

STUDY OF REMOVING PESTICIDES FROM FRUITS AND VEGETABLES

(Project – Report)

Submitted in partial fulfilment of the requirements for the award of

Bachelor of Technology degree in Biotechnology

By

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DEPARTMENT OF BIOTECHNOLGY

SCHOOL OF BIO & CHEMICAL ENGINEERING

SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited with Grade “A” by NAAC

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of S. Kiran (38300010) who carried out the project entitled “**study of removing pesticides from fruits and vegetables**” under our supervision from February 2020 to March 2020.

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DECLARATION

I **S. Kiran** hereby declare that the Project Report entitled “**study of removing pesticides from fruits and vegetables**” done by me under the guidance of **Dr. Thiyagarajendhiran** at **Sathyabama institute of Science and Technology, Chennai** is submitted in partial fulfilment of the requirements for the award of Bachelor of Technology degree in Biotechnology.

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SIGNATURE OF THE CANDIDATE

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ABSTRACT

Pesticides are a numerous and diverse group of chemical compounds, which aroused to eliminate pests in agriculture and households. They enable the quantities and the quality of crops and food to be controlled, and help to limit the many human diseases transmitted by insect or rodent vectors. However, despite their many merits, pesticides are some of the most toxic, environmentally stable and mobile substances in the environment. Their excessive use has a deleterious effect on humans and the environment; their presence in food is particularly dangerous. With their environmental stability, ability to bioaccumulate and toxicity, pesticides may place the human body at greater risk of disease and poisoning [1]. Pesticides enter the environment in various forms (e.g., powders, moistened powders, powders for preparing aqueous solutions, and concentrates for making up emulsions or sprays). Pesticides are of enormous importance in increasing the yields and quality of agricultural products. The intensive development of agriculture means that more and more toxic organic and inorganic compounds are entering the environment. Because of their widespread use, stability, selective toxicity and bio accumulation, pesticides are among the most toxic substances contaminating the environment. They are particularly dangerous in fruit and vegetables, by which people are exposed to them. It is therefore crucial to monitor pesticide residues in fruit and vegetables using all available analytical methods. We present results from the literature in the context of Maximum Residue Levels (MRLs) of target pesticides in fruit and vegetables samples. We also discuss about the presence of pesticide and insecticide in fruit and vegetables.

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CHAPTER 1: INTRODUCTION

1.1 What is a pesticides?

PRESENCE OF PESTICIDES IN FRUITS AND VEGETABLES ABSTRACT The intensive development of agriculture means that more and more toxic organic and inorganic compounds are entering the environment. Because of their widespread use, stability, selective toxicity and bio accumulation, pesticides are among the most toxic substances contaminating the environment. They are particularly dangerous in fruit and vegetables, by which people are exposed to them. It is therefore crucial to monitor pesticide residues in fruit and vegetables using all available analytical methods. We present results from the literature in the context of Maximum Residue Levels (MRLs) of target pesticides in fruit and vegetables samples. We also discuss about the presence of pesticide and insecticide in fruit and vegetables. Pesticides are a numerous and diverse group of chemical compounds, which are used to eliminate pests in agriculture and households. They enable the quantities and the quality of crop s and food to be controlled, and help to limit the many human diseases transmitted by insect or rodent vector. However, despite their many merits, pesticides are some of the most toxic; environmentally stable and mobile substances in the environment. Their excessive use has a deleterious effect on humans and the environment; their presence in food is particularly dangerous. With their environmental stability, ability to bio accumulate and toxicity, pesticides may place the human body at greater risk of disease and poisoning. Pesticides enter the environment in various forms (e.g., powders, moistened powders, powders for preparing aqueous solutions, and concentrates for making up emulsions or sprays).

1.2 PESTICIDES EFFECT OF ENVIRONMENT

We think that eating well gives our body the essential nutrients that it requires when we consume fresh fruits and vegetables. This might come as a surprise to some of the people but most of the foods contain highly contaminated pesticides residue on them. , many people today put pesticides in foods.

Pesticides are used to protect the crops from insects, germs and rodents when the plants are growing up. Residual amount of these chemicals are present on the food when it gets to the grocery store. The pesticide residue cannot easily be removed with plain water. When you

consume a fruit, the pesticide residue goes into the body as they get stuck and can make you sick. Read on to find out

1.3 PESTICIDES METABOLITES AND THEIR USES

A metabolite is a compound or substance formed during the process of chemical reactions (metabolism) by means of enzymes that occur in an organism or cell. Most pesticides are subject to metabolic degradation in plants or the environment. However, a number of currently available pesticides (insecticides and miticides) are converted into metabolites either inside an insect or mite pest, or within plant tissues.

Factors that can affect metabolism of certain insecticides and miticides include plant type and plant health. Insecticides and miticides that have activity against insect or mite pests as metabolites are referred to as pro-insecticides or pro-acaricides (miticides). Many insecticide and miticide metabolites may have no or very minimal insecticidal or miticidal activity due to detoxification or the metabolites are discarded from the insect or mite body during excretion. However, some processes may result in toxic metabolites.

In most cases, alterations to the active ingredient are required for some pesticides to confer toxic effects on insect and mite pests. For instance, most systemic insecticides are converted into metabolites that are more water soluble and are more active against insect pests.

In fact, all the neonicotinoid systemic insecticides registered for use in greenhouses that are applied to the growing medium as drench applications or granules are converted into metabolites. For example, when imidacloprid is applied to plants as a drench or granule, approximately 95 percent of the active ingredient (parent compound) is metabolized almost completely although this depends on the plant species.

The metabolites of imidacloprid are active against insect pests such as aphids. The primary metabolites of imidacloprid include olefine and 4-, and 5-dihydroxy. Olefine is 16 times more active on insect pests than imidacloprid because the metabolite has a higher attraction or affinity for the target site, nicotinic acetylcholine receptor, in certain aphid species. In addition, the water solubility of the metabolites is higher than the active ingredient. Thiamethoxam is converted into a metabolite that is actually another neonicotinoid systemic insecticide, clothianidin. Clothianidin is the least watersoluble of the neonicotinoid systemic insecticides at 327 ppm (327 mg/L) but has a higher binding affinity for the target site (nicotinic acetylcholine receptor). In addition, clothianidin is rapidly taken up in the transpiration stream and accumulates at higher concentrations in plant parts and tissues than other neonicotinoid systemic insecticides. Acetamiprid, which is another neonicotinoid systemic insecticide, but can only be applied to the foliage — not growing medium — is converted into five different metabolites. The metabolites of certain insecticides and miticides used in greenhouses are presented in fruits and vegetables

The importance of matrix pretreatment, sample extraction and clean-up in multi residue methods for pesticide analyses is discussed, with emphasis on alternative new techniques attempted worldwide such as accelerated solvent extraction, microwave-assisted extraction, solid-phase extraction, solid-phase micro-extraction, matrix solid-phase dispersion, supercritical fluid chromatography, ultrasonic

CHAPTER 2: 1.1 REVIEW OF LITERATURE

The main objective of the review is to document, assess and analyze the results of the previously reported data on levels of different pesticides in selected fruits and vegetables from Pakistan. The findings of the previous studies clearly indicated that more than 50 % of the samples were contaminated with organophosphate, parathyroids and organochlorine pesticides. Many studies reported that among fresh fruits and vegetables tomato, apple, melon, mango, grapes, and plum crossed the FAO/WHO permissible limits for these contaminants residual levels. The comparison of other regions showed that observed levels were found above maximum residue limits (MRLs) in 50 % of the samples but were in agreement with the studies from neighboring countries like China and Bangladesh. Higher hazard risk index (HRI) values were calculated for dieldrin, methamidophos, o,p'-DDT, diazinon and p,p'-DDT in apple, mango, banana, melon, potato and onion. The review also highlights that data on pesticide residues in foodstuff is scarce which should be overcome by further extending studies from different areas of Pakistan. In order to ascertain the provision of food suitable for human consumption, it is imperative to monitor pesticides in food commodities by the country's authorities and enforce guidelines based on permissible limits.

In recent years, few environmental issues have aroused the concern of the public as much as pesticides, especially in relation to the health of children. In spite of the many published studies on the subject of pesticides and human health, there remains deep controversy surrounding this issue. This report will try to elucidate the results of the many studies of pesticides and health, and draw conclusions as to the true health effects of pesticides. To understand this controversial issue it is helpful to look at the history of pesticide use. Prior to World War II, the pesticides that we use now did not yet exist. Some pesticides currently in use were in fact developed during the World War II for use in warfare.

The organophosphate insecticides were developed as nerve gases, and the phenoxy herbicides, including 2,4-D (the most commonly used herbicide in Canada), were created to eradicate the Japanese rice crop, and

later used as a component of Agent Orange to defoliate large areas in jungle warfare. After World War II, these chemicals began to be used as pesticides in agricultural production, for environmental spraying of neighborhoods for mosquito eradication, and for individual home and garden use.

During the 1960s and 1970s, epidemiologists in the USA noted a rise in the incidence of non-Hodgkin's lymphoma (NHL). When plotted on a map of the USA these cases were clearly clustered in agricultural areas. This increase in NHL incidence paralleled the rise in pesticide use, prompting some epidemiologists to theorize that there was a causal link. Rachel Carson's revolutionary book, *Silent Spring*

(1), first published in 1962, started the slow process of raising political and public awareness of the hazards posed to wildlife, humans, and the ecosystem by the use of pesticides. This process continued with *Our Stolen Future*

(2), described by then Vice-President Al Gore as the sequel to *Silent Spring*, which documented the health effects of endocrine-disrupting chemicals. Since then there have been hundreds of scientific studies done on all continents to determine if there is a relationship between pesticide use and human health problems. Since 1990,

when the municipality of Hudson, Quebec passed a by-law restricting the use of cosmetic pesticides on public and private property, pesticides have received considerable media attention in Canada. In 1991, two lawn-care companies challenged the Hudson by-law on the grounds that pesticide use was not within municipal jurisdiction. The court affirmed that municipalities do indeed have the power to pass by-laws regarding pesticide use, so the lawn-care companies appealed the ruling. In 2001, the Supreme Court of Canada upheld the municipality's right to pass the by-law. Interestingly, although the health effects of pesticides were not argued during the Supreme Court challenge, the judgement implied that this had been an important factor in the Court's decision

(3). Since then, many municipalities across Canada, including Toronto and Halifax, have passed by-laws restricting the cosmetic use of pesticides. Cosmetic use of pesticides remains a complicated issue involving arguments about the rights of lawn-care and pesticide companies, property owners' rights, and increasingly, the health effects extraction and gel permeation chromatography. Detection employing capillary gas chromatography and high-performance liquid chromatography in conjunction with mass spectrometry, capillary electrophoresis, immunoassay techniques and others is summarized. In the search for review papers, the inclusion criteria were expanded to include reviews conducted between 1990 and 2003. The initial search, using the term "pesticides," yielded 12,061 papers. For the second selection stage, the term "pesticides" was combined with "systematic review," "meta-analysis," and "review" to select those studies that apply a systematic approach. When the papers were limited to review articles only, 1684 articles were found. However, these papers had a number of limitations, and although many were categorized as reviews, most did not describe a systematic approach. In addition, a number of the papers were primarily reviews dealing with organochlorines that had been picked up in the search because they were classified broadly as dealing with pesticides. As a result, many of the papers did not meet our inclusion criteria. From this list of 1684 articles, 49 relevant review papers were selected. Two members of the pesticide review group evaluated these review paper abstracts to determine their relevance to the current project. Of the 49 identified reviews, 30 were selected for further assessment using the quality and relevance criteria. The review articles were collected and categorized according to health effect. We decided to organize the papers according to health effect rather than specific pesticide exposure, since most of the human health effect literature considers people exposed to cumulative or aggregate pesticide mixtures. To ensure that all possible health effects were included, a comprehensive search of medical subject headings (MeSH) in Medline was done early in the review process.

This ensured that all relevant terms were included in the search process, and minimized the exclusion of relevant studies. The health effect categories included in Phase 1 included: cancer, genotoxic, immunologic, neurotoxic, reproductive, and other. Four members of the group reviewed these review articles: two focused on the cancer papers and two reviewed the non-cancer papers. To standardize this process all reviewers used a common assessment tool in an effort to ensure consistent application of the evaluation criteria. After this step, a full project team meeting was held in Toronto on May.

5, 2003 to introduce project members, conduct in-depth assessments of the review papers, and formulate the next phase of the project. This process allowed the group to determine gaps in the literature, and decide on the focus and limits of the review. The group decided to apply the

following guidelines in choosing the health effects for review:

1. For the health effect, absence of a current, methodologically excellent review paper;
2. For cancers, data on incidence, premature loss of life, and increasing incidence were used to select specific tumour types for review; as well, a chosen cancer had to account for a substantial portion of total cancer incidence. Using these guidelines, the following health effects were chosen for review, and categorized broadly as “cancer” or “non-cancer”:

A) Cancer B) Non-Cancer

1. Lung 1. Reproductive effects
2. Breast 2. Genotoxic/immunotoxic
3. Colorectal 3. Dermatologic
4. Pancreas 4. Neurotoxic
5. Non-Hodgkin’s lymphoma
6. Leukemia
7. Brain
8. Prostate
9. Stomach
10. Ovary
11. Kidney
12. Testicular

Over the next month, work proceeded on the quality assessment tool for reviewing the primary studies. This tool, referred to as the data extraction form, was designed through extensive consultation with Andrea Furlan, the Evidence Based Practice Coordinator at the Institute for Work and Health. In addition, all members of the pesticide group took part in a pilot exercise, using the data extraction tool to assess the same article. All ratings of the article used in the pilot exercise were within one point of each other on the global rating scale. This exercise also led to some minor changes that made the form easier to use for the primary studies.

CHAPTER 3: AIM AND SCOPE

3.1 AIM:

Pesticides are used to control various pests and disease carriers, such as mosquitoes, ticks, rats and mice. Pesticides are used in agriculture to control weeds, insect infestation and diseases. There are many different types of pesticides; each is meant to be effective against specific pests and also used to fruits and vegetables because some fruits and vegetables getting easily soggy that’s why using pesticides from fruits and vegetables

3.2 METHOD FOR REMOVING PESTICIDES

Washing



Illustration by : Karno Guhathakurta & Aradhana Gupta

- The first step in the removal of pesticide residues from the food products is washing. Washing with 2% of salt water will remove most of the contact pesticide residues that normally appear on the surface of the vegetables and fruits.
- About 75-80% of pesticide reduces are removed by cold water washing. The pesticide residues that are on the surface of fruits like grapes, apples, guava, plums, mangoes, peaches and pears and fruity vegetables like tomatoes, brinjal and okra require two to three washings.
- The green leafy vegetables must be washed thoroughly. The pesticide residues from green leafy vegetables are removed satisfactorily by normal processing such as washing blanching and cooking

Blanching

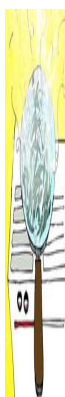


Illustration by : Karno Guhathakurta & Aradhana Gupta

A short treatment in hot water or steam applied to most of the vegetables. Certain pesticide residues can effectively be removed by blanching. But before blanching it is very important to thoroughly pre-wash the vegetables and fruits.

Peeling



Illustration by : KarnoGuhathakurta & Aradhana Gupta

- Both systemic and contact pesticides that appear on the surface of the fruits and vegetables can be removed by peeling.
- Steps such as concentration, dehydration and extraction from the raw product can further reduce pesticide residues in the end product. The net influence of processing almost always results in minimal residues in processed food

Cooking



Illustration by : Karno Guhathakurta & Aradhana Gupta

Animal Products

- Animal products are also the major source of contamination for pesticide residues in human diets since the animals feed on fodder, which are sprayed with pesticides.
- Pressure cooking, frying and baking will remove pesticide residues from the animal fat tissues.

Dairy products

- Boiling of milk at elevated temperatures will destroy the persistent pesticide residues.

Vegetable Oils

- Refined oils will have fewer amounts of pesticide residues.
- Household heating of oils up to a particular flash point will remove pesticide residues.

CHEAPER 4: MATERIALS AND METHODS

4.1 MATERIALS

4.1.1 Equipments used

- 1.vegetables
- 2.fruits
- 3.backing soda
- 4.knife
- 5.vessels
- 6.variety of pesticides chemical

4.2 METHODOLOGY

4.2.1 Sample collection

Sample collection is collected by different locations and different supermarket and with farmers and house garden's

4.2.2 what are the fruits and vegetables using pesticides more.

To test for pesticides, users simply pass a swab over the fruit or vegetable, insert the swab into the detector and wait about 30 seconds. A green light on the face of the device means the pesticide residue is under the EPA tolerance; a red light means the opposite

2.3 To test for pesticides, users simply pass a swab over the fruit or vegetable, insert the swab into the detector and wait about 30 seconds. A green light on the face of the device means the pesticide residue is under the EPA tolerance; a red light means the opposite

4.2.4 who is most risk by using pesticides

Fetuses, infants, growing children, pregnant and nursing mothers, and women of childbearing age are most at risk for adverse health outcomes from exposure to pesticides. Children are more at risk than adults because children eat more relative to their body weight than adults eat. Exposures during vulnerable periods of development can be particularly dangerous. These vulnerable periods include fetal development, infancy, early childhood, and puberty. Fetuses are exposed to pesticides through the mother's diet. Infants are exposed through breast milk. Acute poisoning is a persistent problem among agricultural and occupational workers who handle pesticides and track them into their homes where family members get exposed. People who live near agricultural fields may be exposed by drift from aerial spraying. What Fruits and V

4.4: what is the health risks.

Most studies of the health effects of pesticides have focused on occupationally exposed people, like farmworkers and pesticide applicators. Acute OP pesticide poisonings result in symptoms like nausea, abdominal cramps, diarrhea, dizziness, anxiety and confusion, which can be quite severe but are often reversible. There have also been many studies in groups of people who work with pesticides but who have not experienced acute poisonings serious enough to result in these kinds of symptoms. These studies have found that chronic, lower dose exposure is associated with respiratory problems, memory disorders, skin conditions, depression, miscarriage, birth defects, cancer and neurological conditions such

as Parkinson's disease. There have been fewer studies of people without known occupational exposures, but one study with a nationally representative sample showed increasing odds of ADD/ADHD for 8-15 year olds with increasing levels of OP pesticides metabolites in urine.¹

4.5. what crops used on pesticides.

Pesticides are used on fruits, vegetables, wheat, rice, olives and canola pressed into oil, and on non-food crops such as cotton, grass, and flowers. The OP pesticides malathion and chlorpyrifos are commonly used on all fruits, vegetables, and wheat. Pesticides are used on crops that are fed to animals, although residue from pesticides is generally not found in meat or dairy products

4.6.3 sampling

Sampling Extract cleanup and it is preparation for analysis Identification and determination of analytes Fixing, transport and storage Extraction of pesticides from the sample and/or enrichment of the sample.

4.7.4 sample preparation

The sample-preparation stage and the operations involved in it can affect the final result. Whether the analysis provides the desired information about the sample therefore depends on its proper, correct preparation. It is extremely important that the sample of material for analysis is homogeneous and representative. A representative sample has a chemical composition that resembles as closely as possible the average composition of the entirety of the analyzed material. The sample should be stored frozen and in the dark. Generally speaking, the sample-preparation process consists of a number of steps. In the case of fruit and vegetables, one such step is the removal of surface contaminants by washing the samples in distilled water. The sample is then dried at elevated or ambient temperature or with the aid of a desiccant. In the next step, the sample is broken up and crushed, or ground in a mill or with a pestle and mortar, after which the sample is homogenized. The exact preparation procedure depends on the nature of the material under investigation, and every combination of operations in this procedure can lead to loss of analytes and/or cause additional contamination of the sample

4.8. TABLE OF PESTICIDES

Table 3. Techniques for the final determination of pesticides in samples of fruit and vegetables Analyte Sample Final determination technique + detector Ref.

Organophosphorus pesticides	Apples, tomatoes, apple juice	GC-FPD	Pesticide residues
Fresh fruit (oranges, apples, peaches, pears and grapefruits) and vegetables (lettuce, tomato, cabbage, potato, onion and leek)		GC-MS	Pesticide residues
Oranges		LC-MS	Cyromazine and its metabolites
Beetroot		LC-ESI-MS2	Pesticide residues
Fruits and vegetables		GC-NPD/ECD	Organophosphorus insecticide residues
Strawberries and cherries		GC-MS	10 pesticides of various classes
Oranges, tangerines		LC-MS	Organophosphorus pesticides
Cucumber, potato		GC-TSD	Pesticide residues
Oranges, tangerines, grapefruits, lemons		LC-MS2	Insecticides
Peppers		GC-MS, GC-MS2	252 pesticides of various classes
Tobacco		HPLC-MS2	234 pesticides of various classes
Herbs		GC-MS	Pesticide residues
Fatty vegetable		GC-MS, LC-MS	Fungicides
Fruits (oranges, tangerines, lemons, grapefruits, apples, pears, bananas) and vegetables (potatoes and lettuces)		LC-fluorescence detection	
Organophosphorus pesticides	Olive oil	GC-FPD	Pesticide residues
Cucumber, strawberries		GC-ECD	Pesticides of various classes
Grapes, musts, wines		GC-MS	Pesticides of various

classes Oranges, tangerines, nectarines, peaches, khaki is GC-NPD, GC-ECD, GC-MS Organophosphorus pesticides Cabbage, grapes LC-MS2 160 pesticides of various classes Tomatoes, pears, oranges LC-MS2.

CHAPTER-5

5.1:EXTRACT THE CLEAN UP.

The isolation of analytes from biological samples involves a certain clean-up effect, and, like every clean-up process ensures a certain degree of isolation. Extraction yields not only the target analytes but also interferences (e.g., sugars, fats and chlorophyll), which may distort the result of the analysis. Hence, extract clean up is essential and should always precede analysis of the extract. The usual techniques for cleaning up fruit and vegetable extracts are:

- (1) solid-phase extraction (SPE);
- (2) solid-phase microextraction (SPME);
- (3) matrix solid-phase dispersion extraction (MSPDE);
- (4) stir-bar sorption extraction (SBSE);
- (5) adsorption chromatography; and,
- (6) gel-permeation chromatography (GPC).

SPE is the most popular clean-up technique [31]. As the sample passes through a column of sorbent, the target analytes are adsorbed on the sorbent particles. The compounds retained are then liberated with a solvent and analyzed. A salt, usually NaCl or Na₂SO₄, is often added to the solution to increase its ionic strength, and that increases the proportion of analytes extracted to the sorbent. Sorbents used for SPE include C18, polymers, graphitized non-porous carbon, and ion-exchangers.

The B15C5 sorbent is the best one for determining organophosphorus pesticides. The method is simple and can be readily automated. However, against that, the solvent bed has to be conditioned before each use, and analyte recovery is small. In SPME, analytes are adsorbed on a fiber coated with a suitable solid phase that is pushed out from a micro-syringe. The analyte is then thermally desorbed and transferred to the GC injector. The benefits of this method are that solvents can be eliminated and that it is impossible to overload the column because of the limited volume of adsorbent. Depending on where the fiber is placed in relation to the sample, SPME can be divided

into:

- (1) direct immersion (DI-SPME),
- (2) headspace (HS-SPME).

GPC is just as frequently used as a clean-up technique [33–35]. It enables micromolecular pesticides to be separated from macromolecular substances present in the matrix. While the long lifetime of the columns is an advantage, the poorer resolution compared to adsorption techniques, especially when gradient-elution techniques are used, is a disadvantage. Approaches are being sought to develop pesticide-determination techniques that are quick, easy, cheap, effective, rugged and safe (QuEChERS) [43–54], which is a combination of liquid-liquid extraction (LLE) and SPE. It is based on a number of stages (see Fig. 5). Table 2 lists the most commonly used techniques for

cleaning up extracts prior to the final determination of pesticides in samples of fruit and vegetables. Consumption of sample and toxic solvents with the QuEChERS method is minimal. By applying EChERS to the determination of pesticides in fruit and vegetables, matrix effects are eliminated and high recoveries of target analytes are possible. The method can be modified depending on the type of sample and the target analytes. To improve the extraction of polar organophosphorus pesticides, the method is modified by the addition of acetic acid. When samples of citrus fruit are under investigation, protective wax coatings can be removed by freezing the samples for at least one hour. For the analysis of citrus fruits, blackcurrants and raspberries, it is recommended to add aq NaOH to reach pH = 5 and to improve the analysis. Work is in progress to optimize this method for the analysis of pesticides of various classes. The last stage in the QuEChERS method is the final determination of analytes by GC or LC.

5.2: 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 off 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. Pesticide on plant surface (leaf or fruit) Photolysis

Microbial degradation Volatilization Penetration into the plant surface Transport in the plant Rain wash off 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.

5.3 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

5.4: 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.

5.5: PESTICIDES – RISKS AND BENEFITS

RISKS

- Toxic to humans
- Impact on environment and ecosystems

BENEFITS

- Crop protection
- Food preservation
- Material preservation
- Disease control

CHAPTER 6

6.1:seasonal pesticides uses

simazine, paraquat, 2-4D

WINTER

Fungicides: dinitroor thocresol (DNOC)

Insecticides: organophosphate
compounds (OPs)

SPRING

Fungicides: Cu salts, dithiocar bamates

Insecticides: endosulfan, OPs

SUMMER

Insecticides: OPs

Ref: Dr A. Laborde, Uruguay

EXAMPLE OF SEASONAL PESTICIDE USE

APPLE ORCHARD

CALENDAR

NPS

<<NOTE TO USER: Include your local calendar for pesticide treatment of APPLES or any other agricultural tasks.>>

<<NOTE TO USER: How many pesticides may be found in an apple? Will "Snow-White" be offered a poisoned apple?>>

More than 10 different chemicals may be sprayed on apple trees or other vegetable crops before harvest.

The example of a calendar of pesticide application in apple trees in Uruguay was provided by Dr A. Laborde.

Ref:

•Achard. Fruit growing calendar. Banco de Seguros del Estado Yearbook. Uruguay, 1996.

Picture: www.nps.gov/whmi/gallery/grounds016.htm – NPS – Us Department of the Interior. Apple orchard

6.2:METABOLIC PATHWAYS

Organophosphates

metabolize into:-

Oxones-

Specific inactive

metabolites (ME)

-

Non-specific

metabolites:

dialkylphosphates

(DAPs)

Wessels, EHP (2003) 111 (16): 1939

oxon

DAP

DAP

ME

Metabolism may either activate or inactivate the chemical.

Therefore, immature metabolic pathways may be protective or increase the danger from specific chemicals.

As an example, organophosphates are metabolized to oxones (active metabolite), but also to other specific inactive metabolites (ME) and to non-specific metabolites (the dialkyl phosphates (DAPs)) (shown in the figure).DAPs are used as biomarkers of environmental exposure to all kinds of organophosphate pesticides because DAPs are metabolites of all these pesticides.

Ref:

•Wessels D et al. Use of biomarkers to indicate exposure of children to organophosphate pesticides: implications for a longitudinal study of children's environmental health. Environmental Health Perspectives, 2003, 111:1939. Figure: Reproduced with permission from Environmental Health Perspectives

6.3:Summary and conclusion

The increasingly widespread application of pesticides— substances with different physical and chemical properties – means that ever larger amounts of these compounds are getting into the environment. As a result of the various processes to which they are subject in the environment, they may be converted to even more toxic compounds. They are currently regarded as some of the most dangerous environmental contaminants because of their stability, mobility and long-term effects on living organisms. Pesticides can be absorbed and stored by plants, and their metabolites can likewise be accumulated. As crops are an

essential part of the human diet, the quality of these products is extremely important and is often a factor determining whether or not consumers

will buy them. The aim of controlling pesticide residues is to protect

consumer health from their possible side effects. Safe food should have above all an appropriate nutritious value and contain the least possible amounts of substances that could be hazardous to health. It is therefore crucial to monitor pesticide residues in fruit and vegetables. Because of the difficulties inherent in the determination of pesticides (low concentrations of pesticides in samples), work is in progress to improve existing techniques and to develop new ones, in order to improve the reliability of analytical results.

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