Pesticide Residues in Food and the Environment in the Philippines: Risk Assessment and Management

Cristina M. Bajet
National Crop Protection Center, Crop Protection Cluster
University of the Philippines at Los Banos
College, Laguna 4031, Philippines
email: cmbajet@yahoo.com, cmbajet@uplb.edu.ph

ABSTRACT

The Philippines as a developing country and with limited resources to implement intense monitoring of pesticide residues has focused on other ways to assess and manage risks. The top priority of the Philippines is food production/security and in the local market, pesticide residues analysis as a basis for market acceptance is secondary. Compliance to Maximum Residue Limits (MRLs) of major export crops like banana, pineapple, mango, okra, and asparagus, among others is the main focus of the Government. Rice is the largest consumer of pesticides in terms of volume but the pesticide application in high value crops is more intense.

The paper is a review of Philippines' efforts on pesticide residue related problems. Focus is on pesticide regulation, monitoring and research activities of the Government Laboratories doing pesticide residue analysis on food and/or raw agricultural commodities. Rapid detection tools like colorimetric test kit and enzyme inhibition tests as solution for monitoring residues of organophosphates and carbamates on selected vegetables is the focus of the paper. Discussion includes the results of research on pesticide residues in water and soil and other environmental concerns related to pesticide usage in agriculture, to include ecotoxicological studies on non-target aquatic organisms.

Management options include regulatory control and promotion of organic agriculture through the enactment of the organic act. The food safety law puts together options for safe food available locally and export products by minimizing trade risks due to pesticide residues through generation of locally generated data.

Keywords**:** rapid test kit, regulatory control, organophosphate and carbamate pesticides, dietary risk, environmental risk

INTRODUCTION

The Philippines effort is to monitor various farming activities from conventional (to include traditional, Integrated Pest Management (IPM), Good Agricultural Practices (GAPs), etc.) to organic farming and with limited resources. This situation necessitates a concerted effort by Government in partnership with stakeholders for pesticide residue monitoring and evaluation to ensure consumer protection and food safety. With limited resources to implement intense monitoring of pesticide residues, the Philippines have focused on other ways to assess and manage risks. The top Government priority is food security. Food safety like pesticide residues analysis as a basis for market acceptance is secondary. Compliance to Maximum Residue Limits (MRLs) of major export crops like banana, pineapple, mango, okra, and asparagus, among others is the focus and priority of the Government. Rice is the largest consumer of pesticides in terms of volume but pesticide application in high value crops are more intense, resulting to residues on the crops. Residues on rice resulting from pre harvest are minimal and most residues in rice maybe related to post harvest application. For high value vegetables available in the market, the intensity of pesticide application and the concentration of residues is correlated to the value of the crop, production season and/or consumer demand. During festivities and the Christmas season, consumer demand increases and the farmers are pressured to protect their crops because the value is higher, resulting to higher pesticide residues.

Regulatory control

Pesticide residue risk assessment on food safety and management of pesticide use is regulated through pesticide registration. The government agency mandated to regulate availability and use of pesticides is the Fertilizer and Pesticide Authority (FPA) created with Presidential Decree 1144, now under the Office of the President. All pesticide products are evaluated by a team of experts on pesticide specification, bio-efficacy, toxicology, residues, environmental effects and environmental fate and transport data. In cooperation with FPA, the Bureau of Plant Industry National Pesticide Analytical Laboratory (BPI-NPAL) and its satellite Pesticide Analytical Laboratories (PALs) provide laboratory services for formulation analysis as part of the registration requirements to check the quality of pesticide products for registration. As part of the food safety assessment and regulation and as a requirement for registration, or approval for label expansion to other crops, a local residue data is required and a dietary risk assessment is done based on Filipino diet.

Likewise, BPI NPAL and its five satellite PALs nationwide do residue analysis as part of market basket monitoring of residues. Results of these monitoring activities are also a basis of FPA regulation. Pre export analysis is also done by BPI-NPAL mainly for mango and okra while crops from corporate growers like Dole, Del Monte, Stanfilco, among others, are responsible for their exports in terms of pesticide residues.

Part of FPA’s regulation is training of stakeholders of the pesticide industry. Researchers involved in bio-efficacy and supervised residue trials are to be licensed. Pesticide Industry personnel undergo training and licensure as accredited responsible care officers and are actively involved in the partnership with FPA on the Government’s Stewardship Program. Pesticide Applicators and Pesticide Marketing Personnel are also certified and licensed by FPA.

The setting of Maximum Residue Limits (MRLs) is part of the FPAs regulatory process but the Bureau of Agriculture and Fisheries Standards (BAFS) is the Government agency that is in charge to convene all experts, stakeholders and relevant Government Agencies to set the national MRL based on the existing data and pesticide registered usage as approved by FPA. Regulatory control also include the passing of laws related to food safety Republic Act (RA) 10611 and to organic agriculture act of 2010 RA 10068, which is one of the main focus of the current Secretary of the Department of Agriculture (DA).

Monitoring of residues using rapid detection kits

In support of Government efforts to minimize risk due to the use of pesticide products, research on pesticide residues in food and the environment is part of the research activities at the National Crop Protection Center (NCPC), Crop Protection Cluster (CPC) at the University of the Philippines Los Banos (UPLB).

A colorimetric Rapid Test Kit (RTK) was developed at the Pesticide Toxicology and Chemistry Laboratory, NCPC, CPC, UPLB for organophosphate and carbamate residues (Fig 1). The RTK was initially used as a teaching tool for conventional farmers to understand the concept of residues and pre-harvest interval (PHI) and for them to be able to decide on the right time to harvest.

Fig.1. Rapid test kit (RTK) for the detection of organophosphate and carbamate residues on selected vegetables developed at the National Crop Protection Center, University of the Philippines Los Banos and farmer trying to use the RTK.

The RTK was developed for easy and rapid detection of pesticide residues on vegetables with tests durations of about 8-10 minutes. The RTK was tested on FPA registered organophosphate (OP) and carbamate (CBM) pesticides on vegetable crops which are intensively applied with pesticides. The RTK was tested on registered OP and CBM pesticides on eggplant (*Solanum melongena*), yardlong beans (*Vigna unuiculata*), green beans (*Phaseolus vulgaris*), bittergourd (*Momordica charantia*), pechay (*Brassica chinensis*), tomato (*Solanum lycopersicum*) and okra (*Abelmoschus esculentus*).

The OP and CBM group are the commonly used/cheapest commercially available pesticides with moderate to high toxicity. Pesticide residues are extracted using acetone concentrated and spotted into a filter paper. After the test, the intensity of the color reaction will indicate the concentration of the residues on the vegetable tested. The RTK is a semi quantitative colorimetric test and completed test in a few minutes for immediate action/decision. It is cheap (USD 0.5/test) and easy to handle. The RTK is user friendly and the procedure has been tested and easily followed by ordinary farmers and agricultural technicians (Fig 1).

As part of expanding the applications of the RTK, it was tested on 53 MRLs on seven commonly consumed vegetables where ten pesticides are specifically registered (Table 1). Percentage of detection was from 19-100%. Test was sensitive to MRLs of fenthion and carbaryl and limited sensitivity to triazophos and malathion. For the CBM test, the color of the tomato extract interfered with the analysis of carbofuran and BPMC. However, a positive result for RTK is still a good indication of a high concentration of pesticide residues.

Table 1. RTK tested on MRLs of selected vegetables on ten FPA registered pesticides.

Pesticide	No MRLs tested*	Range of MRLs (mg/kg)	% detection**	Remarks
malathion	6	0.2-8	31	Not sensitive to yardlong beans
fenthion	2	0.1-0.5	100	Pechay and tomato
chlorpyrifos	6	0.2-1	63	Good for eggplant and tomato
traizophos	3	0.1-0.2	19	Not sensitive to yardlong beans and green beans
profenofos	6	0.05-10	54	Not sensitive to yardlong beans and pechay
diazinon	6	0.05-0.5	44	Not sensitive to yardlong beans and green beans
carbaryl	7	0.5-10	100	For all vegetables tested
carbofuran	7	0.1-0.5	87	Tomato color interferes with detection
BPMC	4	0.3-1.5	67	Tomato color interferes with detection
methomyl	6	0.2-5	67	Variable, good for eggplant and green beans

*vegetables tested: eggplant, yardlong beans, green beans, bittergourd, pechay, tomato and okra

**Based on 3 persons with 3 replicates/person

MDL: 0.1 mg/kg for OPs, carbofuran,carbaryl and 1 mg/kg for BPMC and methomyl

Source: Sarmiento and Bajet (2015)

With the current focus of the DA to promote organic agriculture (OA), there is a need for a rapid tool to be able to monitor the compliance of farmer members of organic producers to ensure that no pesticide residues are present in organic produce. For OA farmers, farmers in transition to OA, and new OA farmers, it is necessary to monitor compliance to OA principles. The RTK may be used as a quick test of farmer leaders and organic certifying bodies in monitoring OA farmers and help in their regulatory work. Implementation of OA needs a technology to monitor compliance on the avoidance of use of pesticides.

Both OPs and CBMs are acetylcholinesterase (AChE) inhibitors and most pesticides belong to toxicity category I or II. The Rapid Bioassay for Pesticide Residues (RBPR) developed by the Taiwan Agricultural

Research Institute (TARI) uses housefly head AChE (Chiu *et al*., 1991). RBPR was developed for postharvest monitoring of vegetables for auction before it is sold to major markets in Taiwan. This technology is widely used in Taiwan, including some Asian countries and RBPR will be adopted for pilot testing in the Philippines as part of a project with the Department of Science and Technology.

The RBPR is highly sensitive since it is based on the principle of enzyme inhibition, highly specific for OPs and CBMs. The test is expected to be more sensitive than the currently used RTK. Detection limit is from 0.004 ppm for dichlorvos to 3.4 ppm for methomyl (Chui *et al*., 1991). Pesticides that can be detected include dichlorvos, carbofuran, mevinphos, phenthoate profenofos chlorpyrifos ppirimiphos methyl methomyl methidathion, acephate, fenitrothion, metamidophos, dimethoate, among others. Table 2 is a comparison of RTK and RBPR.

Table 2. Comparison between Rapid Test Kit (RTK) and Rapid Bioassay for Pesticide Residues (RBPR).

Criteria	RTK***	RBPR
Principle of test	Colorimetric	Enzymatic inhibition
Detection	Visual, semi quantitative	Spectrophotometer
Pesticides tested	malathion, fenthion, chlorpyrifos, triazophos, profenofos, diazinon, carbaryl, carbofuran, methomyl	carbofuran, profenofos, chlorpyrifos, methomyl, phenthoate* pirimiphos methyl* acephate*, fenitrothion* dimethoate*, mevinphos**, methidathion**, metamidophos**, dichlorvos**
Time for testing per sample	8-10 minutes	8-12 minutes

*active ingredient registered but not on tested crops

**active ingredient not registered in the Philippines

*** tested on eggplant, yardlong beans, common beans, bittergourd, pechay, tomato and okra

The RBPR and/or RTK can be used by farmers who practice conventional, GAPs or IPM farming to decide when to harvest, by organic and "in-transition organic" farmers to monitor non-compliance of members and by DA technicians, traders and consumers for quick check on the residues of vegetables. With increasing local awareness of pesticide residues and the promotion and mushrooming of "organic farming" without any test except trust and farm visit, the RBPR and/or RTK is expected to partly solve this need. This is cost effective compared to monitoring using classical residue analysis. These rapid detection kits will enable the monitoring of produce prior to and after marketing. Consumers may also opt to use RTK and/or RBPR for personal monitoring of pesticide residues in vegetables bought from markets. Likewise, these rapid detection kits may also be useful in regular residue analytical laboratories to minimize the number of samples to be analyzed resulting to higher sample output and low usage of organic solvents. In this case, only samples with known background and those which come out positive will be analyzed.

Lastly, it can be a complimentary method for use in pesticide regulation programs of FPA, Bureau of Agriculture and Fisheries Standards (BAFS) and Food Development Center (FDC). This is in line with the Government's focus on food safety.

Monitoring of residues using classical analysis

The basis for all regulatory control is classical analysis of pesticide residues. Regulation is based on results of locally generated residue data as part of research or regular monitoring activities. Nationwide market basket sampling is part of monitoring residues done by BPI-NPAL and data generated is a basis for regulatory control. If a specific pesticide residue is detected on a vegetable crop where it is not registered, FPA will call the attention of the pesticide supplier as part of the Pesticide Industry's commitment on Stewardship. In cases when the residues detected are consistently beyond MRL on specific crops, then the pesticide management practices or the usage of the farmers are investigated. Risk management efforts are based on monitoring results and this include dietary risk assessment using maximum residues detected or set MRLs and using Filipino diet as basis. Dietary risk assessment is required for pesticide registration and normally no label expansion is approved if there is $\geq$ 100% of the acceptable daily intake of the pesticide from all possible registered uses. Monitoring and risk management includes generation of local pesticide residue data on specific crop-pesticide uses through supervised residue trials. Rice is the crop more widely cultivated and consumes the highest volume of pesticide products but most of the residue trials show that residues are in the husk compared to the grain. Residues are non detectable at harvest because the last pesticide application is at milk dough stage of the rice. Most residues on rice are due to post harvest application.

Strategies also include studies on enzymatic bioremediation of surface residues of organophosphate insecticides (Scott *et al*., 2011). In the Philippines, the usefulness of the enzyme for bioremediation was tested on mango, tomato and eggplant. Several researches on washing with or without the aid of soap, cooking practices like broiling, boiling, frying was found to reduce pesticide residues depending on crop surface, chemistry of pesticide, type of formulation, and mode of action are among the researches completed to reduce dietary risks (Bajet, 2015). The initiative of the Government to go organic farming is also one of the strategies towards food safety, including the passing of the food safety law.

Export products like banana, pineapple, mango, okra, among others are also analyzed by classical residue analysis for compliance to requirements related to MRLs. The results of the analysis will be the basis for the decision to export or not and to change export destinations. Pesticide residues are problematic especially for crops which are normally consolidated from several farmers of different pesticide management practices like mango and okra. For mango, Japan is the target export destination in terms of value but Hong Kong is the largest importer of mango from the Philippines. Institutional crops like banana, pineapple and asparagus are closely monitored in terms of pesticide and pesticide residue management by the Companies producing these crops.

Environmental risk assessment and management

First line of environmental risk assessment is again through regulatory control. All pesticide products for registration should submit data on environmental effects and environmental fate and transport, as part of the requirements of FPA. Some pesticides result to more environmental risks when applied to specific ecosystems, specific times of application or proximity to waterways and other non-target organisms. Risk management involves knowledge of these situations and to relate to toxicity like lethal dose resulting to 50% mortality (LD_{50}) values of non-target organisms and relate to the measured or expected environmental concentrations.

Researches related to environmental risk monitoring and assessment is based on classical analysis of pesticide residues on targeted ecosystems and organisms. Several studies were done at NCPC, UPLB and other institutions in the country. Environmental risk is greater for rice cultivation since the probability of off site migration is higher due to the irrigation canals which eventually find its way to bodies of water. Rice is also the largest consumer of plant protection products due to the wide area of cultivation although the intensity of usage is lower than high value crops. The pesticide application and resulting residues were documented by Bhuiyan and Castaneda (1995) and Tejada *et al*., (1995) in the early `90s. Recently, Elfman *et al*. (2011) reported that for 34 samples analyzed, 16 samples collected from rice ecosystem exceeded the Swedish guidelines for lambda cyhalothrin, cypermethrin and deltamethrin in San Francisco, Leyte Philippines (Table 3). Mollusicides, also used in rice farming for the control of the Golden Apple Snail, could also be a source of contaminants in shellfish in the coastal regions. Tanabe *et al*., 2000 measured total butyl tins (BTs) in green mussel with concentrations ranging from non detectable to 787 ng/g and an average of 133 ng/g of the 11/13 samples found to contain BTs.

Table 3. Selected measurements of pesticide residues in Philippine environment.

Ecosystem (Place)	Environmental substrates analyzed	Results	Reference
Rice (San Francisco, Leyte)	water	lambda cyhalothrin (0.006 ug/L); cypermethrin and deltamethrin (0.0002 ug/L)	Elfman et al.,2011. Agricultural Water Management 101: 81-87
Vegetable (La Trinidad, Bugias and Atok, Benguet Province)	water soil	1/49 (0.07 mg/L chlorpyrifos) 34/78 samples with residues (endosulfan sulfate, chlorpyrifos, profenofos, cyhalothrin, cypermethrin, endosulfan, chlorothalonil))	Del Prado-Lu. 2010. Archives on Environmental Contamination Toxicology 59:175–181
Vegetable and rice (Pagsanjan-Lumban Watershed, Laguna de Bay)	water	0.85 ug/L average malathion 2008 and 0.113 ug/L in 2009 ＜1.0-15.4 ug/L prefenofos in 2008	Varca, 2012. Agricultural Water Management 106: 35-41
Environmental Monitoring (Metro Manila, Cavite, Leyte, Capiz, Bataan)	Green mussel	Total butyl tins (range: non detectable to 787 ng/g with average of 133 ng/g)	Tanabe et. al., 2000. Ocean and Coastal Management 43:819-839.
Ecotoxicologcal impact (Pagsanjan-Lumban Watershed, Laguna de Bay)	Tilapia fingerlings Shrimps Duckweed	Environmentatl concentration of profenofos and malathion with hazard/ impact on local shrimps species of Laguna de Bay Lesser risk of herbicides to duckweed	Bajet et al., 2012. Agricultural Water Management 106: 42-49.

In Benguet Province, the vegetable bowl of the Philippines, Del Prado-Lu (2010) detected chlorpyrifos in 2% of the water sampled and 43.5% of the soil samples analyzed contain endosulfan sulfate, chlorpyrifos, profenofos, cyhalothrin, cypermethrin, endosulfan and chlorothalonil residues. This is indicative that the soil is really the ultimate sink of pesticide residues. Endosulfan is also already banned for use in the Philippines, which explains the presence of the metabolite endosulfan sulfate.

Varca (2012) monitored the off site migration of pesticides in the Pagsanjan-Lumban watershed which is the fresh water source of Laguna Bay, the second largest freshwater Lake in Southeast Asia. This watershed runs through vegetable and rice production areas and an average of 0.85 ug/L malathion was detected in 2008 and 0.113 ug/L in 2009. A concentration of <1.0-15.4 ug/L prefenofos was also detected in 2008 (Table 3). The maximum measured concentration of malathion and profenofos in water was related by Bajet *et al.* (2012) to toxicity to aquatic non target organisms.

Environmental impact management includes measuring the toxicity of pesticides on local species like fish, shrimps, and duckweed, among others. Toxicity and toxicity index were measured by Tejada *et al*. (1993) on Tilapia fingerlings. Toxicity of non-target aquatic organisms were related to the measured environmental concentration in the Pagsanjan-Lumban watershed which is the main tributary to Laguna Lake and passes through agricultural areas mainly rice, vegetables, plantation crops and ornamentals (Bajet *et al*. 2012). The maximum measured environmental concentration of profenofos and pyrethroids were greater than the 48h LC50 of local shrimp *Macrobrachium* sp. indicating that this species is sensitive to the use of these pesticides in the watershed (Table 3). The local duckweed *Lemna* sp, used as a fish food for *Tilapia* sp. is also used to measure of the impact of herbicides on the aquatic environment (Bajet *et al*., 2010)

CONCLUSION

The Philippine Government's effort towards food and environmental safety in terms of pesticide residues is focused on regulatory control of a number of Government agencies and passing of laws related to food safety and organic agriculture in partnership with stakeholders. In support, monitoring activities through research as well as development of rapid test kit and pilot testing of RBPR are efforts to monitor residues of local markets and farms. Environmental monitoring is also part of researches of Government agencies and Institutions to be able to gain knowledge in management of these risks. Lastly, with limited funds for food monitoring, the effective way to increase food safety is to promote organic agriculture, strengthen programs that can guide farmers on good farming practices, alternative methods for pest control like IPM, GAP, use of plants with pest repellent properties, recognizing beneficial insects, know about pesticide residues and judicious/proper use of pesticides, all of which can reduce violative residues on food resulting to minimal dietary and environmental risk.

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SUMMARY

The Philippines in its effort to promote food safety has mainly focused on Government regulatory control through pesticide registration, monitoring, training and partnership with stakeholders. There is limited monitoring of local markets but data generated is used for regulatory control. Efforts to augment pesticide residue monitoring activities are a consequence of research activities, stakeholders and Industry efforts using classical pesticide residue analysis and rapid detection tools. Environmental safety is also a concern with researches generated through measuring the impact of agricultural activities on water, soil, and other environmental compartments. Ecotoxicological studies on the impact on non target organisms is also determined by measuring toxicity and relate data to expected and/or measured environmental concentrations of pesticide residues.

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