Journal of Environmental Science and Management 20-2: 28-33 (December 2017) ISSN 0119-1144

Detection of Organophosphate Residues in Selected Crops in Benguet and Mt. Province, Philippines

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ABSTRACT

High input agricultural systems refer to food production systems that use inorganic chemicals such as pesticides and fertilizer inputs intensively, with the aim of significantly increasing yield levels. This leads to the accumulation of pesticide residues and heavy metals in the crops and in the environment. This study was undertaken to determine the presence and concentration of toxic pesticide residues in cabbage, potato, and sweet peas in selected farms in Pactil, Mt. Data, Mountain Province and Loo, Buguias, Benguet. Through the use of gas chromatography (GC), findings show that about 18 pesticide residues (organophosphates) were detected in the crop samples. Furthermore, concentrations of toxic organophosphate residues were generally elevated and higher than MRL. A general default MRL of 0.01 mg kg^{-1} applies where a pesticide is not specifically mentioned, which means that there is no established MRL. If the default level of 0.01mg kg^{-1} is applied for those without MRL then almost all samples would be unsafe for consumption. Other vegetables crops, soil and water in the study area may also be analyzed for the presence of active compounds and other toxic chemicals.

Key words: *organophosphate, pesticide residues, pesticide residue accumulation, maximum residue limit (MRL)*

INTRODUCTION

Pesticide poisoning is a serious health problem that disproportionately affects infants and children. Improper use or storage of pesticides can harm humans. Accordingly, key risks are cancer, birth defects, and damage to the nervous system and the functioning of the endocrine system. The World Health Organization in collaboration with United Nations Environment Programme estimates that some three million agricultural workers suffer from acute pesticide poisoning and 20,000 people die each year (*Blacksmith Institute 2010*). The illness and deaths resulted from occupational exposure by people who use pesticides without proper warnings or protective clothing. A research conducted in Belgium, for instance, highlighted the potential exposure of florists to pesticide residues on cut-flower species (*Toumi et al. 2016*). Locally, in a study among cut-flower farmers in La Trinidad, Benguet, *Lu* (*2007*) reported the adverse health effects associated with pesticide exposure. Furthermore, increased pesticide exposure was attributed to non-ergonomically designed tools, unsafe work practices in the vegetable farms (*Lu 2011*) and poor personal protective equipment (PPE) use (*Lu 2009*).

A number of highland vegetable crops have been implicated for pesticide contamination. On the comprehensive assessment of pesticide residues in two vegetable-farming municipalities in Benguet conducted by *Reyes and Laurean* (*2007*), pechay taken from Kapangan, Benguet contained the pyrethroid residue, cypermethrin, with an amount of 0.30 mg kg^{-1}. On the other hand, more residues were identified from the crops collected from the municipality of Buguias. The researchers found out that five out of the nine samples tested were positive for residues at limit of determination (LOD). Celery, however, contained an organophosphate residue (chlorpyrifos) of 0.37 mg kg^{-1} higher than the MRL of 0.05 mg kg^{-1}. A similar study made by Delima (2012) detected high concentrations of organophosphate residues in cabbage, Chinese cabbage (*pechay*) and cauliflower both in Benguet and Nueva Vizcaya.

Similar observations have been documented in other parts of the country, notably in eggplant farms in Sta. Maria, Pangasinan. Several farms in the province tested positive for organophosphate residues such as profenofos, chlorpyrifos, among others, some of which even exceeded the acceptable maximum residue limit (*Del Prado-Lu 2015*).

The use of agrochemicals have been proven to bio-accumulate in many plants. Similarly, in the study of *Briones and Robles* (*2005*), residues of profenofos (an organophosphate), malathion, cypermethrin, among others, were detected in the plant material of roses, one of the more popular in the cutflower farming industry. The highland vegetable industry in the Province of Benguet is characterized to be intensive in terms of chemical farming through the years. Thus, pesticide residues have already contaminated many parts of the ecosystem, a fact that would support the occurrence of bioaccumulation in crops and other plants. This is well-demonstrated in the study on pesticide contamination of soils in Benguet done by *Lu* (*2010b*) showing that technical endosulfan was found to have a mean concentration of 0.025 mg kg^{-1}, chlorpyrifos (0.01 mg kg^{-1}), profenofos (0.003 mg kg^{-1}), among others.

Such studies present relevance on the contemporary discussions on the attainment of sustainable development goals being supported globally and by the national government. Here, the natural environment is seen as a life-support system to society and economy. In order to ensure a continuous flow of these environmental services, the natural environment cannot be in a dysfunctional state. With the rate of acceleration of environmental degradation brought about by a confluence of various factors as population growth, urbanization and industrialization, the nation and the Cordillera Region, in particular, the Local Government Units (LGU), various government and non-government agencies & organizations, and civil society, have called for the preservation and protection of the environment. Benguet alone, as a case in point, has crafted provincial environment codes and several policies which espouse the pro-active protection of the environment in the face of development projects and activities going on in several fronts. The results of the study can be used to identify the implementing strategies and actions that will reduce the negative impact of pesticide on soil and water resources.

This paper focuses on the presentation and discussion of the pesticide residues detected in selected highland vegetables, such as cabbage (*Brassica oleracea*), sweet pea (*Pisum sativum*), and potato (*Ipomoea batatas*). Moreover, it seeks to present the maximum residue level (MRL) permitted for food crops, among the crops sampled in this study.

MATERIALS AND METHODS

The study conducted a survey of farming areas characterized by high-input conventional agriculture, i.e., chemical applications of fertilizers and pesticides. Two sites have been identified: Loo, Buguias, Benguet and Pactil, Mount Data, Bauko, Mt. Province, with the farm as the unit of analysis. Within each barangay, one farm each was designated as sampling site, with the consideration that this was chosen based on increasing distance from road accessibility. A consideration on the fact that these farms have the following crops planted: cabbage (leafy vegetable), potato (root crop), sweet pea (fruit vegetable) was verified, thus, the conduct of studies in these particular sites.

Vegetable samples were sourced (sampled) from an area where these are commonly grown and cultivated for commercial production. Final sample gathering for the wet season, subject to laboratory analysis, was made between June to September 2012, while samples for the dry season were collected from February to May 2012.

One kilo of composite sample of the harvestable crops was taken. In this context, 'harvestable' means that the target crops have reached proper level of maturity and at quality ready for gathering and intended to be sold in the market. For the potatoes, only the tubers were sampled for analysis. For the cabbage and the sweet peas, only the leafy portions and the mature pods were sampled, respectively. These were packed using sterile plastic zip-lock bags which were properly labeled and stored in a cooler to maintain their original composition, as these were transported from the sites to Baguio City in a six-hour trip. Upon gathering, the collected samples were brought immediately to the Natural Science Research Unit Laboratory at Saint Louis University in Baguio City for the gas chromatography (GC) processing and analysis. The prominent and significant pesticide residues were identified based on the compounds recognized by the machine. With this, the levels of concentration of each pesticide residue were determined and ranked accordingly. In cases where two identical pesticide residues peaked in the graph, the amount of concentration level are added and compared to the other compounds present. In cases where no pesticide residues were identified by the machine, initials NPD (no pesticide detected) is written to indicate the absence of which. Each of the crop samples taken as composite sample from each farm had three determinations for the pesticide residue serving as replicates.

RESULTS AND DISCUSSION

Significant amounts of pesticide residues were accumulated in vegetables considering the concentrations in parts per million (ppm). The level of toxicity of the pesticide residues were identified using Maximum Residue Limit (MRL) according to the standards of the World Health Organization (Codex Alimentarius, WHO Standards, *FAO and WHO 1993*). MRL is the standard limit of concentration for a pesticide residue to be considered tolerable. Each residue is supposed to have MRL; however, based on literature search done for this study, very few have identified MRL for each crop sample (**Table 1**).

A total of 18 pesticide residues were identified in the samples, through gas chromatography. A cumulative sum of 24 of which were evident during the dry season, while another 53 during the wet season were present in all of the sampled crops.

With this, a total of 16 organophosphate pesticide residues were identified in the cabbage samples from Mt. Data during the dry season and 12 during the wet season as compared to the samples from Loo, where only four and six were identified during the dry and wet season, respectively. Dichlorvos was not found during the wet season in Loo while fenthion and phorate were identified.

As to concentration level, dichlorvos is very high in both samples from Mt. Data (5.08 mg kg^{-1}) and Loo (5.10 mg kg^{-1}) during the dry season and from Mt. Data during the wet season (5.75 mg kg^{-1}). Other residues with high concentration were disulfoton with 1.14 mg kg^{-1} and 52.85 mg kg^{-1} during the wet and dry season in Mt. Data, respectively; demeton (11.39 mg kg^{-1}) from wet season samples of Mt. Data and dry season sample from Loo (1.55 mg kg^{-1}). If the default limit of 0.01mg kg^{-1} is to be applied, it can be noted that the concentration of the other residues where no MRL is specified is way beyond the MRL.

Based on available samples collected during the dry season, azinphos was identified in potato samples from Mt. Data and stirofos in Loo. The concentration of azinphos (0.13 mg kg^{-1}) is higher than its MRL (0.05 mg kg^{-1}). There were more pesticide residues identified during the wet season such that there were four (4) in Mt. Data samples and ten (10) in Loo. Phorate had the highest concentration (10.48 mg kg^{-1}) in Mt. Data during the wet season which is higher than the prescribed MRL of 0.20 mg kg^{-1}. Potato samples from Loo registered high

Table 1. Pesticide residues present in vegetable samples (mg kg^{-1}) in Mt. Data, Bauko, Mt. Province and Loo, Buguias, Benguet during the dry and wet seasons.

Residues	Cabbage				Potato				Sweet Pea				D	W
	Mt. D		Loo		Mt. D		Loo		Mt. D		Loo			
	D	W	D	W	D	W	D	W	D	W	D	W		
Dichlorvos	5.08	5.75	5.10					1.27	0.63	2.10	0.74	3.23	4	4
Mevinphos	0.56	1.52										0.55	1	2
Ethoprophos	0.08							0.13*				0.08	1	2
Naled	0.21			0.10				0.23		0.47		0.10	1	4
Phorate	0.55	9.24		0.33		10.48*		0.29*				0.11	1	5
Disulfoton	1.14	52.85	0.43	0.32		0.28		0.19		0.25*		0.05	2	6
Methyl parathion	0.45*	0.27*										11.43*	1	2
Fenchlorphos	1.18	0.59				0.67		0.67		0.89		0.21	1	5
Chlorpyrifos	0.32												1	0
Trichloronate	0.66	8.79	0.28	0.21		0.22		0.28		0.37		0.31	2	6
Merphos	1.90	0.79						0.51		.			1	2
Fensulfoton	0.63												1	0
Bolstar (sulprofos)	0.19	0.21						0.13				0.09	1	3
Azinphos methyl	0.57	0.48			0.13*								2	1
Coumaphos	4.18	0.40										0.33	1	2
Demeton	0.88	11.39	1.55	0.06				1.21		1.73		3.23	2	5
Fenthion				0.17									0	1
Stirofos							0.09					0.11	1	1
Diazinon													0	0

* significant values higher than MRL where MRL is specified D=dry season W=wet season

demeton (1.20 mg kg^{-1}) and dichlorvos (1.27 mg kg^{-1}) concentration. Phorate (0.29 mg kg^{-1}) and ethoprophos (0.13mg kg^{-1}) concentrations were higher than their prescribed MRLs at 0.20 mg kg^{-1} and 0.05 mg kg^{-1}, respectively. Potatoes, among fruits and vegetables are the crops said to be likely contaminated by pesticides, such as residues of organophosphorus pesticides –OPPs (*Fenik et al. 2011*). Similar to the cabbage samples, if the default limit is to be applied, it can be inferred that the concentration of the other residues where no MRL is specified is higher than the MRL.

Sweet pea pod samples collected from Mt. Data and Loo during the wet and dry seasons yielded positive results for dichlorvos, although concentrations were higher during the wet season for the samples from Mt. Data (2.10 mg kg^{-1}) and Loo (3.23 mg kg^{-1}). The concentration of demeton during wet season is also high in both Mt. Data (1.73mg kg^{-1}) and Loo (3.23 mg kg^{-1}). Disulfoton in sweet pea samples from Mt. Data (0.25 mg kg^{-1}) is higher than MRL (0.10 mg kg^{-1}) while methyl parathion in Loo (11.43 mg kg^{-1}) is very much higher than MRL (0.30 mg kg^{-1}). For the other residues, the default limit may be applied.

There were a total of 75 pesticide residues seen in the study, 24 during the dry season and 51 in wet season. Forty (40) pesticide residues were identified in samples from Pactil, Mt. Data as compared to 35 samples from Loo, Buguias. The lesser number of toxic residues during the wet season may be attributed to the effect of the rain that tend to wash the pesticides from the plant surfaces. The higher number of residues in Pactil may indicate heavier and more intensive use of agrochemicals by the vegetable farmers.

Not all active components and residues have MRL for different crops. In case no MRL is stated per sample, a default limit is said to be indicated. That is, "the MRL in foodstuff is 0.01 mg kg^{-1} (**Table 2**). The general limit is applicable by default, i.e., in all cases where an MRL has not been specifically set for a product or product type" (*European Union 2005*). Based on this criterion, most of the samples contained pesticide residues higher than 0.01 mg kg^{-1}. Fenthion and dichlorvos were also identified in the samples. Fenthion is generally used for citrus and cherries while dichlorvos is used for cereals. This implies that the pesticide used was not appropriate for the crops used in the study.

The gas chromatographic analysis of selected crops collected from selected farms in Mt. Data, Mt. Province and Loo, Buguias, Benguet revealed the presence of pesticide residues specifically organophosphates. Organophosphate compounds include some of the most toxic chemicals used in agriculture such as disulfoton, phorate, dichlorvos, coumaphos, and chlorpyrifos. The latter residue was implicated to be the most common pesticide residue in crops found by *Lu* (*2010a*) in another study conducted in Benguet. Similarly, this was also found to be the most frequently detected organophosphate residue in soil and water samples from cocoa producing areas in Ghana (*Fosu-Mensah et al. 2016*).

Table 2. Maximum residue limits (MRL) for pesticide residues in vegetables sampled in Mt. Data, Bauko, Mt. Province and Loo, Buguias, Benguet (*Codex Alimentarius, WHO Standards, 2nd ed. Vol.2, 1993*).

Compound Name	Sample	MRL (mg kg^{-1})
Azinphos	Potato	0.05
Chlorpyrifos	Cabbage	1.00
	Pea	0.01
	Potato	2.00
Diazinon	Cabbage	0.50
	Pea	0.20
	Potato	0.01
Disulfoton	Pea	0.01
Ethoprofos	Potato	0.05
Phorate	Potato	0.20
Methyl parathion	Cabbage	0.05
	Potato	
Fenthion	Only for citrus, cherries	
Dichlorvos	Only for cereal grains	

High phorate concentrations were identified on cabbage and potato samples. According to the E*xtension Toxicology Network* (*1993*), phorate is among the most poisonous pesticide and classified under the list of RUP (Restricted Use Pesticide) by EPA.

Another pesticide with high concentration is dichlorvos, which was identified in cabbage, potato and sweet pea samples. The US Department of Labor Occupational Safety and Health Administration (OSHA) classified dichlorvos as toxic causing acetylcholine inhibition, respiratory, gastrointestinal-disorders, muscle weakness, eye-tearing and dermatitis. Disulfoton residues were detected in high concentration in cabbage. This pesticide was cancelled in 2009 by EPA and in 2003 by EU when it was shown to cause avian and fish mortality even at low concentrations according to the *American Bird Conservation* (*2010*).

Trichloronate residue is also high in cabbage sample. It is a cholinesterase inhibitor like other organophosphates. It is a non-systemic insecticide but is not registered as pesticide in US. On the other hand, coumaphos is an acaricide and has no registered agricultural uses. According to the *EPA R.E.D. Facts* (*1996*), this pesticide is used for direct animal treatment only to control ticks that carry bovine and equine piroplasmosis. It is a neurotoxin and obtained direct dermal exposure when mixing and also from eating poultry and beef. Just like coumaphos, diazinon is an acaricide for mites and ticks (*Pesticide Action Network 2000*). It is used to control sucking and chewing insects in vegetables, potatoes and bananas and also for soil-dwelling agricultural insects and to control ectoparasites in sheep. Accordingly, diazinon was phased out on Dec. 31, 2004.

Chlorpyrifos is another acaricide/miticide for foliage and soil-borne insects/pests on crops specifically on corn (*EPA 2002*). It is a cholinesterase inhibitor. A 0.5% solution of chlorpyrifos is utilized as termiticide.

Methyl parathion is used as stomach poison for insects (*Pesticide Action Network 2005*) and effects show similar symptoms like oils organophosphates. Its use was banned in Indonesia, Sri Lanka, Tanzania, Columbia, Korea, China and Japan while in other countries it was made more difficult to obtain. Lastly, mevinphos is used on peas and brassicas and toxicity symptoms are similar to those of other organophosphates. Its use was cancelled in the US in 1994 as shown in the EPA Facts. Also, in a study in the United States, even some foods labeled as organic, presumed to have been produced organically, have demonstrated detectable amounts of pyrethroid and organophosphorus pesticides (*Riederer et al. 2010*).

The above-mentioned facts and discussions clearly state that most of the organophosphate residues accumulated in the crops are harmful to humans and the environment.

CONCLUSIONS AND RECOMMENDATIONS

A total of 104 pesticide residues were identified in the five samples containing active ingredients classified as organophosphates in the study. They include the most toxic chemicals used in agriculture like phorate, dichlorvos, disulfoton, coumaphous, diazinon and chlorpyrifos. Some of them have been banned or cancelled such as methyl parathion and mevinphos. Inappropriate use was also identified as in the case of fenthion and dichlorvos as they are utilized beyond their Maximum Residue Limit (MRL). Most of the residues identified have concentrations higher than MRL or higher than the default limit which means that the vegetable samples are not safe for consumption.

This study, therefore, recommends that agencies concerned in the pesticide use, the environment and agriculture sectors should further evaluate the policies and guidelines of pesticide use and its effects so as to avoid any damages that these compounds may contribute, be it physical, social, environmental, or economic.

Identification of other active components such as carbamates and pyrethroids may be done on the same crops used in the study. Other vegetable species, the soil and water in the area may also be analyzed for the presence of active components and other toxic chemicals.

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ACKNOWLEDGMENT

This research project was not possible without the Commission on Higher Education and its Zonal Research Center for Region 1 and CAR, especially the Program Cluster Implementer at Saint Louis University led by SLU Research Director Dr. Gaston P. Kibiten. To the SLU Natural Science Research Unit, Evelyn E. Oda, Ph.D., NSRU OIC and Jenner M. Butlong, RPh., NSRU Analyst/Technician. Special thanks is given to the farmers of Loo, Buguias, Benguet and Pactil, Mt. Data, Mountain Province for the invaluable collaboration that they gave during the conduct of this study.