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REVIEW

DIETARY RISK ASSESSMENT OF IMIDACLOPRID RESIDUE IN RICE: THE USE OF QUICK, EASY, CHEAP, EFFECTIVE, RUGGED AND SAFE (QUECHERS) METHOD: A REVIEW.

Raihanah, Chokeli[1], Zailina Hashim[1,2*], Ho Yu Bin[1] , Saliza Mohd Elias[1], and Norida Mazlan[3] and Vivien How[1]

[1]*Department of Environmental and Occupational Health, Faculty of Medicine And Health Sciences, Universiti Putra Malaysia 43400 UPM Serdang, Selangor DE, Malaysia*

[2]*Department of Agriculture Technology, Faculty of Agriculture, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia*

*Corresponding Author: Tel: +60389472406 Email: zailina@upm.edu.my

Abstract

In Malaysia, agricultural production is one of the largest and most important economic activities. The introduction of insecticides in agriculture has been found to be immediate and cheaper way to overcome the pest attack problem and has helped farmers to increase productivity of the crop production. However, the risks of using insecticides are serious and unfortunately created numerous problems such as accidental poisoning to human, upset to natural environment balance and toxic residue that are hazardous to health in the environment. In order to measure the health effect from the exposure of insecticides in rice, a dietary risk assessment is needed. In order to analyze insecticides residue in rice samples, a Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method can be used.

Key Words: Imidacloprid pesticides, Dietary Risk Assessment, QuEChERS.
(Not exceeding 200 words)

Introduction

Agricultural production is one of the largest and most important economic activities in the world, particularly in low and middle income countries, where agriculture has a significant impact on GDP growth (Kwadwo et al., 2008). In Malaysia, Agriculture sector contribute 12% to the national Gross Domestic Product (GDP) and providing employment for 16% of the population (Encyclopedia of the Nations, 2013). In agriculture setting, paddy is one of the major crops activity and it is planted area throughout Malaysia by estimation of 672,000 hecter with the average national paddy production is 3.660 metric tonnes per hectare (Department of Agriculture). As rice is a staple foodstuff in the everyday diet of Malaysians and is a symbol of traditional Malay culture, the production of rice, which stood at 1.94 million metric tons in 1998, plays an important part in the country's agriculture. Based on the report from Department of Agriculture in 2011, Selangor, Pulau Pinang and Terengganu show the three highest states of paddy productions compared to the others state in 2010/2011. In order to fulfill the market demand has caused the increasing use of pesticides on rice fields in Malaysia (Mohd Fuad et al., 2012).

The introduction of pesticides in agriculture has been found to be immediate and cheaper way to overcome the pest attack problem and has helped farmers to increase productivity of the crop production. Worldwide approximately 9,000 species of insects and mites, 50,000 species of plant pathogens, and 8,000 species of weeds damage crops. Insect pests cause an estimated 14% of loss, plant pathogen cause a 13% loss, and weeds a 13% loss (Pimentel, 2009a). About one-third of the agricultural products are produced by using pesticides (Liu et al., 2002). Without pesticide application the loss of fruits, vegetables and cereals from pest injury would reach 78%, 54% and 32% respectively (Cai, 2008). Crop loss from pests declines to 35% to 42% when pesticides are used (Pimentel, 1997; Liu and Liu, 1999). Meantime, the risks of using pesticides are serious and unfortunately created numerous problems such as accidental poisoning to human, upset to natural environment balance and toxic residue that are hazardous to health in the environment (Pimentel, 2009b). Most pesticides are not spontaneously generated. Most of them are high toxic to humans and the environment. Pesticides and their degraded products would flow into the atmosphere, soils and rivers, resulting in the accumulation of toxic substances and thus threatening human health and the environment (Zhang et al., 2011). Within the different insecticide classes, the neonicotinoid insecticides, which include imidacloprid, acetamiprid, clothianidin, thiamethoxam, thiacloprid, dinotefuran and nitenpyram, are an important group of neurotoxins specifically acting as antagonists of the insect nicotinic acetylcholine receptors (nAChR) (Matsuda et al. 2001; Elbert et al. 2008).

Imidacloprid, [1-(6-chloro-3-pyridinyl) methyl-4, 5-dihydro-N-nitro-1H-imidazole-2-amine] is a member of neonicotinoid insecticides class which was first introduced by Bayer Agricultural Product (Daraghmeh et al., 2007). Since the introduction of imidacloprid in the early 1990s, the use of different neonicotinoid insecticides has grown considerably. Imidacloprid are used extensively for the control of important agricultural crop pests by spraying and also widely used in seed dressings and soil additions. Imidacloprid can enter human body through ingestion, inhalation and dermal contact (Kumar et al., 2013) described drowsiness, dizziness, vomiting, disorientation, and fever as the signs of toxicity of imidacloprid poisoning. Contamination of the imidacloprid residues through the dietary intake has been the significant issue in many areas of the world (Zhang et al., 2011). Thus, it is essential to monitor pesticides residue in food for the evaluation of food safety in order to avoid any risk to human consumption (Kapoor et al., 2013). Thus it is important to ensure that pesticides levels found in foods remain safely within the limit such as maximum residue limit (MRL).

Pesticides residue in food crops

According to the Pesticide Board Malaysia, (2012), "pesticide residue" means any specified substances in food, agricultural commodities, or animal feed resulting from the use of a pesticide. While defined by the World health organization (WHO), pesticides residue is any substance or mixture of substances in food for man or animals resulting from the use of a pesticide and includes any specified derivatives, such as degradation and conversion products, metabolites, reaction products, and impurities that are considered to be of toxicological significance. Meanwhile, European Crop Protection defined residue is a very small trace amount of pesticides. Once residues are demonstrated to be safe for consumers, one safe value so called Maximum Residue Limit (MRL) are set by independent scientists, based on rigorous evaluation of each pesticide legally authorized.

When a crop is treated with pesticides, a very small amount of the pesticides or its metabolites or degradation products can remain in the crop until after it is harvested. This is known as residue. Residues can rise from the use on a crop legally allowed pesticides according to good agricultural practice (GAP) which it leaves smallest and acceptable amount of residue. The over use of a pesticide or use too close to harvest time and incorrect use of pesticides after harvest to reduce pest infestation in storage or in transit also can contribute to the pesticide residue contamination in crop product. Apart from that, nowadays pesticides have

been used as a performance maximize in achieving better crop productivity. It usually used to enhance and stabilize crop yield, protect the nutritional integrity of food, facilitate storage to assure year-round supplies, and provide attractive and appealing food products. Among which, the use of pesticides and other chemicals has become a common agricultural practice. In general, farmers use pesticides to protect crops from insects, pests, weeds and fungal diseases whilst they are growing and to protect harvested crops from rats, mice, flies and other insects during storage. In this respect, the use of pesticides is can be considered beneficial to public health because of its function to protect crop quality (Hong Kong Food and Environmental Hygiene Department, 2007). As a result of continuous use, at timer the residues find the place in edible parts, soils, water and other environment. Increased use of agrochemical like pesticides has resulted in contamination of the environment thus might associated with long-term effects on human health, ranging from short-term impacts such as headaches and nausea to chronic impacts such as cancer, reproductive harm, and endocrine disruption (Chen et al., 2011).

In general, there are four main reasons behind the overuse of pesticides among the farmers which are ignorance about their environmental impact, lack of alternatives beside of pesticides, an underestimation of the short and long-term costs of pesticide use, and also weak enforcement of laws and regulations relating to pesticide use (South Asian Network for Development and Environmental Economics, 2009). Consumer exposure to pesticide residues in food, *inter alia*, is an issue that is of considerable concern to consumers, food producers, academics and government agencies. In Lucknow India, pesticide residue data demonstrates that food crop, namely fruits, vegetables and cereals, is the major dietary source of pesticide residues for the general population (Kapoor et al., 2012). Most of the consumers are start to aware that they ingest pesticides indirectly with their food nowadays. One of the key issues that interests both regulators and consumers is the question of how much pesticide is consumed. To know either it hazardous or non hazardous to health, dietary intake assessment must to carry out to evaluate the health risk in term of cancer or non cancer risk. The amount of pesticide consumed is termed dietary intake, or simply intake. As the tool for quantifying risk , Dietary Risk Assessment are at the heart of the setting of legally enforceable limits for pesticides (Maximum Residue Levels, MRLs) and they are used to support regulatory decisions that lead to the granting, or refusal, of approval for the use of products containing pesticides (Tucker, 2008). Therefore, monitoring is important in order to increase the food safety along with the reduction in consumption of pesticide residue.

Dietary risk assessment of pesticides

Ingestion of excessive amounts of contaminants such as pesticides through the food supply can have detrimental effects on the health of consumers. Thus, it is essential to analyze the foods we eat for contaminants and other chemicals through regular monitoring and surveillance programs to assure that chemical levels found in foods remain safely within acceptable national and international guidelines. The consumption of pesticide-contaminated foods may pose potential health risks; therefore, contamination of the pesticide residues through the dietary intake is a significant issue in many areas of the world (Rice et al. 2007; Li et al. 2008).Exposure to pesticide residues through the diet consumption considered to be five orders of magnitude higher than other exposure routes, such as air and drinking water (Juraske et al., 2009).

The Codex Alimentarius Commission Procedural Manual (Codex Alimentarius Commission, 2006) defines exposure assessment as “the qualitative and/or quantitative evaluation of the likely intake of biological, chemical, and physical agents via food as well as exposures from other sources if relevant”. The present document deals with dietary exposure assessment of chemicals, including nutrients, present in food. However, some of the principles and approaches described here can have application to biological agents in food as well.

Dietary exposure assessments combine food consumption data with data on the concentration of chemicals in

food. The resulting dietary exposure estimate is then compared with the relevant toxicological reference value for the food chemical of concern. Assessments may be undertaken for acute (short-term) or chronic (long-term) exposures, where acute exposure covers a period of 24 h (reference) and long-term exposure covers average daily exposure over the entire lifetime.

Globally, there are two organizations that are actively involved in formulating guidance of dietary risk assessment which are the Organization for Economic Co-operation and Development (OECD) and the United Nations (Codex Alimentarius by FAO and WHO).

Generally, the process of dietary pesticide risk assessment has been presented and three major components of the process estimation of pesticide residue levels, estimation of food consumption patterns, and characterization of risk based on a comparison of exposure estimates with toxicological criteria (Winter, 1992).

Dietary exposure estimates the quantity of pesticides that people ingest through their diets. Two types of exposure assessment are performed: the short-term assessment which focuses on the amount of a substance that is ingested over a short period of time, usually as part of a single meal or during one day, and the long-term exposure assessment which estimates the intake of a given substance over a long period to assess possible risks which may occur as a consequence of lifetime exposure (EFSA, 2010).

If the exposure is below the relevant health-based guidance value such as acute reference dose (ARfD) and acceptable daily intake (ADI), for acute and chronic exposure, respectively, the use of that pesticide in crop protection is considered acceptable (Boobis et al., 2008).

Method to analyze pesticides residue in rice

A large number of sample preparation methods of rice analysis before QuEChERS an acronyms for Quick, Easy, Cheap, Effective, Rugged and Safe method as an effective option for the determination of pesticides in cereals and its derivatives. Analysis for pesticide residues is often carried out in some steps for pretreatment mainly including solvent extraction, clean-up and concentration (Wang et al., 2012).The extraction step can be classified in two categories: solvent or sorbent-based extraction methods. The examples of solvent- based extraction methods are ultrasound assisted extraction (UAE), supercritical fluid extraction (SFE), and pressurized liquid extraction (PLE), while sorbent-based procedures are solid-phase extraction (SPE), matrix-solid-phase extraction (MSPD), stir-bar sorptive extraction (SBSE) or solid-phase micro extraction (SPME) (Gonzalez_Curbelo et al., 2012). While for the sample clean-up techniques which are the most commonly employed, comprises of liquid–liquid extraction (LLE)introduced by Jansson et al.,(2004);solid-phase extraction (SPE) by Štajnbaher et al.,(2003); solid-phase micro-extraction (SPME) was developed by Cai et al., (2003)and solid matrix partition (Wang et al., 2012).

Among all the methods listed above, LLE (Banerjee et al., 2007); Watanabe et al., (2007) and SPE (Muccio et al., (2006); Seccia et al., (2008) and Xiao et al., (2011) are the most commonly used techniques for the clean-up of the neonicotinoid insecticides. But, LLE suffers from the disadvantage of requiring both large amount of samples and toxic organic solvents, meanwhile SPE also suffers from the disadvantage of large amount of organic solvents, moreover, SPE has the characteristics of tedious purification steps yet costly, many of the published methods for neonicotinoid insecticides determination in foods use a combination of two or more commercially available SPE columns for clean-up (Cazorla-Reyes et al., (2011); Liu et al., (2010); Muccio et al., 2006). To overcome these shortcomings in LLE and SPE, the DSPE method firstly introduced by Anastassiades et al.,(2003) and developed for the extraction of pesticides from fruits and vegetables, consists of an acetonitrile extraction/partitioning and a dispersive solid-phase extraction (Wang et al., 2012). The main advantages of the method include inexpensive procedures that require less labor and organic solvents and high recoveries for wide range polarities of pesticides (Chen et al., 2011). Apart from that, Gas

Chromatography (GC) and Liquid Chromatography (LC) coupled to either electrochemical detector or post-column photochemical reactor were the instruments that are commonly used to quantify the multi residue in matrices. Although the GC multi-residue method is still the primary choice for new pesticides, the LC–MS/MS is undoubtedly indispensable as a complementary technique for monitoring purposes for future needs (Janssons et al., 2004). In the case of neonicotinoid insecticides particularly Imidacloprid, they are unsuitable for the direct analysis by gas chromatography due to their low volatility and high polarity (Wang et al., 2012). They are mainly determined by HPLC-DAD (Obana et al., (2002); Watanabe et al., 2007; Tsochatzis et al.,(2010); Kapoor et al.,(2012) and Wang et al., (2012)or mass spectrometry (Fernández-Alba et al., (2000); Pous et al., (2001); Blasco et al., 2002; Schoning et al., (2003);Obana et al., (2003); Fidente et al., (2005); Di Muccio et al., 2006; Seccia et al., (2008);Liu et al., 2010; Xiao et al., (2011) and Zhang et al., 2012).

QuEChERS method

Anastassiades et al., (2003) have developed an original analytical methodology combining the extraction of pesticides from food matrices and extract cleanup. They coined the acronym QuEChERS which stands for Quick, Easy, Cheap, Effective, Rugged and Safe. This technique involves micro-scale extraction using acetonitrile and purifying the extract using dispersive solid-phase extraction (d-SPE) and direct compatibility with both GC- and LC-MS analyses. Initially, the methodology was developed for the analysis of veterinary drugs in animal tissues but after realizing its great potential in the extraction of polar and particularly basic compounds it was also tested on pesticide residue analysis in plant material with great success (Anastassiades, 2011). It is the method of choice for food analysis because it combines several steps and extends the range of pesticides recovered over older, more tedious extraction techniques, since the development and publication of the method. The method has undergone various modifications and enhancements over the years since its first introduction. The original QuEChERS method has been modified using acetate (Lehotay et al., 2005) or citrate (Paya et al., 2007) buffers to accommodate some of the difficult pesticides. After collaborative studies, these two modifications became AOAC International Official Method 2007.01 (Lehotay, 2007) and CEN standard method EN 15662, respectively (Mastovska et al., 2010). Table 2.3 shows the example of studies that used QuEChERS methods to analyze Imidacloprid residue in rice

Conclusion

As a conclusion, agricultural production is one of the most important economic activities and introduction of pesticides in agriculture has benefited the crop production. However, the use of pesticides can also give an impact to human health and environment. Thus, in order to determine the health effect from the ingestion of the agriculture product, a dietary risk assessment is needed and the QuEChERS method is suitable for the analysis of pesticides food residue.

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Table 1: Example of studies that used QuEChERS methods to analyze Imidacloprid residue in rice.

Sample amount	**Extraction**		**d-SPE (per mL extract)**				**Separation technique**	**Recoveries**	**Results**	**References**
	Solvents	Salts	$MgSO_4$ (mg)	PSA(mg)	GCB (mg)	C_{18}(mg)				
10g	10 mL ACN	4 g $MgSO_4$	150	50	Replaced by 10 mg activated charcoal.	C18 solid-phase extraction cartridges	HPLC-DAD with confirmation using LC-MS	77.5 to 111% for all commodities	33% of cereal samples showed Imidacloprid, but only 3% of samples were above the MRL (0.05 mg/kg).	Kapoor et al., 2012
5 g	15 mL of deionized water and 10mLof ACN	4 g of MgSO4 and 1g of NaCl	150	150	-	50	GC-TOFMS and UPLC-MS/MS	70-120%		Mastovska et al., 2010
10g	10ml water, 20ml ACN (50 µL formic acid).)	4 g of MgSO4 and 1 g of NaCl	-	125	25	125	HPLC-DAD	76–123%.	0.002–0.005 mg/kg	Wang et al., 2012