

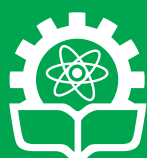
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02 – 06

**DEGRADATION OF THE INSECTICIDES FIPRONIL AND
CYPERMETHRIN IN GREEN ONIONS (*Allium fistulosum*) AND
MUSTARD GREENS (*Brassicajuncea*)**

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ABSTRACT

Pesticide dissipation on food (vegetables, fruits, cereals) is one of the most to be concerned toxicological data, in the aspect of human health risk and food safety, suggesting the suitable pre-harvest interval. A laboratory-scale study was conducted for 2 separated systems (3 replicates per system) of green onions (*allium fistulosum*) and mustard greens (*brassica juncea*) in order to identify the dissipation of the two commonly used insecticides fipronil and cypermethrin under tropical climate. After pesticide application, vegetable samples in these microcosms were collected at day 0, 1, 2, 3, 4, 5, 6 to measure the residue of fipronil and cypermethrin (n = 3). The analytical method was validated with good repeatability and trueness. The decay equations fitted well the first-order kinetics with good correlation coefficient ($R^2 > 0.93$, $p < 0.0005$). The calculated half-life values of fipronil were 2.9 days in green onions and 3.2 days in mustard greens, while those of cypermethrin were 4.5 days and 3.2 days. To meet the maximum residue levels in vegetables of fipronil (0.02 mg/kg) and cypermethrin (0.7 mg/kg), the estimated pre-harvest intervals were up to 23 days and 7.5 days, respectively.

Keywords: dissipation, fipronil, cypermethrin, half-life

1. INTRODUCTION

After the success of Paul Hermann Müller in synthesizing the insecticide DDT in 1948 [1], synthetic pesticides have been applied widely to control and prevent pests and diseases, protect the crops, helping to improve agricultural productivity [2]. Nowadays, new generation pesticides such as groups of synthetic pyrethroids, phenyl pyrazoles, neonicotinoids, etc. have been developed and introduced to the market as replacement for the prohibited organochlorine pesticides or the restricted organophosphate and carbamate pesticides. They are chemically designed to have high selectivity and decompose faster compared to the old-generation ones.

Vietnam, an agricultural-based country under typical tropical climate, is the third world's largest vegetable producer in 2016 [3], in which mustard greens (*Brassica juncea*) and green onion (*Allium fistulosum*) are among the main crops, have been cultivated year-round in every province of the country. However, the abuse and misuse (e.g. overdose, high frequency application, etc) as well as poor toxicity awareness (e.g. shorten the pre-harvest interval) of pesticides used in

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Vietnam [4, 5, 6, 7, 8, 9] would cause high pesticide residue levels in vegetables, suggesting high risk to human health in terms of pesticide intake. Noticeably, both green onions and mustard greens can be used as processing or raw, where the later might bring higher risk of pesticide intake to human body (if hypothesized that pesticide residues on vegetables are decomposed or volatilized by the heat of cooking [10]).

Two of the most frequently applied insecticides in vegetable cultivation in Vietnam are fipronil and cypermethrin (household interviews, data not shown). Fipronil is a member of a relatively new class of pesticides, the phenyl-pyrazole insecticides, while cypermethrin (including 8 isomers) belongs to the group of synthetic pyrethroid insecticides, derived from naturally-occurring pyrethrins, taken from pyrethrum of dried *Chrysanthemum* flowers [11]. The toxicology of these both pesticides is classified at class II - moderately hazardous [12].

Pesticide after application on plants, will partly be transported to the surrounding environment while the rest will persist on the plants and degrade. The residue of a pesticide in a plant is known as mainly defined by the applied dose and its degradation rate – which is strongly affected by environmental conditions (temperature, rainfall, wind, sunlight amount, etc.) and the crop itself [13]. Under tropical climate, pesticides are likely to dissipate faster than in temperate regions [14]. There were publications on the dissipation of pesticides under different climate conditions worldwide, for instance, in Canada [15], in Spain [16], or in different cultivars such as Chinese cabbage [17], mango [18], cowpea [19], tomato [20], and mustard greens [21]. A study of Chai et al. [22] provided evidence of the different pesticide dissipation rates in different weather conditions with the same application technique onto plant. Accordingly, exponential decay equation helped to predict significantly the half life of individual pesticide as well as the theoretical residues of the target pesticide in a plant at a specific time, moreover to recommend a suitable pre-harvest interval. Noticeably, so far there have been no systematic study on the dissipation of pesticides on plant conducted in Vietnam – an agricultural country located in a typical tropical climate region.

Therefore, in this study, a mesocosm experiment was conducted to define the degradation of fipronil and cypermethrin insecticides in green onions and mustard greens as well as to compare the effect of the plant itself toward the dissipation rate of each target pesticide.

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

Table 1. General physical-chemical properties [23] of fipronil and cypermethrin.

Compounds	Chemical class	Formular	Vapour pressure (mmHg, 20°C)	Solubility in water (mg/L, 20 °C)	log(K _{ow})	DT ₅₀ ^(*) in soil (days)	Toxicity (**)	MRL (***) (mg/kg)
Fipronil	Phenyl pyrazole	C ₁₂ H ₄ Cl ₂ F ₆ N ₄ OS (M = 437.2)	3.710 ⁻⁴	3.78	3.7	142	II	0.02 (brassicac)
Cypermethrin	Pyrethroid	C ₂₂ H ₁₉ Cl ₂ NO ₃ (M = 416.3)	3.1 10 ⁻⁹ (25 °C)	0.009	5.3	60	II	0.7 (leafy vegetables)

* Half-life

** Toxicity data announced by WHO [12]

*** Maximum residue level [24]

Fipronil and cypermethrin standards, surrogate standard p,p'-DDT and internal standard fluorene-D10 (>97 % purify) were obtained from Sigma Aldrich (USA). Stock solutions (1000 µg/mL) were prepared in acetone and stored at -20 °C. Working solutions were prepared in toluene. HPLC

grade solvents were ordered from J. T. Baker (Deventer, The Netherlands), including n-hexane, acetone, toluene. Glass fiber filters (Whatman, 47 mm, pore size 1.6 μm) and florisil (1g/6 mL) silica-based reversed phase cartridges from Sigma Aldrich (USA), activated carbon from Merck (Darmstadt, Germany) were used. General physical-chemical properties of fipronil and cypermethrin were demonstrated in *Table 1*.

2.2. Experimental design

The mesocosm experiment was conducted in the garden of the Hue University – College of sciences (16°27'28,32" N, 107°35'29,98" E) in June – July 2018, aiming to get the systems exposed to the natural weather conditions of the typical tropical climate (i.e. high amount of sunlight, high temperature and air humidity, mild wind speed). The experiment included 4 microcosms (one control (no pesticide spraying) and three replicated microcosms with pesticide application) for green onions and 4 ones for mustard greens. Each microcosm was a foam box (90 cm x 60 cm x 30 cm) with small holes at the bottom for water drainage. Porous alluvial topsoil (free of fipronil and cypermethrin) digging from Huong An commune – a traditional cultivation area in Thua Thien Hue province – filled the box. The surface soil of 3 cm was mixed with NPK fertilizer (free of fipronil and cypermethrin, ca. 10 g/box). Seedlings of green onions (15 days old) and mustard greens (10 days old) were transplanted in rows with a distance of 10 cm in between. Plants were watered and weeds were removed on a daily basis. The experiment started from 1st June 2018 and the systems were kept 30 days before pesticide application. Tungent 5SC (fipronil 50 g/L) and Appencyper 35EC (cypermethrin 35% w/w) amounts of 0.5 mL were mixed and dissolved in 1 L water (resulting in 0.025 mg fipronil/L and 0.175 mg cypermethrin/L) to spray onto the 3 replicated microcosms of green onions or mustard greens (total sprayed area was 3.24 m², the control ones were not sprayed). Pre-harvest time suggesting for fipronil is 7 days while for cypermethrin is 14 days. Vegetable samples were collected from each system on 0 (1 hour before pesticide application), 1, 2, 3, 4, 5, 6 days after application. Data on the weather conditions during the experiment were provided by the Hydrometeorological forecasting Center of Thua Thien Hue province (see *Table 2*)

Table 2. Meteorological information during the experimental period

Month	Ave. air temp. (°C) (day/night)	Ave. Sunshine (h)	Ave. Rainfall (mm)	Humidity (%)	Evaporation (mm)
June 2018	34.7/25.3	191	161.9	80	81.7
July 2018	33.4/25.1	163	158.2	84	68.8

2.3. Pesticide analysis

Fipronil and cypermethrin analytical protocol was adopted from the study of Chau et al. , [25] with modification, specifically: Vegetable sample (5g) were chopped, mixed with 60 mL acetone, 20 g Na₂SO₄ and homogenized by a metal blender (Philips, The Neitherland) before ultrasonic extraction in 15 min with 3 replicates. Five hundred ng of the surrogated p,p'-DDT was spiked to the sample at the very beginning. The extract, after filtering (Watmann glassfiber filter, England), were rotary evaporated (Buchi, Switzerland) to 10 mL, before solid phase extracted, including charcoal activated carbon packed column (1 g, Merck, Germany) with 40 mL acetone:toluene (v:v,

1:1) elution, and then florisil cartridge (1g/6mL, Supelco, Sigma Aldrich, USA) with 25 mL acetone:n-hexane (v:v, 1:5) elution. The extract was then evaporated to nearly dryness, taken by toluene to 1 mL amber vial containing 100 ng fluorene-D10 as internal standard before filled up by toluene to 1 mL and stored at -20°C until analysis. Fipronil and cypermethrin were measured using GC/MS QP2010 plus system (Shimadzu, Japan) employing Rtx-CL pesticide capillary column (fused silica, 30m x 0.25mm, film thickness 0.25µm, Restek, USA). The temperature program was as the following: initial 70°C for 1 min, increased to 180°C at a rate of 10°C/min, then to 240 °C at a rate of 5°C/min held for 5 min, finally to 280°C at a rate of 10°C/min held for 15 min. The target ions offipronil, cypermethrin, p,p'-DDT and fluorene-D10 were 367-213-143, 183-165-181, 235-237-165, 121-150-122, respectively. A typical chromatogram of 500 ppb analytes mixture was shown in *Figure 1*.

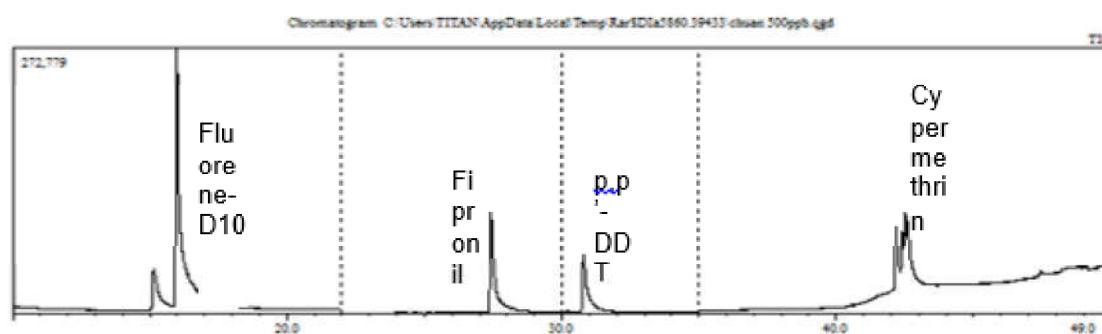


Fig. 1. Chromatogram of standard mixture at 500 ppb

2.4. Quality control

Home-grown green onions and mustard greens were used as blank samples to control the laboratory contamination. The instrument limit of detection (LOD) for each target compound was calculated from seven replicated injections of the standard solution at the lowest concentration in the calibration curve (5 ppb in this study), which was delivered by multiplying the *t-distribution* by the determined standard deviation (SD): $LOD = 3.14 \times SD$ (3.14 is the *t* value for a 99 % confidence interval, with six degrees of freedom) [26]. Accordingly, the respective limit of quantification (LOQ) of the method for an individual compound is $LOQ = 10 \times SD$. Only detected concentrations higher than the specific LOQ values were used for further assessment. The calibration curves for the studied compounds were developed from seven levels (5, 10, 50, 100, 200, 500, 1000 ppb). The trueness (Rev %) and the repeatability (RSD %) of the analytical method were checked by three replicates with a fortification level of 100 ng of each target pesticide onto green onions samples (home-grown). In addition, this study accepted a recovery of the surrogate p,p'-DDT from 80% to 120%.

2.5. Data analysis

Exponential decay equations were fitted to pesticide dissipation data:

$$C_t = C_o \cdot e^{-kt}$$

C_t: the concentration of pesticide at time *t* (ng/g)

C_o: the initial concentration (ng/g)

k: the dissipation rate constant (1/day)

t: the elapsed time (day)

The equation was derived by applying non-linear least-squares regression analysis of concentration against time. Dissipation half-lives (DT50: the time required for 50% of the initial concentration to dissipate) were calculated from the above equation: $DT50 = (\ln(2))/k$. For persistence comparisons, 99% dissipation times were also calculated.

Sigma Plot 11.0 (Systat Software Inc, San Jose, California, USA) was employed for data analysis.

3. RESULTS AND DISCUSSION

3.1. Quality control of analytical method

The quantification limits of fipronil, cypermethrin, and surrogate p,p'-DDT were defined by 3.8, 6.1 and 2.5 ng (Table 3). The LOQ of cypermethrin was the highest due to the long retention time on the Rtx-CL pesticides capillary column (42.1 to 42.9 minute). The trueness (n = 3, fortification level of 100 ng) of analytical method varied from 106% to 115% for fipronil and from 79% to 104% for cypermethrin with repeatabilities (RSD%, n = 3) fluctuated from 5% to 6%, absolutely met the AOAC (Association of Official Analytical Chemists) guideline (RSD < 21% for the measured concentration from 10 ng to 100 ng) [27].

Table 3. Limit of detection (LOD), limit of quantification (LOQ), trueness (Rev) and repeatability (RSD) of the analytical method

Compounds	LOD (ng) (n = 7)	LOQ (ng) (n = 7)	Rev (%) (n = 3)	RSD (%) (n = 3)	Calibration curves; (R ²)
Fipronil	1.1	3.8	106 - 115	4.7	$y = 410^{-5}x + 7 \cdot 10^{-4}$; (0.997)
Cypermethrin	1.8	6.1	79 - 104	5.9	$y = 3 \cdot 10^{-5}x + 9 \cdot 10^{-4}$; (0.996)
p,p'-DDT	0.7	2.5	87 - 98	6.4	$y = 6 \cdot 10^{-4}x - 76 \cdot 10^{-4}$; (0.999)

Injection concentration for LOD, LOQ determination was 5 ng.

Spiked concentration in real vegetable samples for recovery and repeatability tests was 100 ng.

3.2. Dissipation of fipronil

One hour after application, fipronil residue level in green onions and mustard green reached 4.2 and 3.9 mg/kg, respectively (Table 4). Fipronil dissipated exponentially with time (Figure 2), followed first-order kinetic, in which the achieved dissipation equations gained good relative coefficient ($R^2 = 0.96$, $p = 0.0001$).

Table 4. Fipronil dissipation in green onions and mustard greens

Days after application	Green onions		Mustard greens	
	Ave. quantified concentration (mg/kg) (n = 3)	Dissipation rate (%) (n = 3)	Ave. quantified concentration (mg/kg) (n = 3)	Dissipation rate (%) (n = 3)
0	4.2 ± 0.17	-	3.9 ± 0.20	
1	3.2 ± 0.11	22.9	3.3 ± 0.14	15.8
2	2.2 ± 0.08	48.1	2.3 ± 0.18	40.8
3	1.8 ± 0.07	56.6	2.1 ± 0.11	45.9
4	1.4 ± 0.08	65.1	1.3 ± 0.09	66.8
5	1.4 ± 0.07	66.3	1.5 ± 0.05	60.7
6	1.3 ± 0.09	68.8	1.2 ± 0.06	69.4

Concentrations of fipronil in vegetables were calculated based on fresh weight

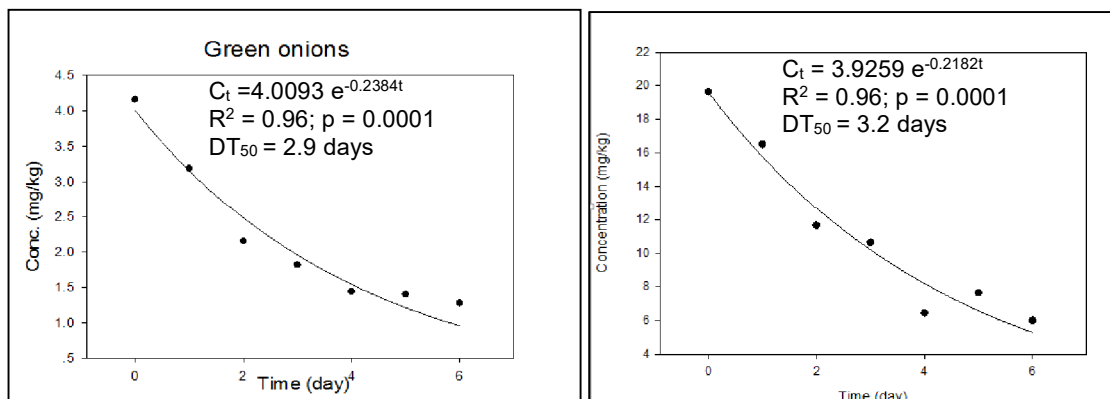


Fig. 2. Dissipation curves of fipronil in green onions and mustard greens

One day after applied onto the mesocosm, 23% (in green onions) and 16% (in mustard greens) fipronil decomposed. The half-lives or time needed for 50% of a chemical compound to degrade from its parent compound for fipronil were from 2.9 and 3.2 days. Eventhough there were rainfall events at day 2 and 5 during the period of experiment, however, at the end of the experiment (7 days after application), nearly 1.3 mg/kg of fipronil were still quantified in green onions and mustard greens, respectively, corresponding to ca. 69% dissipated. Based on the defined exponential equation, theoretically, 99% of fipronil will be decomposed after 19 days. To meet the MRL of fipronil (in brassicas: 0.02 mg/kg, [24]), a period of 22 days (green onions) or 24 days (mustard greens) is needed, which could be considered to replace the currently recommended pre-harvest interval (7 days). In compared with the previous study, fipronil was reported to have a half-life of 2.6 days in mustard greens in the study of Pei et al [17] who mentioned the main processes affected fipronil dissipation were the oxidation and hydrolysis. A work of Kadam et al [21] on the degradation of fipronil in pomegranate fruits concluded that fipronil persisted up to 3 and 5 days in arils, 7 and 10 days in whole fruits at recommended and higher doses, respectively.

3.3. Dissipation of cypermethrin

Cypermethrin is a chiral compound, includes 8 isomers. In this study, cypermethrin concentration was calculated from total cypermethrin isomers. After application, cypermethrin resided at a level of 2.2 mg/kg in green onions, while this figure was recorded higher in mustard greens at 3.1 mg/kg. The interpretation for this difference could be due to the larger and rough leaf surface of mustard greens captured more pesticides. This initial residue levels of cypermethrin in both green onions and mustard greens after spraying were significantly lower than that of fipronil ($p < 0.05$) eventhough the spraying concentration of cypermethrin were seven times higher than that of fipronil (0.175 mg/L versus 0.025 mg/L). This low deposition cypermethrin could be explained by the facts that cypermethrin has very low vapour pressure ($3.1 \cdot 10^{-9}$ mmHg, 25°C), almost insoluble in water (solubility 0.009 mg/L at 20 °C) with high $\log K_{ow}$ (5.3), facilitating a high loss of cypermethrin after application. Meanwhile, fipronil vapour pressure is much higher ($3.7 \cdot 10^{-4}$), its solubility is higher (3.78 mg/L) with lower $\log K_{ow}$ (3.7) (see *Table 1*). In addition to that, fipronil is a systemic insecticide [28, 29]. This property caused a fast absorption of fipronil into the tissues of the leaves after application.

However, the mentioned chemical-physical properties of fipronil and cypermethrin were unlikely to affect their dissipation profiles. The dissipation data of cypermethrin were fitted well by first-order degradation kinetic ($R^2 = 0.99$, $p < 0.0001$ for green onions and $R^2 = 0.93$, $p = 0.0005$ for mustard greens) (*Figure 3*). Cypermethrin half-lives in mustard greens and green onions were 4.5 days

and 3.2 days, respectively. At the end of the experiment, 59% of cypermethrin in green onions and 74% in mustard greens decomposed. It would take 30 days for 99% of cypermethrin to be degraded in green onions, while this period in mustard green was 23.3 days. The required period for cypermethrin to dissipate in both green onions and mustard greens to reach the MRL 0.7 mg/kg [24] was 7.5 days, much shorter than that of fipronil (see section 3.2).

Table 5. Cypermethrin dissipation in green onions and mustard greens

Days after application	Green onions		Mustard greens	
	Ave. quantified concentration (mg/kg) (n = 3)	Dissipation rate (%) (n = 3)	Ave. quantified concentration (mg/kg) (n = 3)	Dissipation rate (%) (n = 3)
0	2.2 ± 0.17	-	3.1 ± 0.23	-
1	1.8 ± 0.12	18.2	2.6 ± 0.18	16.1
2	1.6 ± 0.16	27.3	2.5 ± 0.11	19.4
3	1.4 ± 0.10	36.4	1.6 ± 0.13	48.4
4	1.2 ± 0.06	45.5	1.0 ± 0.12	67.7
5	1.0 ± 0.08	54.5	1.3 ± 0.04	58.1
6	0.9 ± 0.06	59.1	0.8 ± 0.03	74.2

Concentration of cypermethrin in vegetables were calculated based on fresh weight

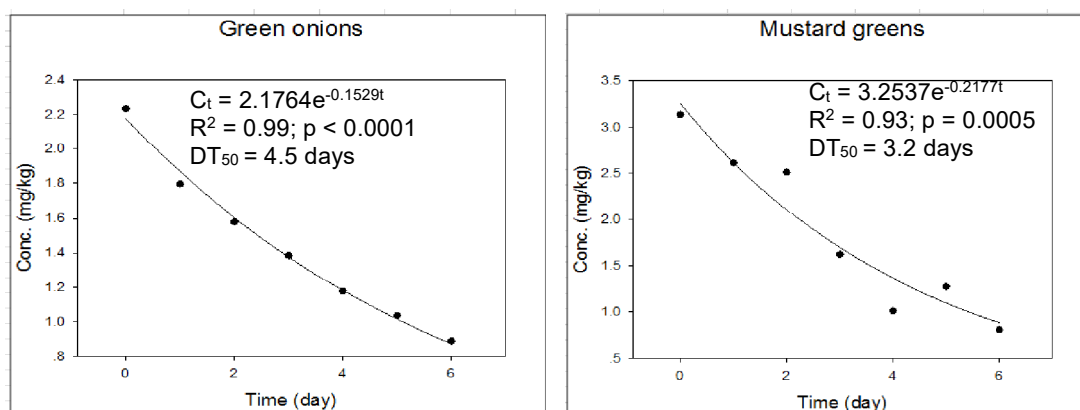


Fig. 3. Dissipation curves of cypermethrin in green onions and mustard green

A study from Chai et al [22] publicited the half-lives of cypermethrin in mustard greens fluctuated from 1.6 days to 2.5 days at different experimental locations in Malaysia. The half-lives for cypermethrin in this study (3.2 to 4.5 days) were also similar to those reported for cabbage (2.6–4.9 days)[30, 31, 32] okra (4.1 days) [19] and head lettuce (2.8–3.3 days) [15] grown in a temperate climate, suggesting that climate conditions were not the main impact factors for the dissipation of cypermethrin in vegetables.

4. CONCLUSIONS

Study on the dissipation of pesticides in vegetables provides the key information for pesticide risk assessment and toxicology. The dissipation rate of fipronil and cypermethrin in both green onions and mustard green could all be fitted by first-order kinetics. Half-lives of the studied pesticides varied from 2.9 days (fipronil in green onions) to 4.5 days (cypermethrin in green onions).

Chemical-physical characteristics of a pesticide strongly affect its deposition onto plant after application, proposing a high application dose should be considered for a non-systemic pesticide with low vapour pressure and less soluble in water (such as cypermethrin). The pre-harvest interval of 7 days is appropriate for cypermethrin, however, 7 days is inadequate to ensure a safe residue level of fipronil (MRL 0.02 mg/kg) in vegetables to be consumed. This study proposes either a lower spraying dose of fipronil or a longer pre-harvest interval. Otherwise, fipronil should not be applied on vegetables, especially for the vegetables that could be directly consumed without cooking such as green onions or mustard greens.

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REFERENCES

- [1]. Nobel Media AB 2014. http://www.nobelprize.org/nobel_prizes/medicine/laureates/1948/press.html, (latest accessed 30/10/2018).
- [2]. Taylor E. L et al, Pesticide Development – A Brief Look at the History, Southern Regional Extension Forestry(2007), Available: <http://www.walterreeves.com/gardening-q-and-a/why-do-we-use-poisons/attachment/pesticide-development-a-brief-look-at-the-history-2/>.
- [3]. Statista, <https://www.statista.com/statistics/264662/top-producers-of-fresh-vegetables-worldwide/>, latest accessed 30/10/2018
- [4]. Hoi P. V., Mol A. P. J., Oosterveer P., van den Brink P. V, Huong P. T. M, Pesticide use in Vietnamese vegetable production: a 10-year study, International Journal of Agricultural Sustainability, (2016), doi: 10.1080/14735903.2015.1134395.
- [5]. Thuy P. T., Van Geluwe S., Nguyen V. A., Van der Bruggen B, Current pesticide practices and environmental issues in Vietnam: management challenges for sustainable use of pesticides for tropical crops in (South-East) Asia to avoid environmental pollution, Journal of Material Cycles and Waste Management, 2012, 14: 379-387.
- [6]. Huong P. T. T., Everaarts A.P., Neeteson J.J., Struik P.C., Vegetable production in the Red River Delta of Vietnam. I. Opportunities and constraints, NJAS - Wageningen Journal of Life Sciences, 2013, 67: 27– 36.
- [7]. Berg H, Pesticide use in rice and rice–fish farms in the Mekong Delta, Vietnam, Crop Protection, 2001, 20:897–905.
- [8]. Toan P. V., Sebesvari Z., Bläsing M., Rosendahl I., Renaud F. G., Pesticide management and their residues in sediments and surface and drinking water in the Mekong Delta, Vietnam. Science of Total Environment, 2013, 452-453: 28–39.
- [9]. Chau N.D.G., Sebesvari Z., Amelung W., Renaud F.G., Pesticide pollution of multiple drinking water sources in the Mekong Delta, Vietnam: evidence from two provinces, Environmental Science and Pollution Research, 2015, 22: 9042-9058.
- [10]. Shahram S., Amirahmadia M., Yazdanpanah H. et al, Effect of cooking process on the residues of three carbamate pesticides in rice, Iranian Journal of Pharmaceutical Research, 2011, 10 (1): 119-126.
- [11]. Thatheyus A. J, Selvam D. G, Synthetic Pyrethroids: Toxicity and Biodegradation, Applied Ecology and Environmental Sciences, 2013, 1 (3): 33–36.
- [12]. WHO (World Health Organization), The WHO recommended classification of pesticides by hazard and guidelines to classification 2009, Geneva: International Program on Chemical Safety (IPCS) & World Health Organization (WHO), 2010. Available: http://www.who.int/ipcs/publications/pesticides_hazard_2009.pdf.
- [13]. Ebeling W., Analysis of the basic processes involved in the deposition, degradation, persistence, and effectiveness of pesticides. Residue Reviews, 1963, 3:35–163.

- [14]. Laabs V., Amelung W., Pinto A. and Zech W., Fate of pesticides in tropical soils of Brazil under field conditions, *Journal of Environmental Quality*, 2002, 31:256–268.
- [15]. Ripley B. D., Ritcey G. M., Harris C. R., Denomme M. A., Brown P. D., Pyrethroid insecticides on vegetable crops, *Pest Management Science*, 2001, 57: 683–687.
- [16]. Chavarri M. J., Herrera A. and Arino A., Pesticide residues in field-sprayed and processed fruits and vegetables, *Journal of the Science of Food and Agriculture*, 2004, 84:1253–1259.
- [17]. Pei Z., Yitong L., Baofeng L., Gan J. J., Dynamics of fipronil residue in vegetable-field ecosystem, *Chemosphere*, 2004, 57:1691–1696.
- [18]. Bhattacharjee A. K. and Dikshit A., Dissipation kinetics and risk assessment of thiamethoxam and dimethoate in mango, *Environmental Monitoring and Assessment*, 2016, 188:165 DOI 10.1007/s10661-016-5160-3.
- [19]. Nath P., Kumari B., Yadav P., RandKathpal T. S., Persistence and dissipation of ready mix formulations of insecticides on okra fruits, *Environmental Monitoring and Assessment*, 2005, 107:173–179 .
- [20]. Preito A., Molero D., Gonzalez G., Buscema I., Ettiene G., Medina D., Persistence of methamidophos, diazinon, and malathion in tomato, *Bulletin of Environmental Contamination and Toxicology Journal*, 2002, 69:479–485.
- [21]. Kadam D. R., Deore B. V., Umate S. M., Residues and dissipation of fipronil and metabolites in pomegranate fruits, *International journal of plant protection*, 2014, 7(2):456-461.
- [22]. Chai L., Mohd-Tahir N., Hansen H. C. B., Dissipation of acephate, chlorpyrifos, cypermethrin and their metabolites in a humid-tropical vegetable production system, *Pest Management Science*, 2009, 65:189–196.
- [23]. University of Hertfordshire, PPDB: Pesticide properties database. Available: <http://sitem.herts.ac.uk/aeru/iupac/index.htm> (latest accessed 30/10/2018), 2009.
- [24]. Codexalimentarius. Pesticide Residues in Food and Feed. Available: <http://www.fao.org/fao-who-codexalimentarius/standards/pestres/pesticides/en/>, (latest accessed 30/10/2018), 2016.
- [25]. Chau N. D. G., Quang H. M., Long H. T., Study on gas chromatographic quantification of currently used pesticides in onion leaves. *Analytica Conference Proceeding*, 2017, 221–230.
- [26]. USP (United States Pharmacopeia), Validation of compendial methods, Twenty-Sixth Revision, National Formulary, 21st ed. Rockville, MD: The United States Pharmacopeial Convention Inc 2013.
- [27]. Association of Official Analytical Chemists (AOAC) International Manual on policies and procedures, Peer Verified methods Program, Arlington, VA, 1993.
- [28]. Simon-Delso et al., Systemic insecticides (neonicotinoids and fipronil): trends, uses, mode of action and metabolites, *Environmental Science and Pollution Resource*, 2015 22:5–34.
- [29]. Bonmatin et al., Environmental fate and exposure; neonicotinoids and fipronil, *Environmental Science and Pollution Resource*, 2015, 22:35–67.
- [30]. Ripley B. D., Ritcey G. M., Harris C. R., Denomme M. A. and Lissemore L. I., Comparative persistence of pesticides on selected cultivars of specialty vegetables. *Journal of Agricultural and Food Chemistry*, 2003, 51:1328–1335.
- [31]. Zhang Z. Y., Liu X. J., Yu X. Y., Zhang C. Z. and Hong X. Y., Pesticide residues in the spring cabbage grown in open fields, *Food Control*, 2007, 18:723–730.
- [32]. Zhang Z. Y., Zhang C. Z., Liu X. J. and Hong X. Y., Dynamics of pesticide residues in the autumn Chinese cabbage grown in open fields. *Pest Management Science*, 2006, 62:350–355 .