

## Degradation of pesticide residues in fruits and vegetables studied using high-performance liquid chromatography/high-resolution mass spectrometry

KAIXUAN TONG – XINGQIANG WU – ZIJUAN ZHANG – YUJIE XIE – HUI CHEN – CHUNLIN FAN

### Summary

In this paper, we report the degradation of 47 pesticides in apple, grape, cabbage and tomato within 77 days under freezing frozen conditions ( $-18\text{ }^{\circ}\text{C}$ ). Pesticides were analysed by liquid chromatography – quadrupole time-of-flight mass spectrometry (LC-Q-TOF-MS). Recovery studies of the pesticides were conducted at limit of quantification (LOQ) level with 5 replicates in the four matrices. They were all in the range of 70–120 % and the relative standard deviation (RSD) was less than 25 %, which indicated acceptable reliability and quantitative accuracy of the proposed method. Spiked samples were prepared at  $50\text{ }\mu\text{g}\cdot\text{kg}^{-1}$  and  $200\text{ }\mu\text{g}\cdot\text{kg}^{-1}$  and stored at  $-18\text{ }^{\circ}\text{C}$ . The degradation curve of these pesticides was drawn based on the summarized results, their degradation rules was logarithmic, polynomial or exponential. The degradation rates in apples and tomatoes were relatively stable with half-lives of 6.8–30.1 days. Most of the pesticides vanished rapidly within 14 days in cabbage and grape. The degradation rule in this work could provide an important reference for risk assessment and measurement accuracy for regulatory agencies.

### Keywords

time-of-flight mass spectrometry; pesticide residue; degradation; agricultural product

It is estimated that more than  $2.5 \times 10^9$  kg of pesticides are used annually in the world, so pesticide residues and their degradation products in food are a non-negligible threat to consumers' life and health [1–3]. To deal with the issues of pesticide residues, some countries and organizations have established monitoring systems and conduct sampling inspection routinely and periodically. In the actual manipulation process, samples are frozen and stored for re-testing. Globally, relevant organizations and institutions will verify the detection methods of pesticide residues in fruits and vegetables every year and evaluate the skill and capability of individual laboratories to fulfill the detection methods [4–6]. Spiked samples are usually distributed to the participating laboratories for verification. However, degradation of pesticide in the samples might cause troubles even under frozen condition. The stability of pesticides depends on physical properties of pesticides, such as volatilization, solubility, octanol-water partition coefficient ( $K_{ow}$ ) and dissociation constant ( $K_a$ ) [7].

Nowadays, the research on the degradation

of pesticide residues mainly focuses on oxidation by strong oxidation gases (ozone [8, 9] or  $\text{ClO}_2$  [10, 11]), photodegradation [12, 13], action of microorganisms [14, 15] and biodegradation [16]. However, studies on the natural degradation rule of multiple pesticides in frozen samples are still rare and limited. Therefore, a dynamic model of pesticide degradation is required to evaluate the degradation of pesticides at a certain frozen storage period.

According to the literature, degradation of individual pesticides in a various matrix has been studied and the key factors of pesticide degradation have been discussed. For example, BIAN et al. [17] investigated the degradation of three organophosphorus pesticides (dichlorvos, diazinon and malathion) in cucumber under various storage conditions and the results showed that the storage temperature had impact on the storage stability. Dichlorvos was stable at  $-20\text{ }^{\circ}\text{C}$  for 180 days (degradation less than 30 %), but stability was reduced to 30 days at  $4\text{ }^{\circ}\text{C}$ . Malathion degraded by more than 70 % at  $-20\text{ }^{\circ}\text{C}$  within

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Kaixuan Tong, Xingqiang Wu, Zijuan Zhang, Yujie Xie, Hui Chen, Chunlin Fan, Chinese Academy of Inspection and Quarantine, No. 11 Ronghua South Road, Daxing District, 100176 Beijing, China.

Correspondence author:

Hui Chen, e-mail: ciqhuichen@163.com

90 days. YING et al. [18] studied the degradation rates of fluroxypyr and halosulfuron-methyl in maize stalks, mature maize grains and fresh maize. The authors reported that the degradation rates of these two herbicides were less than 30 % within 70 days at  $-20\text{ }^{\circ}\text{C}$  in the three matrices. GONZÁLEZ-CURBELO et al. [19] evaluated the dissipation kinetics of four organophosphorus pesticides in maize and wheat flours in the dark at room temperature for 90 days. The results showed that the degradation curves of the four pesticides conformed to the first-order kinetics, while the residual pesticide was 34–86 % in maize flour and 69–92 % in wheat flour. DONG et al. [20] studied the storage stability of eight organophosphorus pesticides in seven matrices and concluded that the storage stability of five organophosphorus pesticides in cabbage and potato could be improved by adjusting pH, addition of copper ion and sulfur powder, as well as by amending with methanol and dichloromethane after sample treatment. Their results showed the storage temperature was the most important factor, and the effect of metal ions on enzyme activity could inhibit the degradation of organophosphorus pesticides in cabbage and potato at a certain level. The above results showed that pesticides would degrade with time but lower temperature could reduce the degradation, especially with unstable or volatile pesticides. Anyway, samples should be tested as soon as possible.

High resolution mass spectrometry (HRMS) has unique advantages in trace level detection and quantification of compounds in complex matrices. Unlike triple quadrupole mass spectrometry, based on full-scan data, HRMS can extract a theoretically unlimited number of analytes without compromising the resulting sensitivity. [21]. In this research, a dynamic study of 47 pesticide residues was carried out at spiking levels of  $50\text{ }\mu\text{g}\cdot\text{kg}^{-1}$  and  $200\text{ }\mu\text{g}\cdot\text{kg}^{-1}$ . The residue contents were determined by liquid chromatography-quadrupole time-of-flight mass spectrometry (LC-Q-TOF-MS). The degradation curves of 47 pesticides in four matrices of apple, tomato, cabbage, and grape within 77 days were established. Dynamic degradation models of pesticide residues were selected based on the fitting curves. Next, the degradation equations and degradation rates were investigated.

## MATERIAL AND METHODS

### Chemicals and reagents

Sodium chloride, magnesium sulfate, and sodium sulfate (analytical purity) were obtained

from Tianjin Fuchen Chemical Reagent (Tianjin, China). Methanol, acetonitrile and toluene (chromatographic purity) were obtained from Anpel Laboratory Technology (Shanghai, China). The 90 standards were obtained from Tianjin Alta Scientific (Tianjin, China). All fruits and vegetables used in the test were purchased from the local market in Beijing, China.

### Apparatus

HPLC-Q-TOF-MS instrument Agilent 1290 and Agilent 6550 equipped with Agilent Dual Jet Stream ESI were used (Agilent Technologies, Santa Clara, California, USA). Milli-Q Ultrapure Water System from Millipore (Milford, Massachusetts, USA) was used to provide deionized water. Further, N-EVAP112 nitrogen blowing concentrator (Organomation Associates, Worcester, Massachusetts, USA), AH-40 automatic homogenizer (China Raykol Scientific Instruments, Xiamen, China), Fotor Plus high-throughput automatic solid phase extractor (China Raykol Scientific Instruments), high-throughput vacuum parallel concentrator (China Raykol Scientific Instruments) and low-temperature refrigerator (Haier, Qingdao, China) were used in this research.

### Samples

The mixed standard solution of 90 pesticides was obtained by diluting 1 ml of  $1\text{ }000\text{ mg}\cdot\text{kg}^{-1}$  each selected pesticide standards in a 100 ml volumetric flask by methanol. Then, the mixed standard solution was stored in the dark at  $4\text{ }^{\circ}\text{C}$ . The content of each pesticide was  $10\text{ mg}\cdot\text{kg}^{-1}$ . Blank samples of the selected matrices (apple, grape, tomato, and cabbage) were prepared and to each matrix, corresponding volumes of the mixed standard were added and homogenized, to obtain aged samples spiked at  $50\text{ }\mu\text{g}\cdot\text{kg}^{-1}$  and  $200\text{ }\mu\text{g}\cdot\text{kg}^{-1}$ , respectively. They were aliquoted and stored at  $-18\text{ }^{\circ}\text{C}$ . For each test, one aliquote would be used.

### Sample preparation

The sample preparation for each matrix (apples, grapes, tomatoes and cabbage) was the same as described previously [22]. Briefly, 10.00 g of the sample was transferred into 80 ml centrifuge tube, 40 ml of 1% acetic acid in acetonitrile was added, homogenized for 1 min at 225 Hz using the automatic homogenizer to bring the sample to a homogenous state, 1 g of NaCl and 4 g of anhydrous magnesium sulfate was added, shaken for 10 min, centrifuged at  $3\text{ }155\times g$  for 5 min, 20 ml of supernatant was removed, evaporated and concentrated to approximately 2 ml in a parallel concentrator at  $37\text{ }^{\circ}\text{C}$ . A purification

step was carried out on a carbon/NH<sub>2</sub> solid phase extraction column with 2 cm anhydrous magnesium sulfate. Before loading, the column was activated with 4 ml of acetonitrile-toluene (3:1, v/v) and the effluent was discarded. After loading, the sample bottle was washed with 2 ml of acetonitrile-toluene (3:1, v/v) three times and the washing solution was loaded. A volume of 25 ml of acetonitrile-toluene (3:1, v/v) was used to elute and the eluent was combined in a test tube. The eluent was concentrated to approximately 0.5 ml at 37 °C in a parallel concentrator and dried under nitrogen. The residue was dissolved in 1 ml of acetonitrile – aqueous solution (2:3, v/v) and filtered through a Nylon membrane filter (0.22 μm pore size).

### Analysis

Separation took place in a Zorbax SB-C18 column (100 mm × 2.1 mm, particle size 3.5 μm; Agilent Technologies) at 40 °C. 5 mmol·l<sup>-1</sup> ammonium acetate aqueous solution and 0.1% (v/v) formic acid acetonitrile were applied as phase A and phase B. The flow rate was set at 0.4 ml·min<sup>-1</sup>. The gradient program was set as follows: 0 min, 1 % B; 3 min, 30 % B; 6 min, 40 % B; 9 min, 40 % B; 15 min, 60 % B; 19 min, 90 % B; 23 min, 90 % B; 23.01 min, 1 % B, 4 min. The equilibrium time was 4 min. The injection volume was 5 μl. Detection was achieved using Dual Jet Stream (AJS) ESI source (Agilent Technologies), positive full scan (m/z 50–1000) mode, capillary voltage was 4 kV; nitrogen was used as nebulizer gas at 0.14 MPa, sheath gas temperature was set at 375 °C with 11.0 l·min<sup>-1</sup>, drying gas flow rate was 12.0 l·min<sup>-1</sup>, drying gas temperature was 325 °C and fragmentation voltage was 145 V. All ions mass/mass data acquisition mode was set to the optimized acquisition mode, in which the collision energy was initially set to 0 V, and then set to 0 V, 15 V and 35 V after 0.5 min, respectively.

### Method precision and accuracy

The recovery rates in four matrices were determined at a level of limit of quantification (*LOQ*) to investigate the accuracy and precision of the method. Five parallels were tested at the spiking level of *LOQ*. The recovery of pesticides in four matrices were in the range of 70–120 %, and the relative standard deviations (*RSD*) were less than 25 %, which indicated that the accuracy and precision of the method met the requirements of accurate quantification.

## RESULTS AND DISCUSSION

### Stability screening

The content of the 90 compounds in the four matrices at two spiking levels were tested on day 0, 1, 7, 14, 21, 28, 35, 42, 49, 56, 63, 70 and 77 of storage. The degradation rate (*DR*) on day *X* of the pesticide is defined as Eq. 1 in percentage:

$$DR_X = \frac{m_0 - m_X}{m_0} \times 100 \quad (1)$$

where *m*<sub>0</sub> is initial content and *m*<sub>*X*</sub> is content on day *X*.

Based on the results obtained, relatively stable pesticides were selected according to the following criteria:

- A – Degradation rate on Day 14 (*DR*<sub>14</sub>) is less than 40 %. It was found that most pesticides degraded quickly in 14 days, then degraded relatively slowly. If the degradation of the candidate pesticide in the four matrices would be too fast, these pesticides would not be suitable for collaborative study between laboratories. Day 14 was considered a cut-off day for candidate pesticides.
- B – The average degradation rate between Day 21 and Day 77 is less than 30 %. Otherwise, it is considered that the degradation of a candidate in the four matrices is unstable and this should be removed from the candidate list.
- C – *RSD* of the content between Day 14 and Day 77 is greater than 30 %. It indicates that the variation of degradation of the pesticide is large. Therefore, pesticides with this property in various matrices should be removed from the candidate list.

Based on the above criteria, 47 candidates were selected as relatively stable pesticides for further evaluation. The degradation equation and other information are summarized in Tab. 1–4, and the mass spectrometric information is shown in supplemental file.

### Pesticide degradation kinetics

The content of the spiked pesticides in four matrices were determined on day 0, 1, 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, 77 with 5 replicates, the average of five was calculated as the result. The degradation curve of each pesticide in individual matrices was plotted as concentration versus time. The degradation equation was obtained. The degradation curves were summarized and classified as three types: exponential, logarithmic and polynomial. Typical degradation curves are shown in Fig. 1, in which the degradation of type A is in

**Tab. 1.** Degradation equation, correlation coefficient and half-life of 47 pesticides in apple.

No	Pesticide	Apple 50 $\mu\text{g}\cdot\text{kg}^{-1}$			Apple 200 $\mu\text{g}\cdot\text{kg}^{-1}$		
		Equation	$R^2$	$t_{1/2}$ [d]	Equation	$R^2$	$t_{1/2}$ [d]
1	Ametryn	$y = 50.055 e^{-0.053x}$	0.775	13.1	$y = 188.99 e^{-0.046x}$	0.840	15.1
2	Atrazine	$y = 48.467 e^{-0.055x}$	0.781	12.6	$y = 172.17 e^{-0.031x}$	0.669	22.4
3	Atrazine-desethyl	$y = 49.679 e^{-0.059x}$	0.737	11.7	$y = 187.11 e^{-0.041x}$	0.623	16.9
4	Azoxystrobin	$y = 43.311 e^{-0.045x}$	0.756	15.4	$y = 178.18 e^{-0.04x}$	0.670	17.3
5	Benalaxyl	$y = 45.342 e^{-0.046x}$	0.894	15.1	$y = 168.82 e^{-0.036x}$	0.585	19.3
6	Benzoylprop-ethyl	$y = 44.367 e^{-0.052x}$	0.803	13.3	$y = 153.99 e^{-0.04x}$	0.628	17.3
7	Bitertanol	$y = -1.4779x + 42.238$	0.716		$y = 205.94 e^{-0.064x}$	0.768	10.8
8	Bupirimate	$y = 45.334 e^{-0.057x}$	0.785	12.2	$y = 161.94 e^{-0.046x}$	0.742	15.1
9	Buprofezin	$y = 41.975 e^{-0.043x}$	0.590	16.1	$y = 146.06 e^{-0.047x}$	0.695	14.7
10	Chlorpyrifos	$y = 47.45 e^{-0.069x}$	0.749	10.0	$y = 0.4251x^2 - 7.39x + 122.5$	0.525	
11	Cyflufenamid	$y = 41.827 e^{-0.049x}$	0.822	14.1	$y = 0.5168x^2 - 11.337x + 158.06$	0.560	
12	Cyprodinil	$y = 45.862 e^{-0.051x}$	0.675	13.6	$y = 146.43 e^{-0.045x}$	0.716	15.4
13	Desmetryn	$y = 51.347 e^{-0.061x}$	0.824	11.4	$y = 187.41 e^{-0.043x}$	0.819	16.1
14	Diethatyl-ethyl	$y = 45.085 e^{-0.048x}$	0.844	14.4	$y = 177.64 e^{-0.04x}$	0.625	17.3
15	Dimethenamid	$y = 51.796 e^{-0.068x}$	0.834	10.2	$y = 184.08 e^{-0.033x}$	0.574	21.0
16	Diphenamid	$y = 49.117 e^{-0.049x}$	0.756	14.1	$y = 183.14 e^{-0.029x}$	0.618	23.9
17	Esprocarb	$y = 43.654 e^{-0.042x}$	0.699	16.5	$y = 0.3063x^2 - 7.8177x + 154.61$	0.605	
18	Fenamidone	$y = 40.586 e^{-0.041x}$	0.783	16.9	$y = 172.19 e^{-0.039x}$	0.619	17.8
19	Fenothiocarb	$y = 47.263 e^{-0.045x}$	0.835	15.4	$y = 172.51 e^{-0.031x}$	0.509	22.4
20	Flutriafol	$y = 47.196 e^{-0.051x}$	0.745	13.6	$y = 184.48 e^{-0.045x}$	0.800	15.4
21	Fluxapyroxad	$y = 45.654 e^{-0.046x}$	0.774	15.1	$y = 179.43 e^{-0.036x}$	0.616	19.3
22	Isoprothiolane	$y = 54.514 e^{-0.059x}$	0.669	11.7	$y = 0.1599x^2 - 5.6447x + 173.29$	0.611	
23	Kresoxim-methyl	$y = 50.519 e^{-0.065x}$	0.778	10.7	$y = 169.39 e^{-0.035x}$	0.585	19.8
24	Mepanipyrim	$y = 46.28 e^{-0.048x}$	0.753	14.4	$y = 169.72 e^{-0.043x}$	0.657	16.1
25	Metalaxyl	$y = 46.66 e^{-0.046x}$	0.651	15.1	$y = 183.7 e^{-0.033x}$	0.720	21.0
26	Methoprotryne	$y = 48.74 e^{-0.051x}$	0.790	13.6	$y = 180.35 e^{-0.039x}$	0.799	17.8
27	Metolachlor	$y = 47.634 e^{-0.049x}$	0.801	14.1	$y = 173.23 e^{-0.03x}$	0.581	23.1
28	Orbencarb	$y = 47.717 e^{-0.05x}$	0.803	13.9	$y = 165.05 e^{-0.03x}$	0.729	23.1
29	Paclobutrazole	$y = 47.597 e^{-0.048x}$	0.663	14.4	$y = 189.75 e^{-0.042x}$	0.768	16.5
30	Penconazole	$y = 44.27 e^{-0.045x}$	0.846	15.4	$y = 199.98 e^{-0.057x}$	0.774	12.2
31	Pentachlor	$y = 46.95 e^{-0.048x}$	0.786	14.4	$y = 162.24 e^{-0.039x}$	0.615	17.8
32	Picoxystrobin	$y = 44.55 e^{-0.054x}$	0.829	12.8	$y = 161.87 e^{-0.032x}$	0.531	21.7
33	Pirimicarb	$y = 50.76 e^{-0.049x}$	0.741	14.1	$y = 174.6 e^{-0.023x}$	0.583	30.1
34	Pirimiphos-methyl	$y = 45.358 e^{-0.047x}$	0.837	14.7	$y = 172.47 e^{-0.035x}$	0.777	19.8
35	Propisochlor	$y = 48.952 e^{-0.056x}$	0.814	12.4	$y = 172.73x^{-0.158}$	0.516	4.4
36	Pyributicarb	$y = 42.437 e^{-0.052x}$	0.662	13.3	$y = 124.58 e^{-0.052x}$	0.590	13.3
37	Quinalphos	$y = 48.466 e^{-0.054x}$	0.889	12.8	$y = 170.29 e^{-0.045x}$	0.696	15.4
38	Sebuthylazine	$y = 47.956 e^{-0.053x}$	0.778	13.1	$y = 159.01 e^{-0.026x}$	0.545	26.7
39	Simeconazole	$y = 46.446 e^{-0.051x}$	0.702	13.6	$y = 186.34 e^{-0.048x}$	0.835	14.4
40	Simeton	$y = 52.296 e^{-0.064x}$	0.778	10.8	$y = 192.71 e^{-0.041x}$	0.769	16.9
41	Tebuconazole	$y = 46.973 e^{-0.06x}$	0.867	11.6	$y = 208.9 e^{-0.069x}$	0.879	10.0
42	Tebufenpyrad	$y = 43.655 e^{-0.046x}$	0.674	15.1	$y = 139.55 e^{-0.038x}$	0.579	18.2
43	Terbuthylazine	$y = 50.419 e^{-0.062x}$	0.827	11.2	$y = 168.22 e^{-0.034x}$	0.604	20.4
44	Tetraconazole	$y = 47.882 e^{-0.056x}$	0.701	12.4	$y = 186.3 e^{-0.045x}$	0.784	15.4
45	Thiazopyr	$y = 43.94 e^{-0.047x}$	0.677	14.7	$y = 161.79 e^{-0.041x}$	0.564	16.9
46	Triazophos	$y = 49.247 e^{-0.061x}$	0.917	11.4	$y = 172.66 e^{-0.039x}$	0.598	17.8
47	Trifloxystrobin	$y = 45.05 e^{-0.057x}$	0.844	12.2	$y = 152.34 e^{-0.04x}$	0.502	17.3

 $R^2$  – correlation coefficient,  $t_{1/2}$  – half-life.

**Tab. 2.** Degradation equation, correlation coefficient and half-life of 47 pesticides in tomato.

No	Pesticide	Tomato 50 $\mu\text{g}\cdot\text{kg}^{-1}$			Tomato 200 $\mu\text{g}\cdot\text{kg}^{-1}$		
		Equation	$R^2$	$t_{1/2}$ [d]	Equation	$R^2$	$t_{1/2}$ [d]
1	Ametryn	$y = 47.054 e^{-0.042x}$	0.566	16.5	$y = 204.44 e^{-0.051x}$	0.840	13.6
2	Atrazine	$y = 44.73 e^{-0.047x}$	0.547	14.7	$y = 187.8 e^{-0.05x}$	0.830	13.9
3	Atrazine-desethyl	$y = 43.588 e^{-0.048x}$	0.601	14.4	$y = 197.97 e^{-0.06x}$	0.793	11.6
4	Azoxystrobin	$y = 55.736 e^{-0.06x}$	0.794	11.6	$y = 193.05 e^{-0.05x}$	0.896	13.9
5	Benalaxyl	$y = 51.783 e^{-0.056x}$	0.795	12.4	$y = 189.48 e^{-0.045x}$	0.825	15.4
6	Benzoylprop-ethyl	$y = 53.4 e^{-0.069x}$	0.755	10.0	$y = 185.33 e^{-0.049x}$	0.881	14.1
7	Bitertanol	$y = 54.283 e^{-0.073x}$	0.864	9.5	$y = 192.7 e^{-0.055x}$	0.781	12.6
8	Bupirimate	$y = 51.151 e^{-0.074x}$	0.879	9.4	$y = 191.66 e^{-0.053x}$	0.871	13.1
9	Buprofezin	$y = 42.052 e^{-0.06x}$	0.664	11.6	$y = 184.35 e^{-0.049x}$	0.753	14.1
10	Chlorpyrifos	$y = 52.751 e^{-0.082x}$	0.699	8.5	$y = 180.7 e^{-0.048x}$	0.523	14.4
11	Cyflufenamid	$y = 44.811 e^{-0.058x}$	0.690	12.0	$y = 190.77 e^{-0.049x}$	0.818	14.1
12	Cyprodinil	$y = 46.994 e^{-0.055x}$	0.617	12.6	$y = 189.97 e^{-0.045x}$	0.691	15.4
13	Desmetryn	$y = 46.691 e^{-0.048x}$	0.638	14.4	$y = 199.37 e^{-0.05x}$	0.794	13.9
14	Diethatyl-ethyl	$y = 45.447 e^{-0.05x}$	0.516	13.9	$y = 179.75 e^{-0.05x}$	0.852	13.9
15	Dimethenamid	$y = 45.039 e^{-0.047x}$	0.534	14.7	$y = 197.01 e^{-0.054x}$	0.833	12.8
16	Diphenamid	$y = 45.688 e^{-0.041x}$	0.516	16.9	$y = 196.52 e^{-0.046x}$	0.866	15.1
17	Esprocarb	$y = 53.349 e^{-0.07x}$	0.632	9.9	$y = 177.61 e^{-0.036x}$	0.688	19.3
18	Fenamidone	$y = 51.162 e^{-0.063x}$	0.885	11.0	$y = 189.82 e^{-0.055x}$	0.872	12.6
19	Fenothiocarb	$y = 53.947 e^{-0.061x}$	0.866	11.4	$y = 176.85 e^{-0.038x}$	0.754	18.2
20	Flutriafol	$y = 50.349 e^{-0.058x}$	0.858	12.0	$y = 179.41 e^{-0.048x}$	0.800	14.4
21	Fluxapyroxad	$y = 53.386 e^{-0.059x}$	0.786	11.7	$y = 192.61 e^{-0.053x}$	0.804	13.1
22	Isoprothiolane	$y = 44.979 e^{-0.057x}$	0.763	12.2	$y = 206.93 e^{-0.055x}$	0.819	12.6
23	Kresoxim-methyl	$y = 49.386 e^{-0.057x}$	0.702	12.2	$y = 183.61 e^{-0.045x}$	0.733	15.4
24	Mepanipyrim	$y = 51.873 e^{-0.065x}$	0.792	10.7	$y = 195.03 e^{-0.052x}$	0.855	13.3
25	Metalaxyl	$y = 47.573 e^{-0.044x}$	0.696	15.8	$y = 196.88 e^{-0.05x}$	0.865	13.9
26	Methoprotryne	$y = 45.729 e^{-0.042x}$	0.611	16.5	$y = 201.58 e^{-0.049x}$	0.813	14.1
27	Metolachlor	$y = 54.771 e^{-0.06x}$	0.787	11.6	$y = 185.8 e^{-0.042x}$	0.822	16.5
28	Orbencarb	$y = 54.701 e^{-0.063x}$	0.769	11.0	$y = 178.16 e^{-0.041x}$	0.833	16.9
29	Paclobutrazole	$y = 51.133 e^{-0.04x}$	0.837	17.3	$y = 188.52 e^{-0.036x}$	0.668	19.3
30	Penconazole	$y = 49.149 e^{-0.051x}$	0.858	13.6	$y = 185.43 e^{-0.043x}$	0.890	16.1
31	Pentachlor	$y = 53.972 e^{-0.068x}$	0.804	10.2	$y = 183.67 e^{-0.048x}$	0.750	14.4
32	Picoxystrobin	$y = 54.21 e^{-0.065x}$	0.801	10.7	$y = 183.27 e^{-0.045x}$	0.862	15.4
33	Pirimicarb	$y = 49.623 e^{-0.043x}$	0.616	16.1	$y = 191.85 e^{-0.04x}$	0.849	17.3
34	Pirimiphos-methyl	$y = 56.51 e^{-0.065x}$	0.721	10.7	$y = 189.39 e^{-0.041x}$	0.846	16.9
35	Propisochlor	$y = 53.833 e^{-0.061x}$	0.803	11.4	$y = 193.17 e^{-0.052x}$	0.814	13.3
36	Pyributicarb	$y = 42.583 e^{-0.054x}$	0.596	12.8	$y = 189.13 e^{-0.051x}$	0.759	13.6
37	Quinalphos	$y = 55.527 e^{-0.069x}$	0.868	10.0	$y = 177.07 e^{-0.047x}$	0.848	14.7
38	Sebuthylazine	$y = 43.962 e^{-0.046x}$	0.586	15.1	$y = 190.14 e^{-0.048x}$	0.840	14.4
39	Simeconazole	$y = 0.1327x^2 - 3.3692x + 47.839$	0.547		$y = 190.22 e^{-0.051x}$	0.856	13.6
40	Simeton	$y = 46.602 e^{-0.046x}$	0.706	15.1	$y = 201.64 e^{-0.051x}$	0.756	13.6
41	Tebuconazole	$y = 50.986 e^{-0.061x}$	0.837	11.4	$y = 191.91 e^{-0.058x}$	0.903	12.0
42	Tebufenpyrad	$y = 45.709 e^{-0.064x}$	0.546	10.8	$y = 185.47 e^{-0.045x}$	0.789	15.4
43	Terbuthylazine	$y = 46.148 e^{-0.046x}$	0.547	15.1	$y = 196.92 e^{-0.049x}$	0.882	14.1
44	Tetraconazole	$y = 49.837 e^{-0.056x}$	0.811	12.4	$y = 187.28 e^{-0.049x}$	0.798	14.1
45	Thiazopyr	$y = 47.003 e^{-0.056x}$	0.511	12.4	$y = 172.13 e^{-0.034x}$	0.704	20.4
46	Triazophos	$y = 56.041 e^{-0.07x}$	0.861	9.9	$y = 186.47 e^{-0.052x}$	0.842	13.3
47	Trifloxystrobin	$y = 42.307 e^{-0.05x}$	0.580	13.9	$y = 188.16 e^{-0.046x}$	0.803	15.1

 $R^2$  – correlation coefficient,  $t_{1/2}$  – half-life.

**Tab. 3.** Degradation equation, correlation coefficient and half-life of 47 pesticides in cabbage.

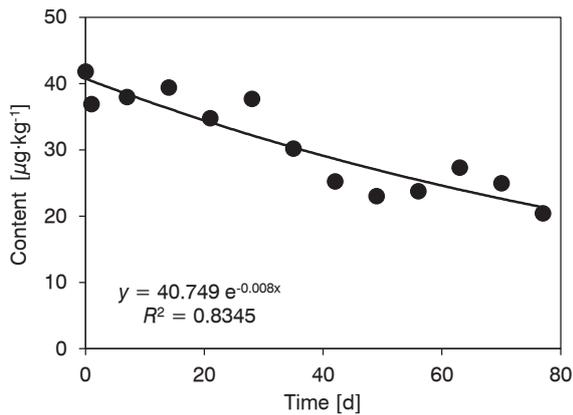
No	Pesticide	Cabbage 50 µg·kg <sup>-1</sup>			Cabbage 200 µg·kg <sup>-1</sup>		
		Equation	R <sup>2</sup>	t <sub>1/2</sub> [d]	Equation	R <sup>2</sup>	t <sub>1/2</sub> [d]
1	Ametryn	$y = 47.527 e^{-0.058x}$	0.807	12.0	$y = 190.05 e^{-0.045x}$	0.775	15.4
2	Atrazine	$y = 47.289 e^{-0.048x}$	0.691	14.4	$y = 186.83 e^{-0.046x}$	0.856	15.1
3	Atrazine-Desethyl	$y = -0.2221x^2 + 1.8016x + 35.904$	0.573		$y = 166.44 e^{-0.037x}$	0.543	18.7
4	Azoxystrobin	$y = 41.821 e^{-0.032x}$	0.416	21.7	$y = -42.12 \ln(x) + 204.89$	0.933	
5	Benalaxyl	$y = 51.494 e^{-0.06x}$	0.845	11.6	$y = -52.62 \ln(x) + 229.38$	0.917	
6	Benzoylprop-ethyl	$y = 46.769 e^{-0.051x}$	0.417	13.6	$y = 0.9116x^2 - 20.613x + 254.97$	0.761	
7	Bitertanol	$y = 58.881 e^{-0.071x}$	0.830	9.8	$y = -70.01 \ln(x) + 256.29$	0.926	
8	Bupirimate	$y = 45.185 e^{-0.062x}$	0.911	11.2	$y = -38.73 \ln(x) + 198.07$	0.916	
9	Buprofezin	$y = 46.341 e^{-0.078x}$	0.742	8.9	$y = 1.0953x^2 - 24.754x + 223.94$	0.910	
10	Chlorpyrifos				$y = 2.7896x^2 - 51.641x + 323.18$	0.886	
11	Cyflufenamid	$y = -0.1086x^2 + 0.2844x + 35.077$	0.525		$y = 1.1104x^2 - 22.152x + 220.71$	0.736	
12	Cyprodinil	$y = 49.962 e^{-0.067x}$	0.808	10.3	$y = 0.9221x^2 - 20.293x + 217.35$	0.938	
13	Desmetyrn	$y = 47.518 e^{-0.061x}$	0.778	11.4	$y = 184.17 e^{-0.049x}$	0.713	14.1
14	Diethatyl-ethyl	$y = -14.1 \ln(x) + 59.077$	0.955		$y = -66.46 \ln(x) + 248.75$	0.925	
15	Dimethenamid	$y = 48.499 e^{-0.051x}$	0.877	13.6	$y = -43.47 \ln(x) + 208.75$	0.976	
16	Diphenamid	$y = 49.307 e^{-0.052x}$	0.858	13.3	$y = -34.71 \ln(x) + 201.37$	0.878	
17	Esprocarb	$y = 44.689 e^{-0.055x}$	0.878	12.6	$y = -43.17 \ln(x) + 199.02$	0.926	
18	Fenamidone	$y = -15.41 \ln(x) + 57.35$	0.932		$y = -69.01 \ln(x) + 235.3$	0.945	
19	Fenothiocarb	$y = 51.478 e^{-0.06x}$	0.910	11.6	$y = -41.95 \ln(x) + 204.34$	0.964	
20	Flutriafol	$y = 48.215 e^{-0.057x}$	0.778	12.2	$y = -37.44 \ln(x) + 196.69$	0.890	
21	Fluxapyroxad	$y = 50.145 e^{-0.061x}$	0.873	11.4	$y = -48.64 \ln(x) + 211.29$	0.925	
22	Isoprothiolane	$y = 49.254 e^{-0.073x}$	0.417	9.5	$y = -72.63 \ln(x) + 284.58$	0.705	
23	Kresoxim-methyl	$y = -12.64 \ln(x) + 53.726$	0.819		$y = -60.83 \ln(x) + 237.97$	0.916	
24	Mepanipyrim	$y = 44.941 e^{-0.052x}$	0.796	13.3	$y = -39.59 \ln(x) + 202.62$	0.862	
25	Metalaxyl	$y = 53.792 e^{-0.062x}$	0.934	11.2	$y = -49.16 \ln(x) + 226.08$	0.937	
26	Methoprotryne	$y = 49.536 e^{-0.062x}$	0.784	11.2	$y = 198.47 e^{-0.049x}$	0.806	14.1
27	Metolachlor	$y = 49.437 e^{-0.049x}$	0.903	14.1	$y = -42.91 \ln(x) + 210.38$	0.941	
28	Orbencarb	$y = 44.327 e^{-0.04x}$	0.654	17.3	$y = 175.38 e^{-0.037x}$	0.625	18.7
29	Paclobutrazole	$y = 51.206 e^{-0.037x}$	0.525	18.7	$y = -42.74 \ln(x) + 219.9$	0.822	
30	Penconazole	$y = 51.385 e^{-0.055x}$	0.846	12.6	$y = -45.85 \ln(x) + 218.7$	0.947	
31	Pentachlor	$y = 53.476 e^{-0.068x}$	0.756	10.2	$y = -46.18 \ln(x) + 208.97$	0.958	
32	Picoxystrobin	$y = 44.825 e^{-0.044x}$	0.868	1.6	$y = -36.95 \ln(x) + 197.8$	0.956	
33	Pirimicarb	$y = 49.756 e^{-0.056x}$	0.736	12.4	$y = 0.8478x^2 - 17.695x + 214.19$	0.859	
34	Pirimiphos-methyl	$y = 48.073 e^{-0.053x}$	0.875	13.1	$y = 0.7441x^2 - 16.355x + 203.77$	0.912	
35	Propisochlor	$y = 50.139 e^{-0.058x}$	0.782	12.0	$y = -43.6 \ln(x) + 209.22$	0.912	
36	Pyributicarb	$y = 42.249 e^{-0.068x}$	0.819	10.2	$y = 175.63 e^{-0.059x}$	0.863	11.7
37	Quinalphos	$y = -14.21 \ln(x) + 57.639$	0.940		$y = -69.77 \ln(x) + 245.25$	0.903	
38	Sebuthylazine	$y = 44.326 e^{-0.044x}$	0.666	15.8	$y = -33.79 \ln(x) + 190.53$	0.799	
39	Simeconazole	$y = 51.669 e^{-0.058x}$	0.881	12.0	$y = 1.2825x^2 - 27.266x + 241.81$	0.972	
40	Simeton	$y = 51.152 e^{-0.058x}$	0.834	12.0	$y = -44.51 \ln(x) + 229.61$	0.807	
41	Tebuconazole	$y = -11.95 \ln(x) + 55.496$	0.937		$y = -65.41 \ln(x) + 244.34$	0.910	
42	Tebufenpyrad	$y = 42.86 e^{-0.057x}$	0.470	12.2	$y = 1.1095x^2 - 23.494x + 233.99$	0.793	
43	Terbuthylazine	$y = 45.302 e^{-0.042x}$	0.662	16.5	$y = -37.16 \ln(x) + 200.06$	0.864	
44	Tetraconazole	$y = 46.228 e^{-0.051x}$	0.855	13.6	$y = -44.83 \ln(x) + 205.48$	0.927	
45	Thiazopyr	$y = -17.72 \ln(x) + 63.038$	0.928		$y = 2.1103x^2 - 41.106x + 274.38$	0.972	
46	Triazophos	$y = -12.85 \ln(x) + 58.956$	0.924		$y = -55.99 \ln(x) + 233.79$	0.967	
47	Trifloxystrobin	$y = 43.485 e^{-0.054x}$	0.588	12.8	$y = 1.1875x^2 - 23.785x + 232.78$	0.842	

R<sup>2</sup> – correlation coefficient, t<sub>1/2</sub> – half-life.

**Tab. 4.** Degradation equation, correlation coefficient and half-life of 47 pesticides in grape.

No	Pesticide	Grape 50 $\mu\text{g}\cdot\text{kg}^{-1}$			Grape 200 $\mu\text{g}\cdot\text{kg}^{-1}$		
		Equation	$R^2$	$t_{1/2}$ [d]	Equation	$R^2$	$t_{1/2}$ [d]
1	Ametryn	$y = -8.712 \ln(x) + 46.55$	0.921		$y = -42.36 \ln(x) + 211.18$	0.928	
2	Atrazine	$y = -14.07 \ln(x) + 56.16$	0.834		$y = -50.74 \ln(x) + 225.52$	0.869	
3	Atrazine-Desethyl	$y = -17.98 \ln(x) + 62.314$	0.902		$y = -70.43 \ln(x) + 256.63$	0.895	
4	Azoxystrobin	$y = -17.2 \ln(x) + 66.394$	0.788		$y = -50.47 \ln(x) + 208.36$	0.931	
5	Benalaxyl	$y = 38.532 e^{-0.038x}$	0.833	18.2	$y = -40.47 \ln(x) + 195.08$	0.861	
6	Benzoylprop-ethyl	$y = 41.929 e^{-0.057x}$	0.899	12.2	$y = -53.52 \ln(x) + 216.06$	0.873	
7	Bitertanol	$y = -0.1693x^2 + 1.4376x + 29.935$	0.687		$y = -39.4 \ln(x) + 182.38$	0.736	
8	Bupirimate	$y = 44.135 e^{-0.071x}$	0.898	9.8	$y = -44.15 \ln(x) + 195.4$	0.936	
9	Buprofezin	$y = -9.32 \ln(x) + 45.584$	0.953		$y = -43.34 \ln(x) + 188.78$	0.828	
10	Chlorpyrifos	$y = 0.5349x^2 - 11.374x + 80.431$	0.607		$y = 2.0256x^2 - 35.681x + 237.5$	0.645	
11	Cyflufenamid	$y = -10.48 \ln(x) + 46.9$	0.925		$y = 2.0199x^2 - 36.271x + 247.97$	0.877	
12	Cyprodinil	$y = -7.757 \ln(x) + 43.129$	0.943		$y = -7.2322x + 167.91$	0.733	
13	Desmetryn	$y = -10.2 \ln(x) + 49.463$	0.918		$y = -48.32 \ln(x) + 220.63$	0.921	
14	Diethatyl-ethyl	$y = 38.146 e^{-0.036x}$	0.778	19.3	$y = -41.37 \ln(x) + 196.15$	0.862	
15	Dimethenamid	$y = -7.466 \ln(x) + 42.785$	0.789		$y = -43.67 \ln(x) + 213.67$	0.947	
16	Diphenamid	$y = -7.452 \ln(x) + 45.808$	0.871		$y = -42.09 \ln(x) + 207.08$	0.893	
17	Esprocarb	$y = -3.969 \ln(x) + 34.537$	0.474		$y = 1.0483x^2 - 18.682x + 193.29$	0.763	
18	Fenamidone	$y = -0.1699x^2 + 1.5669x + 27.83$	0.792		$y = 168.62 e^{-0.061x}$	0.792	11.4
19	Fenothiocarb	$y = -8.386 \ln(x) + 46.403$	0.878		$y = -52.26 \ln(x) + 223.03$	0.900	
20	Flutriafol	$y = -12.37 \ln(x) + 52.662$	0.939		$y = -50.65 \ln(x) + 215.45$	0.953	
21	Fluxapyroxad	$y = -8.887 \ln(x) + 45.721$	0.916		$y = -55.69 \ln(x) + 214.37$	0.925	
22	Isoprothiolane	$y = 41.882 e^{-0.045x}$	0.868	15.4	$y = 1.2896x^2 - 25.811x + 229.81$	0.789	
23	Kresoxim-methyl	$y = 40.937 e^{-0.048x}$	0.772	14.4	$y = 1.4062x^2 - 27.659x + 228.72$	0.925	
24	Mepanipyrim	$y = -6.178 \ln(x) + 39.182$	0.830		$y = -45 \ln(x) + 204.46$	0.935	
25	Metalaxyl	$y = 41.971 e^{-0.043x}$	0.792	16.1	$y = -38.11 \ln(x) + 201.43$	0.843	
26	Methoprotryne	$y = -9.378 \ln(x) + 47.675$	0.834		$y = -42.63 \ln(x) + 210.28$	0.894	
27	Metolachlor	$y = 38.411 e^{-0.03x}$	0.780	23.1	$y = 1.2892x^2 - 25.277x + 231.42$	0.915	
28	Orbencarb	$y = -5.396 \ln(x) + 38.177$	0.608		$y = 1.3407x^2 - 24.614x + 223.04$	0.800	
29	Paclobutrazole	$y = 40.841 e^{-0.039x}$	0.756	17.8	$y = 1.4216x^2 - 26.3x + 220.09$	0.857	
30	Penconazole	$y = 38.25 e^{-0.042x}$	0.770	16.5	$y = -41.31 \ln(x) + 196.1$	0.821	
31	Pentachlor	$y = 38.174 e^{-0.045x}$	0.857	15.4	$y = -41.65 \ln(x) + 194.93$	0.804	
32	Picoxystrobin	$y = -9.685 \ln(x) + 46.112$	0.796		$y = -58.11 \ln(x) + 230.2$	0.807	
33	Pirimicarb	$y = -5.947 \ln(x) + 42.348$	0.561		$y = -34.38 \ln(x) + 201.64$	0.883	
34	Pirimiphos-methyl	$y = -5.396 \ln(x) + 36.373$	0.875		$y = -32.06 \ln(x) + 183.36$	0.857	
35	Propisochlor	$y = 37.176 e^{-0.034x}$	0.672	20.4	$y = -39.09 \ln(x) + 200.61$	0.870	
36	Pyributicarb	$y = 44.327 e^{-0.066x}$	0.939	10.5	$y = -40.64 \ln(x) + 188.9$	0.634	
37	Quinalphos	$y = -0.1236x^2 + 1.1557x + 27.639$	0.550		$y = -35.12 \ln(x) + 182.57$	0.814	
38	Sebuthylazine	$y = -11.5 \ln(x) + 50.924$	0.753		$y = -40.87 \ln(x) + 203.86$	0.772	
39	Simeconazole	$y = 38.928 e^{-0.044x}$	0.808	15.8	$y = -47.01 \ln(x) + 204.53$	0.923	
40	Simeton	$y = -7.928 \ln(x) + 45.86$	0.853		$y = -41.06 \ln(x) + 212.03$	0.862	
41	Tebuconazole	$y = -0.1888x^2 + 1.8315x + 26.592$	0.670		$y = 163.96 e^{-0.054x}$	0.808	12.8
42	Tebufenpyrad	$y = -9.094 \ln(x) + 44.654$	0.913		$y = -42.84 \ln(x) + 191.56$	0.838	
43	Terbuthylazine	$y = -9.988 \ln(x) + 47.212$	0.792		$y = -44.34 \ln(x) + 211.84$	0.827	
44	Tetraconazole	$y = 39.835 e^{-0.049x}$	0.868	14.1	$y = -51.45 \ln(x) + 208.04$	0.892	
45	Thiazopyr	$y = -0.1733x^2 + 1.7495x + 25.513$	0.674		$y = -29.17 \ln(x) + 171.17$	0.643	
46	Triazophos	$y = -0.1435x^2 + 1.1074x + 30.449$	0.724		$y = -40.07 \ln(x) + 189.53$	0.844	
47	Trifloxystrobin	$y = 43.56 e^{-0.064x}$	0.954	10.8	$y = -35.8 \ln(x) + 187.06$	0.875	

 $R^2$  – correlation coefficient,  $t_{1/2}$  – half-life.



**Fig. 1.** Exponential degradation curve of piperonyl butoxide in apple at  $50 \mu\text{g}\cdot\text{kg}^{-1}$  spiking level.

accordance with the first-order kinetic equation as Eq. 2:

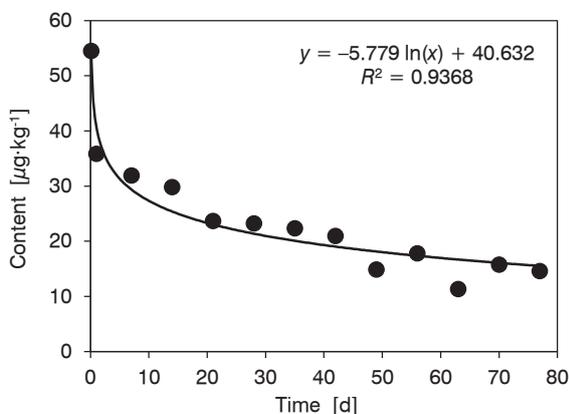
$$C_t = C_0 e^{-kt} \quad (2)$$

herein,  $C_t$  represents the test content of the pesticide at day  $t$ ;  $C_0$  represents the initial test content,  $k$  represents the first-order reaction rate constant.

In this type, the half-life of the pesticide ( $t_{1/2}$ ) was calculated according to Eq. 3 and expressed in days:

$$t_{1/2} = \ln \frac{2}{k} \quad (3)$$

In Fig. 1, type A degradation of piperonyl butoxide in apple spiked at  $50 \mu\text{g}\cdot\text{kg}^{-1}$  is depicted as an example. The degradation rate of piperonyl butoxide was proportional to the initial content during the observation period. The degradation rate of these pesticides showed a downward trend within 77 days. Degradation of butralin in cabbage

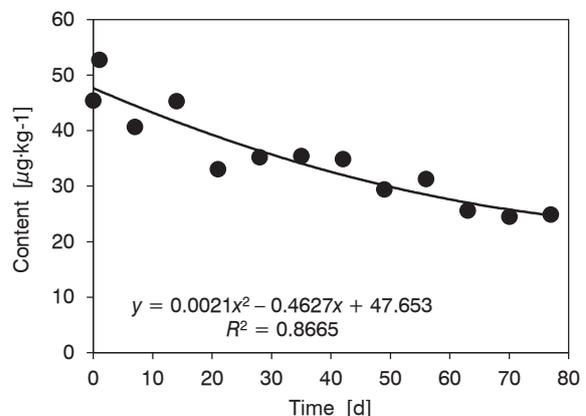


**Fig. 2.** Logarithmic degradation curve of butralin in cabbage at  $50 \mu\text{g}\cdot\text{kg}^{-1}$  spiking level.

spiked at  $50 \mu\text{g}\cdot\text{kg}^{-1}$  was an example of the degradation of type B (Fig. 2). Degradation between Day 0 and Day 14 was significantly faster than that between Day 14 and Day 77, and the difference in degradation between days 0–14 and days 14–77 was large. Simeconazole in cabbage spiked at  $50 \mu\text{g}\cdot\text{kg}^{-1}$  was an example of the degradation of type C (Fig. 3). Degradation was slightly faster between Day 0 and Day 14 then later between Day 14 and Day 77, when it slowed down and tended to be almost stable. The degradation equations of 47 pesticides were obtained for each matrix and, based on this, further study of degradation of these 47 pesticides in various matrices was carried out.

### Pesticide degradation in various matrices

Degradation of pesticides was faster in the first 14 days, therefore, the distribution of the degradation of pesticides in various matrices was investigated between Day 0 and Day 14, and between Day 0 and Day 77, respectively. The degradation curves of the 47 pesticides in the four matrices between Day 0 and Day 14 most closely matched type C kinetics. This phenomenon may be due to the fact that adsorption between most pesticides and the matrices is not particularly strong at the early stage of storage, there is higher oxygen content near the outer layer of the matrices, which is conducive to higher degradation of pesticides [23]. This may lead to faster degradation of pesticides at the early stage. Degradation of pesticides is related to oxygen, temperature, pH, water, light and other factors. Pesticides with weak adsorption to the matrix penetrate deeper into it and are thus less degraded by the environment. In addition, degradation of pesticides also depends on their structure and stability, as more stable compounds



**Fig. 3.** Polynomial degradation curve of simeconazole in cabbage at  $50 \mu\text{g}\cdot\text{kg}^{-1}$  spiking level.

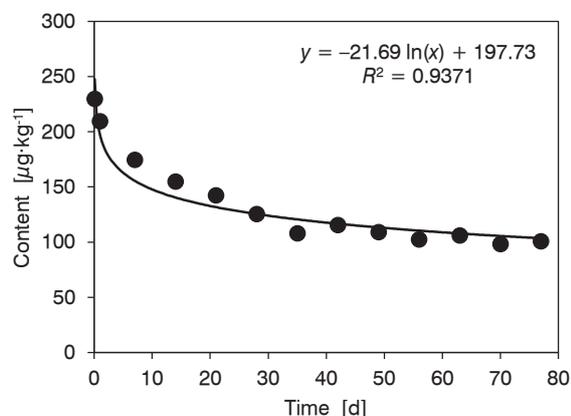
**Tab. 5.** Type of degradation kinetics for 47 pesticides.

Matrix	Level of added pesticides [ $\mu\text{g}\cdot\text{kg}^{-1}$ ]	Number of pesticides		
		Type A	Type B	Type C
Apple	50	46	0	1
	200	43	0	4
Tomato	50	46	0	1
	200	47	0	0
Cabbage	50	39	7	1
	200	7	30	10
Grape	50	14	26	7
	200	2	38	7

degrade slower. Data on degradation of 47 pesticides in various matrices on days 0–77 are summarized in Tab. 5.

In apple, at the low spiking level ( $50 \mu\text{g}\cdot\text{kg}^{-1}$ ), the pesticides exhibited mainly type A degradation kinetics (46 pesticides). Their half-life ( $t_{1/2}$ ) ranged from 10.0 to 16.9 days, the average was 13.5 days. At the high spiking level ( $200 \mu\text{g}\cdot\text{kg}^{-1}$ ), 43 pesticides exhibited degradation of type A with  $t_{1/2}$  values ranging from 10.0 to 30.1 days, the average was 17.8 days. The selected pesticides showed a relatively stable degradation trend in apple.

In tomato, 46 pesticides at  $50 \mu\text{g}\cdot\text{kg}^{-1}$  spiking level conformed to the degradation of type A, while  $t_{1/2}$  ranged from 6.8 to 19.8 days, with an average of 12.7 days. At  $200 \mu\text{g}\cdot\text{kg}^{-1}$  spiking level, all of 47 selected pesticides conformed to the degradation of type A,  $t_{1/2}$  ranged from 11.6 to 20.4 days, the average was 14.6 days, indicating that the selected pesticides were also stable in tomato.

**Fig. 4.** Degradation curve of triazophos in cabbage at  $200 \mu\text{g}\cdot\text{kg}^{-1}$  spiking level.

In cabbage, 39 pesticides at  $50 \mu\text{g}\cdot\text{kg}^{-1}$  spiking level conformed to the degradation of type A,  $t_{1/2}$  was 8.9–21.7 days, with an average of 12.8 days. At  $200 \mu\text{g}\cdot\text{kg}^{-1}$  spiking level, 30 pesticides conformed to the degradation of type B.

In grape at  $50 \mu\text{g}\cdot\text{kg}^{-1}$  spiking level, 26 pesticides conformed to the degradation of type B. At  $200 \mu\text{g}\cdot\text{kg}^{-1}$  spiking level, 38 pesticides also conformed to the degradation of type B. It was determined that the degradation rate of the selected pesticides in grape was fast between Day 0 and Day 14, and then tended to be stable.

Maximum residue limit (*MRL*) is the threshold to compare and judge whether the pesticide in the matrix exceeds the regulation values. Under frozen condition, the pesticide concentration exceeding the standard might be reduced and lower than *MRL* due to the degradation. For example, triazophos in cabbage, shown as Fig. 4. *MRL* of Chinese national standard for triazophos in cabbage is  $100 \mu\text{g}\cdot\text{kg}^{-1}$  [24]. The initial content of triazophos in cabbage was  $200 \mu\text{g}\cdot\text{kg}^{-1}$  and would decrease to  $98.36 \mu\text{g}\cdot\text{kg}^{-1}$  on Day 70, which is lower than *MRL* of the regulation. The time needed for a certain pesticide to degrade below the *MRL* level can be approximately calculated according to the degradation equation of this pesticide. For example, *MRL* of metolachlor in tomato is  $100 \mu\text{g}\cdot\text{kg}^{-1}$ . If its initial content is  $200 \mu\text{g}\cdot\text{kg}^{-1}$ , its degradation equation (Fig. 5) means that approximately 91 days are required to decrease below *MRL*. Similarly, as shown in Fig. 6, *MRL* of metolachlor in cabbage is  $100 \mu\text{g}\cdot\text{kg}^{-1}$ . If its initial content is  $200 \mu\text{g}\cdot\text{kg}^{-1}$ , then according to its degradation equation in cabbage, it needs 148 days to decrease to  $100 \mu\text{g}\cdot\text{kg}^{-1}$ . The time necessary to decrease the content of the selected pesticides to *MRL* in the matrices can be calculated by the degradation equations for the starting contents of  $50 \mu\text{g}\cdot\text{kg}^{-1}$  and  $200 \mu\text{g}\cdot\text{kg}^{-1}$ .

In summary, more than 90 % of 47 selected pesticides in apple and tomato at both spiking levels conformed to the degradation of type A. The pesticides in apple and tomato showed a stable degradation trend fitting to the first-order kinetic equation. More than a half of these pesticides in grape at both spiking levels basically conformed to the degradation of type B, degrading rapidly between Day 0 and Day 14, then slowly in the following observation days. In cabbage, 82 % of the pesticides at the low spiking level ( $50 \mu\text{g}\cdot\text{kg}^{-1}$ ) conformed to the degradation of type A and 64 % of pesticides at the high spiking level ( $200 \mu\text{g}\cdot\text{kg}^{-1}$ ) conformed to the degradation of type B. This may be due to rapid degradation of the high content on days 0–14 and then a tendency stabilize, while the degradation rate at the low content was relatively

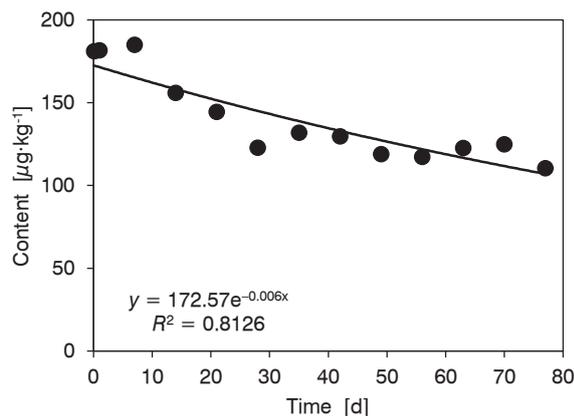


Fig. 5. Degradation curve of metolachlor in tomato at 200  $\mu\text{g}\cdot\text{kg}^{-1}$  spiking level.

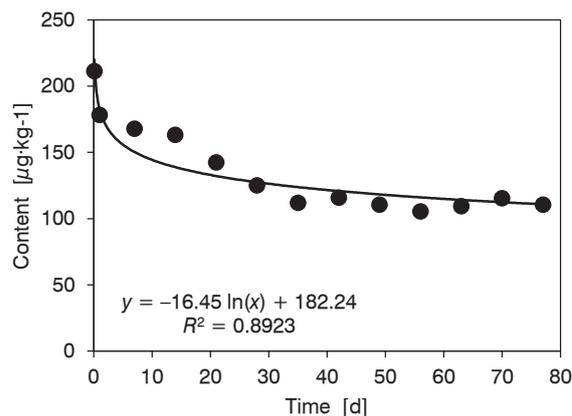


Fig. 6. Degradation curve of metolachlor in cabbage at 200  $\mu\text{g}\cdot\text{kg}^{-1}$  spiking level.

uniform. Overall, degradation of the selected pesticides was relatively stable in apple, tomato and low-spiked cabbage, while it was fast in the early stage in high-spiked cabbage. The pH value and composition of grape may have impact on the degradation of these pesticides, which led to a significant decrease at both spiking levels during the first 14 days.

#### Pesticide degradation depending on their chemical structure

The selected pesticides were classified into 8 chemical groups as amides, triazines, triazoles, carbamates, methoxyacrylates, organophosphates, pyrimidines and others according to their chemical structure. Data on their classification regarding degradation type A, B or C in four matrices at two spiking levels are shown in Fig. 7.

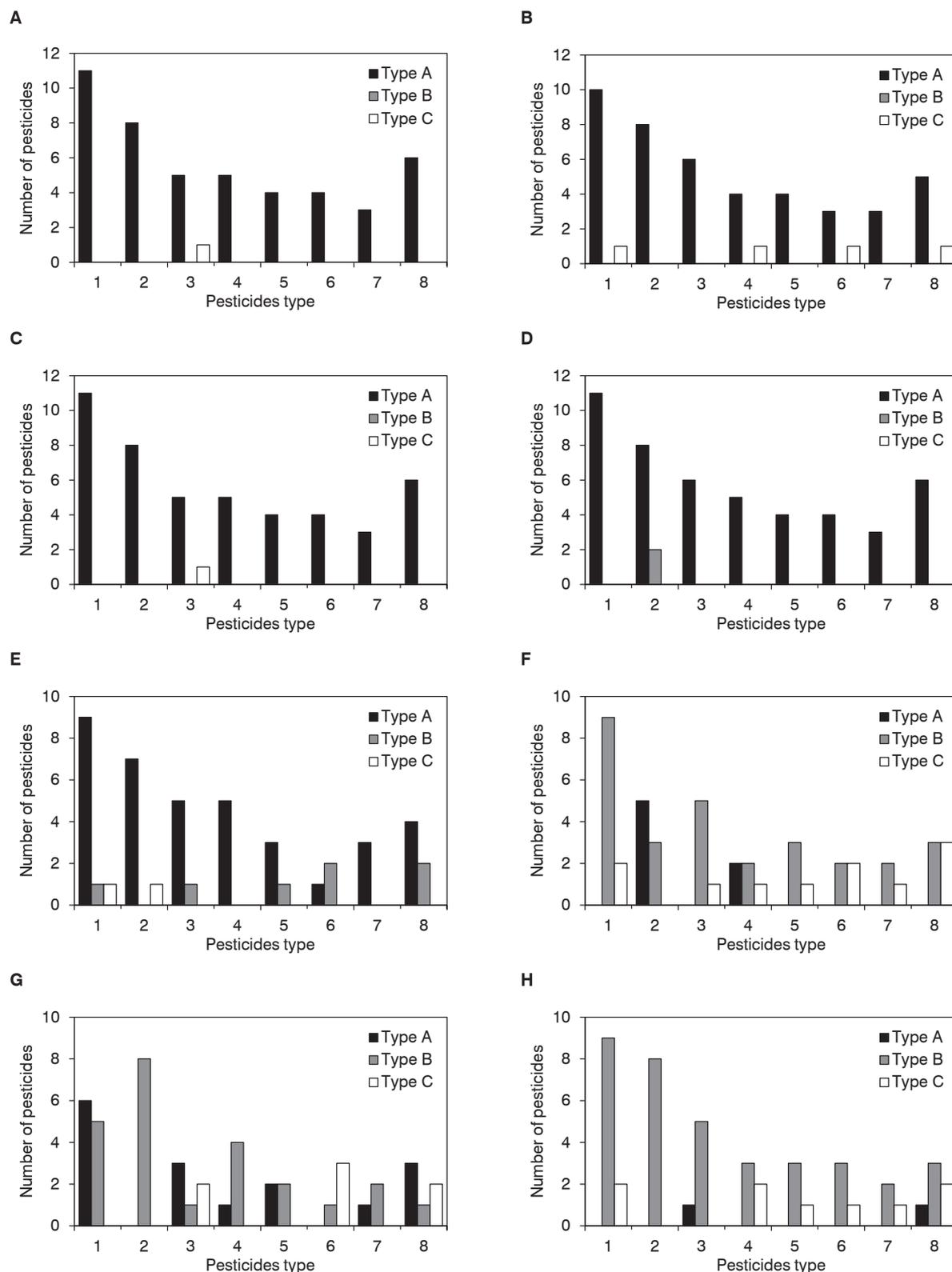
In apple and tomato, the rules of the 8 types of pesticides were obvious. Among them, all of triazines, methoxyacrylates and pyrimidines showed the degradation of type A. Most of the other 5 types of pesticides conformed to the degradation of type A, except for a few that conformed to the degradation of type C, there was no degradation of type B. The classification of the selected pesticides regarding the degradation type was similar in apple and tomato. In cabbage at the low spiking level, 7 types of pesticides, except for organophosphorus, generally conformed to the degradation of type A. However, at the high spiking level, more than 50 % of the 7 types of pesticides, except for triazines, conformed to the degradation of type B and more than 75 % of the amide, triazole and methoxyacrylate pesticides conformed to the degradation of type B. The selected pesticides in cabbage were relatively stable at the low spiking level, and the degradation rate of amides,

triazoles and methoxyacrylates in cabbage was faster in the early stage than in the later stage. In grape, all triazines at both spiking levels conformed to the degradation of type B, indicating that triazines degrade fast in the early stage in grapes. At the low spiking level, more than 80 % of carbamates conformed to the degradation of type B and there was no obvious rule in the other 6 groups. At high spiking level, more than 80 % of amides and triazoles conformed to the degradation of type B and there was no obvious rule in the other 5 groups.

The degradation of amides, triazines, triazoles, carbamates, methoxyacrylates and pyrimidines at the low spiking level was relatively stable in apple, tomato and cabbage. The degradation of selected pesticides at high spiking levels was relatively stable in apple and tomato. The degradation of amides, triazines and triazoles was fast in cabbage and grape in the early stage.

## CONCLUSIONS

The investigation of degradation of selected pesticides was conducted in the matrices of apple, tomato, cabbage and grape. LC-Q-TOF-MS was applied for the determination of pesticides content during storage. Models of degradation of the pesticides were established in four matrices under frozen storage condition ( $-18\text{ }^{\circ}\text{C}$ ). It was shown that 47 out of 90 candidate pesticides were relatively stable and suitable for the study of degradation. Degradation of the 47 pesticides was classified as exponential, logarithmic or polynomial. In general, the degradation rate of pesticides was fast within 14 days. Obvious degradation rule was found in apple and tomato, which was mainly de-



**Fig. 7.** Classification of pesticides according to their degradation type A, B or C.

A – 50  $\mu\text{g}\cdot\text{kg}^{-1}$  in apple, B – 200  $\mu\text{g}\cdot\text{kg}^{-1}$  in apple, C – 50  $\mu\text{g}\cdot\text{kg}^{-1}$  in tomato, D – 200  $\mu\text{g}\cdot\text{kg}^{-1}$  in tomato, E – 50  $\mu\text{g}\cdot\text{kg}^{-1}$  in cabbage, F – 200  $\mu\text{g}\cdot\text{kg}^{-1}$  in cabbage, G – 50  $\mu\text{g}\cdot\text{kg}^{-1}$  in grape, H – 200  $\mu\text{g}\cdot\text{kg}^{-1}$  in grape.

Pesticides types: 1 – amides, 2 – triazines, 3 – triazoles, 4 – carbamates, 5 – methoxyacrylates, 6 – organophosphates, 7 – pyrimidines, 8 – others.

gradation of type A. The degradation rules of the same pesticides in different matrices were not exactly the same. This study provided data on degradation of pesticides in the four matrices. These can be used as a reference for a collaborative study.

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#### Supplementary data

Supplementary data related to this article can be found at <https://www.vup.sk/download.php?bullID=2149>.

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