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Effects of moisture and temperature on pesticide stability in corn flour

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Abstract: Corn flour has been stored at different moisture content (without and with 10 % water) and temperatures (–20, 4 and 25 °C). A modified quick, easy, cheap, effective, rugged and safe (QuEChERS) method was applied to determine the degradation rate of five common pesticides (imidacloprid, carbendazim, triadimefon, acetochlor and metolachlor) during the stored process using high-performance liquid chromatography with a diode array detector and gas chromatography with an electron capture detector. The results showed that there was almost no degradation on five pesticides at –20 °C in corn flour whether with or without water, and the half-life was 69.3–693.2 days. The degradation rate ranged from 1.7 to 7.8 % after ten days of application. Under 25 °C and 10 % moisture content, the half-life was sharply reduced to 5.8–14.4 days. Under this condition, the degradation rate ranged from 40.6 to 68.4 % after ten days of application, and the sequence from high to low of the five pesticides. The degradation rates were as follows: carbendazim, imidacloprid, acetochlor, metolachlor and triadimefon. Therefore, low temperature and drying were beneficial to the storage of corn flour, but unfavorable to the degradation of pesticides in corn flour.

Keywords: pesticides residue; moisture content; temperature; corn flour.

INTRODUCTION

Maize (*Zea mays* L.), also known as corn, is one of the most extensively cultivated cereal crops on earth. More is produced, by weight, than any other grain, and almost every country on earth cultivates maize commercially for a variety of uses.[1] Similar to other crops, corn is attacked by a number of weeds, pathogens, and pests during its growth.[2–4] As an important means to control weeds, pathogens, and pests and to protect crops, pesticide plays an important

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role in agricultural production. But an overdependence on pesticides to control weeds, pathogens, and pests has resulted in serious problems, such as the ubiquity of the improper use of pesticides, the fast development of the pests resistance, and high residue in the corn seeds and corn flour. The ecological environment and human health are threatened immensely.[5] Generally speaking, pesticides mainly are degraded by microorganisms in the soil, also ambient humidity and temperature can affect microorganism activity. The degradation of pesticides is affected by humidity and temperature of the environment.[6] Much research has shown that the degradation rate of pesticides will increase with an increase in water content within a certain range of water-holding capacity. Temperature is another important factor affecting microbial activity;[7] pesticide degradation showed strong sensitivity to temperature, in the tested temperature range, and with an increase in temperature degradation rate of pesticides in the environment speeded up.[8] In addition, temperature can affect the hydrolysis of pesticides.[9] Patsias and Papadopoulou-Mourkidou[10] studied the storage stability of aniline and phenols in water samples at three temperatures (–24, 4 °C and room temperature). Three months later, the results showed that phenols were still stable at room temperature, but the degradation of aniline drugs occurred after one week at room temperature, and no degradation occurred at –20 °C. This indicated that storage temperature has a decisive effect on the storage stability of pesticide residue. Afridi[11] found that under conditions of 13 % humidity and 40 °C, the degradation rate of chlorpyrifos methyl, pirimiphos methyl, and permethrin was the fastest. Thus, it has been proven that both temperature and humidity have a direct effect on the storage stability of pesticides.

During production, transportation, and storage, corn flour also will be exposed to variety of temperature and humidity conditions. The degradation of pesticides in corn flour will be affected by the environment. The effects of temperature and humidity on the degradation of pesticides in various matrixes have been reported widely.[12–16] Few effects in cereals have been reported,[11,17] and in particular, no report has been made for corn flour. Studying the degradation behavior of pesticides in corn flour under different temperature and humidity conditions will clarify significantly the degradation behavior of pesticides in corn flour and ensure the food safety of corn flour.

The QuEChERS – a portmanteau word formed from quick, easy, cheap, effective, rugged, and safe,[18,19] method is a streamlined approach that makes it easier and less expensive for analytical chemists to examine pesticide residue in a variety of agricultural samples. One specific method that has become popular is the QuEChERS technique, which is used to facilitate the rapid screening of numerous food and agricultural samples for pesticide residue.[20] In this study, we selected five pesticides widely used in maize fields. They belong to the three major kinds of pesticides (*i.e.*, herbicide, insecticide, and bactericide): 1) acetochlor (herbicide, CAS: 34256-82-1, $C_{14}H_{20}ClNO_2$, 2-chloro-*N*-(ethoxymethyl)-*N*-(2--ethyl-6-methylphenyl)acetamide), 2) metolachlor (herbicide, CAS: 51218-45-2, $C_{15}H_{22}ClNO_2$, 2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide), 3) imidacloprid (insecticide, CAS: 138261-41-3, $C_9H_{10}ClN_5O_2$, *(2E)*-1-[(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine), 4) triadimefon (bactericide, CAS: 43121-43-3, $C_{14}H_{16}ClN_3O_2$, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone) and 5) carbendazim (bactericide, CAS: 10605-21-7, $C_9H_9N_3O_2$, methyl-1*H*-benzimidazol--2-yl-carbamate). At present, studies have shown that the degradation rate of five pesticides in crops is fast, which belongs to degradable pesticides.[21–25] In this study, we used QuEChERS method combined with high-performance liquid chromatography (HPLC) and gas chromatography (GC) to further study the effects of temperature and humidity on the degradation rates of the five pesticides under storage conditions. The results from monitoring pesticide residue could offer insight into the design of government pesticide control and risk management programs for corn flour or other grains in future.

EXPERIMENTAL

Chemicals and reagents

The carbendazim standard (99.5 % purity), imidacloprid standard (99.9 % purity), metolachlor standard (97.6 % purity), triadimefon standard (98.7 % purity) and acetochlor standard (96.0 % purity) were obtained from Fluka (Sigma–Aldrich Corporation, St. Louis, MO). HPLC-grade methanol and acetonitrile were procured from Merck KGaA (Darmstadt, Germany), and ultrapure water was obtained by a Milli-Q Gradient System from Millipore (Molsheim, France). Primary secondary amine (PSA) and graphitized carbon black (GCB) were purchased from Bonna-Agela Technologies (Tianjin, China). Analytical-grade sodium chloride (NaCl), anhydrous magnesium sulfate ($MgSO_4$), aceticacid and acetone were obtained from Guangfu Fine Chemical Research Institute (Tianjin, China).

The standard stock of acetochlor, metolachlor, and triadimefon were prepared in pure acetone. Then the standard working solutions at the concentration levels between 0.0001 and 1 μg mL^{-1} were prepared from the stock solution by serial dilution with acetone. The standard stock of carbendazim and imidacloprid were prepared in methanol with 1 vol. % acetic acid and 5 vol. % acetonitrile, respectively. The standard working solutions at concentration levels between 0.005 and 10 μg mL^{-1} were prepared from the stock solution by serial dilution with acetonitrile. All standard stock solutions and standard working solutions were stored at 4 °C.

Preparation of experiment

Corn flour samples were purchased from the local market and confirmed that did not have five pesticides, involved in this study, by HPLC and GC (details are given in Supplementary material to this paper). The samples were divided into two parts: nonaqueous and aqueous (dry corn flour mixed with 10 % water). A nonaqueous or aqueous corn flour sample (20.0 g) was weighed into a 50 mL polypropylene centrifuge tube and sprayed with 1 mL mixed standard stock solutions of the five pesticides (100 mg L^{-1}). The centrifuge tube then was lidded and vortexed for 30 min to achieve a residue level of approximately 5.0 mg kg^{-1}. All centrifuge tubes were stored separately in a dark place under frozen (–20 °C), refrigerated (4 °C), and ambient (25 °C) temperatures. This process was repeated three times for each treated sample. The corn flour samples from the centrifuge tubes 0 (calculated as the original concentration), 1, 3, 5 and 10 days after spraying.

Extraction and purification

The samples were treated according to the modified QuEChERS method: 5.0 g of corn flour was treated with 10.0 mL acetonitrile. The mixture was vortexed for 30 min and the extract centrifuged at 3800 rpm for 5 min. An 1.5 mL aliquot of the upper layer was transferred into a 2 mL centrifuge tube containing 150 mg anhydrous $MgSO_4$, 10 mg GCB and 50 mg PSA. The contents were vortexed for 2 min and centrifuged at 6000 rpm for 2 min. The acetonitrile phase passed through a 0.22-μm nylon syringe filter before HPLC and GC analysis.

Instrumental determination

The presence of carbendazim and imidacloprid were determined by an Agilent 1200 series HPLC system (Agilent Technologies, Santa Clara, CA) equipped with a quaternary pump (G1311A), an autosampler (G1329A), a column compartment (G1316A), and a diode array detector (G1315D). The separation of pesticides and interferences were performed on an Ultimate XB C-18 column (250 mm×4.6 mm, 5 μm) obtained from Welch Materials, Inc. (Shanghai, China), operated at 30 °C. The mobile phase was acetonitrile–water (23/77 volume ratio) at a flow rate of 1 mL min^{-1}. Detection wavelengths were at 270 nm (imidacloprid) and 286 nm (carbendazim). The injection volume was 10 μL. Under these experimental conditions, the retention times of carbendazim and imidacloprid were 10.3 and 10.8 min, respectively. The presence of acetochlor, metolachlor, and triadimefon were determined using an Agilent 6890 plus GC (Agilent Technologies) equipped with an electron capture detector and an HP-5 MS (30 m×0.32 mm, 0.25 μm) capillary column. The injector was operated at 260 °C, in a splitless injection mode, and the injection volume was 2 μL. The oven temperature was programmed to increase from 120 °C for 1.5 min, to 220 °C at 15 °C min^{-1}, and then we raised the temperature to 280 °C at 30 °C min^{-1} for 5 min. Nitrogen was used as the carrier gas and makeup gas at a flow rate of 5 and 30 mL min^{-1}, respectively. The detector temperature was 300 °C. The retention times of acetochlor, metolachlor, and triadimefon were 6.85, 7.45 and 7.59 min, respectively.

Calculation

All treatments were replicated three times in the experiments. Microsoft Office Excel 2013 calculated the means and standard deviations (*SD*). The degradation process of five pesticides in corn flour followed the first-order kinetics reactions. The degradation rate constant and half-life were calculated using the first-order rate equation: $c_t = c_0 e^{-kt}$, where c_t represents the concentration of the five pesticides residue at the time of t, c_0 represents the initial deposits after application, and k is the degradation rate constant.[26] The half-life ($t_{1/2}$) was 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 for each experiment, being $t_{1/2} = \ln 2/k$.[26] One-way analysis of variance was carried out with SAS 8.5. When significant effects were found, individual treatments were compared by least significant difference tests. The significance level was defined as $p < 0.05$.

RESULTS AND DISCUSSION

Matrix effect, linearity, recovery, and detection limits

Matrix effect may enhance or suppress the response signal.[27] In this study, we evaluated matrix effect for five pesticides by comparing the slope of the standard and matrix-matched calibration curve. The results are presented in Table I. The matrix-spiked match showed good linearity with correlation coefficients (γ) above 0.9990 for the five pesticides at their concentration ranges.

TABLE I. Calibration curves for five pesticides in organic reagent and corn flour

Pesticide	Matrix	Concentration range, mg L^{-1}	Regression equation	γ
Acetochlor	Acetone	0.0001–1	$y = 1874.3x + 11.360$	0.9998
	Corn flour	0.0001–1	$y = 1719.7x + 45.230$	0.9993
Metolachlor	Acetone	0.0001–1	$y = 1279.5x + 11.108$	0.9997
	Corn flour	0.0001–1	$y = 1091.7x + 32.544$	0.9993
Triadimefon	Acetone	0.0002–1	$y = 8671.5x - 58.666$	0.9997
	Corn flour	0.0002–1	$y = 9098.5x - 200.19$	0.9996
Carbendazim	Acetonitrile	0.005–10	$y = 3.3599x - 0.2997$	1.0000
	Corn flour	0.005–10	$y = 2.8107x - 0.2117$	0.9997
Imidacloprid	Acetonitrile	0.005–10	$y = 4.5332x - 0.2095$	1.0000
	Corn flour	0.005–10	$y = 3.5823x + 0.3542$	0.9995

We spiked the blank corn flour samples with the five pesticides at two concentration levels and performed five replicated analyses for each concentration level. The results are shown in Table II and the chromatograms are shown in Supplementary material. In corn flour, the average recoveries for the five pesticides ranged from 84.1 to 101.7 %, with relative standard deviations of 1.5–6.6 %. These results indicate good precision and accuracy for the method.

TABLE II. Fortified recoveries of five pesticides in corn flour ($n = 5$)

Pesticide	Spiked level, mg kg^{-1}	Average recoveries ± *SD*, %	*RSD* / %
Acetochlor	0.05	97.1±2.5	2.6
	0.5	95.8±2.1	2.2
Metolachlor	0.05	89.5±3.6	4.0
	0.5	91.6±1.7	1.8
Triadimefon	0.05	101.7±1.6	1.5
	0.5	97.1±2.2	2.3
Carbendazim	0.05	90.9±6.0	6.6
	0.5	84.1±3.2	3.8
Imidacloprid	0.05	101.7±5.7	5.7
	0.5	94.3±1.8	1.9

The limit of detection (*LOD*) was the concentration of the spiked sample that produced a signal-to-noise ratio of 3. The *LOD*s were 0.002, 0.002, 0.001, 0.005, and 0.005 mg kg^{-1} for acetochlor, metolachlor, triadimefon, carbendazim and imidacloprid in the corn flour samples, respectively. The limits of quantification that corresponded to the lowest fortification level for acetochlor, metolachlor, triadimefon, carbendazim and imidacloprid were 0.005, 0.005, 0.002, 0.01 and 0.01 mg kg^{-1} in corn flour, respectively.

The effect of water content on the degradation rate of pesticide in corn flour

The dissipation kinetics equations and trends charts for the five pesticides are shown in Table III and Fig. 1. Under anhydrous conditions, the average half-life of the five pesticides in corn flour at –20, 4 and 25 °C was 256.5, 192.5 and 55.5 days, respectively. Under aqueous conditions, the average half-life of the five pesticides in corn flour at –20, 4 and 25 °C was 128.7, 39.4 and 9.8 days, respectively.

TABLE III. The dissipation kinetics equations and half-life of five pesticides in corn flour

Pesticide	Treatments	Regression equation	γ	$t_{1/2}$ / days
Acetochlor	−20 °C/with 10 % water	$y = 0.4876e^{-0.007x}$	0.9879	99.0
	4 °C/with 10 % water	$y = 0.4866e^{-0.022x}$	0.9711	31.5
	25 °C/with 10 % water	$y = 0.4572e^{-0.079x}$	0.9681	8.8
	−20 °C/without water	$y = 0.4700e^{-0.004x}$	0.7258	173.3
	4 °C/without water	$y = 0.4671e^{-0.006x}$	0.9009	115.5
	25 °C/without water	$y = 0.4554e^{-0.017x}$	0.8819	40.8
Metolachlor	−20 °C/with 10 % water	$y = 0.4761e^{-0.004x}$	0.9273	173.3
	4 °C/with 10 % water	$y = 0.4562e^{-0.008x}$	0.8210	86.6
	25 °C/with 10 % water	$y = 0.4335e^{-0.050x}$	0.9156	13.9
	−20 °C/without water	$y = 0.5081e^{-0.001x}$	0.2147	693.2
	4 °C/without water	$y = 0.5075e^{-0.002x}$	0.4674	346.6
	25 °C/without water	$y = 0.5081e^{-0.009x}$	0.8526	77.0
Triadimefon	−20 °C/with 10 % water	$y = 0.4845e^{-0.004x}$	0.8389	173.3
	4 °C/with 10 % water	$y = 0.4661e^{-0.015x}$	0.9545	46.2
	25 °C/with 10 % water	$y = 0.4135e^{-0.048x}$	0.8558	14.4
	−20 °C/without water	$y = 0.4847e^{-0.010x}$	0.9171	69.3
	4 °C/without water	$y = 0.4705e^{-0.009x}$	0.6596	77.0
	25 °C/without water	$y = 0.4804e^{-0.015x}$	0.9005	46.2
Carbendazim	−20 °C/with 10 % water	$y = 0.4343e^{-0.007x}$	0.8964	99.0
	4 °C/with 10 % water	$y = 0.4017e^{-0.041x}$	0.9723	16.9
	25 °C/with 10 % water	$y = 0.3867e^{-0.120x}$	0.9093	5.8
	−20 °C/without water	$y = 0.4992e^{-0.003x}$	0.9916	231.1
	4 °C/without water	$y = 0.4921e^{-0.002x}$	0.4656	346.6
	25 °C/without water	$y = 0.4767e^{-0.019x}$	0.8566	36.5
Imidacloprid	−20 °C/with 10 % water	$y = 0.4653e^{-0.007x}$	0.9882	99.0
	4 °C/with 10 % water	$y = 0.4381e^{-0.044x}$	0.8725	15.8
	25 °C/with 10 % water	$y = 0.4140e^{-0.114x}$	0.9062	6.1
	−20 °C/without water	$y = 0.4744e^{-0.006x}$	0.5998	115.5
	4 °C/without water	$y = 0.4674e^{-0.009x}$	0.5916	77.0
	25 °C/without water	$y = 0.4695e^{-0.009x}$	0.6355	77.0

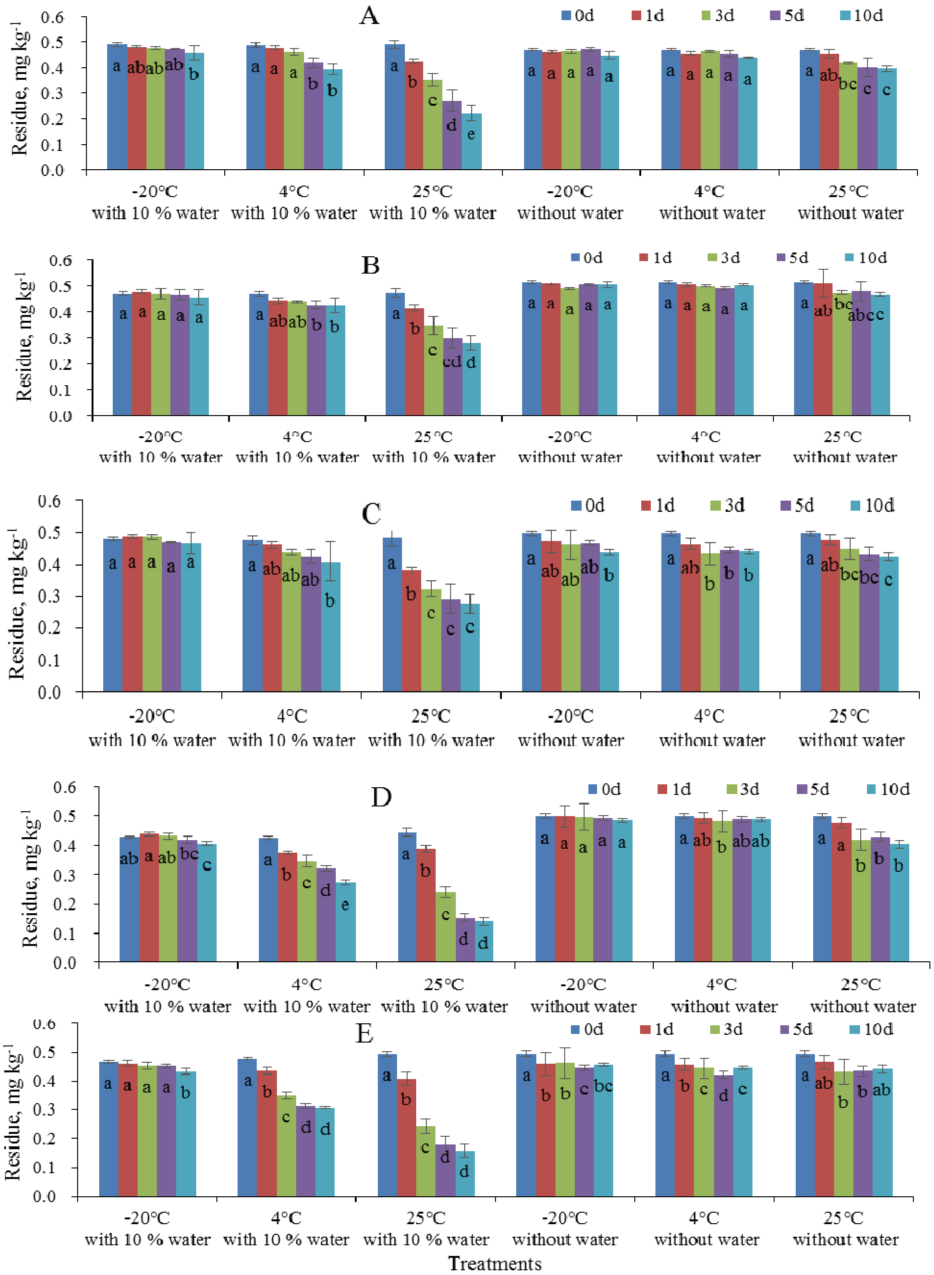

Fig. 1. Residual changes of five pesticides in corn flour under different temperature and humidity conditions: A) acetochlor, B) metolachlor, C) triadimefon, D) carbendazim and E) imidacloprid; d – day; the different letters within the individual error bars indicate that the values are significantly different ($p < 0.05$).

It is evident that, at three temperatures, the dissipation of the five pesticides in aqueous corn flour was faster than in anhydrous corn flour. Reasons for this faster dissipation may include the higher moisture content in corn flour, the stronger bacteria and microbial activity, and the important role bacteria and microbial activity play in the degradation of pesticides. The higher the corn flour moisture content, the faster the degradation rate of pesticide; additionally, different types of bacteria and microbial activity are not the same under the same environmental conditions, and thus their ability to degrade pesticide also is different.

The effect of temperature on the degradation rate of pesticide in corn flour

No matter in anhydrous or hydrous conditions, the dissipation of the five pesticides was faster with rising temperatures. The effect of environmental temperature on bacteria and microbial activity is varied. The higher temperature, the greater bacteria and microbial activity, and the greater degradation ability of pesticides. The higher environmental temperature, the faster natural degradation of pesticides. Bacteria and microbial activity did not have a significant effect on the degradation rate of the five pesticides at –20 °C. Low temperature can inhibit the growth of microorganisms, and microbial activity can affect the stability of pesticide residue storage, so frozen storage is a suitable method.

It can be seen that under –20 °C and aqueous condition, the fastest degradation pesticides were acetochlor, carbendazim, and imidacloprid, followed by metolachlor and triadimefon; under 4 °C and aqueous condition, the fastest degradation pesticide was imidacloprid, followed by carbendazim, acetochlor, triadimefon, and metolachlor; and under 25 °C and aqueous condition, the fastest degradation pesticide was carbendazim, followed by imidacloprid, acetochlor, metolachlor and triadimefon. Under –20 °C and anhydrous condition, the fastest degradation pesticide was triadimefon, followed by imidacloprid, acetochlor, carbendazim and metolachlor; under 4 °C and anhydrous condition, the fastest degradation pesticides were triadimefon and imidacloprid, followed by acetochlor, carbendazim and metolachlor; and under 25 °C and anhydrous condition, the fastest degradation pesticide was carbendazim, followed by acetochlor, triadimefon, imidacloprid and metolachlor.

The difference of storage stability of five pesticides in corn flour

According to the Organisation for Economic Co-operation and Development,[28] based on practical experience, if the degradation rate of some pesticides reaches 30 %, those pesticides are considered not stable in the target matrix.[29] In this study, the degradation rates of the five pesticides in nonaqueous corn flour was less than 30 % under all temperature conditions after being stored for 10 days, and in the aqueous corn flour, it was less than 30 % at −20 and 4 °C, but more than 30 % at 25 °C, after being stored for 5 days.

Under the same conditions, the degradation rates of different pesticides were obviously different. This was related to differences in the physical and chemical properties of the different pesticides. Many studies showed that the degradation rate of different pesticides in the same matrix was not the same, such as those for organochlorine and pyrethroids. Weak polar pesticides in water samples were relatively stable. However, organic phosphorus, carbamate and some other polar pesticides are unstable during storage, and they decompose easily under conditions of 4 and 20 °C.[30] The physical and chemical properties of pesticides, such as saturated vapor pressure and water solubility, can directly affect the stability of pesticides.[31,32]

CONCLUSIONS

The problem of excessive pesticide residue in foods such as corn flour has attracted wide attention. In this study, we have detected the degradation rates of imidacloprid, carbendazim, triadimefon, acetochlor and metolachlor in aqueous and nonaqueous corn flour at −20, 4 and 25 °C in order to evaluate consumer safety and the proper use of these pesticides. We developed a relatively simple and fast method to analyze these five pesticide residues. The results showed that the higher the temperature and water content, the worse the stability of pesticide in corn flour. The five pesticides had almost no degradation at −20 °C in corn flour whether with or without water. Therefore, although low temperature and drying conditions can guarantee the quality of corn flour, it cannot be ignored that pesticide residues could be very serious threat to human health.

SUPPLEMENTARY MATERIAL

Chromatograms of five pesticides in corn flour are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

УТИЦАЈ ВЛАГЕ И ТЕМПЕРАТУРЕ НА СТАБИЛНОСТ ПЕСТИЦИДА У КУКУРУЗНОМ БРАШНУ

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Кукурузно брашно је чувано са различитим садржајем влаге (без 10 % воде и са њим) и на различитим температурама (–20, 4 и 25 °C). Модификован поступак QuEChERS (*quick, easy, cheap, effective, rugged and safe*) је коришћен за утврђивање брзине разлагања пет стандардних пестицида (имидаклоприд, карбендазим, триадимефон, ацетохлор и метолахлор) током складиштења, применом метода HPLC са диодним детектором и GC са детектором захвата електрона. Резултати су показали да није дошло до значајног разлагања пестицида на

–20 °C у кукурузном брашну без влаге или са њом, а њихов полуживот је био 69,3–693,2 дана. Брзина разлагања се кретала између 1,7 и 7,8 % после десет дана. Полуживот пестицида се знатно скратио на 25 °C и уз 10 % влаге, на 5,8–14,4 дана. Под овим условима је брзина разлагања била 40,6 до 68,4 % после десет дана, а редослед степена деградације (од највећег до најмањег) је био следећи: карбендазим, имидаклоприд, ацетохлор, метолахлор и триадимефон. Према томе, ниска температура и одсуство влаге су били погодни услови за чување кукурузног брашна, али неодговарајући за разлагање пестицида у брашну.

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