Characteristics of Pyrethroid Pesticide Residues in Soil of Shenyang, China

Xueying Song\textsuperscript{1,2,a}, Xu Zhang\textsuperscript{1,b}, Mingchao You\textsuperscript{1,c}, Xiaoxu Zhao\textsuperscript{2,d}, Xing Wang\textsuperscript{3,e}

\textsuperscript{1}Key Laboratory of Regional Environment and Eco-Remediation (Ministry of Education), Shenyang University, Shenyang, China
\textsuperscript{2}Key Laboratory of Ecological Environment and Information Atlas (Putian University) Fujian Provincial University, Putian, China
\textsuperscript{3}Liaoning Huadian Environmental Protection Technology Co. Ltd, Shenyang, China.
\textsuperscript{a}Corresponding author: \textsuperscript{a}email: songxy2046@163.com, \textsuperscript{b}email: 973883171@qq.com, \textsuperscript{c}1447565833@qq.com, \textsuperscript{d}email: 185793806@qq.com, \textsuperscript{e}email: 16154518@qq.com

Abstract: Pyrethroid residues in the surface soils and among different soil layers of the open fields and greenhouse soils of Shenyang, China, were analyzed. In addition, the relationship between the soil properties and the pesticide residues was also assessed. Results showed that the detection rates of the pyrethroids were high and multiple pyrethroid pesticides were detected and the average level of trans-cypermethrin was 73.05 μg/kg, which was the highest among the concentration of all test pyrethroids. The detection rate and the residual amount of the same pyrethroid residues were at the low levels in different regions around Shenyang. Comparing the pyrethroid concentrations in greenhouse and the open fields, the residues in greenhouse were higher than those in the open fields. In different soil layers, the pesticide residues were found mainly in the 0-20cm soil layer, and there were no significant differences among the soil depths of 20 cm, 40 cm, 60 cm, 80 cm and 100 cm. Statistical analysis results showed that the residues of fenvalerate were more with the increase of pH value. Organic matter contents were positively correlated with the residues of α-cypermethrin and cypermethrin, and negatively correlated with the residues of lambdacyhalothrin.

1. Introduction

Pyrethroids are a class of pesticides with low toxicity, high efficiency and low residue, developed in recent years. Pyrethroid pesticides play an important role in pest control of crops\textsuperscript{[1-3]}. Increased and unreasonable use of pyrethroid pesticides lead to pyrethroid residues in agricultural products and soils\textsuperscript{[4,5]}. Greenhouse as the main place of vegetable production, the residues of pesticides in vegetables and greenhouse soils can cause potential harm to human health.

Shenyang is the political, economic and cultural center of Northeast China, with a large population and agricultural prosperity. In recent years, the number of greenhouses in the region around Shenyang has been increasing and in some areas crops have been exported abroad, becoming the leading industry in Shenyang. Pesticide residues in greenhouse soil can affect crop safety for a long time, thereby threatening food safety and human health of urban population. So it is very important to study pesticide residue in greenhouse soil around Shenyang. In this study, the residues of several commonly used pyrethroid pesticides in the greenhouse soils around Shenyang was detected in soil, and the distribution characteristics of pyrethroid pesticides in profile soils were studied as so to provide the...
basic data for the rational utilization of pyrethroid pesticides.

2. Materials and methods

2.1. Sampling sites
The greenhouses and the nearby bare land were randomly selected for soil collection in Xinmin, Xinchengzi, Dongling District, Sujiatun and Xinlibao, which were located at the outskirt around Shenyang, China. At the same time, the soil in different soil layers in the nine greenhouses in Xinmin was collected.

2.2. Sample preparation and determination
The soil samples were air dried, mixed, grounded and passed through 60 mesh sieve. Then the mixture of petroleum ether and acetone (v/v, 2:1) was used as extraction agent, soaked overnight, ultrasonic extracted for 20 min. After the sample was standing and stratified, the supernatant was transferred to a 125 mL separation funnel with a funnel. Then 20 mL petroleum ether / acetone (v/v, 2:1) extractant was used for secondary ultrasonic extraction for 20 min. The supernatant was combined, and 50 mL 2% sodium sulfate solution was added to the separation funnel for shaking. The upper organic phase was collected, dried, concentrated to 1 ml by rotary evaporator, to be purified.

The purification experiments were carried out using wet packing columns[7,8]. The 1 ml concentrate and totally 8ml mixture of petroleum ether and ethyl acetate (v/v, 9 : 1) eluent was added to the chromatographic column four times. The eluent was collected and evaporated at room temperature, and dissolved in 1ml n-hexane for testing.

2.3. Conditions for chromatographic analysis
Pre-column pressure was 50 kPa. Carrier gas was high-purity nitrogen, and flow rate was 40 mL/ min. The temperatures of the injection port and detector were 270 ℃ and 320 ℃, respectively. Temperature increasing program: initial temperature 210 ℃ holding for 1 min, rising to 285 ℃ at 10 ℃/ min, holding for 10 min. The injection volume was 1μl.

2.4. Data Statistic analysis
The experimental data were analyzed and counted by Excel and SPSS Statistics 26.

3. Results and discussion

3.1. Pyrethroid residues in soils of different regions
Results showed that 8 pyrethroid pesticides were detected in all five regions, among which fenpropathrin, cyhalothrin, cis-cypermethrin, cypermethrin and fenvalerate were the main pesticides, and the total detection rates were above 70%. The detection rates of trans-cypermethrin, flucythrinate and deltamethrin were significantly different from those of other pesticides, and the detection rate was small. From the regional point of view, pyrethroid pesticides in soil samples were mainly cypermethrin, fenpropothrin and fenvalerate, and the detection rate reached 100%. In addition, the detection rate of the same pesticide varies greatly in different regions, indicating that the types and application amounts of pesticides in regions around Shenyang were not identical.

From table 1, although the total detection rate of trans-cypermethrin, flucythrinate and deltamethrin was relatively lower, the total residue is higher, 73.05μg/kg, 11.03 μg/kg and 23.5μg/kg, respectively. The residue of other pesticides is lower between 2.07-9.74 μg/kg. From different regions, individual pesticide residues in some regions were significantly higher than residues of the same pesticide in other regions. For example, the residue of trans-cypermethrin in Xinmin was as high as 136.38 μg/kg, the residue of flucythrinate in Xinlipu was 68.8 μg/kg, and the residue of deltamethrin in Xinchengzi was 66.94 μg/kg. Due to the large detection of pesticides in Sujiatun area, the pesticide residues in Sujiatun area generally reflect the pesticide residues in the surrounding areas of Shenyang. However,
since no residue limits for pyrethroid pesticides in soil have been established in China, it is unable to evaluate the excessive rate of pyrethroids in soil[9]. But compared with the pesticide residue limits for fruits and vegetables in China, pyrethroid pesticide residues were far lower than the pesticide residue limits for fruits, so the pyrethroid pesticide residues in greenhouse soil around Shenyang were lower.

Table 1 Pyrethroid residues in different sampling sites (μg/kg )

| Pyrethroid       | Sampling sites | Total residues |
|------------------|----------------|----------------|
|                  | Xinmin Xinlipu Dongling Xinchengzi Sujiatun |
| fenpropathrin    | 1.58 3.29 1.74 1.63 3.91 2.07 |
| cyhalothrin      | 3.19 2.28 2.18 5.17 1.95 3.24 |
| cis-cypermethrin | 4.92 33.50 15.55 5.25 5.98 9.74 |
| trans-cypermethrin | 136.38 6.32 6.45 13.62 4.07 73.05 |
| cypermethrin     | 3.33 11.18 2.35 14.30 11.55 7.23 |
| flucythrinate    | - 68.80 - - 17.25 11.03 |
| fenvalerate      | 2.64 1.40 3.54 5.90 7.31 4.13 |
| decamethrin      | 16.49 - 8.55 66.94 - 23.50 |
| bifenthrin       | 3.78 1.47 0.80 0.71 0.44 2.08 |

3.2. Pyrethroid residues in bared and greenhouse soils
The soil samples of greenhouses and bare land in Xinmin area were analyzed. Results in table 3 showed that the detection rate of most pesticides in greenhouses was significantly higher than that in bare land, and the detection rate of fenpropathrin and cypermethrin in greenhouses was lower than that in bare land. Cyfluthrin was not detected in both greenhouses and bare land. The residues of 8 pyrethroids in the greenhouse soil were higher than those in the open fields. The residual content of trans-cypermethrin was 129.7 μg/kg, the highest in the greenhouse. While the residues of cis-cypermethrin in open fields were the highest, with an average residue of 4.65 μg/kg, which was significantly lower than that in greenhouse. The main reason for this result was due to the particularity of the greenhouse. Studies have shown that although pyrethroids have the characteristics of short half-life, the closed nature of greenhouse and high temperature can make the use of pesticides increased, and the long-term use of pesticides increase the residue of pyrethroids in soil. On the other hand, less gas exchange, high humidity and weak light in the greenhouse make pesticide less prone to volatilization, diffusion and photolysis, resulting in a long time of pesticide residues[11], and significantly higher residues in the greenhouse than in the open fields. In addition, environmental conditions in greenhouses can cause pesticide residues by affecting the degradation of pesticides. Wang[12] studied the dynamics of cis-fenvalerate residues in greenhouse and open fields showed that the half-life of cis-fenvalerate in greenhouse soil is 9.8 days, while its half-life in open fields is only 5.7d. The degradation rate in the greenhouse is significantly slower than that in the open fields, so that the pesticide residue in the greenhouse is higher than that in the open fields.

3.3. Pyrethroid residues in different soil layers
The 8 pyrethroids, except deltamethrin, were distributed in different soil layers. In general, the pesticide residues in 0-20 cm soil layer were higher than those in the lower layer (20-100cm), and there was no significant difference in pesticide residues in 20-100 cm soil layer. Studies have shown that pyrethroid pesticides remain mainly in the topsoil after pesticide application, but with agricultural irrigation, water erosion and leaching, a small number of residual pesticides are taken to the lower soil. Moreover, pesticides are greatly influenced by the properties of pesticides during migration. Studies have shown that water-soluble pesticides migrate downwards by adsorption on sediment particles and
are easily infiltrated in the soil profile. In contrast, Fat-soluble pesticides are easily adsorbed by soil clay and organic matter, and are not easy to infiltrate in the soil profile. Pyrethroid pesticides are fat-soluble pesticides, which are easy to be adsorbed and fixed on the soil surface, and are difficult to move in the soil. Therefore, most pyrethroid pesticides are residues in the upper layer, but the multiple-crop index, frequent farming operations, water leaching and deep plowing of soil can cause pesticide residues in the lower layer or irregular pesticide residues in the profile soil in the greenhouse.

3.4. Correlation analysis between pyrethroid residues and soil properties

The correlation between the residues of pyrethroids and soil properties, including soil pH, organic matter, total nitrogen (TN) and total phosphorus (TP), was analyzed in the greenhouse soils around Shenyang. Soil pH was positively correlated with fenvalerate residue. Organic matter content was negatively correlated with cyhalothrin and cypermethrin residues, and positively correlated with cis-cypermethrin residue. The other pesticides were not correlated with pH, organic matter, TP and TN. Studies have shown that the soil property is one of the main factors influencing the degradation of pesticides. After entering the soil, pesticide behaviors will be influenced by temperature, humidity, pH, organic matter content, etc. In general, the higher the organic matter content is, the greater the biological degradation of pesticides occurs, and the higher the soil pH is, the easier the pesticide is degraded. The above results showed that only the residue of cis-cypermethrin increased with the increase of organic matter content, and the residue of fenvalerate increased with the increase of pH. The remaining pesticides were negatively correlated or not correlated with organic matter and pH. In addition, total nitrogen and total phosphorus had no correlation with all pesticide residues, i.e. there was no effect on pesticide residues. Therefore, in general, except for fenvalerate, cyhalothrin, cypermethrin and cis-cypermethrin, the above soil properties had no effect on the residues of most pyrethroids in the greenhouse soils of Shenyang, but the reasons and laws of the effects of organic matter and pH on the above pesticide residues remained to be further studied.

4. Conclusions

The 8 pyrethroids in soil around Shenyang were frequently detected. The trans-cypermethrin concentration was the highest reaching 73.05 μg/kg. The detection rate of pesticides in Sujiatun region was relatively higher, where the detection rates of fenpropathrin, cis-cypermethrin, cypermethrin and fenvalerate reached 100%.

The detection rates of most pyrethroid pesticides in greenhouse soils was higher than those in the open fields, and the pyrethroid residuals in greenhouse soils were significantly higher than that in open fields (p<0.05). The pyrethroid residues in the greenhouse soils around Shenyang were mainly distributed in the 0-20 cm soil layer, and they were also found in the 20-100 cm soil layer with no significant difference in the residual concentrations.

Acknowledgments

This study was financially supported by the Open Fund of Key Laboratory of Ecological Environment and Information Atlas (Putian University) Fujian Provincial University (No.ST18001), and Young and Middle-aged Talent Support Project of Shenyang Science and Technology Bureau (RC190371).

References

[1] Kiraccakali, A.N., Oguz, A.R. (2020) Determination of cytotoxic, genotoxic, and oxidative damage from deltamethrin on primary hepatocyte culture of Lake Van fish, Alburnus tarichi. Chemistry and Ecology, 36: 651-662.

[2] Hozyen, H.F., Khalil, H.M.A., Ghandour, R.A. (2020) Nano selenium protects against deltamethrin-induced reproductive toxicity in male rats. Toxicology and Applied Pharmacology, 408: 115274.

[3] Dader, B., Legarrea, S., Moreno, A. (2014) Control of insect vectors and plant viruses in protected crops by novel pyrethroid-treated nets. Pest Management Science, 70: 3942–3947.
[4] Saeed, S., Albaser, R., Nageswara, R., Swamy, Y.V. (2010) An overview of sample preparation and extraction of synthetic pyrethroids from water, sediment and soil. Journal of Chromatography A, 1217: 5537–5554.

[5] Eiki, W., Koji, B. (2015) Highly sensitive quantification of pyrethroid insecticide etofenprox in vegetables with high-performance liquid chromatography and fluorescence detection. Journal of Chromatography A, 1385: 35-41.

[6] Cui, J., Wang, X., Du, J. (2014) Characteristics and risk assessment of organochlorine pesticide residues in surface soil of Shenyang suburb. Chinese Geology, 41: 1705–1715.

[7] Rahman, M., Hoque, M.S., Bhowmik, S. (2021) Monitoring of pesticide residues from fish feed, fish and vegetables in Bangladesh by GC-MS using the QuEChERS method. Heliyon, DOI: 10.1016/J.HELIYON.2021.E06390.

[8] Huong, D.T.V., Huong, D.T.V., Nga, T.T.H. (2020) Residue Pesticides (Pyrethroid Group) in Vegetable and Their Health Risk Assessment via Digestion on Consumers in Ha Nam Province, Vietnam. IOP Conference Series: Earth and Environmental Science, 505: 012052.

[9] Li, R. (2005) Study on the migration and degradation of pyrethroids in soil. Nanjing: Master's thesis, Nanjing University of Science and Technology. pp. 45-53.

[10] Cai, Q., Mo, C., Li, Y., et al. (2005) The study of PAEs in soils from typical vegetable fields in areas of Guangzhou and Shenzhen, South China [J]. Ecta Ecologica Sinic, 25: 283-288.

[11] Tian, J., Han, B., Li, J., et al. (2002) Experimental study on the relationship between three types of greenhouse and microclimate in Ningxia. Journal of Ningxia Agricultural College, 23: 46-48.

[12] Wang, J., Wan, Y., Xiong, C., et al. (2009) Comparison of residual dynamics of esfenvalerate on cabbage and soil grown in plastic house and open field. Anhui Chemical Industry, 35: 60-62.