countries. This plant is often damaged by many kinds of insects and pathogens such as *Plutella xylostella* (L.) (*9*, *10*), and some selective insecticides were introduced by farmers to reduce economic damage. There is no doubt that the maximum residue limit (MRL) of pesticides in cabbage should be particularly strict as cabbages are simply washed before cooking or eaten directly as fresh vegetables. According to the "Positive List System for Agricultural Chemical Residues in Foods" (2006) ("Positive List System" for short), the MRL of hexaflumuron in cabbage was set at 0.02 mg/kg (*11*). However, hexaflumuron residues above this standard were frequently detected in exported and domestic produce in recent years, which had a potential impact on human health and influenced the export of Chinese cabbage to Japan, Korea, and other countries greatly. On the other hand, pesticides will enter and stay in the soils following field application. A previous study has shown that a significant fraction of atrazine would enter into soil when it was applied by spraying (*12*). Banerjee et al. (*13*) also reported that only 0.1% of the applied agrochemicals reach their target site, whereas the remaining 99.9% move into the environment. Pesticide residues in soils may persist for a long period and pose a serious threat to soil ecosystems, human health, and nontarget animals. Therefore, to ensure food safety and protect the environment, field dissipation studies are needed on the persistence of pesticide in foodstuffs and the residue behavior in agricultural fields before application (*14*).

Although some studies have been published on the insecticidal effects and analytical methods for hexaflumuron (*1*, *4*, *5*, *15*–*17*), few data are available on the dissipation behavior of hexaflumuron in agricultural fields, which is essential to evaluate its persistence and fate in the environment. In this study, field dissipation studies of hexaflumuron with different application regimens based on the worst-case adopted by Chinese farmers were conducted to estimate the dissipation and residue behavior of hexaflumuron in Chinese cabbages and cropped soils. In addition, field surveys in farmers' gardens were investigated to evaluate the application regimen and preharvest interval (PHI) of hexaflumuron that was recommended in this work.

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Table 1. Physicochemical Properties of Soils of Farms I (Hunan) and II (Tianjin)

location	pH	organic carbon (%)	CEC[a] (cmol kg^{-1})	textural class	sand (%)	silt (%)	clay (%)
Hunan (farm I)	5.5	2.71	9.3	loam	27.6	45.9	26.5
Tianjin (farm II)	8.5	3.27	9.0	sandy loam	39.5	39.3	21.2

[a] Cation exchange capacity.

Table 2. Final Residues of Hexaflumuron in Cabbages Grown at Farms I (Hunan) and II (Tianjin)

		residue[a] (mean[b] ± SD, mg kg^{-1})				
location	days after last application	T I	T II	T III	T IV	T V
farm I (Hunan)	21	UD	0.037 ± 0.003	0.053 ± 0.003	0.15 ± 0.007	UD
	24	UD	UD	0.021 ± 0.001	0.095 ± 0.006	UD
	27	UD	UD	UD	0.032 ± 0.002	UD
	30	UD	UD	UD	UD	UD
farm II (Tianjin)	21	UD	0.050 ± 0.005	0.046 ± 0.004	0.31 ± 0.010	UD
	24	UD	0.018 ± 0.001	0.036 ± 0.002	0.10 ± 0.008	UD
	27	UD	UD	UD	0.067 ± 0.003	UD
	30	UD	UD	UD	0.029 ± 0.002	UD

[a] T, treatment. T I and T II, hexaflumuron was sprayed at a rate of 120 g of ai/ha with two and three applications at 7 day intervals, respectively; T III and T IV, hexaflumuron was sprayed at a rate of 180 g of ai/ha with two and three applications at 7 day intervals, respectively; T V, no hexaflumuron was used. UD, undetectable. [b] Mean of three replicates.

MATERIALS AND METHODS

Chemicals and Solvents. Hexaflumuron standard (purity > 99%) and its commercial formulation (hexaflumuron 5 EC) were obtained from Dalian Raiser Pesticides Co., Ltd. (Liaoning, China). The chemical properties of hexaflumuron are as follows: solubility in water, 0.027 mg/L (20 °C); vapor pressure, 0.059 mPa (25 °C); log P_{ow}, 5.68; K_{oc}, 10391 mL/g. All solvents including methanol, dichloromethane, and other reagents were of HPLC grade.

Field Site Description. Field experiments were conducted at two cabbage-growing farms from different areas in China, located at Hunan Agricultural University (farm I, 28° 10′ 47″ N and 113° 4′ 37″ E), South China, and Tianjin Academy of Agricultural Sciences (farm II, 39° 9′ 27″ N and 117° 4′ 56″ E), North China, respectively. None of the farms had been treated with hexaflumuron in the past. The physicochemical properties of the soils from two sites are listed in **Table 1**. The field studies were conducted from October 2005 to January 2006 at farm I and from June 2005 to September 2005 at farm II. During the whole experimental period, there were 12 rainfall events at farm I with an average temperature of 8 °C. Within farm II, there were six rainfall events with an average temperature of 25 °C.

Experimental Design of Dissipation Study. To evaluate the dissipation dynamics of hexaflumuron in cabbages and cropped soils, field experiments were carried out in six plots with an area of 45 m^2 each. The Chinese cabbages were planted on October 25, 2005, at farm I (Hunan, South China) and on June 5, 2005, at farm II (Tianjin, North China). The hexaflumuron was sprayed on December 11, 2005, at farm I and on July 26, 2005, at farm II. Hexaflumuron 5 EC was applied at a rate of 180 g of ai/ha (1.5 times the labeled rate based on field efficacy) in 1000 L of water sprayed by an A2-16 Gongnong backpack sprayer (Taizhou Profit Agricultural Sprayer Factory, China) with three replicates. Meanwhile, three untreated plots were sprayed with water as control group. Then, cabbages and soil samples were collected at 1 h and 1, 2, 3, 5, 7, 10, 14, 21, 28, and 35 days after application. There was no rainfall event within the first week after application. Five unblemished cabbages (about 2 kg each) were harvested randomly with a knife from 2 cm above the soil surface of plants from each of the replicates. Soil samples (about 1 kg) were collected randomly from the surface soil (0−10 cm) using a coring device (5 cm diameter), and stones and plant debris were manually removed. All samples were stored at −4 °C and analyzed within 12 h to determine the hexaflumuron residues.

Experimental Design of Final Residue Study. Field experiments were conducted at farms I and II to evaluate the final residues of hexaflumuron in cabbages and soils. Five different treatments (including a control) were set up, with three replicates each of 45 m^2. Hexaflumuron 5 EC was sprayed at two application rates of 120 g of ai/ha (the labeled rate based on field efficacy) and 180 g of ai/ha and two application frequencies (two and three applications) in 1000 L of water by an A2-16 Gongnong backpack sprayer. A complete randomized block design of three replicates with each treatment was used. The spray rate and frequency of hexaflumuron in each of the treatments are shown in **Table 2**. The representative cabbage and soil samples were obtained on the 21st, 24th, 27th, and 30th days after the last spraying and analyzed immediately. Five unblemished cabbages (about 2 kg) were harvested randomly with a knife from each of the replicates. Soil samples (about 1 kg) were also collected randomly from the surface soil (0−15 cm) using a coring device (5 cm diameter).

Field Survey Design. The main objective of the field survey was to evaluate the application regimen and PHI of hexaflumuron recommended in this work under uncontrolled farm situations. PHI was estimated according to the methods reported by Karmakar et al. (*18*). Two-year field surveys were conducted in farmers' fields during 2006−2007 at Hunan Province and Tianjin City. One field was selected in each region per year, and they were all not far from our experimental farms (farms I and II). There were only slight differences of farm conditions, such as soil properties and climatic conditions, between the selected fields and the experimental farms. Farmers were asked to apply hexaflumuron in cabbage-growing fields at a rate of 120 g of ai/ha with a 7 day interval between two applications. At 21 days after the last spraying, 10 cabbage samples were collected randomly from each field to analyze hexaflumuron in the final produce.

Sample Preparation. Each whole and unwashed cabbage sample was homogenized in a high-speed blender (Kylin-Bell Lab Instruments Co., Ltd., Jiangsu, China). Then, about 20 g samples were taken and transferred into a conical flask with a cap stopper. Cabbage samples were extracted by methanol (60 mL) on a THZ-C shaker (Taicang Experiment Equipment Co., Ltd., China) at 25 (±1) °C for 2 h. The extracts were filtered with a filter paper (Whatman no. 1) and then washed with methanol (20 mL). Tce combined two methanol extracts were concentrated to about 10 mL with an RE-52A rotary vacuum evaporator (Shanghai Biochemical Apparatus Factory, Shanghai, China) at 50 (±1) °C. The concentrated samples were transferred to a 250 mL separating funnel containing 4% sodium chloride solution (50 mL) and extracted by liquid−liquid partitioning with dichloromethane three times (50, 30, and 30 mL), respectively. The dichloromethane phases were separated, combined, and concentrated to about 2 mL with a rotary vacuum evaporator at 30 (±1) °C for further cleanup with column chromatography.

A column (20 cm ×15 mm i.d.) was packed with an absorbent cotton plug at the bottom and covered with 1 cm of anhydrous sodium sulfate. Florisil (5.0 g, about 12 cm in column, 60−100 mesh) and another 1 cm of anhydrous sodium sulfate were placed above the Florisil at the top of the

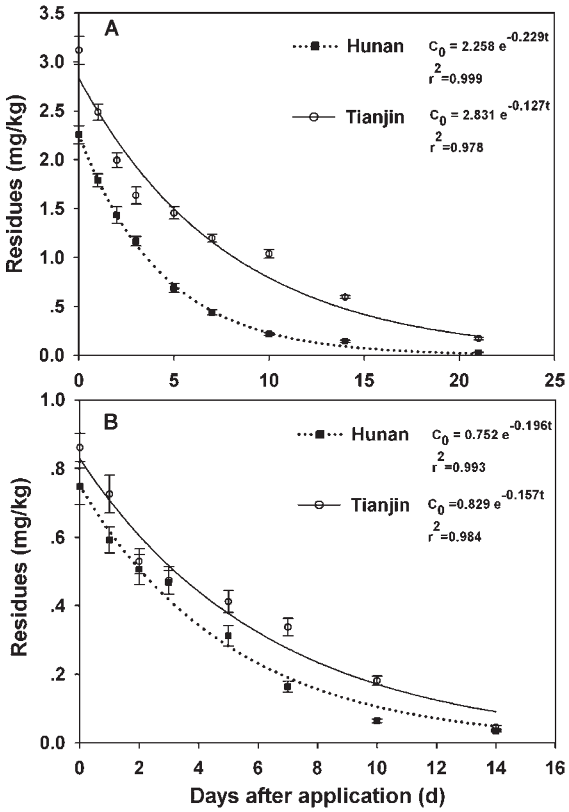

Figure 1. Dynamics of hexaflumuron in cabbage (**A**) and soil (**B**). Points refer to the mean of three replicates. The error bars represent the standard error.

column. Florisil was activated at 650 °C for 4 h and deactivated with 3% deionized water prior to use. The two ends of the column were compacted uniformly. The column was prewetted first with ethyl acetate (20 mL). The concentrated sample was transferred completely to the column, and then the column was eluted with ethyl acetate (50 mL). The eluate was evaporated to about 2 mL with a rotary vacuum evaporator at 50 (±1) °C and was then evaporated to dryness in a KD200 nitrogen evaporator (Hangzhou Allsheng Instruments Co., Ltd., Hangzhou, China). The residue was redissolved in methanol (1 mL). This solution was filtered through a 0.45 μm membrane Teflon filter (Millipore, Bedford, MA) and analyzed immediately by HPLC.

Soil samples were crushed and passed through a mesh (Φ 2 mm). Part of soil was dried at 105 °C to assess the water content. About 20 g soil samples were extracted with methanol (60 mL) by shaking well in conical flasks with cap stoppers for 2 h on a shaker at 25 (±1) °C. The extracts were filtered with filter paper and washed again with methanol (20 mL). The two methanol extracts were combined and concentrated to about 2 mL with a rotary vacuum evaporator at 50 (±1) °C for further cleanup with column chromatography. The following cleanup steps were the same with cabbage samples.

Instrumental Analysis. A high-performance liquid chromatograph (HP1100, Hewlett-Packard, Palo Alto, CA) equipped with a variable-wavelength UV−visible detector was used for hexaflumuron analysis. A 20 μL extract was injected using a manual injector valve. A Hewlett-Packard C_{18} column (250 mm ×4.6 mm i.d., 5 μm) was used to separate compounds of interest, and the column oven temperature was maintained at 38 °C. The mobile phase was an isocratic solvent system composed of methanol/water (73:27 by volume). The flow rate was a gradient starting with 0.8 mL/min, ramped to 0.4 mL/min in 12 min, and held for 5 min, over a total runtime was 17 min. The hexaflumuron eluted at a retention time (RT) of 15.2 min. All samples were determined at a UV wavelength of 215 nm. Quantification of hexaflumuron in real samples was based on the external standard method. The standard calibration curve was linear in the concentration range of 0.084−10.500 mg/L ($R^2 > 0.999$). The limit of detection (LOD, determined on the basis of a signal-to-noise ratio of 3 for blank sample) of hexaflumuron was 0.008 mg/kg for cabbage and soil. The limit of quantification was 0.016 mg/kg for hexaflumuron. The analysis method satisfied the requirement of the "Positive List System" (2006).

Method Validation. For method validation, control and fortified samples were analyzed under the same conditions. Hexaflumuron was spiked in fresh cabbage and soil samples at three concentration levels (0.02, 0.05, and 0.50 mg/kg). The samples were homogenized and analyzed 2 h after application. The number of replications for recovery studies was five for each level of fortification. The mean recoveries of this method ranged from 83.2 to 95.6% and from 87.3 to 97.8% for cabbage and soil, respectively, and coefficients of variation were 1.03−8.84 and 1.15−8.07%, respectively. According to the European Commission (EC) guidelines (*19*), the results in this study are within the accepted range for residue determination.

Data and Statistical Analysis. The dissipation kinetics of the residue data was evaluated by fitting the dynamic degradation models to the data. Exponential relationships were applied for all samples, and results in this work were analyzed using a nonlinear regression. Data and statistical analyses were performed using SPSS version 13.0 (SPSS Inc., Chicago, IL) with statistical significance for all tests set at $p < 0.05$.

RESULTS AND DISCUSSION

Hexaflumuron Dissipation Dynamics. The dissipation dynamics of hexaflumuron in cabbages and soils are shown in **Figure 1**. As expected, a gradual and continuous dissipation of hexaflumuron residues in cabbage and soil was observed as a function of time after application. The first-order decay model fitted well to the dissipation rates, which is in accordance with the observations in zucchini reported by other researchers (*20*). Equation **1** describes the dissipation dynamics, and eq **2** calculates dissipation half-lives of hexaflumuron:

$$C_t = C_0\, \mathrm{e}^{-kt} \tag{1}$$

$$\mathrm{DT}_{50} = \ln 2/k \tag{2}$$

C_t is the concentration (mg/kg) at time t (days) after application, C_0 is the initial concentration (mg/kg), and k is a first-order rate constant (*14*, *21*, *22*).

The persistence of hexaflumuron residues with cabbages grown in Hunan and Tianjin is presented in **Figure 1A**. The initial mean concentrations of hexaflumuron in cabbages were significantly different for the two farms (farm I, 2.26 mg/kg; farm II, 3.12 mg/kg, $p < 0.05$). The major dissipation of hexaflumuron took place within the first week after application, which indicated that hexaflumuron was dissipated rapidly in cabbages. Two weeks after application, the concentrations of hexaflumuron residues declined by 94% at farm I and by 80% at farm II. Hexaflumuron residues were undetectable in cabbages at 28 days after application. The DT_{50} of hexaflumuron in cabbage was 3.37 days at farm I. Compared with 5.58 days at farm II, a sharp decline of residues occurred in cabbage of farm I. The DT_{50} values observed are similar to those reported previously for hexaflumuron in peppers and zucchinis (*20*) and other pesticides in cabbages (*10*). In agricultural fields, growth dilution of the treated plants might play a significant role in the diminution of pesticides in crop plants (*23*). In our study, the time intervals from cabbage planting to hexaflumuron application were similar between farms I and II. Because of the different growth rates, the cabbage at farm I was bigger than that in farm II when hexaflumuron was applied. Therefore, the different initial concentrations of hexaflumuron in cabbage may be, partly, attributed to the different plant sizes between the two farms. However, the growth of cabbage has a limited effect on the dissipation rate of hexaflumuron, because the significant part of dissipation occurred mostly within the first week after application.

Table 3. Final Residues of Hexaflumuron in Soil of Farms I (Hunan) and II (Tianjin)[a]

location	days after last application	residue (mean ± SD, mg kg^{-1})				
		T I	T II	T III	T IV	T V
farm I (Hunan)	21	UD	UD	0.018 ± 0.001	0.086 ± 0.005	UD
	24	UD	UD	UD	0.053 ± 0.004	UD
	27	UD	UD	UD	UD	UD
	30	UD	UD	UD	UD	UD
farm II (Tianjin)	21	UD	UD	0.026 ± 0.001	0.12 ± 0.007	UD
	24	UD	UD	UD	0.041 ± 0.003	UD
	27	UD	UD	UD	UD	UD
	30	UD	UD	UD	UD	UD

[a] See **Table 2** for explanation of codes.

The persistence of hexaflumuron residues in soil is presented in **Figure 1B**. The initial mean concentration of hexaflumuron in soil was 0.75 mg/kg at farm I. The residues decreased to 0.04 mg/kg 14 days after spraying, indicating that 95.3% of the applied hexaflumuron had dissipated. The initial concentration of hexaflumuron in soil was 0.86 mg/kg at farm II, which decreased to 0.05 mg/kg 14 days after spraying; that i, 94.7% of the applied hexaflumuron had dissipated. Hexaflumuron residues were undetectable in soil at 21 days after application. The DT_{50} values of hexaflumuron in soil were 3.01 and 3.68 days in Hunan and Tianjin, respectively. The dissipation rates of hexaflumuron in both soils were much shorter than its degradation rate in soil under laboratory conditions (DT_{50} = 9.3 days, excluding light) reported in our previous study (*24*). Due to the low solubility and low volatility of hexaflumuron, photolysis was the most significant difference in conditions of this study. The degradation of hexaflumuron and other benzoylphenylurea IGRs in water has been previously reported to be rapid (DT_{50} = 5−8.6 h), with a significant fraction of degradation being via photolysis (*2*). Therefore, photodegradation was probably an important dissipation pathway of hexaflumuron in agricultural fields, and another one was microbial degradation by our previous study (*24*). On the other hand, no significant difference was observed in dissipation rates of hexaflumuron in soils between the two sites, although soil properties and physical and chemical conditions, such as temperature and moisture, were varied.

Hexaflumuron has a high K_{oc}, which indicated that it can bind tightly to soil particles and is relatively nonmobile in soil. Therefore, there is a risk of storage of hexaflumuron residues in soil. However, **Figure 1** shows no evidence of hexaflumuron residues that were resistant to degradation in this study. Hexaflumuron has also been previously reported to be degraded quickly through soil microbial degradation and photolysis (*2*, *24*). Therefore, hexaflumuron may not move to or store in the deep layers of soil readily. Of course, the dissipation behavior of pesticides such as hexaflumuron in the environment is a complicated process. They can be dissipated via biological and chemical degradation, photolysis, volatilization, precipitation, runoff, plant uptake, sorption and desorption in soil, and leaching behavior through the soil (*21*, *25*).

Hexaflumuron Residues in Cabbage and Soil. Cabbages were sampled four times during the harvest period to analyze hexaflumuron residues. As shown in **Table 2**, the residues ranged from undetectable to 0.31 mg/kg from the various treatments. At 21 days after the last spraying, hexaflumuron residues in cabbage were undetectable in the samples of treatment I (120 g if ai/ha with two applications at a 7 day interval), but exceeded the proposed MRL standard (0.02 mg kg^{-1}) in other treatments (II, III, and IV). It is worth noting that relatively high concentrations of hexaflumuron residues were detected in treatment IV (180 g of ai/ha with three applications at 7 day intervals) during the harvest period of all sampling time, and the concentrations almost always exceeded the MRL. The results showed a strong positive correlation between the hexaflumuron residues in cabbages and its application rate and frequency (Hunan, r^2 = 0.97, p < 0.05; Tianjin, r^2 = 0.91, p < 0.05, at 21 days after the last spraying). This is consistent with the conclusions reported by Sharma et al. (*26*). A relatively higher application rate and frequency resulted in long PHI, which could be considered harmful to human health.

Soil was sampled on the same collection day as cabbage, and the levels of hexaflumuron residues are presented in **Table 3**. Overall, the residue behavior of hexaflumuron in soil under different treatments was similar to that in cabbages. From the 21st to the 30th day after the last spraying, hexaflumuron were not detectable in the samples of low application regimens (treatments I and II). As we expected, the concentrations of hexaflumuron were higher in treatment IV than in other treatments, and the residues stayed detectable in soil for a long period. This was caused by the relatively higher application regimen of treatment IV. It is well-known that the microbial degradation was responsible for a significant part of pesticide degradation in soil (*27*, *28*). As reported in a previous study, the bioactivity of the degrading microorganisms was suppressed with high application rate of hexaflumuron in soil (*24*). Therefore, the contribution of the biological degradation to the overall hexaflumuron degradation in soil was reduced in treatment IV.

Previous studies have reported that the residual behavior of pesticide can be influenced by many factors, including the frequency and rate of pesticide application, the degradation rate, the weather (temperature, humidity, and wind), micro-organisms, etc. (*10*). Among these factors, the final residual concentrations of hexaflumuron in this research showed the strongest relationship to the application regimen whether in cabbages or in soils. Furthermore, by comparison of treatment II with treatment III, the residual hexaflumuron concentrations were higher in the latter both in cabbages and in soil, although the total spray amounts of the two treatments were same. This implied that increasing the spray frequency may offer an advantage in terms of its lower residue levels as compared with increasing the spray rate under the same total application amount, but the spray rate should also comply with the labeled application rate (120 g of ai/ha) to ensure the insecticidal effect.

Recommended Application Regimen of Hexaflumuron and Field Surveys. As mentioned above, hexaflumuron has fast dissipation rates in cabbages and soils, but the residual period will extend with high application rate and frequency. On the basis of the results of this study, we suggested that the hexaflumuron residues above the "Positive List System" standard detected in exported and domestic produces were most probably attributable to an incorrect application regimen. Farmers may overspray hexaflumuron by excessive amounts and/or at a high frequency to control pests, or even use them right up to crop harvest, thus leading to large hexaflumuron residues in agricultural products. According to the results of the final residue study, a rate of 120 g of ai/ha with two applications at 7 day interval and a 21 day PHI are recommended in uncontrolled Chinese cabbage fields to protect consumer health by minimizing exposure to excessive levels of hexaflumuron residues.

A field survey was conducted to evaluate the recommended application regimen and PHI of hexaflumuron in uncontrolled cabbage fields. Ten unblemished cabbage samples were harvested randomly from each cabbage field per region (Hunan Province and Tianjin City) during 2006−2007, and the fields were shifted in the second year of this study. Of the 40 cabbage samples monitored, hexaflumuron residues were all below the MRL of 0.02 mg/kg. In fact, the residues were not detected in any sample at harvest time. The results indicate that the cabbage products were safe for consumers and comply with the "Position List System". The recommended application regimen and PHI proved to be effective in minimizing hexaflumuron residues in cabbages grown in open fields. However, it is necessary to monitor hexaflumuron residues in Chinese cabbage products under the consideration of human health because it can persist past the harvest time with high application rate and frequency.

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