JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

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Effects of Planting and Processing Modes on the Degradation of Dithianon and Pyraclostrobin in Chinese Yam (*Dioscorea* spp.)

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ABSTRACT: The yam (*Dioscorea* spp.) is widely cultivated in China. The degradation of dithianon and pyraclostrobin in yams with different planting and processing treatments was investigated in this article. An analytical method for two pesticides in yam and yam plant was developed, and recoveries were between 77% and 93%, with relative standard deviations from 0.8% to 7.4%, respectively. On the basis of this method, half-lives for plants grown on stakes versus plants grown without stakes were compared. The results indicated that the half-life for pesticide residues for plants grown on stakes versus plants grown without stakes differed as 6.7 versus 3.1 days for dithianon and 5.4 versus 5.2 days for pyraclostrobin. Dithianon was significantly influenced by planting mode because of its low stability under sunlight. The processing factors of various processing treatments (hot air-drying, vacuum freeze-drying, microwave vacuum-drying, infrared-drying, steaming, and boiling) were all <1, indicating that those processes can reduce residues of two pesticides at different levels. Significant amounts of residues were removed during the boiling treatment, whereas the others showed less effect.

KEYWORDS: *degradation, dithianon, pyraclostrobin, planting mode, processing factor, yam*

INTRODUCTION

Yam (*Dioscorea* spp.) is the fourth major root crop in the world after cassava, potatoes, and sweet potatoes.[1] In China, different yam species are not only a common food but also a traditional Chinese medicine that have also been widely used for the treatment of diabetes, diarrhea, asthma, and other ailments.[2−6] Yams are cultivated either on mounds or on ridges, and the growing plants can be staked or spread on the ground without stakes. Staked yams are more productive; however, the cost of stakes and labor to place them may render the practice uneconomical.[7] Ground yams without stakes are still widely cultivated in rural areas in China.

Fresh yams are consumed in different ways, such as boiled, steamed, or baked products. However, fresh yams are perishable during storage. Consequently, the processed yam products occupy a considerable part of daily consumption. Drying is one of the most important preservation processes for yams to extend their storage life and improve the taste, including air-drying, freeze-drying, far-infrared radiation-assisted freeze-drying, and vacuum-drying.[8−12]

During the growth cycle of yam, the crops are exposed to a wide range of pests and diseases. Yam anthracnose is the most important disease and is caused by *Colletotrichum gloeosporioides* (Popoola et al., Raj et al., and Katoh et al.), which can be effectively controlled by dithianon and pyraclostrobin.[13−17] Dithianon (CAS 3347-22-6, Figure 1A), 5,10-dihydro-5,10-dioxonaphtho-(2,3-*b*)-1,4-dithiin-2,3-dicarbonitrile, is a non-systemic fungicide used against a variety of foliar diseases.[16] Pyraclostrobin (CAS 175013-18-0, Figure 1B), methyl 2-[1-(4-chlorophenyl)pyrazol-3-yloxymethyl]-*N*-methoxycarbanilate, is a broad-spectrum foliar fungicide in the strobilurin chemical class.[18] The combination of these two pesticides shows higher fungicidal activity and longer lifetimes than either alone.[19] In previous studies, residues of dithianon and pyraclostrobin have been determined in various fruits, vegetables, and grain by high-performance liquid chromatography coupled with ultraviolet detector (HPLC-UV), high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS), and gas chromatography coupled with time-of-flight mass spectrometry (GC-TOFMS).[20−25]

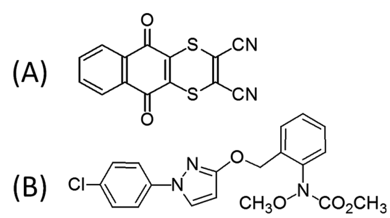

Figure 1. Chemical structures of (A) dithianon and (B) pyraclostrobin.

Pesticide in yams might be concentrated or converted to more toxic metabolites during processing. The processing factors (PFs) are the ratios of residue levels in processed products and their respective raw products, which are important when evaluating the risk associated with intake of pesticide residues.[26] The Joint FAO/WHO Meeting on

Received: August 22, 2017
Revised: October 26, 2017
Accepted: November 13, 2017
Published: November 13, 2017

DOI: 10.1021/acs.jafc.7b03916
J. Agric. Food Chem. 2017, 65, 10439−10444

Pesticide Residues (JMPR) evaluated food-processing data on dithianon and pyraclostrobin residue behaviors where significant residues occur in plant or plant products that are processed into food.[27] To the best of our knowledge, few papers have reported the degradation of dithianon and pyraclostrobin and PFs in yams during different processing procedures.

Therefore, the objectives of this work were as follows: (1) to develop an analytical method for determining the residues of dithianon and pyraclostrobin in yam; (2) to assess the influence of different plant modes (ground and staked) on the dissipation of dithianon and pyraclostrobin in Chinese yam; and (3) to evaluate the degradation of dithianon and pyraclostrobin regarding PFs during different processing treatments, including hot air-drying (HAD), vacuum freeze-drying (VFD), microwave vacuum-drying (MVD), infrared drying (ID), steaming, and boiling.

■ MATERIALS AND METHODS

Chemicals and Reagents. Certified reference standards of dithianon (99.0%) and pyraclostrobin (99.0%) were provided by Dr. Ehrenstorfer Gmbh (Augsburg, German). Water-dispersible granule (WDG) containing 12% dithianon and 4% pyraclostrobin was used. Acetonitrile, methanol, acetone, and chloroform were of chromatography purity and purchased from Thermo Fisher Scientific, Inc. (Waltham, U.S.A.). Hydrochloric acid and sodium chloride were of analytical grade and purchased from Beijing Chemical Reagent Co., Ltd. (Beijing, China). Primary secondary amine (PSA) was purchased from Bonna-Agela Technologies, Ltd. (Tianjin, China).

Apparatus. Several dryers used in this study are as follows: DHG-9070A dryer (Shanghai Keelrein Instruments Co., Ltd., Shanghai, China) for HAD; VirTis lyophilizer (Sentry2.0, SP Industries, Inc., PA, U.S.A.) for VFD; HWZ-2B drier (Hongyuan Microwave Equipment Manufacturing Co., Ltd., Shanghai, China) for MVD; WS70-1 drier (GongyiYuhua Instrument Co., Ltd., Zhengzhou, China) for ID. Extraction and purification of pretreatment were performed using XW-80A vortexer (Haimen QilinBei'er Instrument Manufacturing Co., Ltd., Jiangsu, China) and H-1650 centrifuge (Xiangyi Centrifuge Instrument Co., Ltd., Hunan, China).

Preparation of Standard Solutions. Individual stock standard solutions (1000 mg L^{-1}) were prepared by exact weighing of the solid pesticide and dissolved in 25 mL of acetonitrile. To determine the linearity a 100 mg L^{-1} stock solution was also prepared, and working standard solutions (0.10, 0.25, 0.50, 1.00, 2.00, and 5.00 mg L^{-1} for dithianon; 0.05, 0.10, 0.25, 0.50, 1.00, and 2.00 mg L^{-1} for pyraclostrobin) were prepared by diluting the stock solutions with acetonitrile. All standard solutions were stored at −10 °C before use.

Field Trials. The field trial was conducted in 2014 at Jiaozuo City, Henan Province, China. Each treatment consisted of three replicate plots and a control plot. The area of each plot was 30 m^2. A buffer area was also employed to separate each plot, according to "Guidelines on Pesticide Residue Trials".[28] The fields in this study were previously investigated and determined to be free of the pesticide.

To investigate the dissipation of dithianon and pyraclostrobin in Chinese yam with or without stakes, the WDGs were sprayed once at 800 g a.i. ha^{-1} (two times the recommended dosage) on the surface of the yam plant. Representative yam samples (~1 kg) were collected at 2 h and 1, 2, 3, 5, 7, 10, 14, 21, 28, and 35 days after the application. All samples were homogenized and stored at −20 °C for further analysis.

The physicochemical properties of the soil are as follows: soil type was lu soil; organic matter 1.2−1.6%; pH 6.5−7.5. The average annul precipitation was 552 mm. The average annual temperature was 14.3 °C.

Sample Preparation and Processing. *Pretreatments before Processing.* The whole tubers of yams sampled from the control plot were soaked in water with WDGs at dosage of 1.76 g a.i. L^{-1} for 30 min and then dried in the open air. For hot air-drying (HAD), vacuum freeze-drying (VFD), microwave vacuum-drying (MVD), and infrared drying (ID), the tubers were cut into slices 5 mm in thickness. For steaming and boiling, the tubers were cut into pieces (20 cm long). In this study, the samples in different processing steps were collected to determine the residue. The detailed processing procedures are as follows.

Hot Air-Drying. A DHG-9070A dryer was first allowed to run for 1 h to stabilize at the desired temperature (35 °C) at constant air velocity (1 m s^{-1}). The yam samples were then transferred into the drier and dried for 24 h to constant weight.

Vacuum Freeze-Drying. The yam samples were previously spread on a plate and placed at −80 °C for 24 h and then freeze-dried with a VirTis lyophilizer. The pressure was set to 32 Pa. The temperature of the cold trap was −80 °C. The primary and secondary drying temperatures were 20 and 35 °C, respectively. The yam samples were dried for 12 h to constant weight.

Microwave Vacuum-Drying. The yam slices were spread in one layer on the tray of an HWZ-2B drier. The vacuum degree, drying temperature, and power density were set at 0.95 MPa, 50 °C, and 1.3 W g^{-1}, respectively. The yam samples were dried for 10 h to constant weight.

Infrared Drying. The yam slices were spread in one layer on the tray of a WS70-1 drier. The power was set at 500 W. The yam samples were dried for 24 h to constant weight.

Steaming and Boiling. The yam pieces were steamed or boiled at 100 °C for 10 min.

Extraction and Cleanup. *Extraction and Cleanup for Dithianon.* The homogenized yam sample (5.00 ± 0.01g) was weighed into a 50 mL centrifuge tube (Corning, Inc., NY, U.S.A.). Next, 1 mL of hydrochloric acid (37.2%, w/w), 5 mL of water, and 10 mL of acetonitrile were added in that order. The tube was vortexed vigorously for 1 min with vortexer. After the addition of 5 g of sodium chloride, the tube was vortexed vigorously for another 0.5 min, allowed to stand for 20 min at room temperature, and finally centrifuged for 5 min at 5000 rpm. Subsequently, 2 mL of supernatant was transferred into a 2.5 mL centrifuge tube containing sorbent (100 mg of anhydrous $MgSO_4$ and 50 mg of PSA). The tube was vortexed for 1 min and then centrifuged for 5 min at 4500 rpm with a centrifuge. The resulting supernatant was filtered using a 0.22 μm nylon syringe filter into a colored autosampler vial for analysis.

Extraction and Cleanup for Pyraclostrobin. The homogenized yam or yam plant sample (20.0 g) was weighed into a 100 mL centrifuge tube (Taizhou Weierkang Medical Supplies Co., Ltd., Jiangsu, China), and 5 mL of water and 40 mL of acetonitrile were added. The tube was then shaken in a mechanical shaker for 1 h. After the addition of 5 g of sodium chloride, the tube was vortexed vigorously for 1 min and centrifuged for 5 min at 4500 rpm. Subsequently, 20 mL of supernatant was evaporated to dryness at 40 °C. For cleanup, the NH_2 solid-phase extraction (SPE) cartridge was conditioned with 5 mL of acetone/*n*-hexane (2:3, v/v). The concentrated extracts were dissolved in 5 mL of acetone/*n*-hexane (2:3, v/v), transferred to the cartridge, and then eluted with 15 mL of acetone/*n*-hexane (2:3, v/v). The eluent was collected and evaporated to near dryness at 40 °C. The extract sample was redissolved in 2 mL of acetonitrile and filtered using a 0.22 μm nylon syringe filter into an autosampler vial for analysis.

Both the blanks and spiked samples were treated the same as the samples throughout the study process. Yam samples cultivated in control plots were used as field blanks. The blank samples were analyzed to ensure the absence of interference with retention times of the analytes. Blanks fortified with working solution mixtures of target pesticides at three concentration levels (0.5, 2, and 5 mg kg^{-1} for dithianon and 0.05, 0.5, and 1 mg kg^{-1} for pyraclostrobin) were used for the recovery experiment. All samples were analyzed in quintuplicate.

HPLC Analysis. HPLC determination was performed using a Waters HPLC system equipped with an E2695 separation module and 2998 photodiode array detector (Waters Corporation, MA, U.S.A.). SunFire C_{18} chromatographic column (4.6 mm × 150 mm, 5 μm, Waters Corporation, MA, U.S.A.) was used. The injection volume was

DOI: 10.1021/acs.jafc.7b03916
J. Agric. Food Chem. 2017, 65, 10439−10444

Table 1. Mean Recoveries and RSDs of Dithianon and Pyraclostrobin in Yam and Yam Plant (n = 5)

	yam			yam plant		
pesticide	spiked level (mg kg^{-1})	recovery (%)	RSD (%)	spiked level (mg kg^{-1})	recovery (%)	RSD (%)
dithianon	0.5	77	5.8	0.5	78	4.1
	2	80	0.8	2	82	2.4
	5	93	0.9	90	86	4.0
pyraclostrobin	0.05	88	3.4	0.05	88	5.0
	0.5	91	6.8	0.5	86	5.2
	1	90	7.4	15	82	5.2

20 μL. Mobile phase (A) was acetonitrile, and mobile phase (B) was ultrapure water.

HPLC Conditions for Dithianon. The gradient elution program was as follows: 60% (A) from 0 to 10 min, then 80% (A) from 10 to 20 min, then 100% (A) from 20 to 25 min, then 60% (A) from 25 to 25.1 min. The flow rate was 0.8 mL min^{-1}, and the column temperature was 30 °C. The detection wavelength for dithianon was set at 233 nm.

HPLC Conditions for Pyraclostrobin. The mobile phase of the isocratic elution was 70% (A) and 30% (B). The flow rate was 1 mL min^{-1}, and the column temperature was 25 °C. The detection wavelength for pyraclostrobin was set at 275 nm.

Calculations. *Residue Levels in Fresh Yam.* The residue in this study was expressed as residue in fresh yam, calculated using the following equations (eqs 1 and 2),

$$\omega\% = \frac{W_F - W_D}{W_F} \times 100\% \quad (1)$$

$$C_F = C_D \times (1 - \omega\%) \quad (2)$$

where ω is the water content (%), W_F is the fresh weight (g), W_D is the dry weight (g), C_F is the residue in fresh yam (mg kg^{-1}), and C_D is the residue in dry yam (mg kg^{-1}).[29]

Processing Factor. On the basis of the effects on residue levels and the disposition of the residues in various processed products, the PFs are calculated as follows (eq 3):

$$\text{PF} = \frac{\text{Residues in processed product (mg kg}^{-1})}{\text{Residues in raw agricultural commodity (mg kg}^{-1})} \quad (3)$$

The ratios of residue levels in processed products and their respective raw products are called processing factors (PFs). A PF value <1 indicates a reduction in the amount of residues in the processed commodity, whereas a PF value >1 indicates the concentration effect of processing procedures.[30,31]

Dissipation Kinetics. The dissipation process follows first-order kinetics. The degradation rate constant and half-life were calculated using first-order kinetics equations as follows (eq 4),

$$C_t = C_0\, e^{-kt} \quad (4)$$

where C_t is the concentration of pesticide residue (mg kg^{-1}) at time t (day), C_0 is the initial concentration after application (mg kg^{-1}), and k is the degradation rate constant (day^{-1}). The half-life ($t_{1/2}$) is defined as the time required for the pesticide residue level to fall to half of the initial residue level after application and was calculated from the k value: $t_{1/2} = \ln 2/k$.

Statistical Analysis. All experiments were performed at least three times. Data were statistically evaluated by one-way ANOVA analysis with SPSS base 20.0 software. When significant differences were found between groups ($p < 0.1$), the Duncan test was used to determine the differences among means.

RESULTS AND DISCUSSION

Method Validation. Dithianon and pyraclostrobin in yams were determined by high-performance liquid chromatography coupled with photodiode array detector (HPLC-DAD). Good linearities were achieved for dithianon with a linearity equation of $y = 123836x - 8170.8$ ($\gamma = 0.9997$) in a range of 0.1−5 mg L^{-1}, and for pyraclostrobin with $y = 81155x - 200.45$ ($\gamma = 0.9997$) between 0.05 and 2 mg L^{-1}. The limits of quantification (LOQs), defined as the lowest spiked level, were 0.5 and 0.05 mg kg^{-1} for dithianon and pyraclostrobin, respectively.

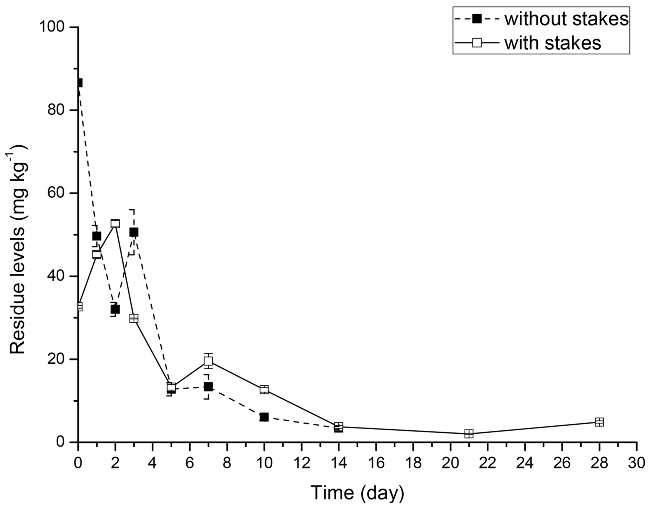

Figure 2. Dissipation of dithianon with different plant modes.

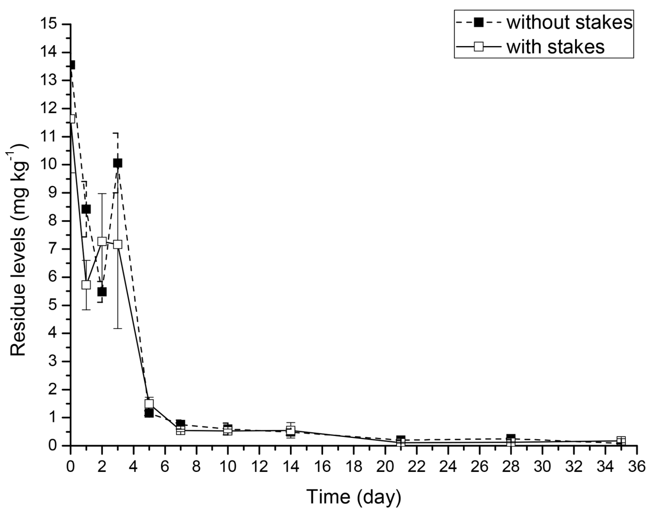

Figure 3. Dissipation of pyraclostrobin with different plant modes.

Recovery studies were performed by spiking the blank samples at different concentration levels with five replicates. As shown in Table 1, the mean recoveries in yam ranged from 77% to 93%, with relative standard deviations (RSDs) between 0.8% and 7.4%, while those in yam plant ranged from 78% to 88%, with RSDs between 2.4% and 5.2%. The recoveries and

DOI: 10.1021/acs.jafc.7b03916
J. Agric. Food Chem. 2017, 65, 10439−10444

Table 2. Dissipation Regression Equations, Half-lives ($t_{1/2}$), and Correlation Coefficients (γ) of Dithianon and Pyraclostrobin (n = 3)

pesticide	planting mode	equation	$t_{1/2}$[a] (days)	γ
dithianon	with stakes	$C = 35.956\ e^{-0.104T}$	6.7 ± 0.2 a	−0.871
	without stakes	$C = 65.075\ e^{-0.226T}$	3.1 ± 0.1 c	−0.964
pyraclostrobin	with stakes	$C = 4.6192\ e^{-0.128T}$	5.4 ± 0.6 b	−0.868
	without stakes	$C = 5.4538\ e^{-0.133T}$	5.2 ± 0.1 b	−0.894

[a]Values with different letters are significantly different ($p < 0.05$).

Table 3. Effect of Some Preparative Processing Methods on Reducing Residues and Processing Factors (Mean ± SD)[a]

	dithianon			pyraclostrobin		
processing methods	residue levels (mg kg^{-1})	reduction (%)	PF	residue levels (mg kg^{-1})	reduction (%)	PF
unprocessed	11.5 ± 1.0 a			18.8 ± 1.2 a		
hot air-drying	7.2 ± 0.6 b	37.4	0.63	16.6 ± 1.1 bc	11.7	0.88
vacuum freeze-drying	6.5 ± 0.4 b	43.5	0.56	17.7 ± 1.4 ab	5.9	0.94
microwave vacuum-drying	7.3 ± 0.6 b	36.5	0.64	16.7 ± 1.1 bc	11.2	0.89
infrared-drying	1.2 ± 0.1 d	89.6	0.10	12.6 ± 0.8 d	33.0	0.67
steaming	2.3 ± 0.2 c	80.0	0.20	15.3 ± 0.1 c	18.6	0.81
boiling	<0.50		n	5.0 ± 0.4 e	73.4	0.27

[a]Values with different letters are significantly different ($p < 0.05$). n = Residues below LOQ, and the processing factor is not calculated.

reproducibility of recovery results confirmed that the method is sufficiently reliable for pesticide analysis in this study.[32]

Dissipation with Different Plant Modes. The dissipation curves of dithianon and pyraclostrobin in yam plants are shown in Figures 2 and 3, respectively. The dissipation regression equations, half-lives ($t_{1/2}$), and correlation coefficients (γ) are summarized in Table 2.

The initial concentration is the quantity of pesticide adhering to the surface of crops after application, which may be influenced by several factors, such as application mode, dosage, growth stage, and planting mode of crop. As shown in the dissipation curves, the initial concentrations in staked yam plant were less than those cultivated on mounds. The staked yam plants were cultivated at a certain height so that the pesticide tended to fall to the ground after application due to gravity. Comparatively, the contact area of yam plants without stakes on the ground was much larger, and the adhered pesticides were much more.

The physical and chemical properties of the pesticide, the planting mode, and the weather, including the light, temperature, and humidity, might play important roles in the degradation rates of pesticides.[33] The regression equations, half-lives, and correlation coefficients are shown in Table 2. On the one hand, under the same planting mode, there was a statistically significant difference between the two pesticides (6.7 vs 5.4 days with stakes, and 3.1 vs 5.2 days without stakes, respectively). The results indicated that the properties of the pesticide played an important role in degradation. On the other hand, the degradation of dithianon was significantly influenced by planting mode (6.7 vs 3.1 days), while the Duncan analysis showed that no distinct difference of degradation rate of pyraclostrobin was found between the two planting modes (5.4 vs 5.2 days). Low stability of dithianon under field conditions (mainly at sunlight) causes relatively fast residue dissipation.[34] The abundant leaves on stakes sheltered yam plant from the strong sunlight, while the yam plant on the ground received more sunshine. Consequently, the degradation rate of dithianon in yam plant with stakes was much slower than for those without stakes. In previous studies, the half-life of dithianon in red pepper was 4.1 days.[35] Furthermore, the half-lives of pyraclostrobinin maize (1.6 days), perilla leaves (4.6 days), and peanut (11.2 days) have been previously reported.[18,36,37] These results show that the dissipation of pesticides is influenced to a certain extent by crop type.

Effect of Processing of Yams on Residues. The effects of different processing methods (HAD, VFD, MVD, ID, steaming, and boiling) on reducing residues and processing factors are summarized in Table 3. As shown in Table 3, all the PFs of dithianon and pyraclostrobin were <1 after the various processing steps, indicating that the residual ratios were reduced during the entire process. All the processing methods resulted in greater reductions in the residues of dithianon than those of pyraclostrobin.

For dithianon, the concentration changed significantly after all the processing methods. The PFs were as follows: MVD (0.64), HAD (0.63), VFD (0.56), steaming (0.20), ID (0.10), and boiling. ANOVA results in Table 3 showed that the residues of HAD, VFD, and MVD were in one class, which indicated little difference between these three treatments. Comparatively, the later three methods, ID, steaming, and boiling, had greater effects on the residues of the target pesticides, especially boiling, after which the residues were below the LOQ. These results were perhaps because of its low stability under heat conditions in which the temperatures of the later three processing methods were all >90 °C, while the first three were <50 °C. Our finding was in agreement with results of Pesticide Manual, in that it decomposed by prolonged heating. The process involving heat treatment causes an increase in volatilization, hydrolysis, and degradation of other chemicals, resulting in the reduction of residue levels.[38]

For pyraclostrobin, the residues were significantly reduced by processing treatments except for VFD. Similar to dithianon, the PFs of pyraclostrobin were decreased by processing treatments in the same order: MVD (0.89), HAD (0.88), steaming (0.81), ID (0.67), and boiling (0.27). The PF after boiling was obviously lower than those after other processes, demonstrating that the boiling process was the most effective for reducing residues of both dithianon and pyraclostrobin while the other processing steps reduced at considerably lower levels. The yams were soaked in water during the boiling treatment; con-

DOI: 10.1021/acs.jafc.7b03916
J. Agric. Food Chem. 2017, 65, 10439−10444

sequently, a part of the residues might be resolved in water. Overall, the results are useful for ascertaining the safety of dithianon and pyraclostrobin in yams cultivated by different planting modes, providing guidance for dietary risk assessment and serving as a reference for yam production.

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS USED

RSDs, relative standard deviations; PFs, processing factors; HPLC-UV, high-performance liquid chromatography coupled with ultraviolet detector; HPLC-MS/MS, high-performance liquid chromatography coupled with tandem mass spectrometry; MRLs, maximum residue limits; HAD, hot air-drying; VFD, vacuum freeze-drying; MVD, microwave vacuum-drying; ID, infrared drying; WDGs, water-dispersible granules; PSA, primary secondary amine; SPE, solid-phase extraction; HPLC-DAD, high-performance liquid chromatography coupled with photodiode array detector; LOQ, limit of quantification; g a.i. L^{-1}, grams of active ingredient per hectare

■ REFERENCES

(1) Akinoso, R.; Olatoye, K. Energy utilization and conservation in instant-pounded yam flour production. *Int. Food Res. J.* **2013**, *20*, 575−579.

(2) Ju, Y.; Xue, Y.; Huang, J.; Zhai, Q.; Wang, X. Antioxidant Chinese yam polysaccharides and its pro-proliferative effect on endometrial epithelial cells. *Int. J. Biol. Macromol.* **2014**, *66*, 81−85.

(3) Fu, Y.; Chen, S.; Huang, P.; Li, Y. Application of bubble separation for quantitative analysis of choline in Dioscorea (yam) tubers. *J. Agric. Food Chem.* **2005**, *53*, 2392−2398.

(4) Wang, S.; Yu, J.; Liu, H.; Chen, W. Characterisation and preliminary lipid-lowering evaluation of starch from Chinese yam. *Food Chem.* **2008**, *108*, 176−181.

(5) Chen, Y.; Zhu, Q.; Wu, S. Preparation of oligosaccharides from Chinese yam and their antioxidant activity. *Food Chem.* **2015**, *173*, 1107−1110.

(6) Han, C.; Lin, Y.; Lin, Y.; Lee, T.; Huang, W.; Lin, S.; Hou, W. Effects of yam tuber protein, dioscorin, on attenuating oxidative status and learning dysfunction in D-galactose-induced BALB/c mice. *Food Chem. Toxicol.* **2014**, *65*, 356−363.

(7) Asiedu, R.; Sartie, A. Crop that feed the world 1. Yams. *Food Security* **2010**, *2*, 305−315.

(8) Fang, Z.; Wu, D.; Yü, D.; Ye, X.; Liu, D.; Chen, J. Phenolic compounds in Chinese purple yam and changes during vacuum frying. *Food Chem.* **2011**, *128*, 943−948.

(9) Fang, S.; Wang, L.; Wu, T. Mathematical modeling and effect of blanching pretreatment on the drying kinetics of Chinese yam. *Chem. Ind. Chem. Eng. Q.* **2015**, *21*, 511−518.

(10) Falade, K. O.; Olurin, T. O.; Ike, E. A.; Aworh, O. C. Effect of pretreatment and temperature on air-drying of Dioscoreaalata and Dioscorearotundata slices. *J. Food Eng.* **2007**, *80*, 1002−1010.

(11) Hsu, C.; Chen, W.; Weng, Y.-M.; Tseng, C.-Y. Chemical composition, physical properties, and antioxidant activities of yam flours as affected by different drying methods. *Food Chem.* **2003**, *83*, 85−92.

(12) Lin, Y.; Lee, T.; Tsen, J.; King, V. A. Dehydration of yam slices using FIR-assisted freeze drying. *J. Food Eng.* **2007**, *79*, 1295−1301.

(13) Popoola, A. R.; Adedibu, B. O.; Ganiyu, S. A. Rapid assessment of resistance of tissue-cultured water yam (Dioscoreaalata) and white guinea yam (Dioscorearotundata) to anthracnose (Colletotrichum-gloeosporioidesPenz.). *Arch. Phytopathology Plant Prot.* **2013**, *46*, 663−669.

(14) Raj, M.; Hegde, V.; Jeeva, M. L.; Senthil, M.; Nath, V. S.; Vidyadharan, P.; Archana, P. V. Molecular diagnosis of Colletotrichumgloeosporioides causing Anthracnose/Dieback disease in Greater Yam (Dioscoreaalata L.). *Arch. Phytopathology Plant Prot.* **2013**, *46*, 927−936.

(15) Katoh, H.; Fukuda, T.; Nishigawa, H.; Natsuaki, T. Rapid detection of Colletotrichumgloeosporioides in infected strawberry plants using loop-mediated isothermal amplification. *J. Gen. Plant Pathol.* **2016**, *82*, 190−198.

(16) Pozzetti, L.; Paolini, M.; Barillari, J.; Cantelli-Forti, G. Induction and suppression of murine CYP-mediated biotransformation by dithianon: organ- and sex-related differences. *Cancer Lett.* **1999**, *141*, 47−56.

(17) Vicentini, C. B.; Romagnoli, C.; Andreotti, E.; Mares, D. Synthetic pyrazole derivatives as growth inhibitors of some phytopathogenic fungi. *J. Agric. Food Chem.* **2007**, *55*, 10331−10338.

(18) Farha, W.; Rahman, M. M.; Abd El-Aty, A. M.; Jung, D.; Kabir, M. H.; Choi, J.; Kim, S.; Jeong Im, S.; Lee, Y.; Shin, H.; Kwon, C.; Son, Y.; Lee, K.; Shim, J. A combination of solid-phase extraction and dispersive solid-phase extraction effectively reduces the matrix interference in liquid chromatography-ultraviolet detection during pyraclostrobin analysis in perilla leaves. *Biomed. Chromatogr.* **2015**, *29*, 1932−1936.

(19) Lan, F.; Liu, C.; Zhou, X.; Wang, Z.; Lu, Z.; Yao, J.; Liu, X.; Jiang, W. Residues and dietary intake risk assessment of dithianon and pyraclostrobin in the jujube. *Chin. J. Pestic. Sci.* **2015**, *17*, 706−714.

(20) Baker, P. G.; Clarke, P. G. Determination of residues of dithianon in apples by high-performance liquid chromatography. *Analyst* **1984**, *109*, 81−83.

(21) Esteve-Turrillas, F. A.; Mercader, J. V.; Agulló, C.; Abad-Somovilla, A.; Abad-Fuentes, A. Development of immunoaffinity columns for pyraclostrobin extraction from fruit juices and analysis by liquid chromatography with UV detection. *J. Chromatogr. A* **2011**, *1218*, 4902−4909.

(22) Ticha, J.; Hajslova, J.; Jech, M.; Honzicek, J.; Lacina, O.; Kohoutkova, J.; Kocourek, V.; Lansky, M.; Kloutvorova, J.; Falta, V. Changes of pesticide residues in apples during cold storage. *Food Control* **2008**, *19*, 247−256.

(23) Pan, X.; Dong, F.; Xu, J.; Liu, X.; Cheng, Y.; Chen, Z.; Liu, N.; Chen, X.; Tao, Y.; Zheng, Y. Comparison of different cleanup procedures for oil crops based on the development of a trace analytical method for the determination of pyraclostrobin and epoxiconazole. *J. Sep. Sci.* **2014**, *37*, 3669−3676.

(24) Niell, S.; Jesús, F.; Pérez, C.; Mendoza, Y.; Díaz, R.; Franco, J.; Cesio, V.; Heinzen, H. QuEChERS adaptability for the analysis of pesticide residues in beehive products seeking the development of an agroecosystem sustainability monitor. *J. Agric. Food Chem.* **2015**, *63*, 4484−4492.

(25) Souza-Silva, E. A.; Pawliszyn, J. Compatible fiber coating for multiresidue pesticide analysisi of grapes by gas chromatography-time-of-flight mass spectrometry (DI-SPME-GC-ToFMS). *J. Agric. Food Chem.* **2015**, *63*, 4464−4477.

(26) Amvrazi, E. G.; Albanis, T. A. Multiclass pesticide determination in olives and their processing factors in olive oil: comparison of different olive oil extraction systems. *J. Agric. Food Chem.* **2008**, *56*, 5700−5709.

(27) FAO/WHO. Updating the principles and methods of risk assessment: MRLs for pesticide and veterinary drugs. FAO/WHO: Rome, 2006.

(28) *Guideline on pesticide residue trials*; NY/T 788-2004; China Agriculture Press: Beijing, China, 2004.

(29) Noh, H. H.; Kim, D. K.; Lee, E. Y.; Chang, M. I.; Im, M. H.; Lee, Y. D.; Kyung, K. S. Effects of oven drying on pesticide residues in

DOI: 10.1021/acs.jafc.7b03916
J. Agric. Food Chem. 2017, 65, 10439−10444

field-grown chili peppers. *J. Korean Soc. Appl. Biol. Chem.* **2015**, *58*, 97−104.

(30) Saber, A. N.; Malhat, F. M.; Badawy, M. M. A.; Barakat, D. A. Dissipation dynamic, residue distribution and processing factor of hexythiazox in strawberry fruits under open field condition. *Food Chem.* **2016**, *196*, 1108−1116.

(31) Aguilera, A.; Valverde, A.; Camacho, F.; Boulaid, M.; García-Fuentes, L. Effect of household processing and unit to unit variability of azoxystrobin, acrinathrin and kresoxim methyl residues in zucchini. *Food Control* **2012**, *25*, 594−600.

(32) OECD; ENV/JM/MONO. Guidance document on pesticiderresidue analytical methods. http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=env/jm/mono(2007)17&doclanguage=en (accessed Oct 25, 2017).

(33) Tewary, D. K.; Kumar, V.; Ravindranath, S. D.; Shanker, A. Dissipation behavior of bifenthrin residues in tea and its brew. *Food Control* **2005**, *16*, 231−237.

(34) Tomlin, C. D. S. *The Pesticide Manual*; The British Crop Protection Council: Hampshire, United Kingdom, 2002.

(35) Jang, J.; Rahman, M. M.; Abd El-Aty, A. M.; Ko, A.; Park, J.; Cho, J. M.; Cho, S.; Seo, Y. M.; Shim, J. A simple and improved HPLC method for the analysis of dithianon in red pepper with tandem mass spectrometry confirmation. *Food Anal. Methods* **2014**, *7*, 653−659.

(36) You, X.; Liu, C.; Liu, F.; Liu, Y.; Dong, J. Dissipation of pyraclostrobin and its metabolite BF-500−3 in maize under field conditions. *Ecotoxicol. Environ. Saf.* **2012**, *80*, 252−257.

(37) Zhang, F.; Wang, L.; Zhou, L.; Wu, D.; Pan, H.; Pan, C. Residue dynamics of pyraclostrobin in peanut and field soil by QuEChERS and LC-MS/MS. *Ecotoxicol. Environ. Saf.* **2012**, *78*, 116−122.

(38) Holland, P.; Hamilton, D.; Ohlin, B.; Skidmore, M. Effects of storage and processing on pesticide residues in plant products. *Pure Appl. Chem.* **1994**, *66*, 335−356.

DOI: 10.1021/acs.jafc.7b03916
J. Agric. Food Chem. 2017, 65, 10439−10444