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Pesticide Residues in Fruits and Vegetables

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1. Introduction

The aim of this chapter is to describe the presence of pesticide residues in fruits and vegetables, mainly how they are introduced, dissipated, degraded, affected by food processing techniques and their risk assessment.

Fruits and vegetables are important components of the human diet since they provide essential nutrients that are required for most of the reactions occurring in the body. A high intake of fruits and vegetables (five or more servings per day) has been encouraged not only to prevent consequences due to vitamin deficiency but also to reduce the incidence of major diseases such as cancer, cardiovascular diseases and obesity. Like other crops, fruits and vegetables are attacked by pests and diseases during production and storage leading to damages that reduce the quality and the yield. In order to reduce the loss and maintain the quality of fruits and vegetables harvest, pesticides are used together with other pest management techniques during cropping to destroy pests and prevent diseases. The use of pesticides have increased because they have rapid action, decrease toxins produced by food infecting organisms and are less labour intensive than other pest control methods. However, the use of pesticides during production often leads to the presence of pesticide residues in fruits and vegetables after harvest.

The presence of pesticide residues is a concern for consumers because pesticides are known to have potential harmful effects to other non-targeted organisms than pests and diseases. The major concerns are their toxic effects such as interfering with the reproductive systems and foetal development as well as their capacity to cause cancer and asthma (Gilden et al, 2010). Some of the pesticides are persistent and therefore remain in the body causing long term exposure. The concern has led to governments setting up monitoring systems in order to assess the safety situation and make informed decisions when passing legislation.

2. Pesticides fate after application to fruits and vegetables

Fate refers to the pattern of distribution of an agent, its derivatives or metabolites in an organism, system, compartment or (sub) population of concern as a result of transport, partitioning, transformation or degradation (OECD, 2003). After pesticides are applied to the crops, they may interact with the plant surfaces, be exposed to the environmental factors such as wind and sun and may be washed of during rainfall. The pesticide may be absorbed by the plant surface (waxy cuticle and root surfaces) and enter the plant transport system (systemic) or stay on the surface of the plant (contact). While still on the surface of the crop, the pesticide can undergo volatilization, photolysis chemical and microbial degradation. These processes are illustrated in Figure 1. All these processes can reduce the original pesticides concentration but can also introduce some metabolites in the crops.

Volatilisation of the pesticide usually occurs immediately after application in the field. The process depends on the vapour pressure of the pesticide. Pesticides with high vapour pressure tend to volatilize rapidly into the air while those with low vapour pressure remain longer on the surface. Volatilization rate also depends on the environmental factors such as wind speed and temperature. The faster the wind speed and the higher the temperature the more the pesticide will evaporate. Photolysis occurs when molecules absorb energy from the sunlight resulting in pesticide degradation. The indirect reaction can also be caused by some other chemicals being broken by the sunlight and their products reacting with pesticides in turn. Some pesticides may be degraded by microbial metabolism. Micro-organisms can use pesticides as nutrients thereby breaking them into carbon dioxide and other components (Holland and Sinclair, 2004). Because of difference between naturally occurring organic chemicals and pesticide structures, they cannot be assimilated by the microbes but they may be altered at reactive sites. The products formed may be less or more toxic than the parent chemical.

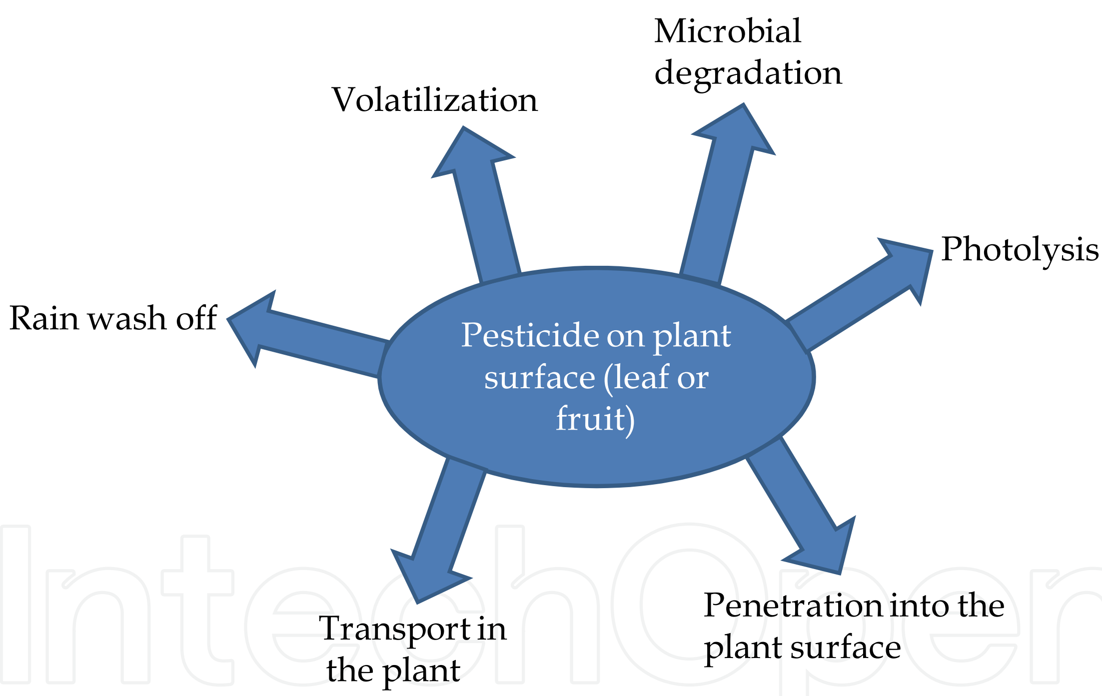

Fig. 1. Fate of pesticides in plant surfaces chemical

Although degradation of pesticides is influenced by different environmental processes, Celik et al, (1995) concluded that under natural field conditions volatilization is the main process that affects pesticides. These researchers applied six pesticides (azinphos-methyl, ethion, diazinon, methidathion, phosalone and pirimicarb) to apples and found that volatilization was the dominant process followed by solar irradiation. Bacterial degradation had the lowest influence except for phosalone. Pirimicarb was highly degraded by solar irradiation. Rain wash off can also be very important when it occurs shortly after application.

3. Monitoring

The purpose of pesticide monitoring programs is to ensure that in fruits and vegetables do not exceed maximum residues levels (MRLs) allowed by the government, no misuse of pesticides that could result in unexpected residues in food and that good agricultural practices (GAP) are maintained. Some programmes, mostly in developing countries, are carried out due to the demands by international trade. The results from these monitoring programmes are also used by regulatory bodies for future developments in setting MRLs and risk assessment exercises for public health. In most countries, the monitoring programs are organised by a single agency designated as the competent authority. The agency designs a monitoring plan based on the previous data available from dietary consumption and risk assessment exercises or pesticide usage in the available fruits and vegetables. In the European Union (EU) there is a coordinated programme for all the member countries to follow from the European commission and the member states national programs. The results are then yearly as a single report by the European Food Safety Authority (EFSA).

In the case of international trade, the monitoring plan is also influenced by the trading partners. For example, partners trading with the EU (normally referred to as third countries) have to incorporate EU standards to their food control programmes. In addition to monitoring, the agencies can engage in follow up sampling (enforcement actions) where some discrepancies had been observed. Laboratories carrying out pesticide residues analysis should be accredited or have started accreditation procedures to some quality standard. Pesticide legislation in developing countries is generally lacking or not implemented and this also affects pesticide monitoring since it relies on legislation to be effective (Ecobichon 2001). The other problem is lack of trained personnel to enforce laws and monitor the use of pesticides and residue levels in food and the environment. However, pesticide monitoring in some developing countries with high agricultural output is driven by international trade. Failure to adhere to trade standards can result in a loss of revenue for the population supported by the affected agricultural industry. This can be illustrated by using the Kenya’s green bean farmers. These Kenyan bean farmers implemented developed country pesticide standards and are required by the UK retailers to show evidence of compliance with UK pesticide legislation (Okello 2001). In the same study, it was also noted that since the 1990s the arrangement saw Kenya increasingly becoming one of the leading countries in green bean production and supplier to developing countries. This also saw the benefits of reduced pesticide related cost of illnesses and incidences of acute symptoms of pesticide exposure in monitored farmers than compared to unmonitored farmers. This was attributed to the education the farmers received about the use and handling of pesticide as well as adhering to protective measures.

4. Maximum residue level

Maximum residue levels are the highest levels of residues expected to be in the food when the pesticide is used according to authorised agricultural practices (EFSA 2010). The MRLs are always set far below levels considered to be safe for humans. It should be understood that MRLs are not safety limits, a food residue can have higher level than MRL but can still be safe for consumption. Safety limits are assessed in comparison with acceptable daily intake (ADI) for short term exposure or acute reference dose (ARfD). MRLs are subject to legal requirements in most of the countries. In developed regions like Europe the responsibility of the legislation is lead by the European Commission (EC) with input from the member states, EFSA and the standing committee on the Food Chain and Animal Health. In the US, the leading agency is Environmental Protection Agency (EPA) with input from the United States Department of Agriculture (USDA) and the Scientific Advisory Panel while in New Zealand the leading agency is the New Zealand Food Safety Authority (NZFSA) with input from the Environmental Risk Management Authority.

MRL setting can be the responsibility of one or more authorities in a country and normally involves the health, agriculture and environmental agencies. MRL enforcement can be a responsibility of one or more agencies and may also depend on different food types. MRL setting is based on the national registered good agriculture practice (GAP) data combined with the estimated likely residue from the supervised trials mean residue (STMR), ADI and ARfD. The information is then evaluated by the risk assessment agency like EFSA in EU or JMPR for CODEX Alimentarius. The JMPR procedure is shown in Figure 2. Where national or regional MRLs are not available, internationally recognised bodies such as the United Nations Codex Alimentarius Commission MRLs can be used as guidance. MRLs are generally published in open literature or websites of the regulatory bodies for public usage. MRLs may be exceeded because of pesticide misuse, false positives due to naturally occurring substances, differences in national MRLs, lack of registered pesticides and incorrect pesticide application (EFSA, 2010).

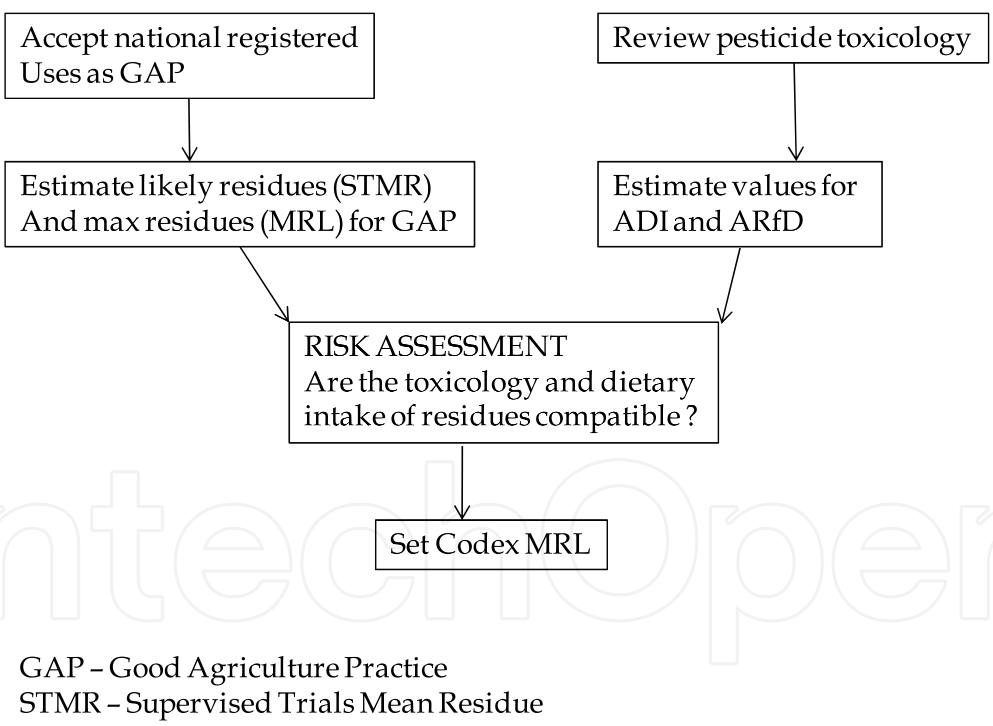

Fig. 2. Procedure for setting JMPR MRLs

The emerging trend is to harmonize MRL in each region or globally and is highly supported by international organisations such as FAO, WHO, CCPR and OECD. In the EU the MRLs are already harmonised as from the beginning of September 2008 under the new regulation EC No. 396/2005 (OECD 2010). In developing regions like Africa, efforts were initiated under the Global MRL Harmonization Initiative – Africa Project that was supported by US Department of Agriculture – Foreign Service, IR-4 Project and USEPA. A summary of the questionnaire from the same project indicated that most of the African countries have adopted the CODEX MRLs with South Africa establishing some of its own in addition (Anonymous 2009).

5. Food processing

Fruits and vegetables like other foods pass through culinary and food processing treatments before they are consumed. The effects of these culinary and food processing techniques have been investigated by various researchers and they have been found to reduce the pesticide residue levels except in cases where there is concentration of the product like in juicing frying and oil production. Some toxic metabolites may be produced during processing treatments, especially thermal processing. One of the extensively studied metabolite is ETU that result from thermal processing of dithiocarbamates. However, the consumers can still be encouraged to employ those processing methods that reduce pesticide residues.

Food processing studies often results in transfer factors or food processing factors (PF) of the pesticide residue in the transition from raw agriculture commodity to the processed product. These processing factors are expressed as the concentration of pesticide after processing divided by the concentration before processing. Some processing factors are available in public literature while others are only available from the pesticide registering bodies. Processing studies have become a part of pesticide registration requirements. Effect of processing in fruits and vegetables are said to be influenced by the physico-chemical properties of the pesticide as well as the processing method (Holland et al., 1994).

Processing factors for a particular processing technique and a group of pesticides are not easily available in literature. These become important when researchers want to perform risk assessment for a group of pesticide in the population. An example can be illustrated by risk assessment of exposure of organophosphorus pesticides in the Dutch diet (Boon et. al, 2008). The authors could not find the general processing factor for a group of organophosphorus pesticide. However, they managed to derive the general processing factors for washing (0.76), peeling (0.44) and canning(0.74) for fruits and vegetables. The authors could not find the general processing factor for a group of organophosphorus

Processing	**R***	**95% CI**	**99.5% CI**
Baking	1.38	0.91 -2.09	0.76 - 2.51
Blanching	0.21	0.10 - 0.44	0.07 - 0.61
Boiling	0.82	0.58 - 1.15	0.50 - 1.33
Canning	0.71	0.46 - 1.09	0.38 - 1.31
Frying	0.1	0.02 - 0.46	0.01 - 0.90
Juicing	0.59	0.32 - 1.09	0.24 - 1.42
Peeling	0.41	0.30 - 0.54	0.27 - 0.61
Washing	0.68	0.52 - 0.82	0.52 - 0.89

R* - processing factor
CI – confidence interval

Table 1. Average processing factors for different processing methods

pesticide their risk assessment, however, they managed to derive the general processing factors for washing (0.76), peeling (0.44) and canning(0.74) for fruits and vegetables. We attempted to summarize the processing factors for fruits and vegetables according to different processing methods using meta-analysis (Keikotlhaile et al, 2010). The results are shown in Table 1. However, the results were generalized and we recommended that the same procedure could be used for a group pesticides applied to similar vegetables for more refined processing factors.

6. Risk assessment

Risk assessment of chemicals is described as a process intended to calculate or estimate the risk to a given target organism, system or (sub) population, including identification of attendant uncertainties, following exposure to a particular agent taking into account the inherent characteristics of the agent of concern as well as the characteristics of the specific target system (OECD 2003). Risk assessment process includes four steps: hazard identification, hazard characterisation (dose-response assessment), exposure assessment and risk characterisation. In that context the risk assessment of pesticide residues in fruits and vegetables is tackled.

6.1 Hazard identification

Hazard identification is the first step in risk assessment and it involves the identification of the type and the nature of adverse effects that an agent has as inherent capacity to cause in an organism, system or (sub) population (OECD 2003). Recent regulations require that hazard identification be performed before a pesticide can be approved for usage in agriculture or other areas. Therefore the information on hazards posed by pesticides is readily available from the pesticide registering bodies and on their websites for public usage. Most of the information is also available from international organisations such as JMPR, OECD and EC. The hazards that have been identified concerning pesticide include reproductive and endocrine disruption, neurodevelopmental delays, immune system, cancer and respiratory distress (Gilden 2010). Studies are carried out in test organisms (microbial, cells or animals) and the exposure level is increased until an adverse effect is produced. The highest dose of the pesticide that does not cause detectable toxic effects on the test organisms is called the no-observed-adverse-effect-level (NOAEL) and is expressed in milligrams per kilogram of body weight per day (WHO 1997)). This is important because it is used in calculation of the ADI or the ARfD.

6.2 Hazard characterisation

Hazard characterisation is the qualitative and, wherever possible, quantitative description of the inherent properties of an agent or situation having the potential to cause adverse effects. This should, wherever possible, include a dose response assessment and its attendant uncertainties (OECD 2003). Hazard characterisation involves comparing the pesticide exposure concentration with the ADI or the ARfD. The ADI is the estimate of the amount of a substance in food (mg/kg body weight/day) that can be ingested daily over a lifetime without appreciable health risk to the consumer (WHO 1997). ADI is calculated by dividing the NOAEL for animal studies with an uncertainty factor of 100 to convert to a safe level for humans. A factor 100 (10 x 10) mostly used to account for species differences and individual variability in sensitivity to the chemicals (Renwick 2002). ARfD is the estimate of the amount of a substance in food that can be ingested over a short period of time, usually during one meal or one day, without appreciable health risk to the consumer (WHO 1997).

6.3 Exposure assessment

Evaluation of the concentration or the amount of a particular agent that reaches a target organism, system or (sub) population in a specific frequency for defined duration (OECD 2003). The potential intake or consumption of pesticide residues is divided by the body weight and compared to ADI or ARfD in exposure assessment.

Exposure = (Concentration of pesticide residue x Food consumed)/ body weight

The input data used in exposure assessment comes from supervised field residue trials, national pesticide monitoring programs and food consumption surveys. The residue levels from pesticide monitoring programs mighty not cover the whole food supply but they are always available in most countries and they reflect samples available for consumers. However, targeted sampling data may over-estimate exposure because it is biased against suspect samples.

6.3.1 Consumption data

Food consumption data are essential component of dietary risk assessment. The data used depend upon the type of population being assessed: children, special ethnic groups, geographical regions and estimation of the quantity of food eaten. Food consumption data may be obtained during food supply surveys (food balance sheets), household inventories, household food use and individual food intake surveys (Hamilton, 2004). According to EFSA guidance document on collection of food consumption data (EFSA, 2009), there are four types of dietary assessment methods, namely: diet history, food frequency, dietary records and dietary recall. In diet history, the history of the whole daily food intake of an individual and the usual meal pattern is assessed over a period of days, months and up to one year. Food frequency involves asking the consumers to estimate the usual frequency of consumption during a specified time for the foods that are listed on the questionnaire. In dietary records, the consumers weigh and record all the food including beverages before eating and also the leftovers after eating. Dietary recall involves asking the consumers to recall the actual food intake for the past 24 or 48 hours or previous days. The quantities are described using household measures, food models or photographs. The most common dietary recall method is the 24-hour recall. The methods that are suitable for both acute and chronic risk assessment are dietary records and dietary recall.

The most appropriate source is the one that measures actual consumption instead of available food supply. Average daily consumption is the most used in exposure assessment calculations, however there are others such as percentile consumption values, average consumption (weekly, monthly, etc) and long term consumption habits. The latter is mostly important in calculation of chronic exposure. In cases where national food consumption data are not available, food balance sheets from FAO can be used even though they might be too generalised.

6.3.2 Dietary exposure models

Dietary intake exposure models are mainly conducted in deterministic and probabilistic assessment. Deterministic exposure assessment is based on single point estimate, usually the mean or worst case scenario (97.5 percentile). Probabilistic exposure assessment is based on the probability of occurrence of the risk and results in a distribution of risk values. Deterministic exposure is generally used as a low tier approach to determine whether there is a course for concern for the defined exposure. It is easy to perform and requires less time to complete. The disadvantage is that it gives single estimate of the risk and does not give an insight of other possible risks for lower levels. Therefore it does not contain information about variability in potential exposure to the exposed population. Probabilistic assessment is based on simulations of potential exposures using computer software and allows more inputs to come up with the final exposure. Most of these distributional models are based on Monte Carlo simulations and are referred to as Monte Carlo models (Hamilton, 2004). These distributional models provide a range of risks throughout the population distribution and provide quantitative information about variability and uncertainty. The disadvantage is that they require time and resources for additional data generation. A brief overview is outlined by Hamilton et al., (2004). Since deterministic models gives an over-estimated exposure assessment by assuming all time consumption of higher concentration the pesticide a more realistic approach of probabilistic assessment is preferred when resources allow.

6.4 Risk characterisation

The qualitative and, wherever possible, quantitative determination, including attendant uncertainties, of the probability of occurrence of known and potential adverse effects of an agent in a given organism, system or (sub) population, under defined exposure conditions (OECD 2003). The international estimate daily intake (IEDI) has been used to characterise the risk of pesticides. It is expressed as:

$$IEDI = \sum STMR \times E \times P \times F$$

Where
STMR = supervised trial median residue level
E = Edible portion
P = processing factor
F = consumption of the food commodity
When the IEDI is more than the ADI the food involved is considered a risk to the concerned consumers. For the national estimated short term intake (NESTI), the risk characterisation is compared with the ARfD.

7. Future work

In pesticide residues research, future work involves mainly the improvement of risk assessment of dietary exposure methods and harmonisation of data collection in as many countries as possible. The methods are also aimed at incorporating all the factors that contribute to exposure assessment in the final model predictions so that it can be realistic. Common methods of dietary exposure assessment were based on deterministic calculations and those have been found to have short comings of only providing exposure for average consumers while excluding higher consumers. The most preferred method is the probabilistic risk assessment since it considers all exposure throughout the entire consumer distribution. Recently risk assessment studies have focused on simultaneous exposure to multiple pesticides instead of only on a single pesticide (Van Klaveren and Boon, 2009). In their paper, the authors discuss the risk trade-offs, risk benefits and the use of integrated probabilistic risk assessment model (IPRA). The model integrates exposure and health effect modelling while incorporating variability and uncertainty.

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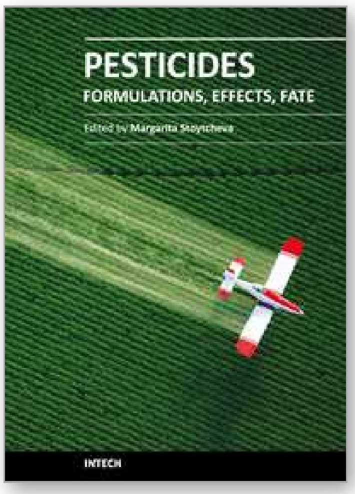

Pesticides - Formulations, Effects, Fate
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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.