Degradation of Dicofol and Chlorpyrifos Residues in Kale Plots

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ABSTRACT

Degradation of Dicofol and Chlorpyrifos were studied in terms of time for the chemical degraded in organic plots, Good Agricultural Practice (GAP) plots, and controlled plots. Kale was chosen for the reference of annual crop to study the degradation in Chiang Mai and Sing Buri for 6 months. Dicofol had degraded within 2-3 months in control plot, 4-5 months in GAP plot and not detected in organic plot. Chlorpyrifos had degraded within 2 months in control plot, 4-5 months in GAP plot and not detected in organic plot. The pH of Kale plots was about Neutral to Slightly Alkaline. Understanding of the fate and behavior of pesticides under tropical conditions was important both in agronomical and environmental terms. The results can used as a scientific data base to determine time for appropriated transition periods of conventional agriculture to organic production in Thailand.

Key words: Kale, pesticide, Dicofol, Chlorpyrifos, transition period, Good Agricultural practice, Organic plant

Introduction

The trend towards organic cultivation in Thailand is growing fast since producers and consumers are becoming aware in health and environment (Lombardi *et al.,* 2010). The principal guidelines for organic production are to use materials and practices that enhance the ecological balance of natural systems and that integrate the parts of the

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farming system into an ecological whole (Fabian *et al*., 2012). The organic crop production certification standard requires that land must not have any prohibited substances applied to it for at least 36 months before harvesting (USDA, 2014). The standards are set under the management of the National Bureau of Agricultural Commodity and Food Standards (ACFS). This organization is responsible for determining the standards and controlling agricultural practices in order to compare to the international organic standards. However, there is one issue that is not officially accepted in Thailand; that is the time spent in the decay of residual agricultural chemicals. This affects the indication of time from the start of organic production to containing a guarantee on the goods as being organic, called transition period. There are two aspects to the conversion. First, is the grower skills and experience in farming and the second is transition of the land. This period, according to the Department of Agriculture and International Federation of Organic Agriculture Movements (IFOAM), is defined as "the provision of the method in organic production that is practiced throughout the transition period at least 12 months before the planting of annual crops and 18 months before the first harvest of the perennials." However, the standard of Codex had difference defined, that transition period should be at least two years for annual crops and three years for perennials. This large difference has affected the acceptance of Thai agricultural product into the international markets which rely on the standard of Codex as a reference limit. The international markets include The European Union (EU), Japan, The United States of America etc.

Kale (*Brassica oleracea* L.) is a popular and an economic crop in Southeast Asia that belongs to the Brassicaceae family. It grows well in strong, moist soil that is enriched with organic matter (Oyugi, 2012). However, kale is mostly vulnerable to insect pests such as diamondback moth [*Plutella xylostella* (Linnaeus)], beet armyworm (*Spodoptera exigua* (Hbner), common cutworm [*Spodoptera litura* (Fabricius)], cabbage looper (*Trichoplusia ni* Hbner), cabbage webworm [*Hellula undalis* (Fabricius)], leaf eating beetle (*Phyllotreta chontanica* Duvivier & *P. sinuata* Steph.)

(Kianmeesuk *et al*., 1999). Tall varieties of kale are transplanted when they are ten to fifteen centimeters (four to six inches) high. The whole plant can be harvested at once or extend the harvest by picking individual leaves. Kale can be harvested at any time as soon as the leaves are large enough (21-28 days) (Oyugi, 2012). It is mostly vulnerable to insect pests such as diamondback moth, beet armyworm, common cutworm, cabbage looper, cabbage webworm and leaf eating beetle (Kianmeesuk *et al*., 1999). Indiscriminate use of pesticides is very common in this crop culture (Kumar and Moorthy, 2001), which leads to destruction of beneficial insects and other non-target organisms, accumulation of toxic residues on produce and human poisoning.

In Thailand, Food and Drug Administration of Thailand had found Dicofol in the super market by testing in Kale (FDA, 2012). Moreover, Kale in the North market fair, Thailand had detected Chlorpyrifos in all samples about 0.02-0.88 ppm (Kanjanamangsak *et al*., 2010). According to the study in Northeast Thailand, Chlorpyrifos was the most 42 percent that can detected in vegetable and fruit by test in 559 samples (Jarupong *et al*., 2012). Chinese-Kale has been reported in commodities of high pesticide residue; with 20% of samples examined were found to exceed the FAO's allowable maximum residue level (Rerkasem, 2004). Therefore, the main purposes of this work were study the degraded of Dicofol and Chlorpyrifos in kale plots for use as reference to indicate an appropriate transition period to organic production (annual) in Thailand.

Materials and Methods

Experimental sites

The trial plots to test the degradation of agricultural residual chemicals was selected by considering the landscape which provided appropriate factors for the experiment. Good Agricultural Practice plot, organic plot and chemical spraying plot in Thumbon Nongyaeng, Amphur Sansai, Chiang Mai Province, and Thumbon Srajaeng, Amphur Bangrachan, Sing Buri Province were chosen as the trial kale plantations.

Experimental plan

The experiment were conducted in Randomized Complete Block Design

(RCBD) with 3 replications. Three treatments were 1. control treatment with spraying Dicofol and Chlorpyrifos only one time 2. GAP treatment with spraying Dicofol and Chlorpyrifos two times and 3. organic treatment with out spraying insecticides by the rule of organic certification. The details of 3 treatments at each trail plot were shown in Table 1, 2, 3 and 4. Data was recorded very month for 6 months

Soil sampling and Pesticide analysis

The soil samples in the trial plots of the annual crops in the selected areas, Chiang Mai and Sing Buri, were sampling by auger equipment under the appropriate depths of kale about 0.6-1.2 inches (DOA, 2014). The amount of Dicofol and Chlorpyrifos were analyzed by AOAC method (2003).Fifty grams of sampling soils mixed with 100 ml. of acetonitriles and blended for 1 min. The mixture was filtered through paper no.1 and transferred to a plastic bottle which contained 5 gm of sodium chloride. The bottles were shaken for 1 min and left it until the solution was separated. The supernatant was transferred to a centrifuge tube which contained 0.5 gm of magnesium sulfate, 0.1 gm of PSA and 0.05 gm of activated charcoal and shaken by vortex for 1 min. The mixture was then centrifuged at 2,500 rpm for 10 min. Ten milliliter was pipetted into a new tube and evaporated by N-Evaporator at 45 °C until it was almost dried. After that, the volume of the solution was adjusted by 5 ml. of hexane and filtered by Nylon Disc filter 0.45 m into vial for 2 ml. The solution was analyzed by GC-ECD (6890N, Agilent Technology), and the result was ensured by GC/MS (5973 inter, Agilent Technology) (AOAC, 2003). The data was reported until it not detected (LOD lower than 0.01 mg/kg).

Statistical analysis

The data was analyzed by SPSS (Statistical Package for the Social Sciences version 17) in Duncan’s new multiple range tests. The different result between the experimental groups was considered at a 95% confidence interval.

Results and Discussion

Dicofol

The amounts of Dicofol in kale plot of Chiang Mai and Sing Buri Province were shown in Table 5 and 6,

Table 1 The activity of kale plot in Chiang Mai for study Dicofol degradation

Treatment	Soil sampling times (months)						
	0	1	2	3	4	5	6
Control	-	Spraying Dicofol	-	Harvest	-	Harvest	-
GAP	-	Spraying Dicofol	Spraying Dicofol	Harvest	Spraying Dicofol	Harvest	-
Organic	-	-	-	Harvest	-	Harvest	-

Table 2 The activity of kale plot in Sing Buri for study Dicofol degradation

Treatment	Soil sampling times (months)						
	0	1	2	3	4	5	6
Control	-	Spraying Dicofol	Harvest	-	-	-	Harvest
GAP	-	Spraying Dicofol	Harvest	-	Spraying Dicofol	-	Harvest
Organic	-	-	Harvest	-	-	-	Harvest

Table 3 The activity of kale plot in Chiang Mai for study Chlopyrifos degradation

Treatment	Soil sampling times (months)						
	0	1	2	3	4	5	6
Control	-	Spraying Chlopyrifos	-	Harvest	-	Harvest	-
GAP	-	Spraying Chlopyrifos	Spraying Chlopyrifos	Harvest	Spraying Chlopyrifos	Harvest	-
Organic	-	-	-	Harvest	-	Harvest	-

Table 4 The activity of kale plot in Sing Buri for study Chlopyrifos degradation

Treatment	Soil sampling times (months)						
	0	1	2	3	4	5	6
Control	-	Spraying Chlopyrifos	Harvest	-	-	-	Harvest
GAP	-	Spraying Chlopyrifos	Harvest	Spraying Chlopyrifos	-	-	Harvest
Organic	-	-	Harvest	-	-	-	Harvest

Table 5 Amount of Dicofol (mg/kg) in the kale plot, Chiang Mai

Treatment	Soil sampling times (months)						
	0	1	2	3	4	5	6
Control	ND	9.3038 0.0018[ab]	1.0119 0.0012[c]	ND	ND	ND	ND
GAP	ND	9.3146 0.0021[ab]	14.0243 0.0015[a]	6.1899 0.0029[b]	2.1356 0.0011[c]	ND	ND
Organic	ND	ND	ND	ND	ND	ND	ND

Values were mean S.D. (n=3).

Mean in the same column, followed by a common letter are not significantly different at 5% level by DMRT or LDS.

ND = Not detected (LOD lower than 0.01 ppm).

Table 6 Amount of Dicofol (mg/kg) in the kale plot, Sing Buri

Treatment	Soil sampling times (months)						
	0	1	2	3	4	5	6
Control	ND	7.0198 0.0027[a]	1.0087 0.0024[b]	0.0217 0.0019[c]	ND	ND	ND
GAP	ND	8.1282 0.0013[a]	1.1101 0.0016[b]	0.0146 0.0020[c]	5.4377 0.0022[a]	1.0023 0.0014[b]	ND
Organic	ND	ND	ND	ND	ND	ND	ND

Values were mean S.D. (n=3).

Mean in the same column, followed by a common letter are not significantly different at 5% level by DMRT or LDS.

ND = Not detected (LOD lower than 0.01 ppm).

respectively. Kale plot in Chiang Mai Province, Amount of detected Dicofol in control treatment was decreased from 9.3038 to 1.0119 mg/kg and could not detected after 3 months. Although Dicofol was sprayed 3 times in 1st, 2nd and 4th month in GAP treatment but detected Dicofol was decreased from 9.3146 to 2.1356 mg/kg in 4 month and not detected after 5 months. Whereas no Dicofol was detected in organic treatment because of no chemical used in this plot.

In Sing Buri Province, detected Dicofol was decreased from 7.0198 to 0.0217 mg/kg and not detected after 3 months in control treatment. GAP treatment showed decreasing of Dicofol from 8.1282 to 1.0023 mg/kg in 5 months and not detected after 6 months even though spraying 2 times in 1st and 4th month were done . Similarly to Chiang Mai kale plot, no Dicofol or any other residual agricultural chemicals was detected in the soil. FAO (1992) reported that, Dicofol was found to disappear quickly and the half-life was 62 days. Soil acts like an active filter, where chemical compounds are degraded by physical, chemical and biological processes. It is also a selective filter because of its capacity to retain chemicals and avoid their seepage into aquifers (Cornejo *et al*., 2000).. The half-lives of pesticides have been reported to increase with decreasing soil water content and temperature (Ou *et al*., 1983).

Chlorpyrifos

Detected Chlorpyrifos in kale plot of Chiang Mai and Sing Buri Province was shown in Table 7 and 8 respectively. In Chiang Mai Province, decreasing in the amount of Chlorpyrifos from 18.1281 to 1.0119 mg/kg in 2 month and not detected after 3 months was expressed in kale plot under control treatment . Under GAP treatment, detected Chlorpyrifos was decreased from 17.1678 to 1.1904 mg/kg in 5 months and not detected after 6 months.

Similar result was also obtained from kale plot in Sing Buri Province. Detected Chlorpyrifos in control treatment was decreased from 14.5311 to 0.1871 and not detected after 3 months. Decreasing was also found in GAP

Table 7 Amount of Chlopyrifos (mg/kg) in the kale plot, Chiang Mai

Treatment	Soil sampling times (months)						
	0	1	2	3	4	5	6
Control	ND	18.1281 0.0031^{a}	1.0173 0.0025^{b}	ND	ND	ND	ND
GAP	ND	17.1678 0.0028^{a}	20.0260 0.0027^{a}	1.2193 0.0019^{b}	16.4025 0.0026^{a}	1.1904 0.0017^{b}	ND
Organic	ND	ND	ND	ND	ND	ND	ND

Values were mean S.D. (n=3).

Mean in the same column, followed by a common letter are not significantly different at 5% level by DMRT or LDS.

ND = Not detected (LOD lower than 0.01 ppm).

Table 8 Amount of Chlopyrifos (mg/kg) in the kale plot, Sing Buri

Treatment	Soil sampling times (months)						
	0	1	2	3	4	5	6
Control	ND	14.5311 0.0012[b]	0.1871 0.0013[c]	ND	ND	ND	ND
GAP	ND	12.0485 0.0010[b]	0.0485 0.0017[d]	20.0001 0.0014[a]	0.0821 0.0010[cd]	ND	ND
Organic	ND	ND	ND	ND	ND	ND	ND

Values were mean S.D. (n=3).

Mean in the same column, followed by a common letter are not significantly different at 5% level by DMRT or LDS.ND = Not detected (LOD lower than 0.01 ppm).

treatment from 12.0485 to 0.0821 mg/kg in 4 month and not detected after 5 months. Chlorpyrifos was not detected from Organic plot in Chiang Mai and Sing Buri Province Fang (2009) mentioned that degradation rate of chlorpyrifos was the first order and half-life was significantly extended with increasing chlorpyrifos concentration. It was between 60 and 120 days but it could range from 2 weeks to over 1 year depending on the soil type, soil micro-organisms, and climatic condition (Singh *et al*., 2002).

Conclusion

Complete degradation of Dicofol and Chlorpyrifos in kale plot were shown after 3 months in both Chiang Mai and Sing Buri Provinces under control treatment. GAP treatment, Dicofol and Chlorpyrifos were not detected after 5 and 6 months. Kale plots cultivated under organic agricultural practice in Chiang Mai and Sing Buri Province were not shown any detectable Dicofol and Chlorpyrifos or any other residual agricultural chemicals in the soil. Information on the actual input of pesticides into the environment is crucial for proper risk assessment and the rational design of risk reduction measures. Understanding of the fate and behavior of pesticides under tropical conditions was important both in agronomical and environmental terms. Degradation time of the pesticide residues depended on area, pH and temperature.The results of this study can be used as a scientific-supported data base to determine the appropriate transition period to organic production in Thailand.

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