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The Degradation of Pesticide Residues in Agriculture Fields to Specify the Organic Transition Period

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Abstract

The degradation of Dicofol, an insecticide of Organochlorine compound, and Chlorpyrifos, an insecticide of Organophosphate, were studied in terms of the time consumed for the chemical decayed in the agricultural plots for organic plant production, Good Agricultural Practice (GAP) plots, and controlled plots. The studied on annual crops including rice in the area of Chiang Mai and Sing Buri Province shown that the Dicofol substance took 4-5 months to decayed, starting from the day of the first used the chemical on both annual crops and perennials crops. However, Chlorpyrifos took only 1-2 months to decayed. The results of this study can be further use as a scientific data base to determine time for appropriate transition periods of conventional agriculture to organic production in Thailand.

Keywords: Dicofol, chlorpyrifos, organochlorine, organophosphate, translation period.

Introduction

Global population is growing faster than agricultural products[1]. The trend towards organic cultivation in Thailand is growing fast since both producers and consumers are becoming more aware in health and environment[2]. The aim of organic agriculture is to increase efficiency the health and productivity of soil, plants, animals and people. The principal processes for organic production are use materials and procedure for increase the ecological balance of natural system[3]. The certification standard of organic production have requires that land must not have any prohibited substances such as non-approved pesticides and synthetic fertilizers to use it for at least 36 months before harvest an organic crop. In addition, soil fertility and crop nutrients should be handling through tillage and cultivation practices, crop rotations, crop waste materials, cover crops, synthetic materials, crop pests, weeds and diseases, mechanical and biological controls. The use of genetic engineering, ionizing radiation and sewage sludge is also prohibited[4].

The standards of agricultural 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 meet organic standards in accordance with and comparable to international organic standards. However, there is one issue that is not officially accepted in Thailand; it 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. One 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 is different. Codex is defined as the transition period as at least two years for annual crops and three years for perennials. This much difference has affected the acceptance of Thai agricultural goods in to the international markets which rely on the standard of Codex as a reference limit. These markets are the European Union (EU), Japan, the United States of America, etc.

Furthermore, because of the producers' loss of opportunity due to the organic status of their products and due to the consideration of Agricultural Commodity and Food Standards on organic agriculture, which includes stakeholders, it is recommended that there should be the study on agricultural residual chemicals' degradation. This is to achieve a scientific data base which could be a foundation for a reference of the determination of the appropriate transition period to organic production in Thailand. Generally, the environment and the factors relating to the decay of agricultural residual chemicals in soil are different than those in countries with colder climates.

Pesticides can be classified into five chemical groups which are organochlorine, organophosphate, carbamate, synthetic pyrethroids, avermectin and formamidine[5-7]. In 2007, about 2363 million kg of pesticides was used in the world with herbicides constituting the highest share of 950.7 million kg followed by 404.6 million kg of insecticides followed by 262.17 million kg of fungicides[8]. The current research is focused on the insecticides of Organochlorine and Organophosphate compounds since these chemicals can stay in the soil longer than pesticides of other compounds. Repeated use of these chemicals is causing severe concern from the health and environment[9].

Insecticides made from the Organochlorine compound, are known by many other names such as Dicofol, DDT (the first banned because it readily accumulated in the animal tissues)[10], HTC, HCB, Dieldren, and Endrin. However, many countries have banned the import and usage of these chemicals since their toxins remain longer than other compounds in food and the environment[11,12]. Dicofol (2,2,2-trichloro-1, 1-bis (4-chlorophenyl) ethanol) is an organochlorine acaricide used to control the cause of damage in plant[13,14]. It was produced from CCl_3CHO and C_6H_5Cl, through condensation, alkalization, chlorination, and hydrolyzation processes[15].

Most insecticides made from Organophosphate compounds, are composed of Phosphate derivatives. There are 140 different kinds of these insecticides and they have more than 100 commercial names worldwide, such as Chlorpyrifos, Paraoxon, Parathion, Malathion, Diazion, and Dichlorvos. Chlorpyrifos (O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl) Phosphorothionate, CPF) is a broad-spectrum organophosphate insecticide used to control insect pests[16,17]. It has a melting point around 41.5–44 $^{\circ}$C. The dissipation, adsorption, leaching, photolysis and biodegradation of CPF in soil ecosystems have been widely investigated[18-22]. However, the use of CPF has bring to contamination of the environmental and food matrix in some regions[23].

The toxicity of pesticides from contaminated food is mostly unknown but there is growing evidence of cancer, neurological damage, endocrine disruption and birth defects consequential from exposure[24,10]. These chemicals can block the work of acetylcholinesterase enzymes which are related to the work of neurotransmitters. As a result, these chemicals are dangerous to systems in the human body if they are accumulated in high value. For instance, they lead to muscle weakness and induce cancer in the human body[25].

Information on the fate of pesticides under the specific geography and typical soil environment of the tropics area is rather limited, particularly in rice soils[26]. Rice (*Oryza sativa* L.) being one of the most important cereals grown almost exclusively in tropical regions of Asia and Africa especially it was an important in agro-ecosystem of Thailand. Global rice production was 468.1 million tons during the year 2010 and it rose to a record 480 million tons in 2011[9]. Therefore, the main purposes of this work were held to indicate an appropriate transition period to organic production in Thailand.

Material and Methods

Materials: Acetronitriles (CH_3CN, analyzed grade), Sodium chlorides (NaCl, analyzed grade), Hexanes (C_6H_{14}, analyzed grade), Magnesium sulfates ($MgSo_4$, analyzed grade), Prostate-specific antigens (PSA, analyzed grade) and Activated charcoals (analyzed grade) were purchased from Merck, Thailand.

Experimental sites: The researcher selected trial plots to test the degradation of agricultural residual chemicals by considering the landscape which provided appropriate factors for the experiment. These factors were season, weather, soil condition and planting system. Fields in Thumbon Nongyaeng, Amphur Sansai, Chiang Mai Province, and Thumbon Srajaeng, Amphur Bangrachan, Sing Buri Province were chosen as the trial rice plantations.

Experimental plan: Randomized Complete Block Design (RCBD) was used in this studied by collecting the data every months. This was to provide experimental results for the various agricultural activities of each area such as spraying insecticides; Because of the annual crops had short lived. The soil samples of the selected areas were collected twice during production to ensure the results.

Soil sampling and Pesticide analysis: The soil in the trial plots of the annual crops in the selected areas, Chiang Mai and Sing Buri, were collected by auger equipment under the appropriate depths of each kind of plant, about 0.6-1.2 inches[27]. The amount of Dicofol and Chlorpyrifos were analyzed by using 50 grams of sampling soils mixed with 100 ml. of acetonitriles and blended for 1 minute. The mixture was filtered by paper no.1 and transferred to a plastic bottle which contained 5 grams of sodium chloride. The bottles were shaken for 1 minute and left it until the solution was separated. The supernatant was transferred to a centrifuge tube which contained 0.5 grams of magnesium sulfate, 0.1 grams of PSA and 0.05 grams of activated charcoal and shaken by vortex for 1 minute. The mixture was centrifuged at 2,500 rpm for 10 minutes. 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 µm into vial for 2 ml. The solution was analyzed by GC-µECD (6890N, Agilent Technology), and the result was ensured by GC/MS (5973 inter, Agilent Technology)[28]. The data was reported until it not detected (LOD lower than 0.01 ppm; nil).

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 ($p>0.05$).

Results and Discussion

The Degradation of Organochlorine Compound; Dicofol: The amount of Dicofol (Organochlorine compounds) in Chiang Mai Province's rice fields between 1st and 4th months were shown in table-1. They were not significant ($p>0.05$) in control plots and GAP plots. The insecticides had been decomposing and were not found after five month. Although, it was found again on 6th month of the GAP plots (47.6850 ppm.) after the rice fields had a second sprayed of insecticide. The Dicofol has degraded again and not detected in the 9th month. In Sing Buri Province, the amounts of Dicofol in the rice fields were reported in table-2. They had significantly ($p<0.05$) in control plots and GAP plots. It was clear that the amount of Dicofol in 1st, 4th, and 6th month were higher than other months (89.4557, 56.2157, and

57.0002 ppm, respectively). Moreover, each month had high Dicofol in the period of spraying insecticide in the GAP rice plots and not detected in the 9th month. This result demonstrated that the amount of Dicofol in Sing Buri Province has slowly degraded than Chiang Mai Province. According to the studied from The Coastal Aquatic Animal Health Research Institute (2007)[29], the remaining amount of Dichlorodiphenyl-trichloroethane (DDT), which is an insecticide made from the organochlorine compound, were depended on the condition of the environment. In colder climates, DDT was remained in the soil longer than tropical zones. This is because the bacteria in soil are more active in higher temperature[25]. Thermal degradation of pesticides could undergo simple evaporation or sublimation, chemical changes and oxidation reactions[30,31]. However, several physico-chemical factors such as temperature, pH, organic carbon content, moisture content, and pesticide formulation might also had influenced on degradation of a pesticide molecule[32].

The Degradation of Organophosphate Compound; Chlorpyrifos: The amount of Chlorpyrifos (Organophosphate compounds) in Chiang Mai Province's rice fields were reported in table-3. They had significant ($p>0.05$) in control plots and GAP plots. The beginning periods were 23.4362 and 32.4484 ppm, respectively. The chemical continued decreased until becoming undetected within two months. Regarding to the degradation trend of Chlorpyrifos in Sing Buri Province was similar to the result of Chiang Mai Province as shown in table-4. Moreover, it was found that the amount of Chlorpyrifos in control plots and GAP plots in Sing Buri Province were not significant ($p>0.05$) in the 1st month of soil collection. According to Fang (2009)[17], the degradation of chlorpyrifos was the first order reaction. Half-life was increasing with increased the 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 microorganisms, and climatic condition[33,34]. Firstly, it was observed to be hydrolyzed to TCP under alkaline conditions[35], but later, the microorganism in the hydrolysis of chlorpyrifos was described[36]. It was decayed faster due to the activity of microorganisms in the soil and the period of dissolution was around 10-14 days[25]. Chlorpyrifos bound may broken-down by abiotic factors like UV light, chemical hydrolysis and dechlorination[37,38].

Table-1
Amount of Dicofol (ppm) in the rice field, Chiang Mai

Treatment	Soil sampling times (months)									
	0	1	2	3	4	5	6	7	8	9
Control	nil	54.9863 ±0.0059^{a}	28.6161 ±0.0042^{b}	12.1718 ±0.0015^{c}	1.1718 ±0.0088^{d}	nil	nil	nil	nil	nil
GAP	nil	57.7776 ±0.0012^{a}	33.6358 ±0.0011^{b}	13.1465 ±0.0091^{c}	2.1465 ±0.0052^{d}	nil	47.6850 ±0.0059^{a}	20.4651 ±0.0013^{bc}	1.0865 ±0.0013^{d}	nil
Organic	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil

Values were mean ± S.D. (n=5). Different letter (a-d) in the same column indicated significant differences ($p<0.05$) between samples. nil = Not detected (LOD lower than 0.01 ppm).

Table-2
Amount of Dicofol (ppm) in the rice field, Sing Buri

Treatment	Soil sampling times (months)									
	0	1	2	3	4	5	6	7	8	9
Control	nil	45.6588 ±0.0011^{b}	24.2716 ±0.0017^{c}	13.6673 ±0.0013^{d}	2.4311 ±0.0019^{f}	nil	nil	nil	nil	nil
GAP	nil	89.4557 ±0.0021^{a}	36.0943 ±0.0016^{c}	19.1121 ±0.0024^{cd}	56.2157 ±0.0027^{b}	21.6744 ±0.0039^{c}	57.0002 ±0.0016^{b}	22.7854 ±0.0031^{c}	4.5423 ±0.0011^{e}	nil
Organic	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil

Values were mean ± S.D. (n=5). Different letter (a-d) in the same column indicated significant differences ($p<0.05$) between samples. nil = Not detected (LOD lower than 0.01 ppm).

Table-3
Amount of Chlorpyrifos (ppm) in the rice field, Chiang Mai

Treatment	Soil sampling times (months)									
	0	1	2	3	4	5	6	7	8	9
Control	nil	23.4362 ±0.0017^{b}	nil	nil	nil	nil	nil	nil	nil	nil
GAP	nil	32.4484 ±0.0019^{a}	0.0659 ±0.0013^{c}	nil	nil	nil	30.7774 ±0.0021^{a}	nil	nil	nil
Organic	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil

Values were mean ± S.D. (n=5). Different letter (a-d) in the same column indicated significant differences ($p<0.05$) between samples. nil = Not detected (LOD lower than 0.01 ppm).

Table-4
Amount of Chlorpyrifos (ppm) in the rice field, Sing Buri

Treatment	Soil sampling times (months)									
	0	1	2	3	4	5	6	7	8	9
Control	nil	29.0548 ±0.0028[a]	nil	nil	nil	nil	nil	nil	nil	nil
GAP	nil	33.0426 ±0.0015[a]	0.0276 ±0.0013[b]	nil	30.0497 ±0.0041[a]	nil	32.9431 ±0.0017[a]	nil	nil	nil
Organic	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil

Values were mean ± S.D. (n=5). Different letter (a-d) in the same column indicated significant differences ($p<0.05$) between samples. nil = Not detected (LOD lower than 0.01 ppm).

Conclusion

The degradation of pesticide residues in agriculture could be concluded that the decayed of Dicofol (Organochlorine compound) took 4-5 months for dissolution counting from the first day of spraying the chemical on annual crop plots. According to the decomposition of Chlorpyrifos (Organophosphate Compound), the chemical could decayed within 1-2 months, which was much shorter than the dissolution time used by the pesticides made from Organochlorine compounds. Understanding of the fate and behavior of pesticides under tropical conditions was important both in agronomic and environmental terms. Degradation time of the pesticide residues was depending on area, pH and temperature. Therefore, the pesticide residues, which use to predict the organic transition period in Europe and Thailand were not the same because of the different geography. 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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