RAPID DETECTION OF PESTICIDES AND HEAVY METALS IN CANNED FRUITS AND VEGETABLES AND ESTIMATION OF HEALTH RISK

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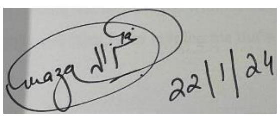

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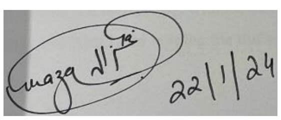

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ABSTRACT

A rainbow of fruits and vegetables in diet supports overall wellbeing and health of humans and reduces the risk of chronic diseases. However, the presence of pesticide residues and heavy metal accumulation in fruits and vegetables has raised concerns about potential risk to human health. This study was carried out to identify concentration of pesticides and heavy metals in canned fruits and vegetables and estimate the potential health risk to humans. Different types of canned fruits and vegetable samples were purchased from Al Fatah, Imtiaz super market and Risen store. Total seventeen samples, ten canned vegetables (sweet corn, green peas, mushrooms, green olives, red kidney beans, garlic, red chili, cauliflower, carrot, lemon) and seven canned fruits (peach, grapes, pear, pineapple, red cherry, papaya, lychee) of different local and international brands were taken. By using (HPLC) four types of pesticides i.e. Glyphosate, Bifenthrin, Imidacloprid, Difenoconazole were analyzed in these samples and five heavy metals i.e zinc, manganese, chromium, cobalt and copper were determined by Atomic Absorption. The results showed that concentration of glyphosate in vegetables sweet corn (0.4 ppm), green peas (0.3 ppm), mushrooms (0.15 ppm), green olives (0.21 ppm) , red kidney beans (0.6 ppm), garlic clove (0.60 ppm), red chilli (0.3 ppm), cauliflower (0.66 ppm), carrot (0.34 ppm) and lemon (0.65 ppm), and fruit peach (0.195 ppm) , grapes (0.21 ppm), pear (0.39 ppm), concentration of bifenthrin in vegetable green olives (0.11 ppm) and fruit pear (0.158 ppm) , lychee (0.171 ppm), concentration of imidacloprid in vegetable mushroom (0.15 ppm) and cauliflower (0.10 ppm) and fruit peach (0.29 ppm) and concentration of difenoconazole in vegetable mushroom (0.67 ppm) , green olives (0.13 ppm), garlic clove (0.3 ppm), lemon (0.416 ppm) and fruit peach (0.123 ppm) , grapes (0.133 ppm), pear (0.25 ppm)**,** red cherry **(**0.25 ppm)**,** papaya **(**0.11 ppm) **,** lychee (0.11 ppm) exceeded the MRL values set by WHO and FAO. While for heavy metals, concentration of zinc in all the vegetables sweet corn (0.062 ppm), green peas (0.049 ppm), mushroom (0.069 ppm), green olives (0.83 ppm), red kidney beans (0.031 ppm), garlic clove (0.251 ppm), red chilli (0.086 ppm) , cauliflower (0.022 ppm), carrot (0.041 ppm), lemon (0.017 ppm) and fruits peach (0.021 ppm) , grapes (0.18 ppm), pear (0.034 ppm), pineapple (0.256 ppm), red cherry (0.068 ppm), papaya (0.715 ppm), lychee (0.012 ppm) exceeded the Maximum Residue Limit set by FAO and WHO, concentration of manganese in vegetable sweet corn (0.208 ppm), green peas (0.247 ppm), mushrooms (0.184 ppm), garlic clove (0.04 ppm), red chilli (0.379 ppm), cauliflower (0.224 ppm) and concentration of cobalt in vegetable sweet corn (0.048 ppm), green peas (0.048 ppm), garlic clove (0.08 ppm) and fruit peach (0.048 ppm) exceeded the MRL values while concentration of chromium in vegetable mushroom , cauliflower, lemon and fruits pineapple, lychee were below detection limit (BDL). For copper no vegetable and fruit samples exceeded the MRL values.

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LIST OF ABBREVIATION

AAS	Atomic Absorption Spectrometry
ADI	Acceptable Daily Intake
BDL	Below Detection Limit
EDI	Estimated Daily Intake
HI	Health Index
HPLC	High Performance Liquid Chromatography
HRI	Health Risk Index
MRL	Maximum Residue Limit
WHO	World Health Organization

CHAPTER I

INTRODUCTION

1.1 Background

Food consumption has been recognized as the primary method for human exposure to several environmental toxins (pesticides, herbicides, fungicides, insecticides and heavy metals), accounting for >90% of intake compared to inhalation or dermal routes of exposure. Many foodborne diseases are linked to the consumption of fruits and vegetables so food quality and safety is a major public concern around the globe. Due to the presence of various pathogens, pesticides are widely used to handle and control these pests and improve the quality and quantity of agricultural products. Pest infestation would have caused 30-40% reduction in worldwide agricultural productivity without pesticides. Pesticides are very helpful in maintaining food security but excess use of pesticides leaves the chemical residues on the surface of fruits and vegetables. These residues have been directly linked to the harmful health issues [1].

1.2 Importance of fruits and vegetables

From an agricultural perspective, Pakistan is one of the largest agricultural countries around the globe. Pakistan is blessed with ideal climatic conditions for commercial yield of various fruit and vegetable crops [2]. Fruits and vegetables are recognized as essential parts of a balanced diet because they provide vital nutrients that are required for the majority of the processes occurring in the body. They are low fat and high energy foods that are relatively rich in vitamins (A, B, C, E, thiamine, niacin), minerals and other bioactive components. They are also rich in fiber. It has been suggested that a high intake of fruits and vegetables (five or more servings per day) is positively linked to a lower risk of diabetes, cancer, heart disease, obesity and osteoporosis. As a result of these health benefits, the consumption of fruits and vegetables has grown significantly worldwide in recent years, making them a significant economic asset. Like other crops, fruits and vegetables are also targeted by pests and diseases that lower its quality and yield [3]. There is also a risk of contamination in fruits and vegetables from various microorganisms at any stage of the production process, particularly if they are grown outdoors in a field [4].

1.3 Pesticide contamination

In order to maintain the quality of fruits and vegetables and reduce their loss from the invasion of insects, infections and various weeds, biological or chemical agents are used more often. They are the significant tools for managing the pest, weed and pathogen attacks, boosting crop yield, enhancing crop quality and lengthen the storage life of food crops [5]. During cropping, pesticides are applied with other pest management practices on crops to eradicate pests, prevent diseases, minimize harvest loss and preserve the quality of crops [3]. Due to their rapid action, the ability to reduce toxins produced by food infecting organisms and labor saving nature compared to other pest management techniques numerous types of pesticides are extensively used in many agricultural areas which contaminate the crops with their chemical residues. There have been reports and a large body of evidence on pesticide residues in a variety of fruits and vegetables, both raw and processed [5]. Herbicide, fungicide, carbamate and parathyroid residues are also found in fruits and vegetables crops [6]. Fungicides and herbicides make up a significant percentage of the pesticide residue. Insecticides are the most commonly used pesticides in developing countries, while herbicides are more commonly employed in industrialized nations [7].

When crops grow up, they are more likely to be affected by rodents, germs and insects so pesticides are sprayed to protect crops from all of them. More than 1000 pesticides are globally used to ensure the fruits and vegetables are not destroyed or damaged by the various pests when the food is exposed to during the growing process. When food items are sent to grocery stores to be sold to the consumers, the residual amount of the sprayed chemicals are still present on them. Plain water alone does not prove to be useful for the removal of the pesticide residue easily. When a consumer ingests a fruit the pesticide residue gets into the body causing higher risk of poor health [8]. So, pesticide is a concern for consumers as they have potentially detrimental effects on other non targeted organisms than pests and disease [3]. Although the use of pesticides provides unquestionably numerous advantages, their improper application may leave hazardous residues that can pose a risk to human health and environment, particularly presence on food is dangerous [13]. Pesticides are environmentally stable, mobile, and most toxic chemical agents. They are capable of bioaccumulation; their intake puts the human bodies at critical risk of falling prey to poisoning and different diseases [9]. About 6.7 million deaths in 2010 were reported worldwide due to the lesser intake of the vegetables and fruits, resulting in increased risk of being affected by non-communicable illnesses and poor health status. Most people, adults and children are vulnerable to pesticides by consuming the pesticide residue containing food. Workers performing their duties in occupational and agricultural settings and vicinity breath in and touch these pesticides, which put them at risk of getting affected by chronic and acute poisoning [10]. The intensive use of pesticides results in the contamination of air, degradation of soil, deterioration of agro ecosystem, groundwater contamination, disruption of natural balance, endangering the health and safety of humans and animals. Some of the less expensive pesticides such as lindane and dichlorodiphenyltrichloroethane (DDT) can linger in soil and water for years. Moreover, these get accumulated in crops, vegetables and fruits. Rain and wind are mainly responsible for the transportation of the pesticides to neighboring land and crops from their point of application, where the presence of pesticides can prove to be harmful or undesirable. Their intake can lead to abdominal cramps, dizziness, nausea, confusion, diarrhea, and anxiety resulting from acute pesticide poisoning that can be sometimes severe but are reversible more often. Researchers have identified that dose exposure which is low and chronic is related to memory disorders, respiratory problems, depression, skin conditions, birth defects, cancer, miscarriage, and including neurological conditions like Parkinson 's disease. There are lesser or quite rare studies of individuals without the known occupational exposures despite the one study with the state representative sample revealing increasing odds of ADD/ADHD for eight to fifteen year olds with higher pesticide metabolites levels in urine. Through mother's, infants get exposed to the pesticides as they are breastfed. Among occupational and agricultural workers handling pesticides, acute poisoning is a persistent problem that tracks them into their homes, attacking their family members as well. Due to the drift from aerial spray, individuals living near the agricultural areas are more likely to get exposed to the pesticides [11].

Therefore, it is extremely important to find simple and cost effective methods to eliminate the residues present in the primary raw material [12]. As a result, the International Organizations and Governments have established (MRLs) for pesticides in food commodities [13]. The MRL is the maximum level of pesticide residue in or on food or animal feed, expressed in milligrams per kilogram $mg \cdot kg^{-1}$. Governments also implement regulatory and enforcement measures to keep an eye on MRL compliance in food commodities [14].

1.4 Heavy Metals contamination

Heavy metals along with pesticides also get stuck on the fruits and vegetables. In the last few years, exposure of human beings to heavy metals has gained critical attention as a significant health issue. The severity of this issue is increasing worldwide, particularly in developing nations. Naturally occurring metallic elements with high atomic weights and densities at least five times higher than water are termed as heavy metals. They are metals with metallic properties and have atomic numbers greater than 20. Potentially harmful metal content in soil comes not only from bedrock itself but also from anthropogenic sources such as agricultural inputs, solid or liquid waste deposit, mining, automobile exhaust and industrial discharge, irrigation with polluted water, fertilizer and metal based pesticide addition, harvesting procedure, storage and sale [15]. The continuous use of the heavy metals as starting products in various industrial processes has resulted in a significantly increasing ratio of human exposure to these agents. Heavy metals are not biodegradable. They have lengthy biological half-lives and can accumulate in various human organs leading to unwanted effects [16].

Generally, the heavy metals include Copper (Cu), Manganese (Mn), Iron (Fe), Zinc (Zn), Cobalt (Co), Tin (Sn), Lead (Pb), Mercury (Hg), Molybdenum (Mo), Cadmium (Cd), Arsenic (As), and Chromium (Cr). Both higher concentrations and deficiency of these heavy metals can have serious effects on the health of human beings. Consequently, the accurate estimation of the toxic heavy metal's concentration present in food samples and environment has been a critical hot topic receiving greater and significant attention [17]. Plants that grow in heavy metals poisoned areas may show biochemical processes, physiological and altered metabolism resulting in lower biomass production, metal accumulation and growth reduction. Vegetables absorb heavy metals and store them in both edible and non-edible portions of their bodies in amounts that can pose a health risk to humans and animals [18]. Human beings who are exposed to greater levels of heavy metals contamination may suffer from different types of diseases such as cardiovascular problems, cancers, gastrointestinal and renal failure, hematic, depression, tubular and glomerular dysfunction and osteoporosis. Adolescents, children, and infants are more vulnerable to heavy metals contamination leading to the low intelligence quotients and various developmental challenges [19].

Heavy metals which are emitted from vehicles and industries may get deposited on the surfaces of vegetables and fruits while transporting to the market. The current study has pointed out that atmospheric deposition may greatly increase the ratio of heavy metals poisoning in the vegetables [20]. The excessive intake of harmful heavy metals through food items can result in the chronic accumulation in the liver and kidneys of the human being resulting in disruption of the various biochemical problems causing nervous, kidneys, bones, and cardiovascular issues. Quite a few heavy metals for example Manganese, Zinc, Molybdenum, Cobalt, and Copper serve as micronutrients for human beings and animals' growth if present in trace quantities, while others for example Arsenic, Chromium and Cadmium leads to cancer and skin lesions [21].

Long term exposure to cadmium can result in renal damage, abnormal protein excretion in urine, and reduction in the calcium level in bones. Though zinc is an essential mineral yet too much of it can be harmful. Arsenic is ranked third on the periodic table and the twentieth most prevalent element on Earth. Food, water and the air can expose humans to arsenic. Blood vessel destruction, stomach and intestinal issues, heart and brain dysfunction, skin discoloration and cancers of skin, bladder, lungs, liver, colon and kidney can all result from prolonged exposure to arsenic, Mercury's high toxicity and its ability to bioaccumulate make it dangerous even at very low concentrations. Among the trace metals that have been investigated, it is one of the most toxic ones and exposure to high levels can cause permanent damage to the immune system, brain, kidney, liver, and pituitary gland and developing fetus. Excess of zinc can cause copper deficiency, autism, nausea, vomiting, stomach pain and diarrhea. A high copper diet may result in parenchymatous damage to liver, kidney and heart [15].

The poisoning of the vegetables with heavy metals because of atmospheric and soil contamination put forth a serious threat to its safety and quality. Intake of the heavy metals through diet also contributes to the critical risk to the health of the humans and animals. Heavy metals, for example Cadmium and Lead have been observed to be containing carcinogenic effects. Higher concentrations of the heavy metals such as Lead, Cadmium and Copper in vegetables and fruits were found to be related to the high prevalence of the upper gastrointestinal cancer [22]. In order to avoid the spread of the above mentioned dreadful diseases, it is necessary to control heavy metals contamination or otherwise it will keep on increasing and will continue to damage animals, environment, humans and plants.

1.5 Need for Monitoring

Pesticides are commonly applied in agricultural techniques to safeguard crops from pests, illness and weeds. However, their residues can remain in fruits and vegetables which can pose a risk to human health. Fruits and vegetables are consumed in such great amounts that it becomes obligatory for the concerned authorities to take some serious actions to control the spread of contaminants through effective management techniques. If the use of pesticides and heavy metals in fruits and vegetables goes on increasing, then the negative health impacts due to their consumption will increase and their severity in terms of toxicity will increase as well. Careful and smart techniques in pest management can be introduced based on the data generated through monitoring. Various alternatives can be adopted instead of pesticides so that the dependency on these chemicals can be reduced and ultimately eliminated. Pesticide monitoring programs are designed to make sure that the maximum residue levels MRLs permitted by the government don't exceed in fruits and vegetables. MRLs are the maximum levels of pesticide residue that are legally permitted in food products. Monitoring programs involve the regular testing of food products for pesticide residue, and the results are compared to the MRLs to determine if any action needs to be taken. This cannot be ignored because the contamination in fruits and vegetables can lead to several significant health issues.

1.6 Analytical techniques used for detection of pesticides and heavy metals

For detection of pesticides, High Performance Liquid Chromatography (HPLC) was used and for detection of heavy metals Atomic Absorption Spectrometry (AAS) and microwave digestion were used. Both the techniques were used under the supervision of the expert.

RATIONALE

Pesticides are the chemicals or the substances that are used to eradicate pests. Fruits that have been treated with pesticides may still contain the residues, which are toxicologically significant when consumed. More than1000 pesticides are used globally to protect the food from the pest attack. Each pesticide has a unique characteristic and level of toxicity. Asian nations are more vulnerable to this problem than other impoverished nations in the world. Improper dealing of fruits with respect to pesticide lead to various health problems especially in outlying areas of Punjab because of improper inspection of fruit crops. On the other hand, toxic heavy metal poisoning is a serious environmental issue that has a significant impact on human health. They can be fatal to humans when combined with various environmental components like soil, water and air. Humans are exposed to these toxic substances through the food chain. This study would help in determination of pesticide residues and heavy metals in the selected fruits along with the evaluation of health problems arising due to ingestion of these infected fruits and vegetables.

OBJECTIVES

The objectives of the study were:

- Quantification of pesticide residues in canned fruits and vegetables.
- Quantification of heavy metals in canned fruits and vegetables.
- Assessment of health risk index associated with the contaminants to calculate the possible health risk to humans consuming these foods by calculating the health risk index.

CHAPTER II

LITERATURE REVIEW

Numerous pesticide remnants and heavy metals are found in the majority of the frozen vegetables, various kinds of jams and canned food samples, consequently threatening the consumer's health at the high risk of facing detrimental health problems. It is fairly obvious that this critical health threatening problem demands the practice of cost effective, high speed analytical and more precise techniques which are proficient or effective for the identification of minimum concentrations in a number of pesticide remnants or residues.

So, a study was conducted to highlight the proficiency of using the SFE (Supercritical Fluid Extraction) and SFC (Supercritical Fluid Chromatography) methods for the analysis of pesticide remnants or residues levels in frozen vegetables, fruits and canned foods; and secondly to put up the advocacy of consumer's safety by discarding pesticide remnants poisoning present in markets. Around 15 varieties of frozen vegetables and fruits along with imported canned food items were collected from the local food markets of Houston for identification and investigation purposes. The most important kinds of pesticides investigated were carbamates, herbicides, pyrethroids and fungicides. By using the identification techniques such as SFE and SFC, the overall analysis indicated that almost 60.82 % of food samples under investigation had shown no presence of any pesticide remnants or residues. Whereas on the contrary 39.15% of the collected food samples were observed to be poisoned by 4 various pyrethroid residues± RSD% which ranges from 0.03± 0.005 to 0.03ppm, out of which majority of pyrethroid residues were identified in strawberry jams and frozen vegetables. The range of herbicide residues in tested samples was found to be 0.03± 0.005 to 0.8± 0.01ppm. Almost five varieties of fungicides in the range between 0.05±0.02 to 0.8 ± 0.1 ppm were observed in five collected samples of frozen vegetables. In almost sixty percent of the investigated food samples carbamate residues were not identified. So it was assumed and concluded that Supercritical Fluid Extraction (SFE) and Supercritical Fluid Chromatography (SFC) were found to be reliable, cost effective, accurate and less time consuming for the analysis of frozen fruits and vegetables along with imported canned foods items and are consequently recommended for investigation of the pesticide contaminations. [7]

Examination of pesticide remnants or residues in vegetables and fruits along with their derivatives such as juices, jams, ketchup, pickles, canned products and dried products was conducted. Another study was undertaken to analyze the after effects of peeling, washing, cooking and heating on a variety of pesticides concentration. The stability of different pesticides in collected samples along with their subsequent products was analyzed. For the extraction of pesticide remnants or residues Quenchers method whereas for the analysis GC-MS method were used. For potato and tomato, pesticides such as carbofuran and mancozeb were observed to be stable whereas mancozeb, chlorpyrifos and captain were observed to be unstable. It was indicated that pomace and peels were found to be having pesticide residues in remarkably highest levels. In the current study in hand it was observed that for the pesticide residue dissipation; peeling, heat processes such as blanching and boiling; and washing were the most effective methods. [12]

For the analysis of pesticide remnants or residues in the vegetables of Hyderabad located in Pakistan a study was undertaken. The concentrations of almost 6 pesticides were identified by using GC-MS (Gas Chromatography coupled with Mass Selective Detector) in vegetables produced locally collected from wholesale markets. Almost two hundred samples of 8 vegetables such as green chili, peas, cauliflower, eggplant, bitter gourd, tomato, apple gourd and spinach were examined for the analysis of pesticide remnants or residues. The findings showed that almost all the samples were found to be containing pesticides, out of which only thirty-nine percent (39%) were indicated to be having pesticide residues at or below MRLs (Maximum Residue Limits) whereas sixty-one percent (61%) of the samples were found to be having pesticide residues above the maximum residue limits (MRLs). Out of the 6 examined pesticides chlorpyrifos and carbofuran were observed to have concentration range between 0.01-0.39 and 0.05-0.96mg/kg respectively. The observations and conclusions pointed out important details regarding the prevailing pesticide contamination levels of a number of most commonly used vegetables, moreover emphasized the dire need of controlling the excessive use of chlorpyrifos and carbofuran which are applied and potentially persistent pesticides [23].

Likewise, another study was undertaken in an attempt to analyze the injurious health hazards being imposed on the consumers resulting from possible consumption of harmful chemicals present in the vegetables and fruits. In the following cross sectional study to be done analytically, cucumber, apple and tomato samples were taken from the 4 leading marketplaces of Lahore and were tested one by one for the identification of 9 pesticide remnants or residues levels by making use of the LCMS system (Liquid Chromatography Mass Spectrometry system). The comparison of the identified levels was made with the standard MRLs (Maximum Residue Limits) as set by World Health Organization (WHO) in respective items of all the pesticides. The results drawn indicated that majority of the samples under investigation were not found to be having any remnants or residues of 9 collected pesticides and moreover only 2 tomato samples were found to be having detectable residues of 1 pesticide namely Imidacloprid which were also within the standard limits as set by the World Health Organization (WHO). Consequently, the conclusion was drawn that vegetables and fruits samples taken for analysis didn't pose a critical threat to the consumer's health [24].

Another study was carried out in order to evaluate the amount of pesticide residues and analyze the variance between different sources in Henan Province, China. In 2021, 3307 samples of 24 fruits and vegetables were gathered from 18 distinct regions. Gas chromatography mass spectrometry (GC-MS) was used to evaluate thirteen different pesticide types, and the chi-square test was used to compare the detection rates. Pesticide residues were identified in every sample except yam, pimento, ginger and edible fungus. The detection rates of difenoconazole, acetamiprid, carbendazim,procymidone, emamectin, benzoate, lambda cyhalothrin, cypermethrin and dimethomorph were different in supermarkets and traditional farmer’s market. Both the dimethomorph and the difenoconazole group showed statistically significant differences ($P < 0.05$). This study established a solid foundation for the assessment of popular fruits and vegetables that contained pesticide residues in Henan Province. Various sources adopt different regulatory measures to control pesticide residues in order to ensure food security [25].

Using the Liquid Chromatography - tandem Mass Spectrometry (LC-MS/MS) multi residue analysis approach and Quenchers extraction method 158 fruit and vegetable samples grown in Jordan were analyzed for the detection of pesticide residues. Out of total samples, 73 (46%) had no detectable residues while 85 (54%) had residues. Out of the samples that were examined 34 (22%) had residues that were higher than the Maximum Residue Level MRLs and 51 (32%) had residues that were at or below MRLs. Samples of sweet peppers, peaches and apricots had the majority of the residues that were observed. Tomato and melon samples showed contaminants below MRLs, while only watermelon samples had no detectable residues. Out of 113 pesticides that were tested, 22 were found exceeding the limit of detection, nine of which (hexaconazole, propargite, propiconazole, myclobutanil, thiamethoxam, thiacloprid, clothianidin clofentezine and pyridaben) had residues that exceeded maximum residual limit MRLs according to European regulations. It is strongly advised to implement an ongoing pesticide residue monitoring program for Jordanian fruits and vegetables [26].

It is now possible to determine the presence of pesticide residues in fruits and vegetables using an extraction and analytical procedure. Ultra high Performance Liquid Chromatography linked to tandem mass spectrometry UPLC/MS/MS is the technology used for pesticide identification and quantification. The extraction process uses a pressurized liquid solvent that contains a mixture of 1,1,1,2-tetrafluoroethane and toluene. To assess the effectiveness of methods for identifying 71 distinct pesticides and their metabolites in tomato, cucumber, pepper, spinach, zucchini, grape, cherry, peach and apricot, validation experiments were carried out. After using matrix matched calibration curves, correlation coefficients were found to be higher than 0.99. The maximum residue limit MRLs as per Turkish laws were found to be higher than the limit of quantification (LOQ) values of active compounds. The results showed that the recovery values had relative standard deviations of less than 20% and ranges from 70% to 120%. These findings suggest that the suggested approach is quick, less expensive, robust and produces quantitative data without the need for further cleanup steps [27].

The aim of this study was to investigate the pesticide residue in Turkish Aegean fruits and vegetables. Between 2010 and 2012, a total of 1423 fresh fruit and vegetable samples were collected. The samples were analyzed to determine the concentration of 2 86 pesticide residue. Utilizing a multi residue extraction process (the Quenchers method), the analyses used Ultra High Performance Liquid Chromatography coupled with tandem mass spectrometry UPLC/MS/MS and gas chromatography with an electron capture detector (GC-ECD), confirmed by gas chromatography and mass spectrometry (GC-MS). The results were evaluated according to the maximum residue limits MRLs for each commodity and pesticide by Turkish regulations. Every sample of cabbage, cauliflower and pomegranates was free of pesticides. Out of 754 samples that had detectable residues at or below MRLs, 48 (8.4%) of the fruit samples and 83 (9.8%) of the vegetable samples had pesticide levels over MRLs. The commodities with the highest MRL values were grape, cucumber, lemon and arugula. In apricot, carrot, kiwifruit and leek every pesticide found was below the maximum residual levels. Carbendazim, chlorpyrifos, and acetamiprid were the most often found pesticide residues [28].

This study was carried out to evaluate the danger to human health associated with pesticide residue in vegetables. Therefore, residues from 23 pesticides (organophosphate, organochlorines, acaricides, fungicides and insecticides of biological origin) were examined in three main vegetable crops grown in Southern Nepal: 27 eggplants, 27 chili and 32 tomato samples representing (i) conventional (N=67) and (ii) integrated pest management (IPM) fields (N=19). 93 % of the eggplant samples and all of the tomato and chili samples contained pesticide residue. In the 56% of the eggplant, 96% of the chili samples and every tomato sample, multiple residues were found. The range of total pesticide residues found (μg/kg) in tomatoes, eggplants and chilies was 13.13465, 4.97-507, and 1.71 -231 respectively. These veggies were found to contain the greatest insecticides, carbendazim and chlorpyrifos. Pesticide residues exceeded EU maximum residue limit MRLs in 4% of the eggplant, 44% of tomato, and 19% of the chili samples. The EU MRLs were exceeded by the residues of triazophos, omethoate, chlorpyrifos, and carbendazim. Tomato crops received a higher dosage of carbendazim spraying (p0.005) in comparison to eggplant and chili crops. Hazard Index (HI) and Hazard Quotient (HQ) formula was used for the identification of pesticides to evaluate the dietary exposure of adolescents and adults. Chlorpyrifos, triazophos, dimethoate, omethoate, carbendazim, and profenofos in eggplant, dichlorvos and chlorpyrifos in chillies and dimethoate, carbendazim, and chlorpyrifos in tomatoes were all found to be at HQ > 1. The greatest acute HQ (aHQ) for triazophos (tomato) was found in adults (aHQ=677) and adolescents (aHQ=657) out of all the HQs, indicating the highest hazards for dietary exposure. A greater HI for organophosphates (HI >83) and a lower HI for organochlorines, acaricides, and biological insecticides (HI <1) were seen in cumulative dietary exposure. The IPM field's vegetable crops had significantly lower concentrations of pesticide residues, indicating that IPM systems are more effective at lowering the dangers that pesticide exposure poses to human health [29].

Sixty pesticides were analyzed in fruit and vegetable samples using a multiresidue approach based upon solid phase extraction cartridges for sample preparation and ultra-high performance liquid chromatography/ time of flight mass spectrometry (UHPLC/TOF-MS) for detection. It is possible to do UHPLC/TOF-MS quantitation by precisely determining the accurate mass of the protonated molecules [M+H] (+). Usually the mass accuracy is obtained to be better than 2 ppm. At concentrations below 10μgkg (-1) the pesticides recovery rates were found to be good, with a range of 74% to 111% and a relative standard deviation (RSD) of less than 13.2 %. For the majority of the chemicals the method limit of quantification (MLOQ) was lower than the MRLs set by the European Union and the Food Safety Standard Authority of India. Data from each pesticide's calibration, recovery and repeatability curves were used to calculate the uncertainty. The method illustrated is appropriate for routine quantitative studies of pesticides in food samples [30].

Globally all around the world in the last few years' exposure of human beings to heavy metals has gained significant importance as a critical health threatening problem. Due to the use of these heavy metals in different industrial processes as starting products human exposure to them has increased drastically. So, a study was conducted to find the concentrations of some selected heavy metals such as Lead, Zinc, Chromium, Nickel, Copper, Arsenic and Cadmium in various brands of the canned fruits and vegetables including canned ketchup (tomato sauce), canned whole carrots, canned juice for example pineapple, canned green beans imported to the Jordanian market were identified by the atomic absorption spectroscopy and acid digestion methods. For the collection of samples (11 samples of each type) the popular Jordanian markets, Irbid city, Northern Jordan were selected. The concentrations of the metals in the samples tested were observed to be in the range of 0.50-0.60 mg/kg for Cadmium, 2.6-3.0 mg/kg for Lead, 0.84-0.91 mg /kg for Copper, 2.50-5.10 mg/kg for Arsenic, 0.66-1.71 mg/kg for Chromium, 0.32-3.02 mg/kg for Zinc and 0.97-2.94 mg/kg for Nickel. The results collected revealed that Lead and Arsenic were found to be having the highest concentrations in the mostly analyzed samples whereas mainly in Cadmium the concentrations were found to be lowest. In canned tomato sauce for example the mean concentrations of the heavy metals are 1.02 mg /kg for Zinc, 2.95 mg/kg for Lead, 1.15 mg/kg for Nickel, 0.89 mg/kg for Copper, 0.66 mg/kg for Chromium, 0.50 mg/kg for Cadmium, and 3.50 mg/kg for Arsenic. The conclusions drawn by this study pointed out that the concentration of some heavy metals such as Lead, Chromium, Nickel, Arsenic and Cadmium in canned fruits and vegetables samples being sold in the markets of Jordan were found to exceed the permissible limits as set by the various health organizations [31].

Similarly, in one more study, the concentration of almost twenty-seven toxic heavy metals and mineral elements have been identified in almost fifty-five samples of corresponding and canned fresh food for the comparison purpose. These samples out of which thirty are canned and the rest being fresh food were taken from the various local markets of the western district of Saudi Arabia. For precise, accurate and reliable measurements ICP-AES (Inductively Coupled Plasma -

Atomic Emission Spectrometer) has been put into practice for the quantification of the studied metal levels present in food samples after digestion by making use of the microwave system. The obtained results indicated that the average ranges of the analyzed elements in mg/kg -1 between the canned and fresh food are reported to be as follows: Sodium (Na) 9918-23787, Magnesium (Mg) 16691206, Calcium (Ca) 1611-8557, Copper(Cu)6.22-8.03, Zinc(Zn)24.14-26.76, Lead (Pb) 2.31-7.11, Manganese (Mn) 11.73-17.95, Aluminum (Al) 6.63-41.14, Iron (Fe) 34.35-164.1 respectively. Some of the measured and observed values were found to be not only relatively higher in canned foods as compared to the fresh food samples but also found to be exceeding the international tolerance levels. The monitorization of heavy metals and minerals in canned food along with fresh food items is a critical challenge in controlling and improving the strategies of the food industry [32].

Worldwide the safety of food is a major concern as human beings are more frequently exposed to PTMs (Potentially Toxic Metals) by consuming cereal crops, fruits and vegetables growing in areas contaminated with a variety of pesticides. The current study aims to investigate the concentrations of Potentially Toxic Metals for example Cr(Chromium), Ni(Nickel), As(Arsenic), Cd(Cadmium), and Pb(Lead) present in the food items such as cereals, vegetables and fruits taken from various markets of Khyber Pakhtunkhwa province of Pakistan. Fruit samples such as tangerine, onion, tomato, lady finger, peas and potato along with cereals such as chickpeas, kidney beans and rice were analyzed and acidically extracted by making use of ICP -MS technique. The concentrations of Chromium, Zinc, Lead, Arsenic and Cadmium were found to be 54, 50, 50, 45, and 4% of the samples respectively whereas in vegetables found to be 53, 43, 63, 80, and 46%respectively and moreover in cereals found to be 37, 62, 25, 70 and 25% exceeding the respective permissible limits as set by the Food and Agriculture Organization /World Health Organization (FAO/WHO) in 2001. The findings indicated that the highest average concentration was found to be for Cadmium (CD) 0.27mg/kg, Lead(Pb) 0.57mg/kg, and Nickel (Ni) 14.95mg/kg in vegetables followed by cereals and fruits. Moreover, the highest average concentration of Arsenic (As) 0.44mg/kg was indicated in cereal crops followed by fruits and vegetables. The Potentially Toxic Metals imposing their individual health risk through cereals, fruits and vegetables intake was observed within safe limits for children and adults. Although the total Health Related Items (HRI) values for Nickel(Ni), Arsenic (As) and Cadmium

(CD) for both children and adults were found to be less than 1 and might have imposed serious potential risk to the community consuming these foods on a regular basis [33].

In another study, 135 canned tomato paste samples and 30 of tomato sauces such as ketchup samples with 23 of paste and 10 of ketchup of different brands respectively were purchased in Tehran, Iran from the wholesale marketplaces during the period 2010 - 2013 for analysis and testing. Cadmium and Lead levels were identified by GF-AAS (graphite furnace atomic absorption spectrometer) and HG-AAS or VGA (Mercury absorption spectrometer and Video Graphics Array). The arsenic 's average concentration found to be in tomato paste and ketchup samples was 62± 14 and 48± 12 ng-1, respectively. The values of Cadmium in almost 7 percent of the tomato paste and the 10 percent of the ketchup samples were found to be below the standard limit of quantification (LOQ). Lead concentrations were found to be below the limit of quantification in almost 75 %of the tomato paste and 77 %of the ketchup samples. Values observed for these heavy metals in all the samples were lower than the standard international and national limits [34].

Fruits and vegetable samples were collected from the markets of Al- Karak, Jordan. Atomic Absorption Spectrometry was used to evaluate the concentrations of specific hazardous metals (Pb, Ni, Cd, and Cr) in digested samples of various commonly consumed fruits (banana, orange and apple) and vegetables (green pepper, cucumber, potato, onion and tomato). According to the findings, samples Pb, Ni, Cd, and Cr contents differed greatly. The analysis of the samples revealed that the Pb, Ni, Cd, and Cr contents ranged from 0.33 to 1.00 µg/g-dw, 0.81 to 2.13 µg/g-dw, 0.07 to 1.25 µg/g-dw and 0.81 to 2.43 µg/g-dw in that order. Pb (1.0 µg/g-dw) and Cd (1.25 µg/g-dw) has the greatest mean levels in potatoes, whereas apple had the lowest values (0.33 µg-Pb/g-dw and 0.07 µg-Cd/g-dw). Green pepper and banana had the lowest quantities of Ni (0.81 µg/g-dw) and Cr (0.81 µg/g-dw) respectively, whereas orange had the highest levels of Ni (2.13 µg/g-dw) and Cr (2.43 µg/g-dw) bioaccumulation. It was discovered that the most prevalent metals in all the examined samples were within the safe range for human consumption, the level of Pb, Cd and Cr in all the samples exceeded the maximum allowable amounts of heavy metals as advised by FAO/WHO [35].

Another study was conducted that used multivariate approaches to evaluate and compare the essential and heavy metal levels of 98 fresh fruits that came from various geographic locations that were sold commercially. Using flame atomic absorption spectrometry with deuterium background correction, the amount of twelve elements (calcium, magnesium, potassium, sodium, phosphorus, sodium, cobalt, manganese, iron, chromium, nickel, zinc and copper) were ascertained. A spectrophotometric technique was used to determine the phosphorus in the form of phosphomolybdate. The procedure's reliability was verified by analyzing the certified reference materials tea (NCS DC 73351), cabbage (IAEA-359) and spinach leaves (NIST-1570). The precisions for the reference materials ranged from 0.13 to 6.08 percent, whereas the recoveries of the elements analyzed varied from 85.5 to 103%. Based on recommended dietary allowance and adequate intake estimated for essential elements, it was determined that accessory fruits such as strawberries, raspberries, and pineapples provide the maximum amounts of bio elements to the organisms. Despite the fact that among all the fruits examined accessory fruits were also shown to be the best source of Ni, Ni was discovered to be more prevalent in all the fruits than Cr and Co. Between the quantities of certain metals in fresh fruits , significant correlation coefficients ($p < 0.001$, $p < 0.01$, and $p < 0.05$) were discovered and were able to distinguish between distinct fruit varieties and botanical families by using multivariate approaches like factor analysis and cluster analysis in conjunction with the ANOVA Kruskal-Wallis test [36].

Using X-ray fluorescence (XRF) spectrometry, the concentration of heavy metals in the top and subsoil as well as in specific fruits and vegetables growing in the abandoned Enyigba lead zinc mine was examined. Arsenic (Ar), Chromium (Cr), Cadmium (Cd), Copper (Cu), Manganese (Mg), Lead (Pb), and zinc (Zn) contents were measured in samples of fruits and leaves of the plant under study over a two-year period (2008-2010). Corresponding Pollution Indices (PI) and Bioaccumulation Factors (BAF) were also assessed. The average soil pH was determined to be 6.5, and the average metal concentrations measured in mg/kg in plants under investigation were Pb (0.22 - 6.72), As (0.10 -10.6), Cd (0.10 - 12.4), Cu (12.6 - 82.1), Cr (0.01- 1.02), Zn (34.2 - 162.1), Mn (412.1 - 42.6) and Ni (12.8 - 72.8). High pollution indices of 22.4, 12.37, 8.67, 7.27, and 6.13 were observed in *Nauclea latifolia* (African Peach), Sesamum *indicum* (Beni seed), *Lactuca Sativa* (Lettuce), *Psidium Guajava* (Guava) and *C. Annum* (Pepper). As a result, they were deemed unfit for human consumption. Some of the plants under study showed bioaccumulation factors (BAF > 1), indicating that they might make effective phytoremediation agents. ANOVA or statistical analysis of variance, was used to detect differences in level of heavy metals across and within groups. Fisher's Least Significant Difference (LSD) correlation analysis revealed a substantial correlation between the soil samples and the plant under investigation [37].

Information about heavy metal concentrations in food products and their dietary intake are essential to determine how much health risk the population is facing. The current study's main goals were to determine the levels of zinc, copper, lead and mercury in various fruits and vegetables grown in the Baia Mare mining area (Romania), compute the daily intake rate (DIR) and target hazard quotient (THQ) to estimate the risk to human health associated with eating contaminated fruits and vegetables and develop dietary guidelines to ensure improved food safety. Zn>Cu>Pb>Cd was the heavy metal concentration order found in the examined vegetable and fruit samples. The findings indicated that as compared to fruits (4.9 - 55.9 mg/kg dw for Zn), 1.9 - 24.7 mg/kg dw for Cu, 0.04 - 8.83 mg/kg dw for Pb, and 0.01 - 0.81 mg/kg dw for Cd, vegetables have a higher likelihood of accumulating heavy metals 10.8 - 630.6 mg/kg dw for Zn, 1.4 - 196.6 mg/kg dw for Cu, 0.2 - 1.55.7 mg/kg dw for Pb, and 0.03 - 6.61 mg/kg dw for Cd. It was found that lettuce, kohlrabi, and parsley were excellent heavy metal accumulators. By calculating DIR and THQ the data showed that regular consumption of parsley, kohlrabi, and lettuce from the area may present a high risk to the health of the local population, particularly in the area near the tailings ponds of Tăuţii de Sus and the non ferrous metallurgical plants Romplumb SA and Cuprom SA. While the DIR for Pb (0.6 - 3.1 μg/day kg body weight) and Cd (0.22 - 0.82 μg/day kg body weight) was higher in urban areas near the non ferrous metallurgical plants SC Romplumb SA and
SC Cuprom SA, it was higher in rural areas for Zn (85.3 - 231.6 μg/day kg body weight) and Cu (25.0 - 44.6 μg/day kg body weight). For <1, <1, 12 and 6% of samples, the THQ for Zn, Cu, Pb, and Cd was greater than 5, indicating that those consumers may be at serious risk for health problems [38].

The research on the concentrations of certain heavy metals and gamma radioactive elements in fruits, vegetables and plants from the Lublin town agglomeration are reported in this study. Out of all the samples studied, the potassium 40K isotope was the most abundant. It was primarily concentrated in the above ground portions of certain crops, such as the leaves of red beetroot and leek, as well as the carrot and parsley stalk (from 1135 to 1940 Bq/kg). Vegetable roots showed a noticeably lower content of this element, ranging from 210 to 448 Bq/kg of the dry matter. The 40K levels in the fruit under examination varied from 490 to 510 Bq/kg. 40K transfer coefficients varied from 0.3 to 2.9 from the soil to the fruit and vegetables. About 17% of the overall activity is provided by the naturally occurring isotopes in the uranium series, whereas 19-20% is provided by the thorium series. In fact, cesium 137 Cs was not found in raspberry, red and black currants or the vegetable roots under examination, although it was found in trace amounts in the green sections of the vegetables (4.0 to 8.4 Bq/kg of the dry matter). The range of the 137 Cs transfer factor from the soil to the samples under examination was 0.03 to 0.4. No legitimate safety criteria were exceeded for any of the heavy metal contents in any of the samples that were evaluated [39].

Foodborne chemical contamination presents a serious concern to the consumers. Consuming products contaminated with heavy metals like lead (Pb), and cadmium (Cd) is a source to increase risk. The main goal of the study was to investigate the amounts of lead and mercury contamination in specific fruit and vegetable species that are fresh, processed, frozen, and dried and finding out which of these food groups had higher levels of heavy metal contamination. A total of 370 fruit and vegetable samples were examined in the study including beetroot, celery, carrots, tomatoes, apples, pears, grapes, raspberries, strawberries and cranberries. The atomic absorption spectrometry was used to determine the amounts of Pb and Cd. Statistical models, such as analysis of variance, outlier analysis and post hoc multiple comparison Tukey test, were used to analyze the quantitative data. The result of the testing demonstrated that there were significant differences in the concentrations of Cd and Pb in the samples of dry, frozen, processed and fresh fruits and vegetables. Dried items had the highest amounts seen in the data. A number of fruit and vegetable samples had the levels of Cd and Pb over the maximum allowable limit. When these products are consumed, the contamination of these goods may be a major cause of heavy metal exposure for consumers [40].

CHAPTER III

METHODOLOGY

For the quantification of pesticides and heavy metals in canned fruits and vegetables following steps for methodology were adopted i-e from data collection to lab analysis which are further described in detail.

3.1 Data Collection

The data collection was done in following steps

1. Secondary data
2. Primary data
3. Sample Collection
4. Sample preparation

The data that was gathered consisted of literature review. The aim of this study was to determine how using certain types of canned fruits and vegetables impact consumers' general health.

3.2 Selection of Study Area

Firstly, a study area was chosen for the collection of samples of canned fruits and vegetables. Grocery Stores and markets made up the chosen study area. The samples were collected from the retailers Al- Fatah, Risen Cash and Carry and Imtiaz super store.

3.3 Collection of Samples

Canned fruits and vegetables samples were taken from the regional market in the study area from adjacent local markets of Lahore. Table **3.1** showing the name and sources of samples.

Table 3.1 Canned fruits and Vegetable samples from the source and brands

Location	Sample No	Brand name	Type of sample	Brand type
Risen store	V1	Dew Drop	Sweet corn	International
Al Fatah store	V2	Green Farm	Green peas	International
Risen store	V3	Nature's home	Mushroom	International
Risen store	V4	Dew Drop	Green Olives	International
Risen store	V5	Nature's home	Red Kidney beans	International
Risen store	V6	Dew Drop	Garlic clove	International
Risen store	V7	Dew Drop	Red Chilli	International
Risen store	V8	Dew Drop	Cauliflower	International
Risen store	V9	Dew Drop	Carrot	International
Risen store	V10	Dew Drop	Lemon	International
Al Fatah	V11	Shezan	Peach	International
Al Fatah	V12	Shezan	Grapes	International
Al Fatah	V13	Shezan	Pear	International
Risen store	V14	Malapine	Pineapple	International
Risen store	V15	Cresco	Red Cherry	Local
Risen store	V16	Malapine	Papaya	International
Imtiaz super store	V17	Arizona fields	Lychee	Local

3.4 Lab Analysis

To measure the amount of pesticides and heavy metals residue in canned fruits and vegetables samples were taken to the lab.

3.5 Analysis for Pesticide Detection

High Performance Liquid Chromatography **(HPLC)** method was used for the detection of pesticides in canned fruits and vegetables.

Table 3.2 Detected pesticide with chemical formula

Sr No	Pesticide	Formula
1	Glyphosate	$C_3 H_8 NO_5 P$
2	Bifenthrin	$C_{23} H_{22} ClF_3 O_2$
3	Imidacloprid	$C_9 H_{10} ClN_5 O_2$
4	Difenoconazole	$C_{19} H_{17} Cl_2 N_3 O_3$

Equipment used: Equipment used for the preparation of samples were Round bottom flask, separating funnel, Funnel, Stirrer (simple and magnetic), beakers, hot plate, filter paper, flask, tripod stand and measuring cylinder.

Chemical used: Chemical used for the preparation of samples were Ethyl acetate, Dichloromethane, Distilled water, Sodium chloride, Sodium anhydrous sulfate and methanol.

3.6 Pesticide Analysis Procedure

Firstly, 5 grams of each sample were taken and placed in a round bottom flask. Then, 20 ml each of dichloromethane and ethyl acetate were added. Furthermore, 5 grams of sodium chloride (NaCI) was added to this mixture, along with another 150 ml of distilled water. This round bottom flask was then placed on a hot plate and given 15 minutes to thoroughly mix. The solution within the round bottom flask was transferred to a separate funnel after 15 minutes. The separating funnel was shaken after the solution had been added to ensure that the ingredients were thoroughly mixed. The mixture in the separate funnel was then let to stand until two different layers, the aqueous layer and the organic layer, had formed. They were then separated into flasks after the layers had formed. The aqueous layer was then returned to the separating funnel, where 20ml each of ethyl acetate and dichloromethane was added. This mixture was shaken again, and it was given time in the separate funnel to form two layers. Again, the organic and aqueous layers were separated and collected in separate flasks. Following that, the first and second collected organic layers were combined and filtered out in a separate flask. Anhydrous sodium sulfate was added to the filtered solution in order to eliminate any remaining water content as anhydrous sodium absorbs water. After that, this solution was once again filtered in a separate flask or beaker before being sent to the rotary evaporator to finish drying. Once it had all dried, 10 ml of methanol was mixed, and the solution was transported to and stored in a vial for further HPLC analysis.

3.7 Heavy Metal Analysis

3.7.1. Standard Preparation

Heavy metals that were analyzed in this study include chromium, zinc, copper, cobalt and manganese. The stock solution was prepared from a metal salt containing that specific metal. The salts used for the metals are given below in the table.

Table 3.3 List of metals and salts

SR no	**Metal**	**Metal salt**	**Chemical Formula**
1	Chromium	Potassium Dichromate	$K_2Cr_2O_7$
2	Zinc	Zinc Sulphate Heptahydrate	$ZnSO_4.7H_2O$
3	Copper	Copper II Sulphate	$CuSO_4$
4	Cobalt	Cobalt nitrate	$Co (NO_3)2$
5	Manganese	Manganese II Sulphate	$MnSO_4$

The amount of salt used for the preparation of the stock solution, was calculated by using a formula given below.

$X/Y \times 1000 = Z$ mg

Here,

X = Molecular Weight of the Salt

Y = Atomic Weight of the Metal

Z= Amount of salt in Milligrams

The stock solution of 1000 ppm was prepared, once the amount of salt is determined further it will be dissolved in 1000 ml of distilled water. Small quantities of solution will be taken with the help of pipette and diluted with 100ml of distilled water to produce a standard of desired ppm level.

3.7.2. Sample Preparation

By using hydrogen peroxide, distilled water and nitric acid two solutions were prepared for the sample. Solution A contained 30 ml of hydrogen peroxide and 70 ml of distilled water whereas solution B contained 50 ml of nitric acid and 50 ml of distilled water. After the preparation of these solutions, one gram of each fruit and vegetable sample was taken in a flask and 5 ml of solution A, 5 ml of solution B and 10 ml of deionized water were added to it. This mixture was then shifted into a round bottom flask and placed in a beaker containing silica gel. To keep the round bottom flask stable a thermocol sheet was cut down to form support and a lid.

Table 3.4 Equipment and Chemical used

Equipment	1000ml Volumetric flasks, 5 and 10 ml Pipette, Weighing machine, Spatula, 100 ml volumetric flasks, 50 ml Round bottom flasks, 100 ml Measuring cylinder, 50ml and 500ml Beakers, Thermocol sheet, Microwave
Chemicals	Metal salts, Nitric acid, Hydrogen peroxide, Deionized water, Distilled water

3.7.3. Microwave Digestion

EPA method number 3015A is applied with few modifications according to the lab conditions and conditions are fully optimized by peers. Microwave digestion was applied on the samples made under specific conditions and requirements. Once the solution of heavy metals was made, then the flask containing the beaker was microwaved for 40 seconds to digest the solution.

However, after every 10 seconds the flask was taken out and allowed to cool down. Once digested the solution was filtered and shifted into a volumetric flask and diluted with 100ml of distilled water. Required amount of solution is then poured in the vial for further analysis by atomic absorption.

Note: The gap of every 10 seconds is must in the digestion process due to the use of acid, bursting can occur. The cork usually bursts out of a not given gap or any other explosion.

3.7.4. Atomic absorption

EPA method number 7000B was applied for the atomic absorption process. The model of atomic absorption spectrometer used was 210VGP. Its detector range is 190-930m with acetylene air flame. The use of atomic absorption spectroscopy determined the concentration of heavy metal in each sample. AAS determines the chemical elements using absorption of optical radiation or light vy presence of free atoms in gaseous state, it is quantitative analysis of elements. AAS was used for Zn, Cr, Mn, Co and Cu. To avoid any hazards or loss of analytes the chemical modifiers were very helpful in any step or decrease of matrix effects. Different matrix modifiers were used for different heavy metals.

3.8. Formula used for Quantitative Analysis

The formula used for quantitative analysis of canned fruit and vegetable samples is given as:

Response Factor = Peak Area of Standard/ Standard Amount

Amount of Standard in Sample = Peak Area of Sample/ Response Factor (eq i)

3.9. Formula used for Health Risk Index

Health risk index is calculated by the given formula

HRI= estimated daily intake/acceptable daily intake

HRI = EDI/ADI

Where, estimated daily intake = concentration of detected pesticide × food consumption /body weight kgs (eq ii)

The average daily intake of vegetables by adults was considered 0.35 kgs and the average daily intake of fruits by adults was considered 0.4 kgs.

Body weight of adults was considered 60kgs.

3.10. Data Analysis

The collected samples were compiled and presented by graphical illustrations.

3.11. Results, Discussion and Conclusions

Results were deducted, critical analysis of data was done in discussion and in the end conclusion was drawn

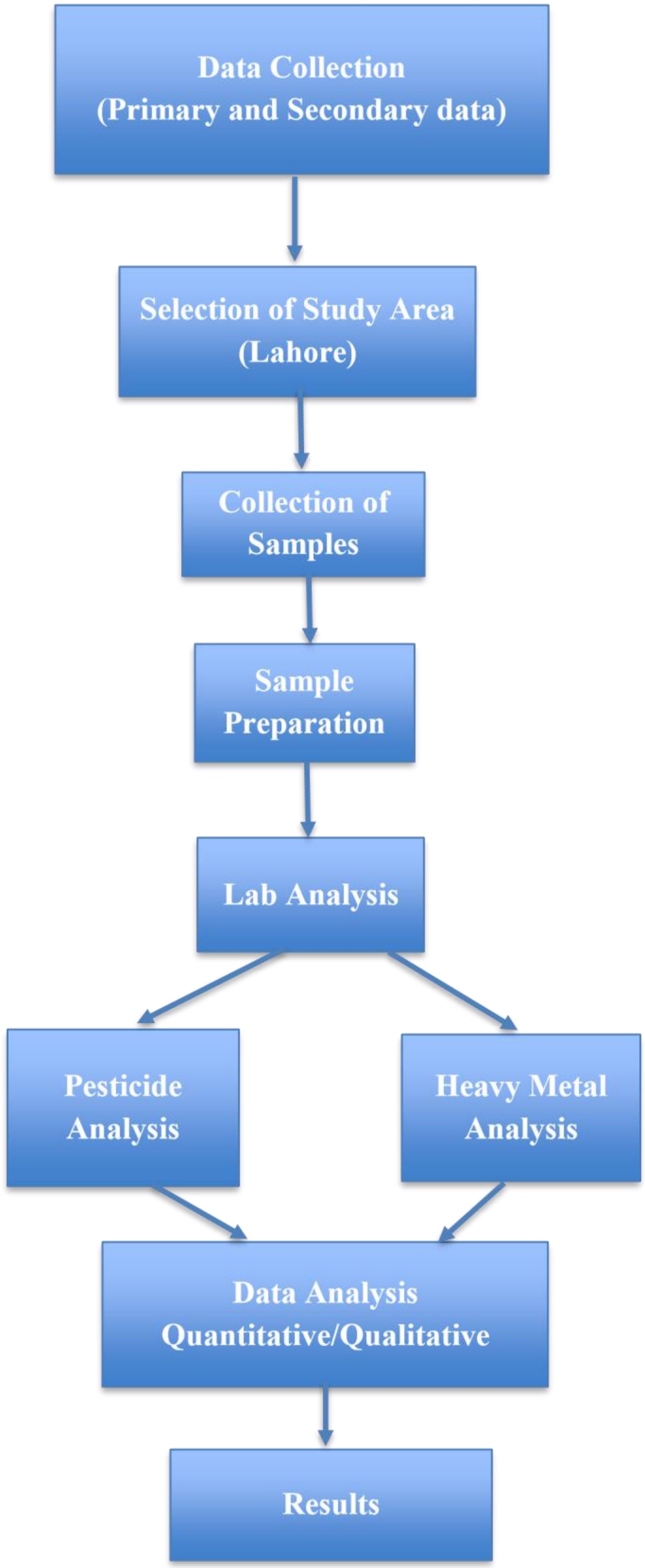

Figure 3.1 Flow Diagram of Methodology

CHAPTER IV

RESULTS

4.1 Results of Pesticide Analysis

To determine the pesticide content present in the selected samples, a pesticide analysis was conducted using HPLC. The pesticide detected was glyphosate, bifenthrin, imidacloprid and difenoconazole Figure 4.1, 4.2, 4.3, 4.4 shows a chromatogram of standards of pesticides and table 4.1, 4.2, 4.3, 4.4 is showing peak values of the standards of the pesticides.

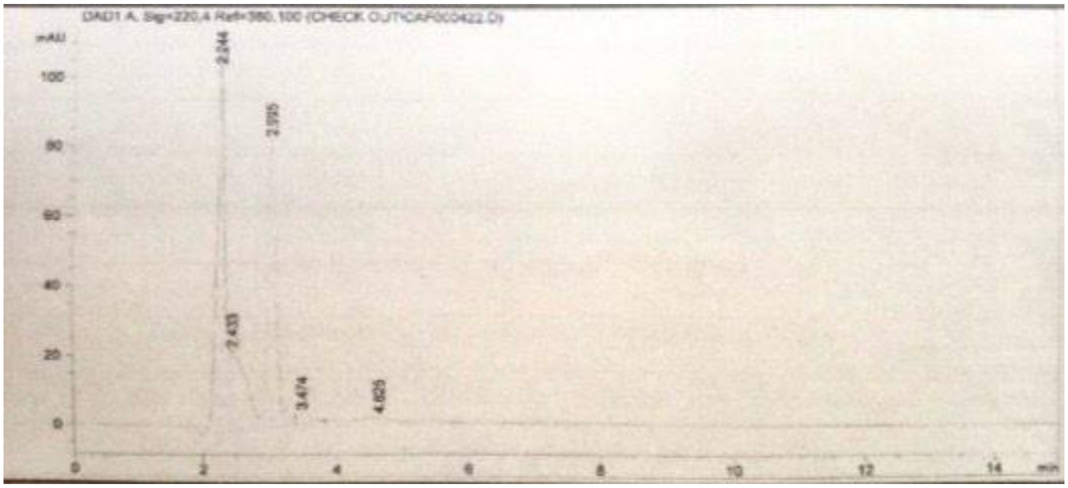

Figure 4.1 Chromatogram of Glyphosate showing peak values

Table 4.1 Standard values Glyphosate pesticide showing peaks

Peak #	Ret time (min)	Type	Width (min)	Area (mAU *s)	Heigh (mAU)	Area %
1	2.24	B V	0.11	913.09	110.51	44.63

2	2.43	VV	0.22	368.26	23.07	18.00
3	2.99	VV	0.12	720.353	84.44	35.21
4	3.47	VB	0.16	33.30	2.72	1.62
5	4.62	VB	0.13	10.72	1.13	0.52
Total				**2045.74087**	**219.89526**	

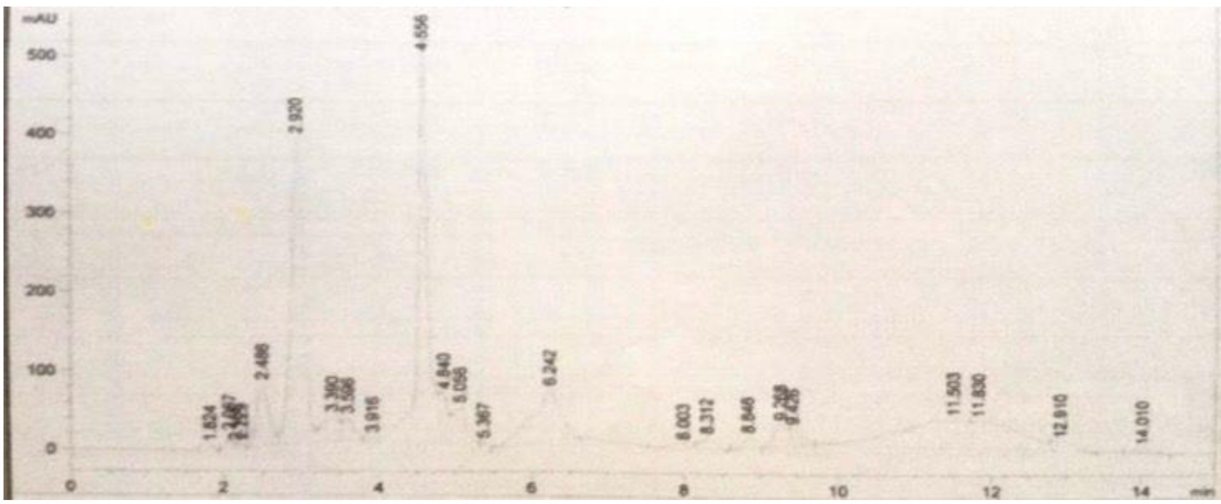

Figure 4.2 Chromatogram of Bifenthrin showing peak values

Table 4.2 Standard values of Bifenthrin showing peaks

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	1.82	BB	0.09	30.98	5.64	0.16
2	2.06	BV	0.05	72.88	18.95	0.39
3	2.15	VV	0.04	13.68	4.32	0.07
4	2.22	VB	0.05	17.37	4.43	0.09

5	2.48	BV	0.16	867.61	78.15	4.64
6	2.92	VV	0.17	4326.41	389.16	23.18
7	3.39	VV	0.22	502.84	31.37	2.69
8	3.59	VB	0.13	254.84	28.18	1.35
9	3.91	BB	0.08	24.42	4.65	0.13
10	4.55	BV	0.12	4735.81	521.68	25.37
11	4.84	BB	0.10	441.96	62.84	2.36
12	5.05	VB	0.17	528.55	45.50	2.83
13	5.36	BB	0.08	12.80	2.39	0.06
14	6.24	BB	0.35	1783.83	65.47	9.31
15	8.00	BV	0.37	134.74	5.71	0.72
16	8.31	VB	0.18	172.38	13.52	0.92
17	8.84	BB	0.15	149.80	14.92	0.80
18	9.26	BV	0.19	3607128.26	28.26	1.93
19	9.42	VB	0.15	211.89	21.58	1.13
20	11.50	BV	0.77	2189.21	35.78	11.73
21	11.83	VV	0.65	1553.26	35.13	8.32
22	12.91	VB	0.28	225.68	11.68	1.20
Total				**1.866606 e^4**	**1434.73702**	

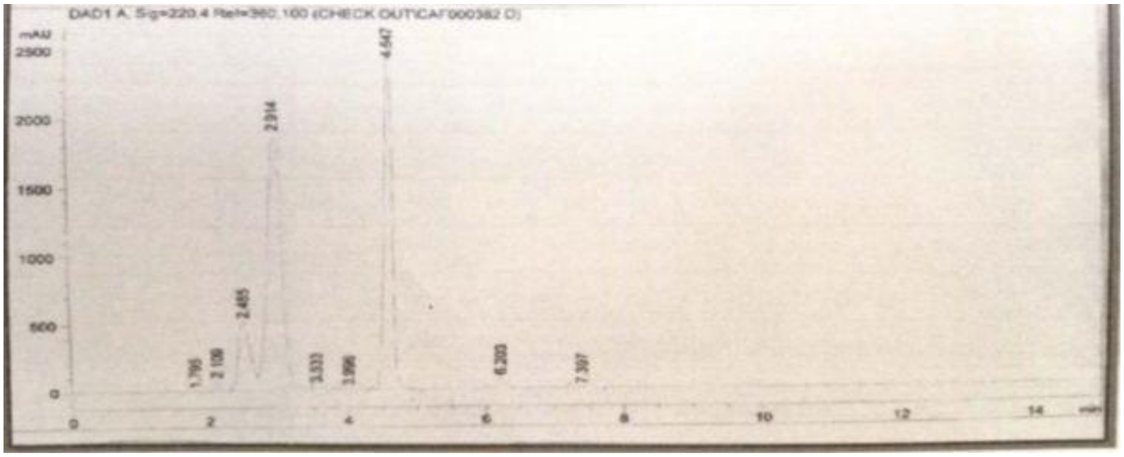

Figure 4.3 Chromatogram of Imidacloprid showing peak values

Table 4.3 Standard values of Imidacloprid pesticide showing peaks

Peak #	**Ret time (min)**	**Type**	**Width (min)**	**Area (mAU*s)**	**Height (mAU)**	**Area %**
1	1.79	BB	0.09	13.05	2.29	0.02
2	2.10	BB	0.06	324.92	74.27	0.59
3	2.48	BV	0.18	6071.84	513.27	11.14
4	2.91	VV	0.22	2.68	1884.20	49.19
5	3.53	VB	0.13	240.68	24.27	0.44
6	3.99	BB	0.17	33.38	2.92	0.06
7	4.54	BB	0.12	2.03	2546.50	37.37
8	6.20	BB	0.13	618.34	71.56	1.13
9	7.039	BB	0.14	14.53	1.49	0.02
Total				**5.44878e^4**	**5120.82236**	

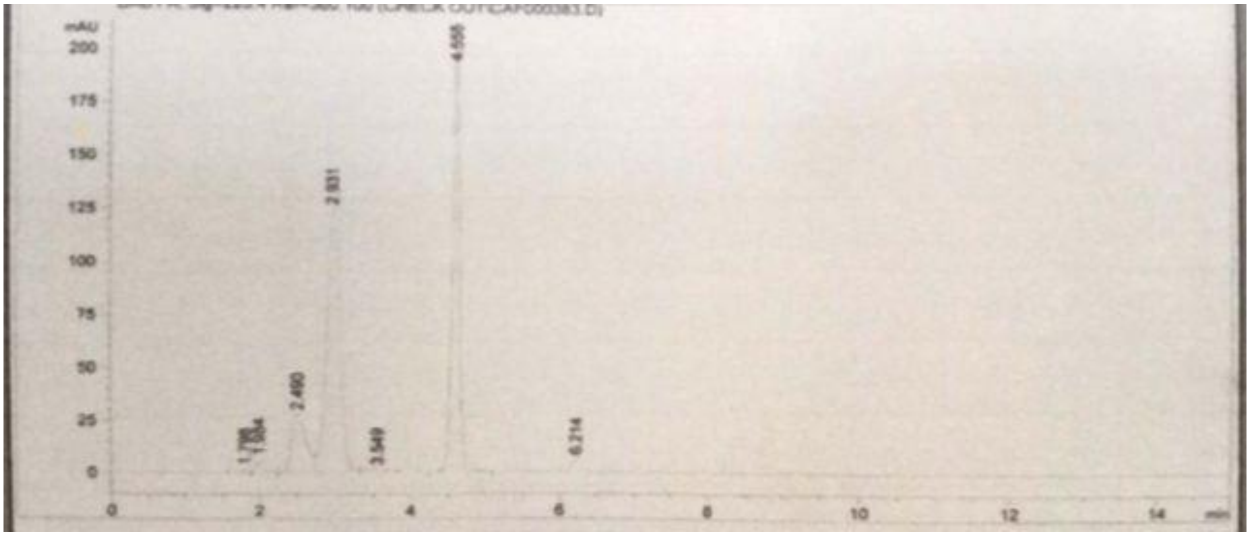

Figure 4.4 Chromatogram of Difenoconazole showing peak values

Table 4.4 Standard values of Difenoconazole pesticide showing peaks

Peak #	**Ret time (min)**	**Type**	**Width (min)**	**Area (mAU*s)**	**Height (mAU)**	**Area %**
1	1.79	BB	0.07	9.40	1.94	0.28
2	1.98	BB	0.07	34.45	6.58	1.05
3	2.49	BV	0.19	365.43	27.86	11.21
4	2.39	VB	0.17	1441.07	124.57	44.24
5	3.54	BB	0.16	13.38	1.05	0.41
6	4.55	BB	0.09	1339.83	203.60	41.13
7	6.21	BB	0.13	53.67	6.15	1.64
Total				**3257.25624**	**371.78160**	

Table 4.5 Quantitative Analysis of Pesticides

Sample ID	Glyphosate (ppm)	Bifenthrin (ppm)	Imidacloprid (ppm)	Difenoconazole (ppm)
V1	0.4	0.007	0.006	0.025
V2	0.3	0.007	0.005	0.021
V3	0.15	0.008	0.15	0.67
V4	0.21	0.11	0.003	0.13
V5	0.6	0.008	0.009	0.039
V6	0.60	0.005	0.009	0.3
V7	0.3	0.005	0.005	0.023
V8	0.66	0.007	0.10	0.042
V9	0.34	0.008	0.005	0.022
V10	0.65	0.0092	0.009	0.416
V11	0.195	0.0069	0.29	0.123
V12	0.21	0.005	0.003	0.133
V13	0.39	0.158	0.006	0.25
V14	0.024	0.006	0.003	0.015
V15	0.039	0.005	0.005	0.25
V16	0.0179	0.007	0.002	0.11
V17	0.0186	0.171	0.002	0.11
MRL	**0.1**	**0.01**	**0.01**	**0.05**

Table 4.6 Qualitative analysis of Pesticides

Sample ID	Glyphosate (ppm)	Bifenthrin (ppm)	Imidacloprid (ppm)	Difenoconazole (ppm)
V1	✔	✔	✔	✔
V2	✔	✔	✔	✔
V3	✔	✔	✔	✔
V4	✔	✔	✔	✔
V5	✔	✔	✔	✔
V6	✔	✔	✔	✔
V7	✔	✔	✔	✔
V8	✔	✔	✔	✔
V9	✔	✔	✔	✔
V10	✔	✔	✔	✔
V11	✔	✔	✔	✔
V12	✔	✔	✔	✔
V13	✔	✔	✔	✔
V14	✔	✔	✔	✔
V15	✔	✔	✔	✔
V16	✔	✔	✔	✔
V17	✔	✔	✔	✔

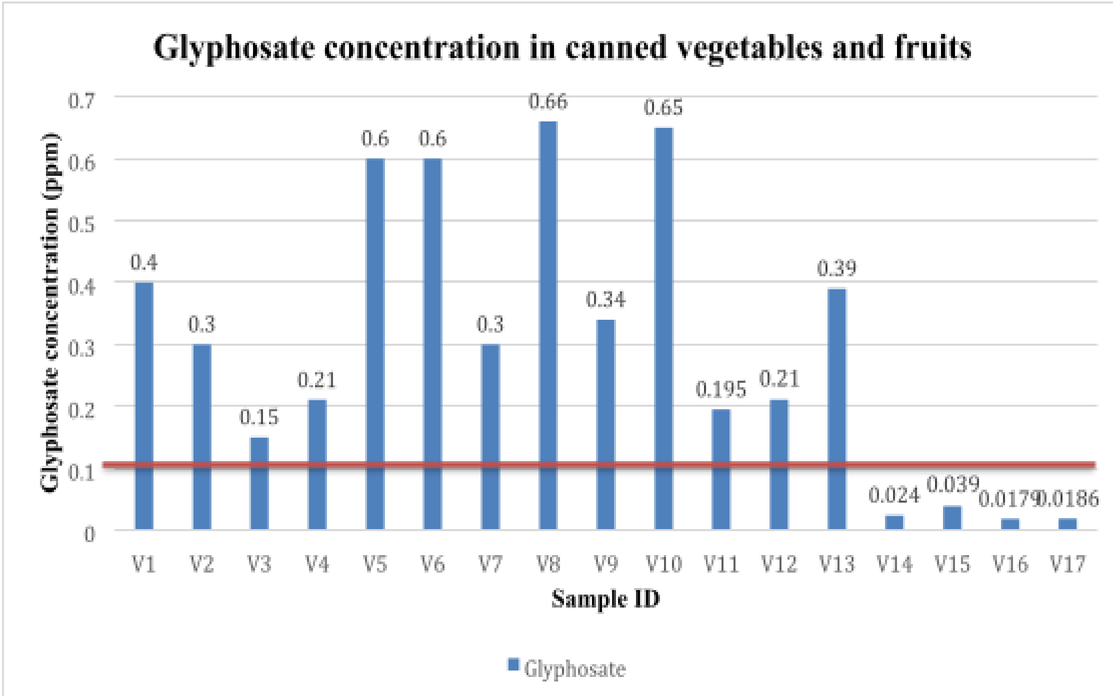

Figure 4.5 Glyphosate concentration in canned vegetables and fruits

The figure 4.5 illustrates that vegetable samples sweet corn **(V1)**, green peas **(V2)**, mushroom **(V3)**, green olives **(V4)**, red kidney beans **(V5)**, garlic clove **(V6)**, red chilli **(V7)**, cauliflower **(V8)**, carrot **(V9)**, lemon **(V10)**, and fruit samples peach **(V11)**, grapes **(V12)** , pear **(V13)** for glyphosate are exceeding the MRL values but no sample posed health risk to the consumers while fruit samples pineapple **(V14)**, red cherry **(V15)**, papaya **(V16)**, lychee **(V17)** didn't exceed the MRL values.

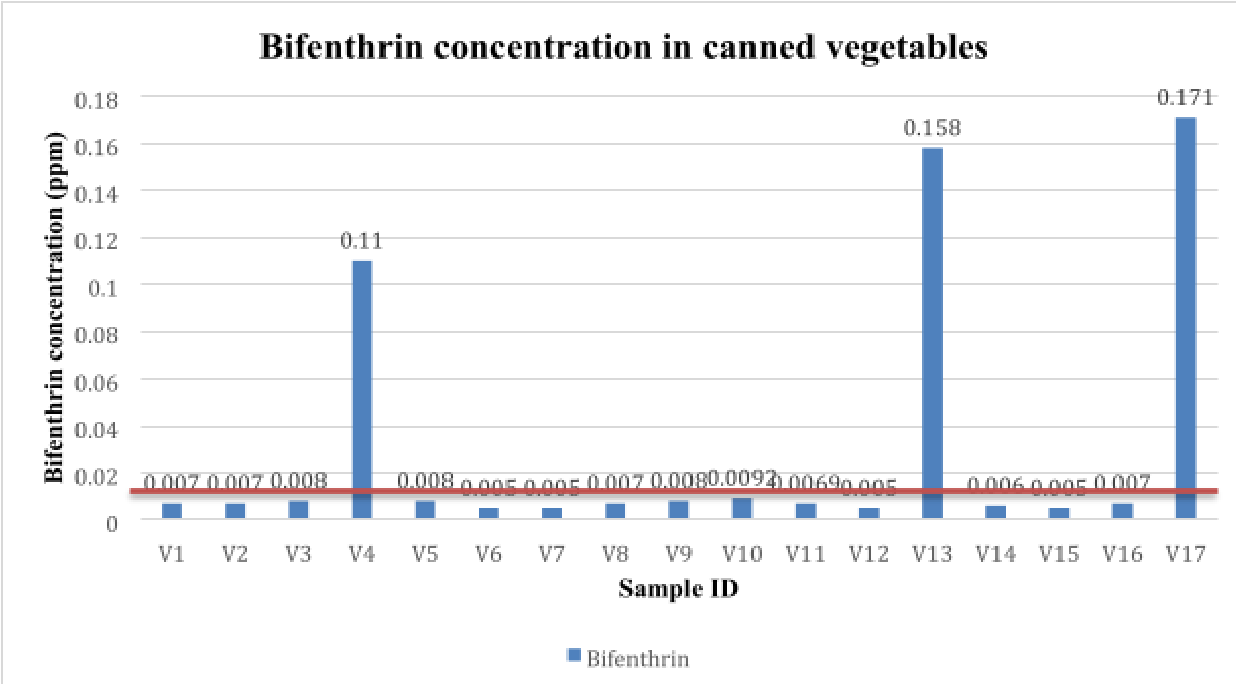

Figure 4.6 Bifenthrin concentration in canned vegetables and fruits

The figure 4.6 shows that vegetable sample green olives **(V4)** and fruit samples pear **(V13)**, lychee **(V17)** for bifenthrin were exceeding the MRL values but no health risk was posed to the consumers. While vegetable samples sweet corn **(V1)**, green peas **(V2)**, mushroom **(V3)**, red kidney beans (**V5)**, garlic clove **(V6)**, red chilli (**V7)**, cauliflower (**V8)**, carrot **(V9)**, lemon **(V10)** and fruit samples peach **(V11)** , grapes **(V12)**, pineapple **(V14)**, red cherry **(V15)**, papaya **(V16)** were below the MRL values.

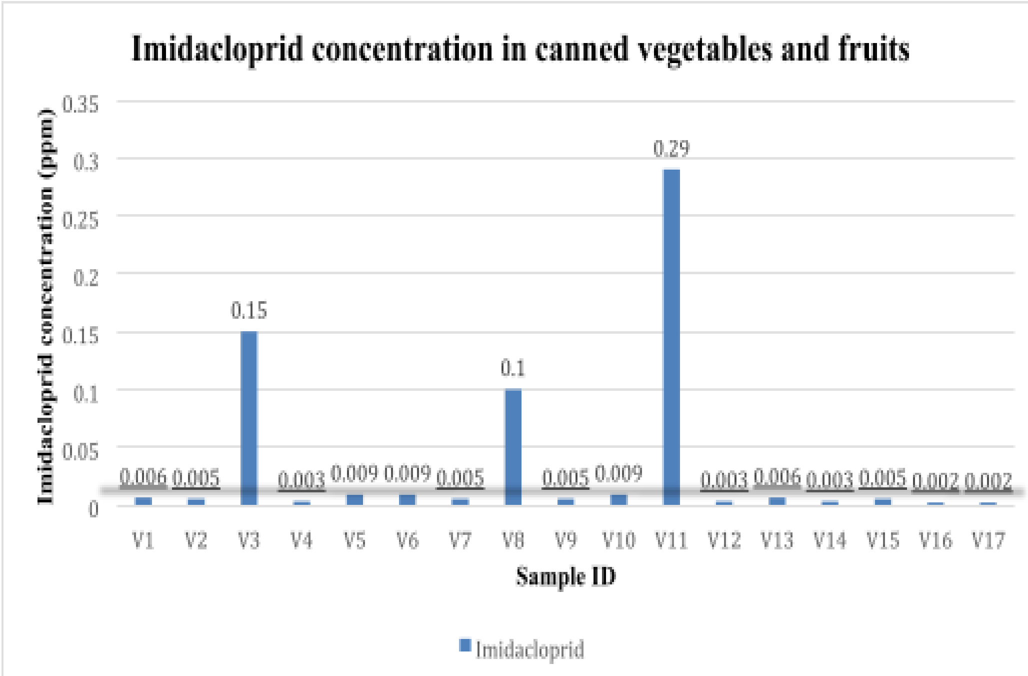

Figure 4.7 Imidacloprid concentration in canned vegetables and fruits

The figure 4.7 illustrates that vegetable samples mushroom **(V3)**, cauliflower **(V8)** and fruit sample peach **(V11)** for imidacloprid exceeded the MRL values but didn't pose any health risk to the consumers. Although vegetable samples sweet corn **(V1)**, green peas **(V2)**, green olives **(V4)**, red kidney beans **(V5)**, garlic clove **(V6)**, red chilli **(V7)**, carrot **(V9)**, lemon **(V10)** and fruit samples grapes **(V12)**, pear **(V13)**, pineapple **(V14)**, red cherry **(V15)**, papaya **(V16)**, lychee (**V17)** were within the MRL limits.

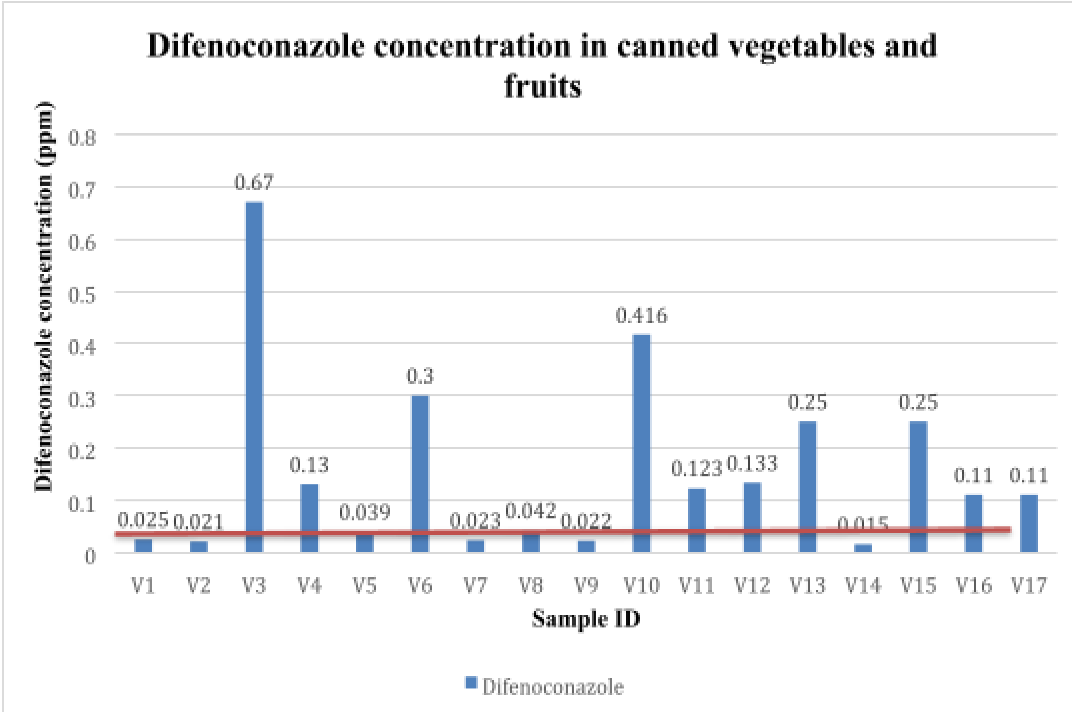

Figure 4.8 Difenoconazole concentration in canned vegetables and fruits

Figure 4.8 shows that vegetable samples mushroom **(V3)**, green olives **(V4)**, garlic clove **(V6)**, lemon **(V10)** and fruit samples peach **(V11)**, grapes **(V12)**, pear **(V13)**, red cherry **(V15)**, papaya **(V16)**, lychee **(V17)** for difenoconazole exceeded the MRL limits but didn't pose health risk to the consumers. However, vegetable samples sweet corn **(V1)**, green peas **(V2)**, red kidney beans **(V5)**, red chilli **(V7)**, cauliflower **(V8),** carrot **(V9)** and fruit sample pineapple **(V14)** didn't exceed the MRL values set by WHO and FAO.

4.2 HRI of detected pesticides

Health Risk Index was calculated in given samples for each pesticide detected to evaluate which sample will pose a serious hazard. Following samples were detected with pesticides in the given table. Tables and graphs are showing exceeding limits of HRI.

Table 4.7 Health Risk Index of Glyphostae in canned vegetables

Sample ID	Conc (ppm)	ADI	EDI	HRI= EDI/ADI
V1	0.4	0.3	0.00233333	0.00233333/0.3 = 0.00777777
V2	0.3	0.3	0.00175	0.00175/0.3 = 0.00583333
V3	0.15	0.3	0.000875	0.000875/0.3 = 0.00291667
V4	0.21	0.3	0.001225	0.001225/0.3 = 0.00408333
V5	0.6	0.3	0.0035	0.0035/0.3 = 0.01166667
V6	0.60	0.3	0.0035	0.0035/0.3 = 0.01166667
V7	0.3	0.3	0.00175	0.00175/0.3 = 0.00583333
V8	0.66	0.3	0.00385	0.00385/0.3 = 0.01283333
V9	0.34	0.3	0.00198333	0.00198333/0.3 = 0.0066111
V10	0.65	0.3	0.00379167	0.00379167/0.3 = 0.0126389

Table 4.8 Health Risk of Glyphosate in canned vegetables

Sample ID	Glyphosate (conc) ppm	Health Risk Index	Health Risk
V1	0.4	0.00777777	No
V2	0.3	0.00583333	No
V3	0.15	0.00291667	No

V4	0.21	0.00408333	No
V5	0.6	0.01166667	No
V6	0.60	0.01166667	No
V7	0.3	0.00583333	No
V8	0.66	0.01283333	No
V9	0.34	0.0066111	No
V10	0.65	0.0126389	No
MRL	**0.1**		

Table 4.9 Health Risk Index of Bifenthrin in canned vegetables

Sample ID	Conc (ppm)	ADI	EDI	HRI= EDI/ADI
V1	0.007	0.01	0.00004083	0.00004083/0/01 = 0.004083
V2	0.007	0.01	0.00004083	0.00004083/0.01 = 0.004083
V3	0.008	0.01	0.00004667	0.00004667/0.01 = 0.004667
V4	0.11	0.01	0.00064167	0.00064167/0.01 = 0.064167
V5	0.008	0.01	0.00004667	0.00004667/0.01 = 0.004667
V6	0.005	0.01	0.00002917	0.00002917/0.01 = 0.002917
V7	0.005	0.01	0.00002917	0.00002917/0.01 = 0.002917
V8	0.007	0.01	0.00004083	0.00004083/0.01 = 0.004083
V9	0.008	0.01	0.00004667	0.00004667/0.01 = 0.004667
V10	0.0092	0.01	0.00005367	0.00005367/0.01 = 0.005367

Table 4.10 Health Risk of Bifenthrin in canned vegetables

Sample ID	Bifenthrin (conc) ppm	Health Risk Index	Health Risk
V1	0.007	0.004083	No
V2	0.007	0.004083	No
V3	0.008	0.004667	No
V4	0.11	0.064167	No
V5	0.008	0.004667	No
V6	0.005	0.002917	No
V7	0.005	0.002917	No
V8	0.007	0.004083	No
V9	0.008	0.004667	No
V10	0.0092	0.005367	No
MRL	**0.01**		

Table 4.11 Health Risk Index of Imidacloprid in canned vegetables

Sample ID	Conc (ppm)	ADI	EDI	HRI= EDI/ADI
V1	0.006	0.06	0.000035	0.000035/ 0.06 = 0.00058333
V2	0.005	0.06	0.00002917	0.00002917/0.06 = 0.00048617
V3	0.15	0.06	0.000875	0.000875/0.06 = 0.01458333
V4	0.003	0.06	0.0000175	0.0000175/0.06 = 0.00029167
V5	0.009	0.06	0.0000525	0.0000525/0.06 = 0.000875
V6	0.009	0.06	0.0000525	0.0000525/0.06 = 0.000875
V7	0.005	0.06	0.00002917	0.00002917/0.06 = 0.00048617
V8	0.10	0.06	0.00058333	0.00058333/0.06 = 0.00972217

V9	0.005	0.06	0.00002917	0.00002917/0.06 = 0.00048617
V10	0.009	0.06	0.0000525	0.0000525/0.06 = 0.000875

Table 4.12 Health Risk of Imidacloprid in canned vegetables

Sample ID	Imidacloprid (conc) ppm	Health Risk Index	Health Risk
V1	0.006	0.00058333	No
V2	0.005	0.00048617	No
V3	0.15	0.01458333	No
V4	0.003	0.00029167	No
V5	0.009	0.000875	No
V6	0.009	0.000875	No
V7	0.005	0.00048617	No
V8	0.10	0.00972217	No
V9	0.005	0.00048617	No
V10	0.009	0.000875	No
MRL	**0.01**		

Table 4.13 Health Risk Index of Difenoconazole in canned vegetables

Sample ID	Conc (ppm)	ADI	EDI	HRI= EDI/ADI
V1	0.025	0.01	0.00014583	0.00014583/0.01 = 0.014583
V2	0.021	0.01	0.0001225	0.0001225/0.01 = 0.01225
V3	0.67	0.01	0.00390833	0.00390833/0.01 = 0.390833
V4	0.13	0.01	0.00075833	0.00075833/0.01 = 0.075833
V5	0.039	0.01	0.0002275	0.0002275/0.01 = 0.02275
V6	0.3	0.01	0.00175	0.00175/0.01 = 0.175
V7	0.023	0.01	0.00013417	0.00013417/0.01 = 0.013417
V8	0.042	0.01	0.000245	0.000245/0.01 = 0.0245
V9	0.022	0.01	0.00012833	0.00012833/0.01 = 0.012833
V10	0.416	0.01	0.00242667	0.00242667/0.01 = 0.242667

Table 4.14 Health Risk of Difenoconazole in canned vegetables

Sample ID	Difenoconazole (conc) ppm	Health Risk Index	Health Risk
V1	0.025	0.014583	No
V2	0.021	0.01225	No
V3	0.67	0.390833	No
V4	0.13	0.075833	No
V5	0.039	0.02275	No
V6	0.3	0.175	No
V7	0.023	0.013417	No
V8	0.042	0.0245	No
V9	0.022	0.012833	No
V10	0.416	0.242667	No
MRL	**0.05**		

Table 4.15 Health Risk Index of Glyphosate in canned fruits

Sample ID	Conc (ppm)	ADI	EDI	HRI= EDI/ADI
V11	0.195	0.3	0.0013	0.0013/0.3 = 0.00433333
V12	0.21	0.3	0.0014	0.0014/0.3 = 0.00466667
V13	0.39	0.3	0.0026	0.0026/0.3 = 0.00866667
V14	0.024	0.3	0.00016	0.00016/0.3 =0.00053333
V15	0.039	0.3	0.00026	0.00026/0.3 = 0.00086667
V16	0.0179	0.3	0.00011933	0.00011933/0.3 = 0.00039777
V17	0.0186	0.3	0.000124	0.000124/0.3= 0.00041333

Table 4.16 Health Risk of Glyphosate in canned fruits

Sample ID	Glyphosate (conc) ppm	Health Risk Index	Health Risk
V11	0.195	0.00433333	No
V12	0.21	0.00466667	No
V13	0.39	0.00866667	No
V14	0.024	0.00053333	No
V15	0.039	0.00086667	No
V16	0.0179	0.00039777	No
V17	0.0186	0.00041333	No
MRL	**0.1**		

Table 4.17 Health Risk Index of Bifenthrin in canned fruits

Sample ID	Conc (ppm)	ADI	EDI	HRI= EDI/ADI
V11	0.0069	0.01	0.000046	0.000046/0.01 = 0.0046
V12	0.005	0.01	0.00003333	0.00003333/0.01 = 0.003333
V13	0.158	0.01	0.00105333	0.00105333/0.01 = 0.105333
V14	0.006	0.01	0.00004	0.00004/0.01 = 0.004
V15	0.005	0.01	0.00003333	0.00003333/0.01= 0.003333
V16	0.007	0.01	0.00004667	0.00004667/0.01 = 0.004667
V17	0.171	0.01	0.00114	0.00114/0.01 = 0.114

Table 4.18 Health Risk of Bifenthrin in canned fruits

Sample ID	Bifenthrin (conc) ppm	Health Risk Index	Health Risk
V11	0.0069	0.0046	No
V12	0.005	0.003333	No
V13	0.158	0.105333	No
V14	0.006	0.004	No
V15	0.005	0.003333	No
V16	0.007	0.004667	No
V17	0.171	0.114	No
MRL	**0.01**		

Table 4.19 Health Risk Index of Imidacloprid in canned fruits

Sample ID	Conc (ppm)	ADI	EDI	HRI= EDI/ADI
V11	0.29	0.06	0.00193333	0.00193333/0.06 = 0.03222217
V12	0.003	0.06	0.00002	0.00002/0.06 = 0.00033333
V13	0.006	0.06	0.00004	0.00004/0.06 = 0.00066667
V14	0.003	0.06	0.00002	0.00002/0.06 = 0.00033333
V15	0.005	0.06	0.00003333	0.00003333/0.06 = 0.0005555
V16	0.002	0.06	0.00001333	0.00001333/0.06 = 0.00022217
V17	0.002	0.06	0.00001333	0.00001333/0.06 = 0.00022217

Table 4.20 Health Risk of Imidacloprid in canned fruits

Sample ID	Imidacloprid (conc) ppm	Health Risk Index	Health Risk
V11	0.29	0.03222217	No
V12	0.003	0.00033333	No
V13	0.006	0.00066667	No
V14	0.003	0.00033333	No
V15	0.005	0.0005555	No
V16	0.002	0.00022217	No
V17	0.002	0.00022217	No
MRL	**0.01**		

Table 4.21 Health Risk Index of Difenoconazole in canned fruits

Sample ID	Conc (ppm)	ADI	EDI	HRI= EDI/ADI
V11	0.123	0.01	0.00082	0.00082/0.01 = 0.082
V12	0.133	0.01	0.00088667	0.00088667/0.01 = 0.088667
V13	0.25	0.01	0.00166667	0.00166667/0.01 = 0.166667
V14	0.015	0.01	0.0001	0.0001/0.01 = 0.01
V15	0.25	0.01	0.00166667	0.00166667/0.01 = 0.166667
V16	0.11	0.01	0.00073333	0.00073333/0.01 = 0.073333
V17	0.11	0.01	0.00073333	0.00073333/0.01 = 0.073333

Table 4.22 Health Risk of Difenoconazole in canned fruits

Sample ID	Difenoconazole (conc) ppm	Health Risk Index	Health Risk
V11	0.123	0.082	No
V12	0.133	0.088667	No
V13	0.25	0.166667	No
V14	0.015	0.01	No
V15	0.25	0.166667	No
V16	0.11	0.073333	No
V17	0.11	0.073333	No
MRL	**0.05**		

4.3 Heavy Metal Results

Metal analysis for canned fruits and vegetables samples was carried out using atomic absorption spectrometry. Concentration levels of all the standards and samples for five different metals were determined. The detected metals were zinc, manganese, chromium, cobalt, and copper.

Table 4.23 Concentration of heavy metals in canned fruits and vegetables

Sr No	Sample code	Zinc (ppm)	Manganese (ppm)	Chromium (ppm)	Cobalt (ppm)	Copper (ppm)
1	V1	0.062	0.208	0.004	0.048	0.007
2	V2	0.049	0.247	0.001	0.048	0.012
3	V3	0.069	0.184	BDL	0.006	0.006
4	V4	0.83	0.145	0.004	0.007	0.07
5	V5	0.031	0.101	0.003	0.008	0.120
6	V6	0.251	0.04	0.003	0.08	0.005
7	V7	0.086	0.379	0.001	0.001	0.008
8	V8	0.022	0.224	BDL	0.007	0.011
9	V9	0.041	0.008	0.006	0.005	0.007
10	V10	0.017	0.021	BDL	0.001	0.009
11	V11	0.021	0.068	0.002	0.048	0.004
12	V12	0.18	0.105	0.003	0.005	0.011
13	V13	0.034	0.009	0.001	0.002	0.003
14	V14	0.256	0.089	BDL	0.007	0.006
15	V15	0.068	0.102	0.003	0.003	0.002
16	V16	0.715	0.131	0.001	0.009	0.08
17	V17	0.012	0.073	BDL	0.002	0.004
MRL		**0.01**	**0.16**	**2.3**	**0.01**	**1**

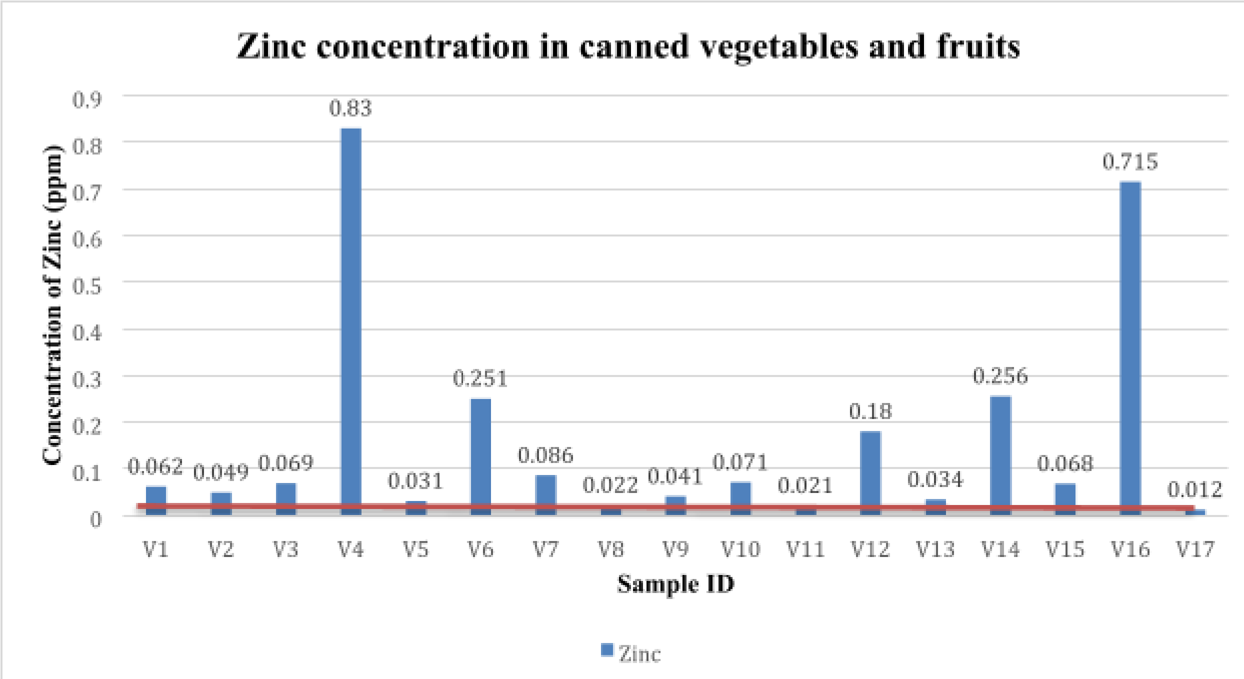

Figure 4.9 Zinc concentration in canned vegetables and fruits

Figure 4.9 shows that zinc concentration in all the vegetable samples sweet corn **(V1)**, green peas **(V2)**, mushroom **(V3)**, green olives **(V4)**, red kidney beans **(V5)**, garlic clove **(V6),** red chilli **(V7)**, cauliflower **(V8)**, carrot **(V9)**, lemon **(V10)** and fruit samples peach **(V11)**, grapes **(V12)**, pear **(V13)**, pineapple **(V14)**, red cherry **(V15)**, papaya **(V16)**, lychee **(V17)** were exceeding the MRL values but no health risk was posed to consumers.

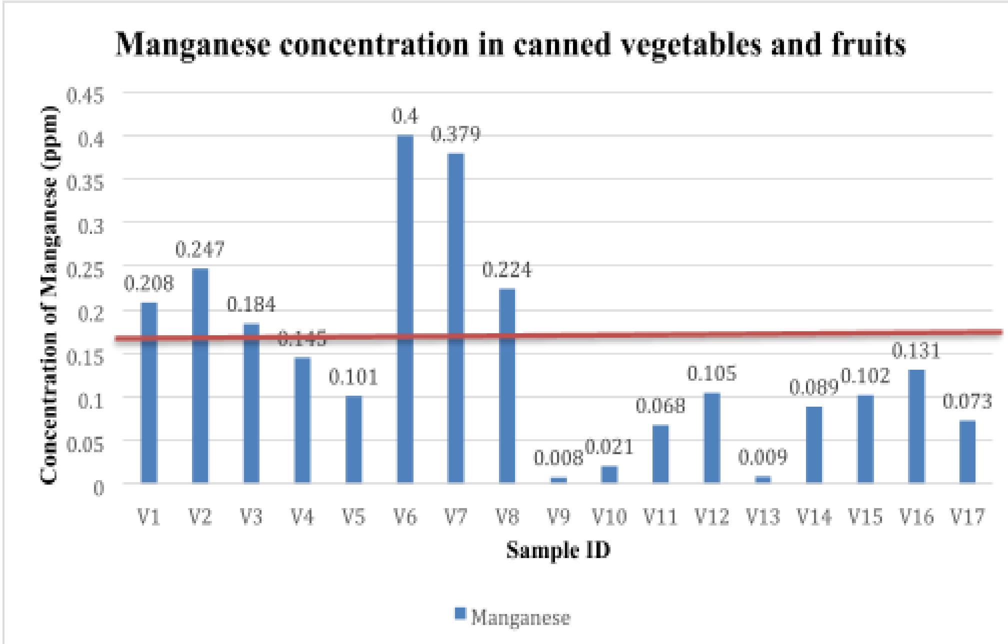

Figure 4.10 Manganese concentration in canned vegetables and fruits

Figure 4.10 illustrates that concentration of manganese in vegetable samples sweet corn **(V1)**, green peas **(V2)**, mushroom **(V3)**, garlic clove **(V6)**, red chilli **(V7)**, cauliflower **(V8)** were exceeding the MRL values but no health risk was posed to consumers while all other samples were within the limit.

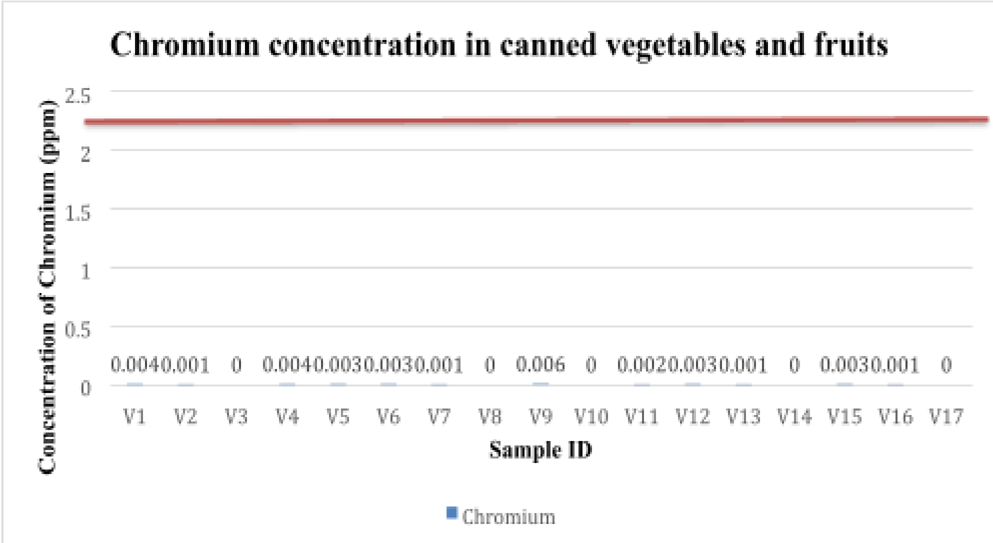

Figure 4.11 Chromium concentration in canned vegetables and fruits

Figure 4.11 shows that the concentration of chromium in all the samples were below the MRL values hence no health risk was posed to the consumers while vegetable samples mushroom **(V3)**, cauliflower **(V8)**, lemon **(V10)** and fruit samples pineapple (**V14)**, lychee **(V17)** were below detection limit **BDL.**

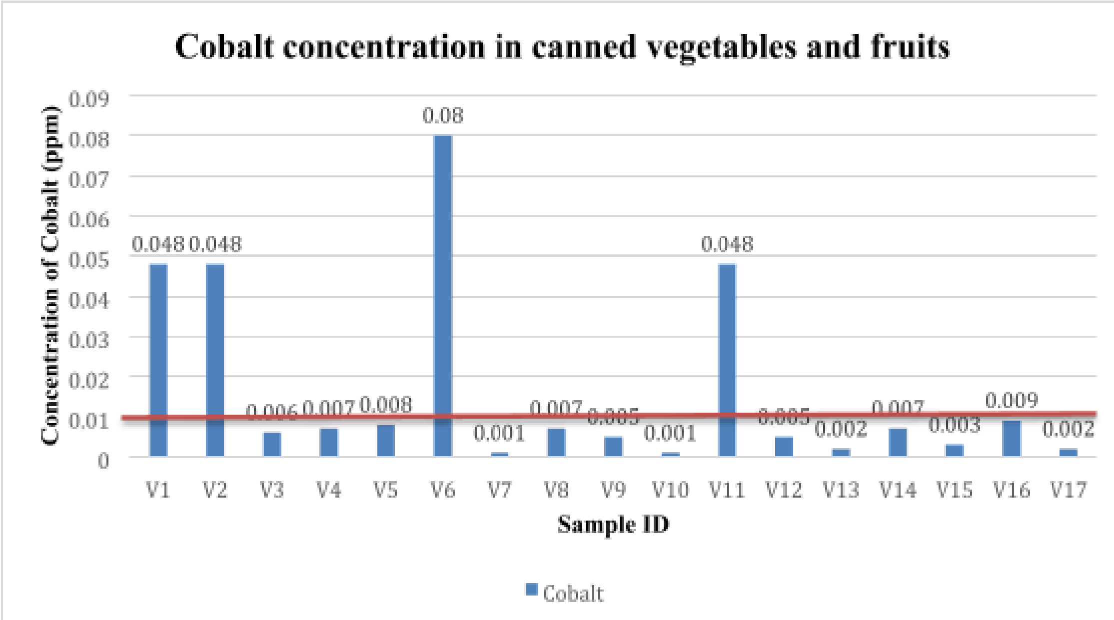

Figure 4.12 Cobalt concentration in canned vegetables and fruits

Figure 4.12 illustrates that concentration of cobalt in vegetable samples sweet corn **(V1)**, green peas **(V2)**, garlic clove **(V6)** and fruit sample peach **(V11)** were exceeding the MRL values but no health risk was posed to the humans while all other samples were within the range.

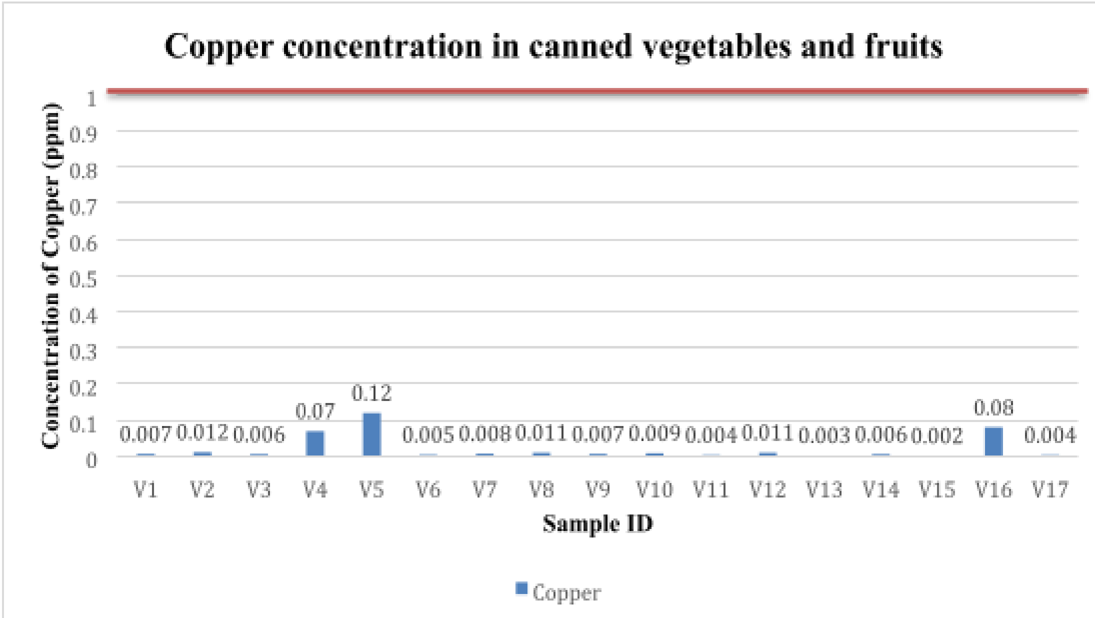

Figure 4.13 Copper concentration in canned vegetables and fruits

Figure 4.13 shows that all the fruits and vegetable samples were within the range and no sample exceeded the MRL values, thus no health risk was imposed on consumers.

MRL = Maximum residue limit

BDL = Below detection limit

4.4 HRI of detected heavy metals

Health risk index is calculated by the given formula

HRI= estimated daily intake/acceptable daily intake

HRI = EDI/ADI

Where, estimated daily intake = concentration of metal × food consumption /body weight kgs. The average daily intake of vegetables by adults was considered 0.35 kgs and the average daily intake of fruits by adults was considered 0.4 kgs.

Body weight of adults was considered 60kgs.

Table 4.24 Health Risk Index of Zinc in canned vegetables

Sample ID	Zinc (ppm)	ADI	EDI	HRI= EDI/ADI
V1	0.062	0.3	0.00036167	0.00036167/0.3 = 0.00120557
V2	0.049	0.3	0.00028583	0.00028583/0.3 = 0.00095277
V3	0.069	0.3	0.0004025	0.0004025/0.3 = 0.00134167
V4	0.83	0.3	0.00484167	0.00484167/0.3 = 0.0161389
V5	0.031	0.3	0.00018083	0.00018083/0.3 = 0.00060277
V6	0.251	0.3	0.00146417	0.00146417/0.3 = 0.00488057
V7	0.086	0.3	0.00050167	0.00050167/0.3 = 0.00167223
V8	0.022	0.3	0.00012833	0.00012833/0.3 = 0.00042777
V9	0.041	0.3	0.00023917	0.00023917/0.3 = 0.00079723
V10	0.017	0.3	0.00009917	0.00009917/0.3 = 0.00033057

Table 4.25 Health Risk of Zinc in canned vegetables

Sample ID	Zinc (ppm)	Health Risk Index	Health Risk
V1	0.062	0.00120557	No
V2	0.049	0.00095277	No
V3	0.069	0.00134167	No
V4	0.83	0.0161389	No
V5	0.031	0.00060277	No
V6	0.251	0.00488057	No
V7	0.086	0.00167223	No
V8	0.022	0.00042777	No
V9	0.041	0.00079723	No
V10	0.017	0.00033057	No
MRL 0.01			

Table 4.26 Health Risk Index of Manganese in canned vegetables

Sample ID	Manganese (ppm)	ADI	EDI	HRI= EDI/ADI
V1	0.208	0.36	0.00121333	0.00121333/0.36 = 0.00337036
V2	0.247	0.36	0.00144083	0.00144083/0.36 = 0.00400231
V3	0.184	0.36	0.00107333	0.00107333/0.36 = 0.00298147
V4	0.145	0.36	0.00084583	0.00084583/0.36 = 0.00234953
V5	0.101	0.36	0.00058917	0.00058917/0.36 = 0.00163658
V6	0.04	0.36	0.00023333	0.00023333/0.36 = 0.00064814
V7	0.379	0.36	0.00221083	0.00221083/0.36 = 0.00614119
V8	0.224	0.36	0.00130667	0.00130667/0.36 = 0.00362964

V9	0.008	0.36	0.00004667	0.00004667/0.36 = 0.00012964
V10	0.021	0.36	0.0001225	0.0001225/0.36 = 0.00034028

Table 4.27 Health Risk of Manganese in canned vegetables

Sample ID	Manganese (ppm)	Health Risk Index	Health Risk
V1	0.208	0.00337036	No
V2	0.247	0.00400231	No
V3	0.184	0.00298147	No
V4	0.145	0.00234953	No
V5	0.101	0.00163658	No
V6	0.04	0.00064814	No
V7	0.379	0.00614119	No
V8	0.224	0.00362964	No
V9	0.008	0.00012964	No
V10	0.021	0.00034028	No
MRL 0.16			

Table 4.28 Health Risk Index of Chromium in canned vegetables

Sample ID	Chromium (ppm)	ADI	EDI	HRI= EDI/ADI
V1	0.004	0.10	0.00002333	0.00002333/0.10 = 0.0002333
V2	0.001	0.10	0.00000583	0.00000583/0.10 = 0.0000583
V3	BDL	-	-	-
V4	0.004	0.10	0.00002333	0.00002333/0.10 = 0.0002333
V5	0.003	0.10	0.0000175	0.0000175/0.10 = 0.000175
V6	0.003	0.10	0.0000175	0.0000175/0.10 = 0.000175

V7	0.001	0.10	0.00000583	0.00000583/0.10 = 0.0000583
V8	BDL	-	-	-
V9	0.006	0.10	0.000035	0.000035/0.10 = 0.00035
V10	BDL	-	-	-

Table 4.29 Health Risk of Chromium in canned vegetables

Sample ID	Chromium (ppm)	Health Risk Index	Health Risk
V1	0.004	0.0002333	No
V2	0.001	0.0000583	No
V3	BDL	-	-
V4	0.004	0.0002333	No
V5	0.003	0.000175	No
V6	0.003	0.000175	No
V7	0.001	0.0000583	No
V8	BDL	-	-
V9	0.006	0.00035	No
V10	BDL	-	-
MRL 2.3			

Table 4.30 Health Risk Index of Cobalt in canned vegetables

Sample ID	Cobalt (ppm)	ADI	EDI	HRI= EDI/ADI
V1	0.048	0.1	0.00028	0.00028/0.1 = 0.0028
V2	0.048	0.1	0.00028	0.00028/0.1 = 0.0028
V3	0.006	0.1	0.000035	0.000035/0.1 = 0.00035
V4	0.007	0.1	0.00004038	0.00004038/0.1 = 0.0004083
V5	0.008	0.1	0.00004667	0.00004667/0.1 = 0.0004667
V6	0.08	0.1	0.00046667	0.00046667/0.1 = 0.0046667
V7	0.001	0.1	0.00000583	0.00000583/0.1 = 0.0000583
V8	0.007	0.1	0.00004083	0.00004083/0.1 = 0.0004083
V9	0.005	0.1	0.00002917	0.00002917/0.1 =0.0002917
V10	0.001	0.1	0.00000583	0.00000583/0.1 = 0.0000583

Table 4.31 Health Risk of Cobalt in canned vegetables

Sample ID	Cobalt (ppm)	Health Risk Index	Health Risk
V1	0.048	0.0028	No
V2	0.048	0.0028	No
V3	0.006	0.00035	No
V4	0.007	0.0004083	No
V5	0.008	0.0004667	No
V6	0.08	0.0046667	No
V7	0.001	0.0000583	No
V8	0.007	0.0004083	No
V9	0.005	0.0002917	No

V10	0.001	0.0000583	No
MRL 0.01			

Table 4.32 Health Risk Index of Copper in canned vegetables

Sample ID	Copper (ppm)	ADI	EDI	HRI= EDI/ADI
V1	0.007	0.5	0.00004083	0.00004083/0.5 = 0.00008166
V2	0.012	0.5	0.00007	0.00007/0.5 = 0.00014
V3	0.006	0.5	0.000035	0.000035/0.5 = 0.00007
V4	0.07	0.5	0.00040833	0.00040833/0.5 = 0.00081666
V5	0.120	0.5	0.0007	0.0007/0.5 = 0.0014
V6	0.005	0.5	0.00002917	0.00002917/0.5 = 0.00005834
V7	0.008	0.5	0.00004667	0.00004667/0.5 = 0.00009334
V8	0.011	0.5	0.00006417	0.00006417/0.5 = 0.00012834
V9	0.007	0.5	0.00004083	0.00004083/0.5 = 0.00008166
V10	0.009	0.5	0.0000525	0.0000525/0.5 = 0.000105

Table 4.33 Health Risk of Copper in canned vegetables

Sample ID	Copper (ppm)	Health Risk Index	Health Risk
V1	0.007	0.00008166	No
V2	0.012	0.00014	No
V3	0.006	0.00007	No

V4	0.07	0.00081666	No
V5	0.120	0.0014	No
V6	0.005	0.00005834	No
V7	0.008	0.00009334	No
V8	0.011	0.00012834	No
V9	0.007	0.00008166	No
V10	0.009	0.000105	No
MRL 1			

Table 4.34 Health Risk Index of Zinc in canned fruits

Sample ID	Zinc (ppm)	ADI	EDI	HRI= EDI/ADI
V11	0.021	0.3	0.00014	0.00014/0.3 = 0.00046667
V12	0.18	0.3	0.0012	0.0012/0.3 = 0.004
V13	0.034	0.3	0.00022667	0.00022667/0.3 = 0.00075557
V14	0.256	0.3	0.00170667	0.00170667/0.3 = 0.0056889
V15	0.068	0.3	0.00045333	0.00045333/0.3 = 0.0015111
V16	0.715	0.3	0.00476667	0.00476667/0.3 = 0.0158889
V17	0.012	0.3	0.00008	0.00008/0.3 = 0.00026667

Table 4.35 Health Risk of Zinc in canned fruits

Sample ID	Zinc (ppm)	Health Risk Index	Health Risk
V11	0.021	0.00046667	No
V12	0.18	0.004	No
V13	0.034	0.00075557	No
V14	0.256	0.0056889	No
V15	0.068	0.0015111	No
V16	0.715	0.0158889	No
V17	0.012	0.00026667	No
MRL 0.01			

Table 4.36 Health Risk Index of Manganese in canned fruits

Sample ID	Manganese (ppm)	ADI	EDI	HRI= EDI/ADI
V11	0.068	0.36	0.00045333	0.00045333/0.36 = 0.00125925
V12	0.105	0.36	0.0007	0.0007/0.36 = 0.00194444
V13	0.009	0.36	0.00006	0.00006/0.36 = 0.00016667
V14	0.089	0.36	0.00059333	0.00059333/0.36 = 0.00164814
V15	0.102	0.36	0.00068	0.00068/0.36 = 0.00188889
V16	0.131	0.36	0.00087333	0.00087333/0.36 = 0.00242592
V17	0.073	0.36	0.00048667	0.00048667/0.36 = 0.00135186

Table 4.37 Health Risk of Manganese in canned fruits

Sample ID	Manganese (ppm)	Health Risk Index	Health Risk
V11	0.068	0.00125925	No
V12	0.105	0.00194444	No
V13	0.009	0.00016667	No
V14	0.089	0.00164814	No
V15	0.102	0.00188889	No
V16	0.131	0.00242592	No
V17	0.073	0.00135186	No
MRL 0.16			

Table 4.38 Health Risk Index of Chromium in canned fruits

Sample ID	Chromium (ppm)	ADI	EDI	HRI= EDI/ADI
V11	0.002	0.10	0.00001333	0.00001333/0.10 = 0.0001333
V12	0.003	0.10	0.0002	0.0002/0.10 = 0.0002
V13	0.001	0.10	0.00000667	0.00000667/0.10 = 0.0000667
V14	BDL	-	-	-
V15	0.003	0.10	0.00002	0.00002/0.10 = 0.0002
V16	0.001	0.10	0.00000667	0.00000667/0.10 = 0.0000667
V17	BDL	-	-	-

Table 4.39 Health Risk of Chromium in canned fruits

Sample ID	Chromium (ppm)	Health Risk Index	Health Risk
V11	0.002	0.0001333	No
V12	0.003	0.0002	No
V13	0.001	0.0000667	No
V14	BDL	-	-
V15	0.003	0.0002	No
V16	0.001	0.0000667	No
V17	BDL	-	-
MRL 2.3			

Table 4.40 Health Risk Index of Cobalt in canned fruits

Sample ID	Cobalt (ppm)	ADI	EDI	HRI= EDI/ADI
V11	0.048	0.1	0.00032	0.00032/0.1= 0.0032
V12	0.005	0.1	0.00003333	0.00003333/0.1= 0.0003333
V13	0.002	0.1	0.00001333	0.00001333/0.1= 0.0001333
V14	0.007	0.1	0.00004667	0.00004667/0.1= 0.0004667
V15	0.003	0.1	0.00002	0.00002/0.1= 0.0002
V16	0.009	0.1	0.00006	0.00006/0.1= 0.0006
V17	0.002	0.1	0.00001333	0.00001333/0.1 = 0.0001333

Table 4.41 Health Risk of Cobalt in canned fruits

Sample ID	Cobalt (ppm)	Health Risk Index	Health Risk
V11	0.048	0.0032	No
V12	0.005	0.0003333	No
V13	0.002	0.0001333	No
V14	0.007	0.0004667	No
V15	0.003	0.0002	No
V16	0.009	0.0006	No
V17	0.002	0.0001333	No
MRL 0.01			

Table 4.42 Health Risk Index of Copper in canned fruits

Sample ID	Copper (ppm)	ADI	EDI	HRI= EDI/ADI
V11	0.004	0.5	0.00002667	0.00002667/0.5 = 0.00005334
V12	0.011	0.5	0.00007333	0.00007333/0.5 = 0.00014666
V13	0.003	0.5	0.00002	0.00002/0.5 = 0.00004
V14	0.006	0.5	0.00004	0.00004/0.5 = 0.00008
V15	0.002	0.5	0.00001333	0.00001333/0.5 = 0.00002666
V16	0.08	0.5	0.00053333	0.00053333/0.5 = 0.00106666
V17	0.004	0.5	0.00002667	0.00002667/0.5 = 0.00005334

Table 4.43 Health Risk of Copper in canned fruits

Sample ID	Copper (ppm)	Health Risk Index	Health Risk
V11	0.004	0.00005334	No
V12	0.011	0.00014666	No
V13	0.003	0.00004	No
V14	0.006	0.00008	No
V15	0.002	0.00002666	No
V16	0.08	0.00106666	No
V17	0.004	0.00005334	No
MRL 1			

CHAPTER V

DISCUSSION

Pesticides are either naturally occurring or chemically synthesized compounds used to manage a range of pests. Numerous industries, including food, forestry, and agriculture use these chemical compounds [41]. The use of pesticide affects the production of about one third of agricultural products. If pesticides are not used there would be 78% loss of fruit production, a 54% loss of vegetable production, and cereal production would decline by 32%. Therefore, pesticides play an essential role in raising the crop yield and reducing the diseases [42]. Almost all humans are exposed to some levels of pesticides and they are dangerous to the people who consume these foods. Even after being cleaned or peeled, a lot of food products like fruits and vegetables still have pesticide residues on them. Extensive study revealed that pesticide exposure increases the risk of mental health issues and cancer by 25-30%. Similarly, the parental exposure to pesticide is associated with a 50% increased risk of leukemia, lymphoma and brain cancer in children.

Workers who handle pesticides may experience acute health issues, including headaches, nausea, vomiting, skin and eye infection as well as abdominal pain and disorientation. There are reports available on increased rates of cancers in the farmers who use these pesticides [43]. While most developed countries have been monitoring pesticide residues in fruits, vegetables and food for decades, the same is not properly recorded in underdeveloped nations [44]. This investigation was carried out to determine the pesticides and heavy metals concentrations in canned fruits and vegetables and also the health risk index. The samples under study were gathered from sources namely Al Fatah store, Risen store and Imtiaz superstore. The samples included were taken from the national and international canned fruit and vegetables brands. Total four types of pesticides were to be determined in all the samples i.e. Glyphosate, Bifenthrin, Imidacloprid and Difenoconazole by using High Performance Liquid Chromatography (HPLC) [45].

The quantitative and qualitative analysis of pesticides was done as shown in **Table 4.5** and **4.6** respectively. Assessment showed that the pesticides were found in different canned fruits and vegetables. Maximum Residue Limit (MRL) of glyphosate in fruits and vegetables is 0.1 ppm according to WHO and FAO of the United Nations. Vegetable samples **(V1, V2, V3, V4, V5, V6, V7, V8, V9, V10)** exceeded the MRL values and showed no health risk and fruit samples **(V11,**

V12, V13) exceeded the MRL values but didn't pose health risk to the consumers. Similar research was conducted in Canada in the beginning of 2015, the prevalence and compliance rates of glyphosate were determined through liquid chromatography/tandem mass spectrometry (LC-MS/MS) that permits accurate and repeatable detection of glyphosate. This study reports on the glyphosate residue concentrations of 7955 samples of milled grain products, processed foods, fresh fruits and vegetables, and pulse products that were gathered in the Canadian retail market between April 2015 and March 2017. A total of 3366 samples (42.3%) had glyphosate residues. 46 samples were found to be noncompliant. Health Canada concluded that amounts of glyphosate detected in the samples of a variety of food surveyed didn't pose a health risk to the Canadian consumers [46]. Likewise a similar study was conducted in Hyderabad for analysis of pesticides residues in the vegetables. The concentration of six pesticides were identified by using GC-MS (Gas Chromatography coupled with Mass Selective Detector) in vegetables. Findings showed that 61% samples had pesticide residues above the MRL values while 39% samples were below the MRL values [23].

The most popular herbicide in the world is glyphosate. It was introduced in 1947 to manage weeds in agricultural producing fields. It is a broad spectrum, non-selective systemic biocide. Due to the extensive use of glyphosate in forestry and agriculture many commercial formulations containing glyphosate have been developed. According to several studies, the presence of glyphosate has been detected in many food crops even after a year after spraying. Their presence in food and water can pose serious health hazards to humans and animals both. This has been verified by the presence of glyphosate in the urine and organs of farmers and farm animals in significant numbers. Furthermore, residues were discovered in average and maximum amounts of 2-3 and 233 μg/L respectively in urine of 60-80% of people. Likewise, residues were also detected in the urine of 44% of the people, although their average and maximum concentrations were lower (<1 and 5 μg/L) respectively. Based on data on the chronic adverse effects of glyphosate, the World Health Organization's (WHO) International Agency for data on cancer (IARC) categorized glyphosate as possibly carcinogenic to humans [47].

MRL for Bifenthrin in fruits and vegetables is 0.01ppm according to the standards determined by WHO and FAO of the United Nations. The results showed that **(V4)** vegetable samples exceeded the MRL values but didn't pose any health risk to the consumers. Fruit samples **(V13)** and **(V17)** exceeded the MRL values but didn't pose any health risk to the consumers. A study was carried out in Italy, using a multi residue method based on modified Quick Easy Cheap Effective Rugged and Safe (Quenchers) sample preparation method and liquid chromatography coupled to mass spectrometry (LC-MS/MS), 14 pesticides were analyzed in 145 vegetable samples from the intensive Sele agricultural plain in the Southwest region of Campania, Italy. The plants were farmed using integrated pest management practices and were intended to supply the fresh cut commercial market in Italy. The results showed that 49.9% of the samples had pesticide residues at or below the maximum residue level (MRL), 2.1% had residues exceeding MRL, 4.8% containing no approved products due to improper farming methods. In this instance, amounts exceeding the MRLs were employed for Etofenprox and Dimethomorph. Boscalid, cyprodinil and propamocarb were detected in 10% of the samples examined. When an indicator of quality for residues was used in the data analysis, it was found that the majority of the examined samples fell into the excellent good category range, indicating that the goods were suitable for the fresh cut market [48].

The MRL value of Imidacloprid in vegetables and fruits was 0.01 ppm according to the standards given by WHO and FAO of the United Nations. Assessment showed that vegetable samples **(V3, V8)** exceeded the MRL values and didn’t pose any health risk but in fruit samples (**V11)** samples exceeded the MRL values but didn’t impose any health. Imidacloprid is an extensively used pesticide in agriculture that works well against a wide range of insect pests. However, its usage has sparked concerns about potential environmental impacts and calls for cautious monitoring and appropriate application to guarantee sustainable farming practices. A study was carried out in Jordan for the examination of imidacloprid using gas chromatography mass spectrometry (GC-MS) on 300 vegetable and fruit samples that were acquired from 15 significant wholesalers spread over four areas of Amman, the capital of Jordan. It was discovered that 39.7% of the samples under examination contained imidacloprid residues. The quantities of imidacloprid in various edible fruits and vegetables varied ranging from less than the Limit of Quantification (LOQ) to 0.40 mg kg-1. The greatest average concentrations were found in apples and eggplant (0.40 and 0.25 mg kg-1) respectively. Lower quantities were seen in grapes (0.07 mg kg-1), potatoes (0.05 mg kg), bananas (0.04 mg kg-1) and cabbage (0.07 mg kg-1). In samples of okra, peaches, apricots and carrots, imidacloprid was found to be below the detection limit (BD). Imidacloprid exceeded the Codex maximum residue limit (MRL) in 25 samples (8.3%). Additionally, 8 out of 300 samples (2.7%) went above the Pest Management

Regulatory Agency's (PMRA) MRL. The largest residual levels were found in the fruits of the eggplant and apple, with 1.30 and 0.83 mg kg-1 respectively, significantly exceeding the MRLs for CODEX and PMRA. Furthermore, the highest amount of imidacloprid residue found in bananas (0.25 mg kg-1) was 500% greater than the CODEX MRLs. The Amman population's estimated average daily intake (EDI) varied across different goods, ranging from 0.00 to 0.144 μg kg -1 body weight day -1. The hazard index (HI) for Imidacloprid ranged from 0.00 to 0.24, with all samples having an HI below unity (<1). In conclusion the study shows that commonly consumed fruits and vegetables have low HI levels of Imidacloprid residues. On the other hand, the notable existence of imidacloprid residues in certain samples emphasizes the pressing requirement for all encompassing efforts to restrict potential health risks to consumers [49]. Similar study was undertaken in Lahore to analyze the injurious health hazards being imposed on consumers by consumption of harmful chemicals present in vegetables and fruits by using LCMS system (Liquid Chromatography Mass Spectrometry system). The results indicated that the majority of the samples under investigation were not found to have pesticide residues , only two tomato samples were found to have concentration of imidacloprid but didn't pose a critical threat to consumers' health [24].

The MRL value of Difenoconazole in vegetables and fruits was 0.05 ppm according to the standards determined by WHO and FAO of the United Nations. The results showed that **(V3, V4, V6, V10)** vegetable samples exceeded the MRL values but didn't pose any health risk to consumers and fruit samples **(V11, V12, V13, V15, V16, V17)** exceeded the MRL values but didn't pose health risk to the consumers. In 2020 under field conditions in China, the dissipation and terminal residues of difenoconazole in whole pulp and banana were examined. Following a quick and easy pretreatment, the residual levels of difenoconazole in different sections of bananas cultivated in Guangdong, Hainan and Yunnan were assessed using a GC-ECD detection method. The relative standard deviation was 3.36-9.84% and the mean recovery was 80.66 - 107.40%. The finding revealed that the half-lives of difenoconazole were 12.16 - 13.33 days for whole bananas and 17.77 - 20.38 days for the pulp, respectively. At harvest intervals of 28 and 35 days after the last application difenoconazole terminal residues in whole bananas and pulp were 0.45 - 0.84 mg/kg and 0.19 - 0.37 mg/kg respectively. These values were below China's maximum residue level. The distribution of difenoconazole in banana pulp and peel was investigated. The findings demonstrated that the residue in peels was consistently 2.19 - 12.30

times more than the pulp up until harvesting. Banana peels absorbed the majority of the difenoconazole, while it didn't easily penetrate into the pulp. The residue levels of difenoconazole at the sample interval of 28 days following the last application were within the acceptable limits for both acute and chronic dietary risk assessment. This study can serve as a guide for future investigations into the safe and practical use of banana peels and pulps as fungicides, as well as for the use of difenoconazole [50]. Likewise, in 2021 a similar study was undertaken in China in order to evaluate the amount of pesticides in Henan. 3307 samples of fruits and vegetables were gathered from 18 distinct regions. Gas Chromatography mass spectrometry (GC-MS) was used to evaluate thirteen different pesticides . Pesticide residues were identified in every sample. The results showed that the difenoconazole group showed statistically significant differences ($P<0.05$) [25].

Health Risk was estimated by dividing estimated daily intake (EDI) of vegetables and fruits with acceptable daily intake (ADI). While EDI was estimated by multiplying the concentration of detected pesticide with the average daily food consumption by adults and dividing it with the body weight of adults.

For detection of heavy metals five metals were selected that are zinc, manganese, chromium, cobalt and copper. The technique used for heavy metal detection was atomic absorption spectrometry and microwave digestion. The detection was done in seventeen samples. Ten were canned vegetable samples (sweet corn, green peas, mushrooms, green olives, red kidney beans, garlic, red chili, cauliflower, carrot and lemon) and seven were canned fruit samples (peach, grapes, pear, pineapple, red cherry, papaya and lychee). Maximum residue limit of zinc is 0.01 ppm and all the vegetable samples **(V1, V2, V3, V4, V5, V6, V7, V8, V9, V10)** and fruit samples **(V11, V12, V13, V14, V15, V16, V17)** were exceeding the standard limit. Many enzymes like human alkaline phosphatase, alcohol dehydrogenase, ribonucleic polymerases and carbonic anhydrase are composed of zinc [51]. Symptoms of exposure to excessive levels of zinc might include nausea, vomiting, cramping in the stomach, and metal fume fever. Consuming large amounts of zinc for several months at a time might lower HDL cholesterol levels, damage pancreas and can cause anemia. On the other hand, zinc deficiency can result in skin ulcers, sluggish wound healing, diminished taste and smell perception, appetite loss and weakened immunity. It may also result in poor development of sex organs and stunted growth in young men. Furthermore, zinc deficiency may result in birth defects in pregnant women [52]. Zinc is one of the less hazardous metals and is necessary for the maintenance of body processes, development of fetal growth, brain and immune system. Greater levels of heavy metal contamination in the soil lead to an increase in zinc uptake [53]. In 2014 a study was carried out in Saudi Arabia and the concentration of almost 27 toxic heavy metals was identified in almost 55 samples of canned and fresh foods for comparison. The 30 canned samples and the rest being fresh food were analyzed using ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometer). The heavy metals detected were Zn, Pb,Cu, Mg, Mn, Fe.The results showed that canned and fresh foods were contaminated with toxic metals and their concentration was exceeding the international tolerance levels [32].

The maximum residue limit for manganese is 0.16 ppm. Samples **(V1**, **V2**, **V3, V6, V7**, **V8)** of vegetables were exceeding the standard value of MRL while they didn't pose any health risk. No fruit samples were exceeding the standard value of MRL and no health risk was imposed to the consumers. Mn is the twelfth most abundant element in the earth crust and is present in food, water and soil. Mammal tissues contain this essential element in the number of oxidative states of two different forms (Mn_{2+} and Mn_{3+}). Mn is engaged in a wide range of roles in the body including the metabolism of amino acids, lipids, proteins and carbohydrates, immunological response, growth and development, regulation of blood glucose and cellular energy, reproduction and detoxification of reactive oxygen species [54]. On the other hand, over exposure to this metal might result in Mn toxicity. Mn toxicity mostly affects the brain, liver, pancreas, bones, kidney. Patients with Mn poisoning have been documented to exhibit dystonia, hypermagnesemia, polycythemia, hepatic cirrhosis and Parkinsonism symptoms [55]. People are exposed to these heavy metals through industrialization, fertilizer application in agriculture and sewage sludge application [56]. During 2008-2010, a study was carried out to examine the Enyigba mine in Nigeria for the detection of heavy metals on specific fruits and vegetables as well as in top and subsoil. X-ray fluorescence (XRF) spectrometry was used to examine the concentration of toxic heavy metals in fruits and vegetables. Manganese, zinc, lead, chromium, cadmium, and arsenic contents were measured in samples of fruits and leaves of plants. Corresponding Pollution Indices (PI) and Bioaccumulation Factor (BAF) were also assessed. Results concluded that High Pollution Indices were observed in peach, guava, lettuce and pepper and they were deemed unfit for human consumption [37].

The maximum residue limit for Chromium is 2.3 ppm. Vegetable samples **(V3**, **V8)**, **V10)** were below detection limit BDL while other samples were not exceeding the standard limits. Fruit samples **(V14)** and **(V17)** were below the detection limit **BDL** and other samples were not exceeding the MRL values. No vegetable and fruit samples posed health risk to the consumers. Chromium is an essential component to encourage insulin's action in body tissue so that it can use carbohydrates, proteins and lipids. Chromium plays a major role in modifying the immune response through immunostimulatory or immunosuppressive mechanisms. The gastrointestinal system, lungs and skin allow chromium to enter the body. The most significant method of occupational exposure is inhalation, while non occupational exposure happens when chromium containing food and water are consumed. Excessive amounts of chromium and prolonged exposure to this can result in a variety of cytotoxic and genotoxic effects that impact the immune system of the body. Inhalation and dermal exposure to chromium can be extremely hazardous and can lead to lung cancer, nasal irritation, nasal ulcers, and hypersensitivity reactions such as asthma and contact dermatitis [57]. A study was carried out in Khyber Pakhtunkhwa province of Pakistan to investigate the concentration of potentially toxic metals present in vegetables, fruits and cereals. The samples were taken from various markets of KPK. Tangerine, onion, tomato, lady finger, peas, potatoes, kidney beans, chickpeas were analyzed and acidically extracted by ICP-MS technique. The samples were contaminated with chromium, lead, zinc and arsenic.The results showed that vegetable intake was observed within safe limits for children and adults. HRI values of Cr, Zn and As for both children and adults were found to be less than 1 and might have imposed serious potential risk to the community consuming these foods on a regular basis [33].

The Maximum Residue Limit for cobalt is 0.01 ppm. Vegetable samples **(V1), (V2)** and **(V6)** were exceeding the MRL values while no health risk was posed by any of them. While in fruit samples only **(V11)** was exceeding the standard limits. The detected values of HRI are less than 1 which are not causing any threat to humans. Cobalt is a necessary trace element for human health and exists in both organic and inorganic forms. The organic form of vitamin B12 Is essential for the formation of nerve cells of amino acids and certain proteins, as well as the synthesis of neurotransmitters, which are critical for the proper functioning of the body. Cobalt enters the body through food, respiratory system, and skin. Excess and shortage of cobalt both will have a negative effect on the body [58].

The Maximum Residue Limit for copper is 1.00 ppm according to the standards determined by WHO and FAO. No vegetable and fruits samples exceeded the standard value of MRL and didn't pose a threat to the humans. Copper is one of the vital trace elements. Copper is an essential component for optimal health maintenance. It creates red blood cells when paired with iron.

Additionally, it also keeps the immune system healthy, supporting bones, neurons, and blood vessels. Copper is generally consumed by humans through nuts, some fruits and vegetables, seafood, red meat and drinking water through the copper pipes [59]. High copper levels as well as deficiencies are harmful to human health. Acute copper poisoning can put a person at risk for several diseases. Prolonged exposure to copper can cause serious neurological defects, liver damage and anemia [60].

The next part was to carry out a health risk index in the samples from the formula HRI = estimated daily intake/acceptable daily intake. Where estimated daily intake = heavy metal concentration x food ingestion rate/ body weight. The standard value for Health Risk Index HRI is 1. The recorded values of Health Risk Index of all the detected heavy metals (zinc, manganese, chromium, cobalt and copper) were less than 1 which means that intake of these metals has no health effects.

A study conducted in China examined 5785 vegetable samples for detection of heavy metals (As, Pb, Cd, Cr, Ni and Hg). Deterministic (point estimate) methods were used to evaluate the health risk to local consumers. The element level varied in different vegetables. As, Cd, Cr, Ni, Hg, and Pb had average concentrations of 0.013, 0.017, 0.057, 0.002, 0.094 and 0.034 mg/kg respectively. The samples with Cd values of 0.25% and Pb concentrations of 1.56% exceeded the Chinese Health Ministry's maximum permissible concentrations (MACs). No clear regular geographical distribution for these heavy metals in vegetables was found in Zhejiang, China. The assessment of high exposure was presented using the mean and 97.5 percentile levels of metalloids and heavy metals. Both the mean and high exposure assessments showed that the health indices (HIs) were below the threshold of 1. This suggests that eating vegetables has a very low health risk to As, Cd, Cr, Pb, Ni and Mg for the general public [61].

A similar study was conducted in São Paulo State, Brazil. The purpose of this study was to compare the levels of heavy metals with the permissible limits by analyzing the amounts of cadmium, nickel, lead, cobalt and chromium in the most commonly consumed foods. In order to determine the risk to human health, the amount of heavy metal consumption from food was calculated. At the São Paulo General Warehousing and Centers Company, vegetable samples were gathered and atomic absorption spectrophotometry was used to quantify the amounts of heavy metals present. The average quantities of Cd and Ni found in all vegetables were lower than the acceptable limits set by Brazilian law. In 44% of the examined samples, Pb and Cr levels were higher than the allowed limit. The maximum amount of Co content was not established by Brazilian law. It may be concluded that eating these veggies is safe and poses no health risk to the consumers [18].

Another study was conducted in southern districts of Khyber Pakhtunkhwa Province, Pakistan. The aim of this study was to investigate the concentrations of heavy metals including copper, zinc, chromium, nickel and manganese in fruit crops (fruit, leaf and root vegetables) and agricultural soils and the health risk these metals pose to the local people. The chosen metal's concentration in soil ranged widely and was found in the following descending order Zn>Cr>Ni>Cu>Mn. The bioaccumulation of heavy metals in vegetables were within the acceptable levels but Cr showed higher concentration in the tested food crops. The calculated daily intake of metals (DIM) in adults and children was in the decreasing order of Mn>Zn>Ni>Cr>Cu but the trend of metal transfer factor for vegetables was in the order of Cu>Ni>Cr>Mn>Zn. For both adults and children, the health risk index (HRI) values for heavy metals were less than 1. Therefore, eating these food crops will not pose a serious health danger to the people [62].

Another study was carried out in Bangladesh and the concentration of Sapodilla (Manilkara zapota), Stone apple (Aegle marmelos), Indian gooseberry (Phyllanthus emblica), Guava (Psidium guajava), Bilimbi (Averrhoa bilimbi), Elephant apple (Dillenia indica), Tamarind fruit (Tamarindus indica), Mango (Mangifera indica), Litchi (Litchi chinensis) and Strawberry (Fragaria X ananassa) were determined using standard procedure. The finding indicates that the chosen tropical fruits were a good source of minerals. Tamarind fruit was a good source of iron, sodium, potassium, calcium and magnesium. Mango had the highest manganese content with 06.16 ± 1.19 mg. Guava had the highest concentrations of sodium, zinc and copper (19.30 ± 2.12 mg, 2.07 ± 0.15 mg, and 62.78 ± 1.24 mg). The concentration of heavy metals i.e. arsenic, cadmium, lead, mercury and chromium were determined for 10 tropical fruits. The study findings suggest that these tropical fruits may be useful in reducing micronutrient deficiencies particularly in rural populations where they are a potent source of minerals and the concentrations of these metals in fresh fruits were lower than the recommended daily intake. However, consumers should be cautious when consuming fresh fruit because excessive consumption may be harmful [63].

Consumers have a right to anticipate that the meals they purchase and eat will be healthy and of the best possible quality. People have a right to express their views regarding the food control practices, guidelines and initiatives that the government and the industrial sector employ to ensure that the food supply satisfies requirements. Though consumers, government and other stakeholders have a significant role to play, in free market societies the food industry is ultimately responsible for allocating the financial and human resources required to implement the necessary controls. This industry is responsible for monitoring and processing of food from raw ingredients to final products on a daily basis. The company must clearly label the products with contaminants information. The companies must pay attention to the customer's feedback in order to make continuous improvements. These measures can help in enhancing food quality and ensuring consumer safety [64].

CONCLUSION

This research concludes that fruits and vegetables are an important part of a diet. This diet is consumed by all the age groups (children and adults). A diet high in fruit and vegetables protects humans against cancer, diabetes and heart diseases. A number of fertilizers are applied and pesticides are sprayed on fruits and vegetables crops that have contaminated it greatly. The results revealed that most of the canned fruits and vegetables were contaminated with four pesticides (glyphosate bifenthrin, imidacloprid, difenoconazole), and five heavy metals (zinc, manganese, chromium, cobalt, copper).Concentration of glyphosate in vegetables sweet corn (0.4 ppm), green peas (0.3 ppm), mushrooms (0.15 ppm), green olives (0.21 ppm) , red kidney beans (0.6 ppm), garlic clove (0.60 ppm), red chilli (0.3 ppm), cauliflower (0.66 ppm), carrot (0.34 ppm) and lemon (0.65 ppm), and fruit peach (0.195 ppm) , grapes (0.21 ppm), pear (0.39 ppm), concentration of bifenthrin in vegetable green olives (0.11 ppm) and fruit pear (0.158 ppm) , lychee (0.171 ppm), concentration of imidacloprid in vegetable mushroom (0.15 ppm) and cauliflower (0.10 ppm) and fruit peach (0.29 ppm) and concentration of difenoconazole in vegetable mushroom (0.67 ppm) , green olives (0.13 ppm), garlic clove (0.3 ppm), lemon (0.416 ppm) and fruit peach (0.123 ppm) , grapes (0.133 ppm), pear (0.25 ppm)**,** red cherry **(**0.25 ppm)**,** papaya **(**0.11 ppm) **,** lychee (0.11 ppm) exceeded the MRL values set by WHO and FAO. While for heavy metals, concentration of zinc in all the vegetables sweet corn (0.062 ppm), green peas (0.049 ppm), mushroom (0.069 ppm), green olives (0.83 ppm), red kidney beans (0.031 ppm), garlic clove (0.251 ppm), red chilli (0.086 ppm) , cauliflower (0.022 ppm), carrot (0.041 ppm), lemon (0.017 ppm) and fruits peach (0.021 ppm) , grapes (0.18 ppm), pear (0.034 ppm), pineapple (0.256 ppm), red cherry (0.068 ppm), papaya (0.715 ppm), lychee (0.012 ppm), concentration of manganese in vegetable sweet corn (0.208 ppm), green peas (0.247 ppm), mushrooms (0.184 ppm), garlic clove (0.04 ppm), red chilli (0.379 ppm), cauliflower (0.224 ppm) and concentration of cobalt in vegetable sweet corn (0.048 ppm), green peas (0.048 ppm), garlic clove (0.08 ppm) and fruit peach (0.048 ppm) exceeded the MRL values while concentration of chromium in vegetable mushroom , cauliflower, lemon and fruits pineapple, lychee were below detection limit (BDL). For copper no vegetable and fruit samples exceeded the MRL values. If these samples are consumed with these rates, there is a chance of an increase of adverse health impacts. Therefore, it is necessary to control the risk and manage application of pesticides as well as heavy metals to a safer limit in order to reduce the serious health impacts.

RECOMMENDATIONS

- This investigation was carried out to detect the pesticide residues and concentration of heavy metals in canned vegetables and fruits samples and also estimate the risk associated with these samples. Similar methods can be used to examine the risk that is associated with other food crops.
- Food safety departments and governments must take immediate proper actions to stop the frequent application of pesticides in agriculture.
- Farmers must use eco-friendly bio pesticides in adequate amounts rather than using harmful and dangerous compounds.
- All agricultural crops intended for human consumption must undergo risk assessment and pesticides and heavy metals monitoring before they are made available to the public.
- Establish comprehensive monitoring systems for pesticides residue in food products and heavy metal concentration in soils, water, air and crops.
- Ensure transparent reporting of monitoring results to the public and relevant authorities.
- Allocate resources for the development and implementation of contamination prevention and remediation programs.
- Implement proper disposal and recycling methods for pesticides containers and industrial wastes containing heavy metals.

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ANNEXURE I

Peak identification in Samples

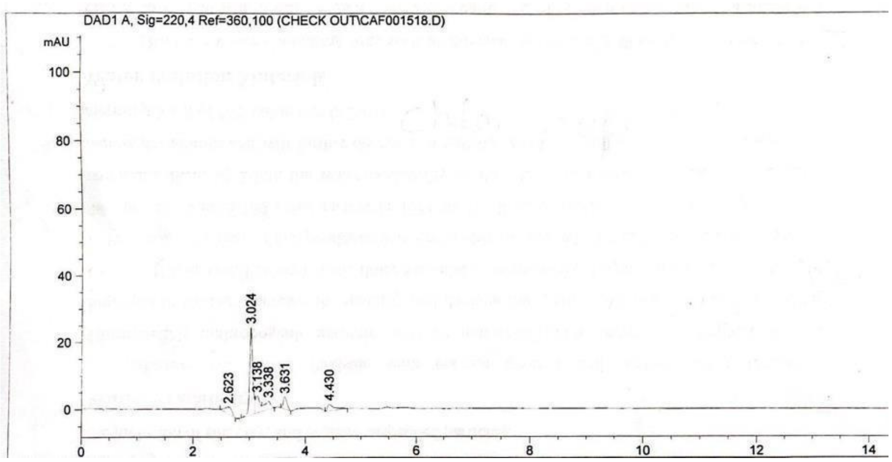


Figure 4.14 Chromatogram of Sample V1

Table 4.44 Sample V1 showing peak value

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.623	BB	0.1416	18.28794	2.02000	1.2831
2	3.024	BV	0.0584	99.48019	26.11206	6.9796
3	3.138	VV	0.0761	25.65788	4.97764	1.8002
4	3.338	VB	0.1113	19.43327	2.37887	1.3634
5	3.631	BB	0.0728	16.56952	3.52629	1.1625
6	4.430	BB	0.1215	16.61216	1.94734	1.1655
7	14.750	BBA	0.2555	1229.26013	80.80587	86.2456
Total				**1425.30109**	**121.76807**	

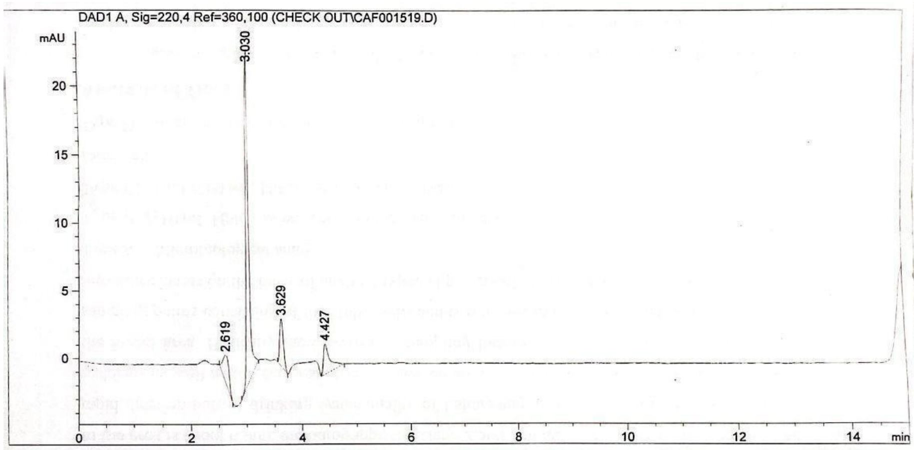


Figure 4.15 Chromatogram of Sample V2

Table 4.45 Sample V2 showing peak values

Peak #	**Ret time (min)**	**Type**	**Width (min)**	**Area (mAU*s)**	**Height (mAU)**	**Area %**
1	2.619	BB	0.1265	15.63454	2.01447	11.2583
2	3.030	BB	0.0536	88.15069	24.71314	63.4764
3	3.629	BB	0.0711	16.22677	3.56221	11.6847
4	4.427	BB	0.1170	18.85967	2.26792	13.5806
T tal				**138.87167**	**32.55774**	

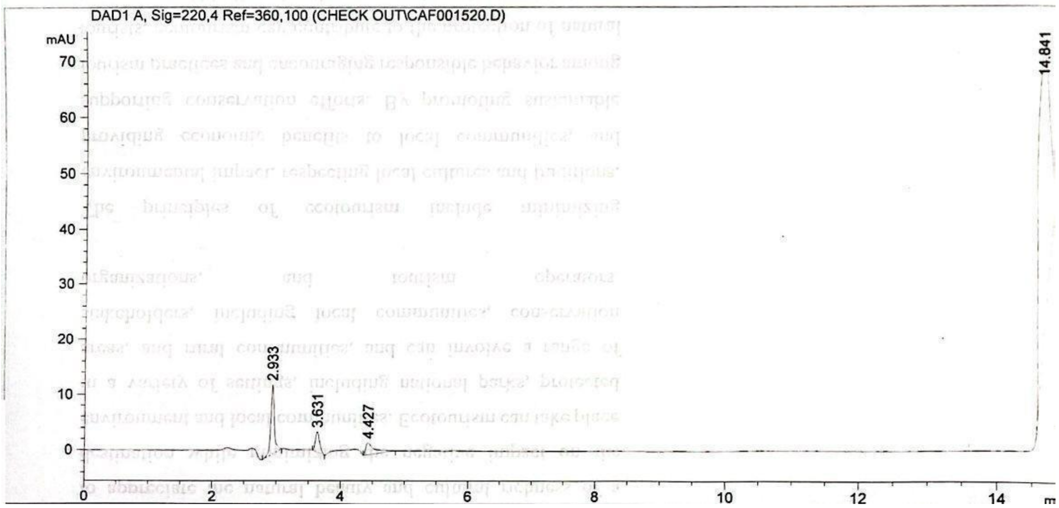


Figure 4.16 Chromatogram of Sample V3

Table 4.46 Sample V3 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.933	BB	0.0586	48.34819	12.65395	7.5152
2	3.631	BB	0.0719	17.07172	3.69292	2.6536
3	4.427	BB	0.1366	21.24115	2.20161	3.3017
4	14.841	BBA	0.2286	556.68115	43.70764	86.5296
Total				**643.34222**	**62.25613**	

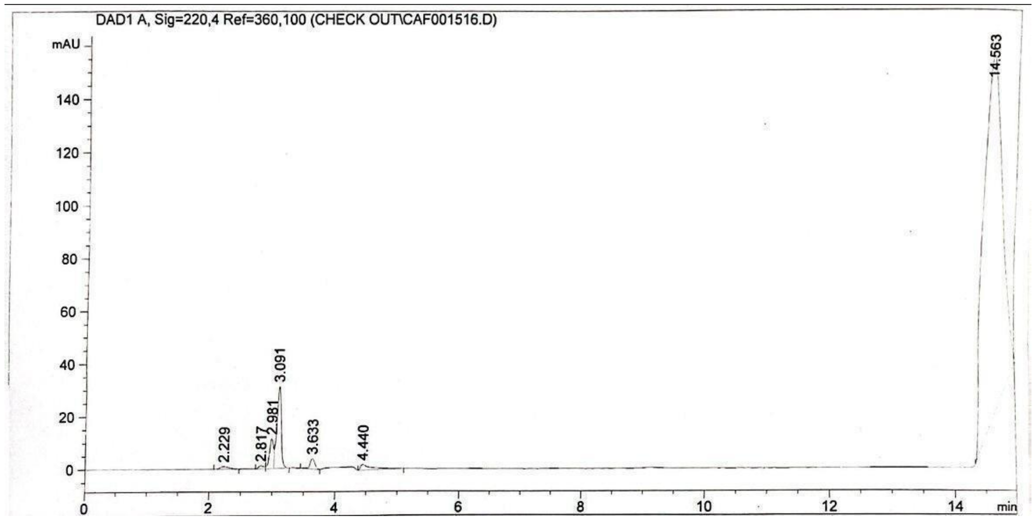


Figure 4.17 Chromatogram of Sample V4

Table 4.47 Sample V4 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.229	BB	0.1538	9.88730	1.01327	0.3191
2	2.817	BV	0.0886	6.79724	1.12307	0.2194
3	2.981	VV	0.0660	48.24749	11.25815	1.5572
4	3.091	VB	0.0719	149.66013	31.21620	4.8303
5	3.633	BB	0.0800	20.77379	3.90682	0.6705
6	4.440	BB	0.1746	28.15936	2.15232	0.9089
7	14.563	BBA	0.3162	2834.80811	141.19344	91.4946
Total				**3098.33341**	**191.86327**	

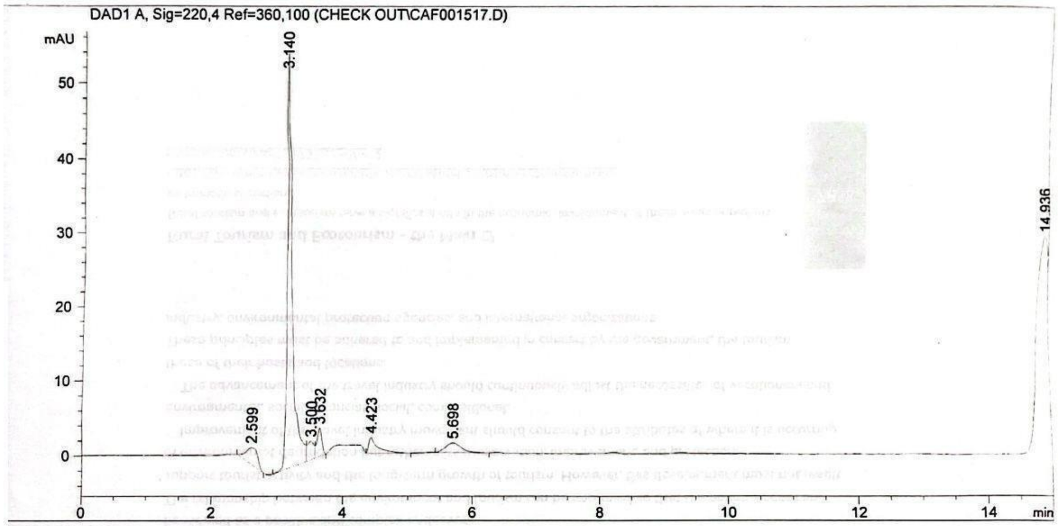


Figure 4.18 Chromatogram of Sample V5

Table 4.48 Sample V5 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.599	BB	0.1984	28.56579	2.21552	5.7812
2	3.140	BV	0.0737	294.47098	55.69358	59.5955
3	3.500	VV	0.1007	17.22739	2.48951	3.4865
4	3.632	VB	0.0809	20.44963	3.79466	4.1386
5	4.423	BB	0.1334	20.88772	2.14893	4.2273
6	5.698	BB	0.2449	21.90371	1.28509	4.4329
7	14.936	BBA	0.1848	90.61079	8.17008	18.3380
Total				**494.11600**	**75.79737**	

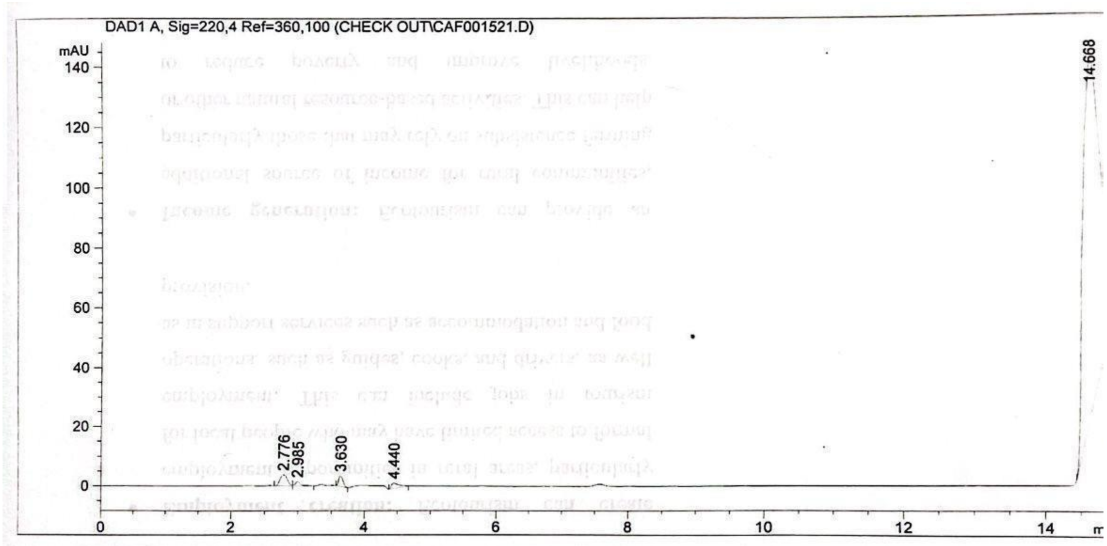


Figure 4.19 Chromatogram of Sample V6

Table 4.49 Sample V6 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.776	BV	0.1239	27.82915	3.69410	1.3388
2	2.985	VB	0.0793	7.54701	1.39041	0.3631
3	3.630	BB	0.0711	16.19549	3.55827	0.7791
4	4.440	BB	0.1107	13.88338	1.82610	0.6679
5	14.668	BBA	0.2821	2013.25610	117.39761	96.8512
Total				**2078.71113**	**127.86649**	

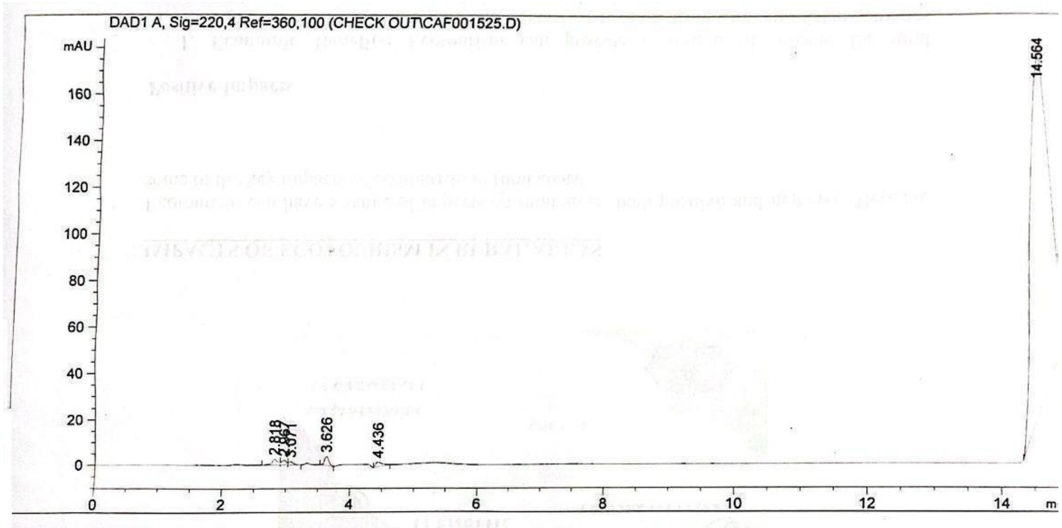


Figure 4.20 Chromatogram of Sample V7

Table 4.50 Sample V7 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.818	BV	0.0924	16.73910	2.55598	0.5251
2	2.967	VV	0.0767	11.26300	2.16506	0.3533
3	3.071	VB	0.0718	7.10113	1.43261	0.2227
4	3.626	BB	0.0731	18.39361	3.89210	0.5769
5	4.436	BB	0.1013	13.59839	2.00080	0.4265
6	14.564	BBA	0.3173	3120.99487	156.08226	97.8954
Total				**3188.09011**	**168.12880**	

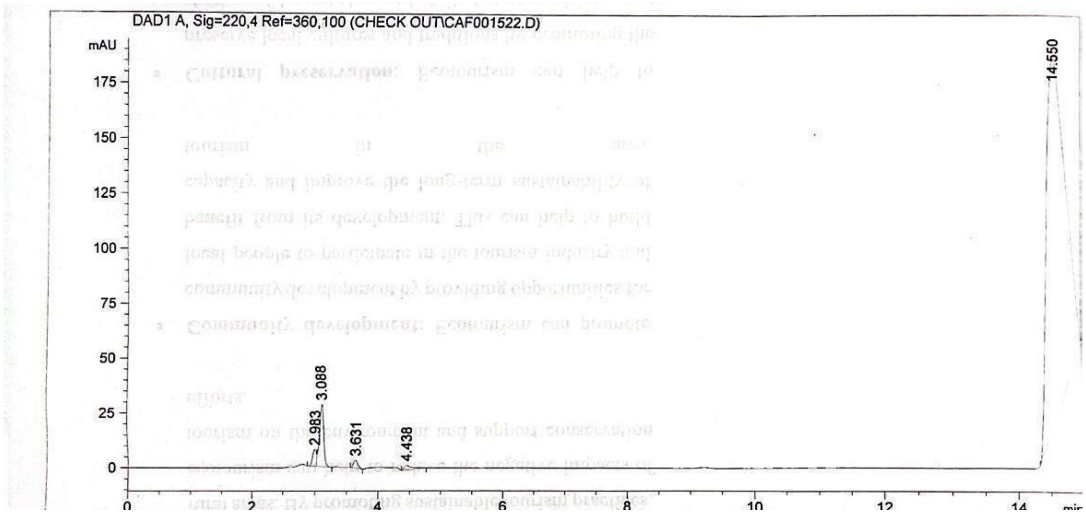


Figure 4.21 Chromatogram of Sample V8

Table 4.51 Sample V8 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.983	BV	0.0620	30.50590	7.74176	0.8425
2	3.088	VB	0.0700	132.79271	28.67330	3.6676
3	3.631	BB	0.0722	17.32559	3.72718	0.4785
4	4.438	BB	0.1256	18.77937	2.11492	0.5187
5	14.550	BBA	0.3220	3421.31812	166.31152	94.4927
Total				**3620.72169**	**208.56868**	

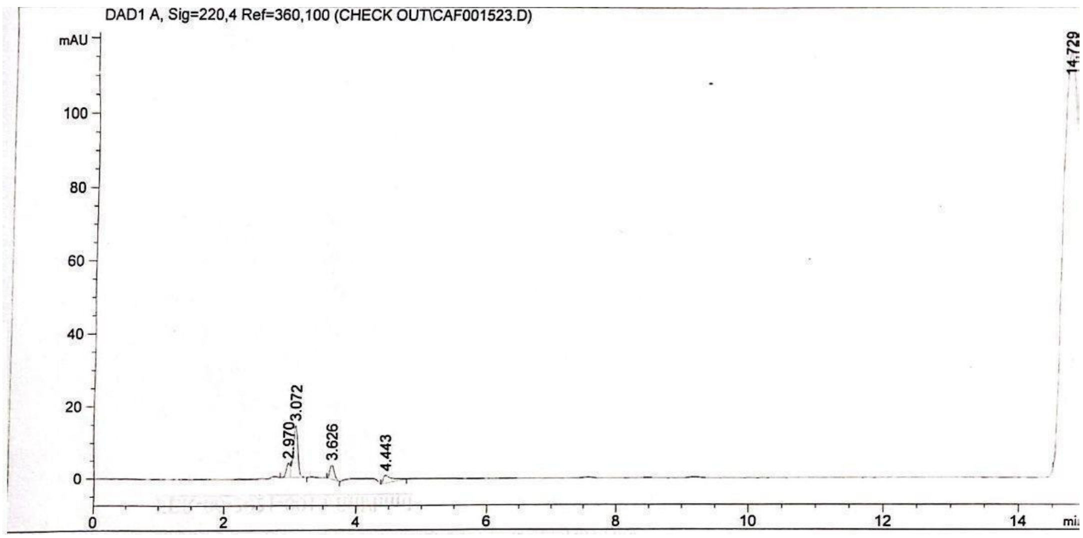


Figure 4.22 Chromatogram of Sample V9

Table 4.52 Sample V9 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.970	BV	0.0624	15.88967	3.99949	1.0420
2	3.072	VB	0.0738	67.94402	14.20111	4.4556
3	3.626	BB	0.0728	18.25790	3.88650	1.1973
4	4.443	BB	0.1319	20.50433	2.17663	1.3446
5	14.729	BBA	0.2608	1402.30469	90.50765	91.9604
Total				**1524.90062**	**114.77139**	

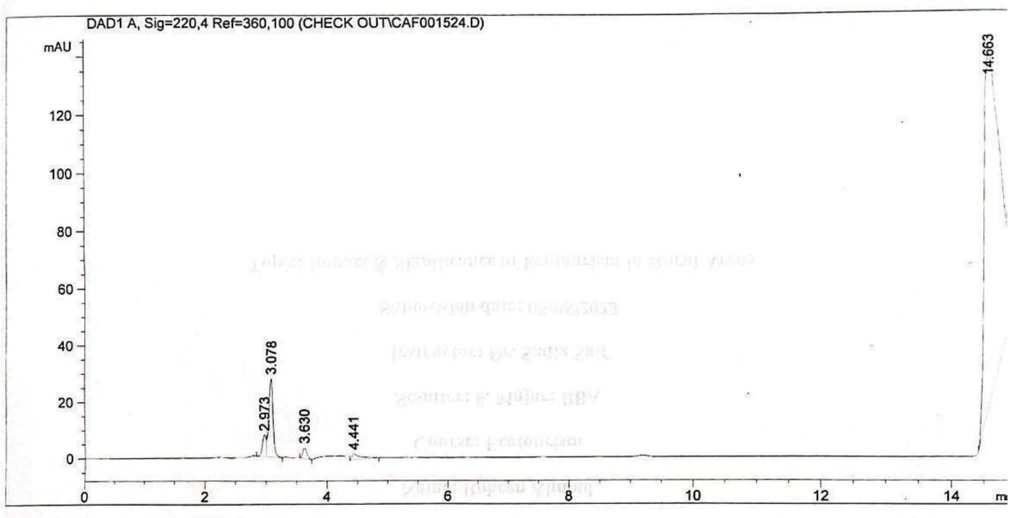


Figure 4.23 Chromatogram of Sample V10

Table 4.53 Sample V10 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.973	BV	0.0609	30.00417	7.47015	1.3299
2	3.078	VB	0.0718	130.97873	27.39395	5.8055
3	3.630	BB	0.0747	17.75589	3.78968	0.7870
4	4.441	BB	0.1366	21.81554	2.18330	0.9669
5	14.663	BBA	0.2859	2055.56812	117.62542	91.1107
Total				**2256.12244**	**158.46250**	

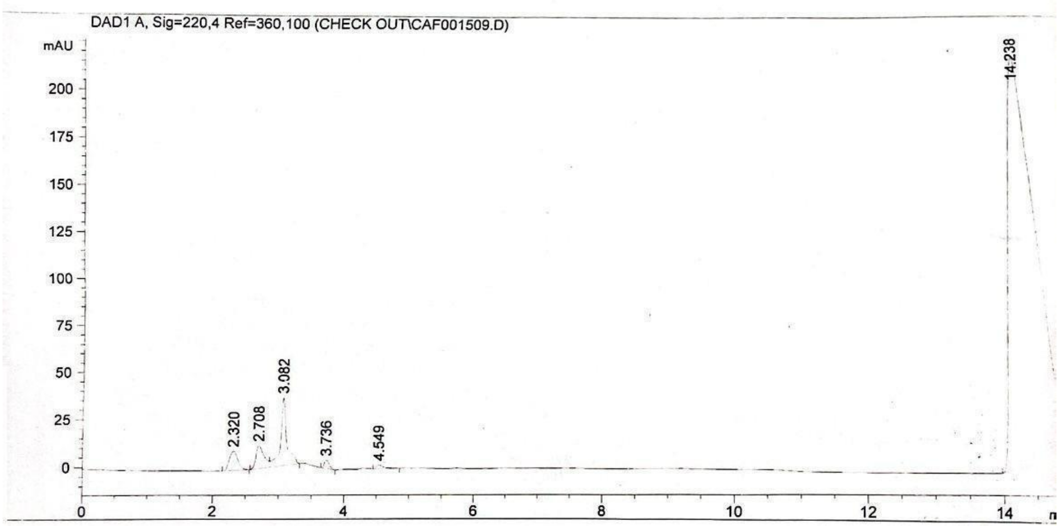


Figure 4.24 Chromatogram of Sample V11

Table 4.54 Sample V11 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.320	BB	0.1418	89.31460	10.03381	1.4017
2	2.708	BV	0.1211	101.99502	12.00347	1.6007
3	3.082	VB	0.0919	238.49159	35.72165	3.7428
4	3.736	BB	0.0836	23.94886	4.39293	0.3758
5	4.549	BB	0.1189	16.53387	2.07540	0.2595
6	14.238	BBA	0.4027	5901.77783	216.05241	92.6196
Total				**6372.06178**	**280.27967**	

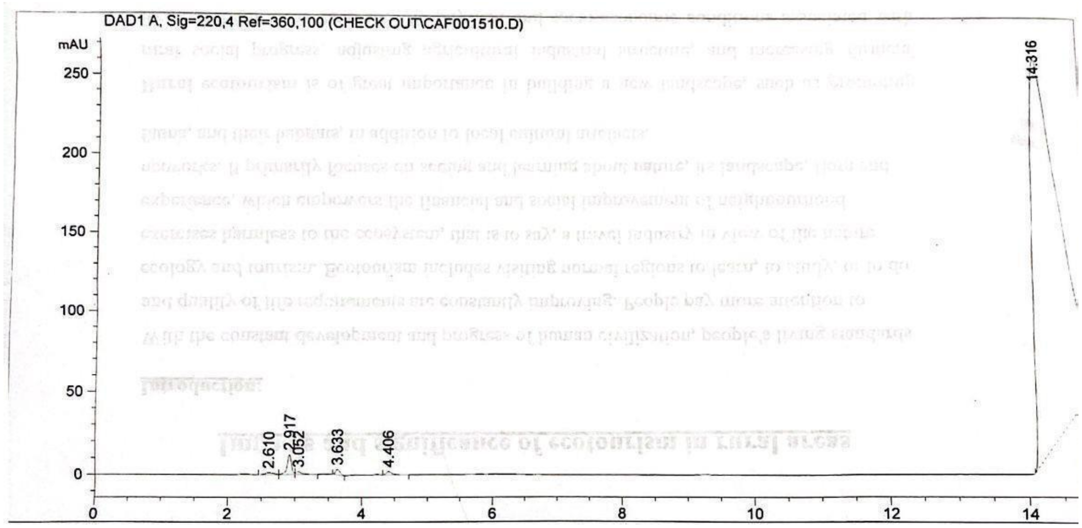


Figure 4.25 Chromatogram of Sample V12

Table 4.55 Sample V12 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.610	BV	0.1127	9.62621	1.18639	0.1425
2	2.917	VV	0.0637	51.30963	12.03950	0.7598
3	3.052	VB	0.0840	9.89390	1.69842	0.1465
4	3.633	BB	0.0722	15.02514	3.23657	0.2225
5	4.406	BB	0.0854	12.42664	2.14985	0.1840
6	14.316	BBA	0.4004	6655.08789	246.97656	98.5447
Total				**6753.36941**	**267.28730**	

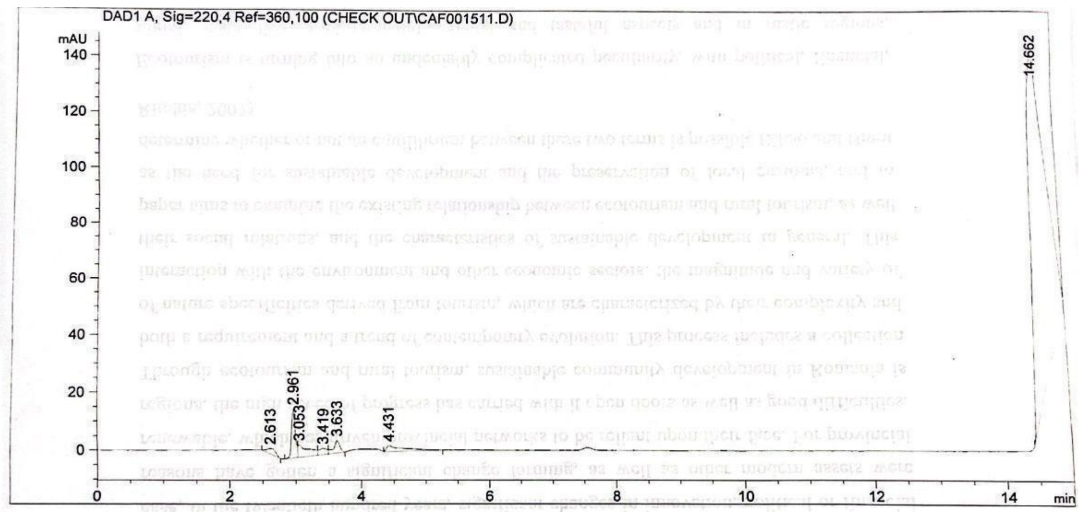


Figure 4.26 Chromatogram of Sample V13

Table 4.56 Sample V13 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.613	BB	0.1537	18.21938	1.86913	0.7921
2	2.961	BV	0.0592	65.69281	16.96075	2.8561
3	3.053	VV	0.1486	49.17717	4.26098	2.1381
4	3.419	VV	0.1141	18.17749	2.16194	0.7903
5	3.633	VB	0.0968	29.24701	4.32805	1.2716
6	4.431	BB	0.2344	37.61656	2.04674	1.6354
7	14.662	BBA	0.2845	2081.95581	118.75890	90.5164
Total				**2300.08623**	**150.38649**	

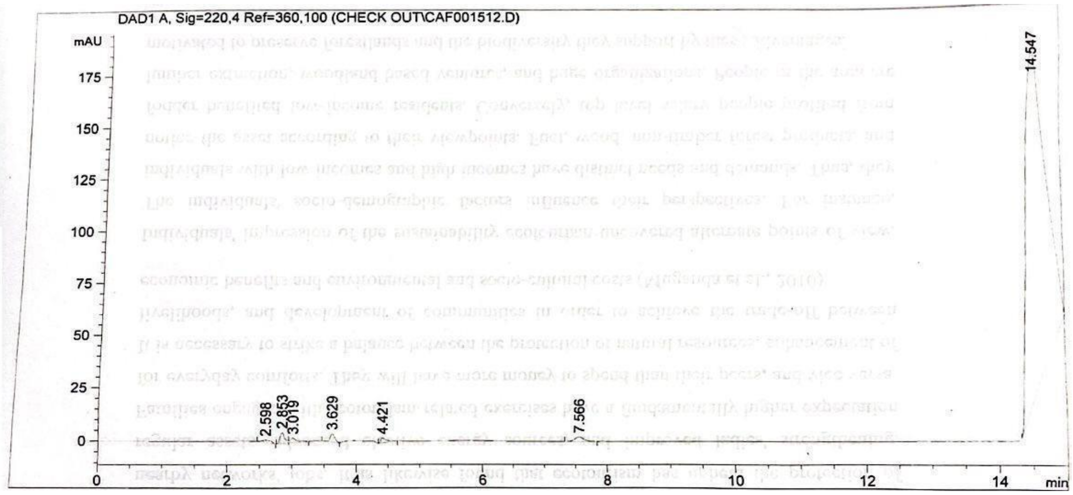


Figure 4.27 Chromatogram of Sample V14

Table 4.57 Sample V14 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.598	BB	0.1375	10.96420	1.05307	0.3105
2	2.853	BV	0.0757	26.02865	5.09035	0.7372
3	3.019	VB	0.1004	14.77654	2.04170	0.4185
4	3.629	BB	0.0786	19.02084	3.78619	0.5387
5	4.421	BB	0.0934	14.38594	2.16830	0.4074
6	7.566	BB	0.1516	20.56632	2.11228	0.5825
7	14.547	BBA	0.3217	3425.03784	166.70491	97.0051
Total				**3530.78034**	**182.95679**	

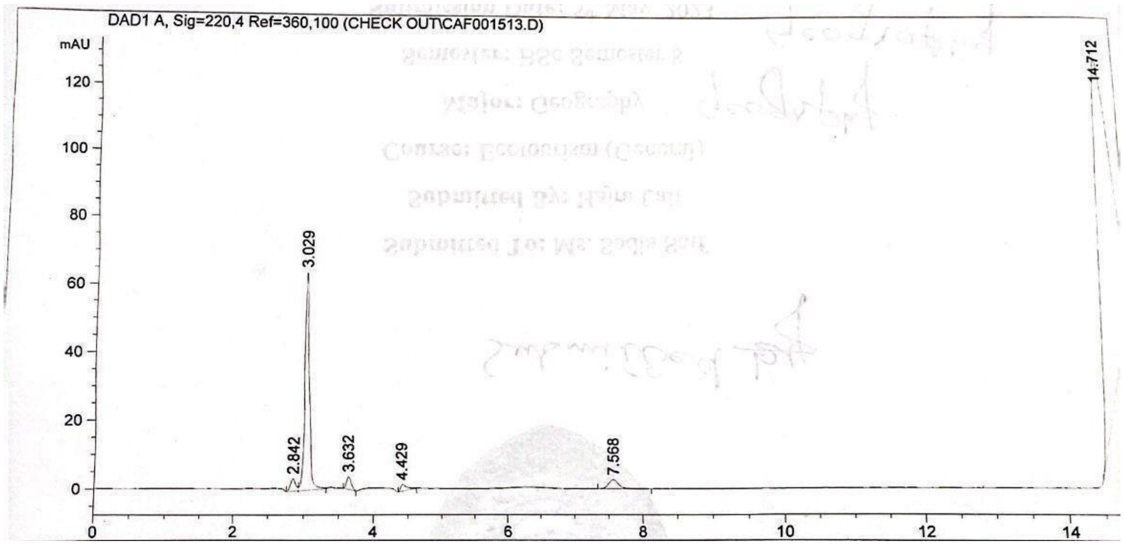


Figure 4.28 Chromatogram of Sample V15

Table 4.58 Sample V15 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.842	BV	0.0764	18.16793	3.62954	0.9004
2	3.029	VV	0.0690	292.57132	64.39332	14.4999
3	3.632	BB	0.0719	16.94736	3.67043	0.8399
4	4.429	BB	0.1001	13.06678	1.95230	0.6476
5	7.568	BB	0.1537	26.57337	2.63372	1.3170
6	14.712	BBA	0.2651	1650.42578	101.83400	81.7953
Total				**2017.75255**	**178.11331**	

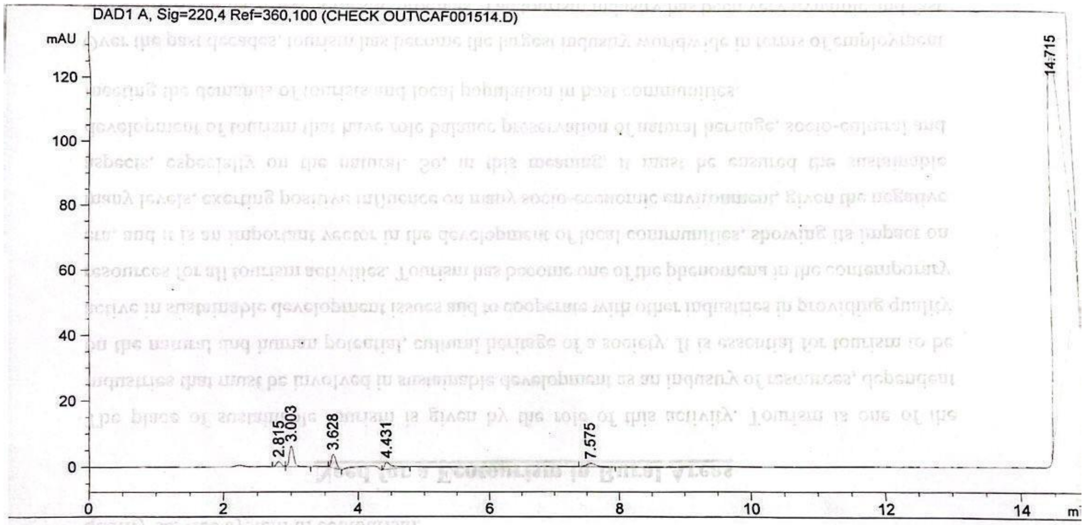


Figure 4.29 Chromatogram of Sample V16

Table 4.59 Sample V3 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	2.815	BV	0.0818	8.18510	1.59795	0.4860
2	3.003	VB	0.0703	29.25653	6.28752	1.7372
3	3.628	BB	0.0762	19.67602	4.08264	1.1683
4	4.431	BB	0.1194	18.76095	2.20204	1.1140
5	7.575	BB	0.1551	10.30226	1.04456	0.6117
6	14.715	BBA	0.2655	1597.93726	100.49239	94.8827
Total				**1684.11811**	**115.70709**	

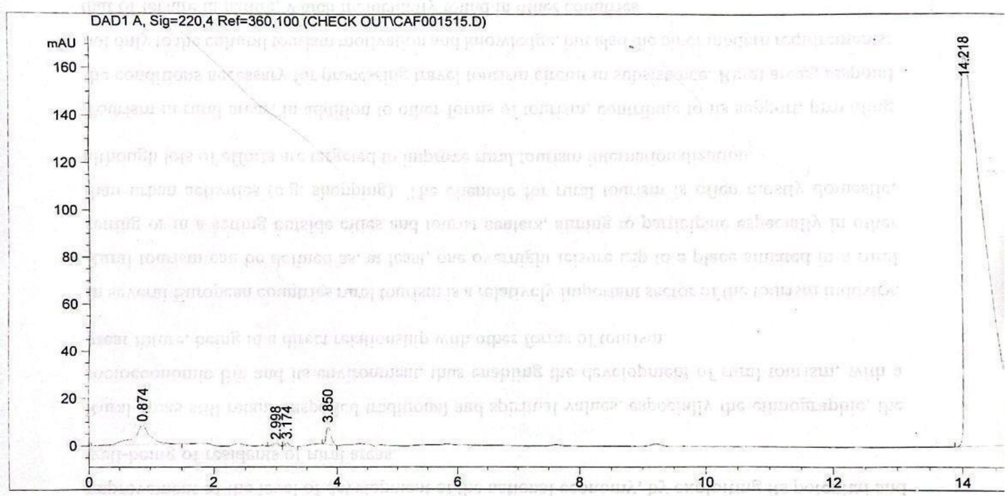


Figure 4.30 Chromatogram of Sample V17

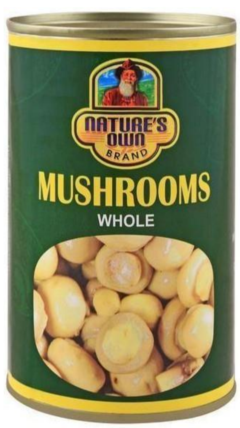
Table 4.60 Sample V17 showing peak values

Peak #	Ret time (min)	Type	Width (min)	Area (mAU*s)	Height (mAU)	Area %
1	0.874	BB	0.2553	151.64714	8.14232	3.5880
2	2.998	BV	0.1096	8.49474	1.21451	0.2010
3	3.174	VB	0.0741	7.01544	1.45939	0.1660
4	3.850	BB	0.0845	40.49654	7.55499	0.9582
5	14.218	BBA	0.3639	4018.86279	165.16431	95.0869
Total				**4226.51665**	**183.53552**	

Annexure II

Sample 1 Sweet Corn

Sample 2 Green Peas



Sample 3 Mushrooms

Sample 4 Green Olives

Sample 5 Red kidney beans

Sample 6 Garlic Clove

Sample 7 Red Chilli

Sample 8,9 Cauliflower, Carrot

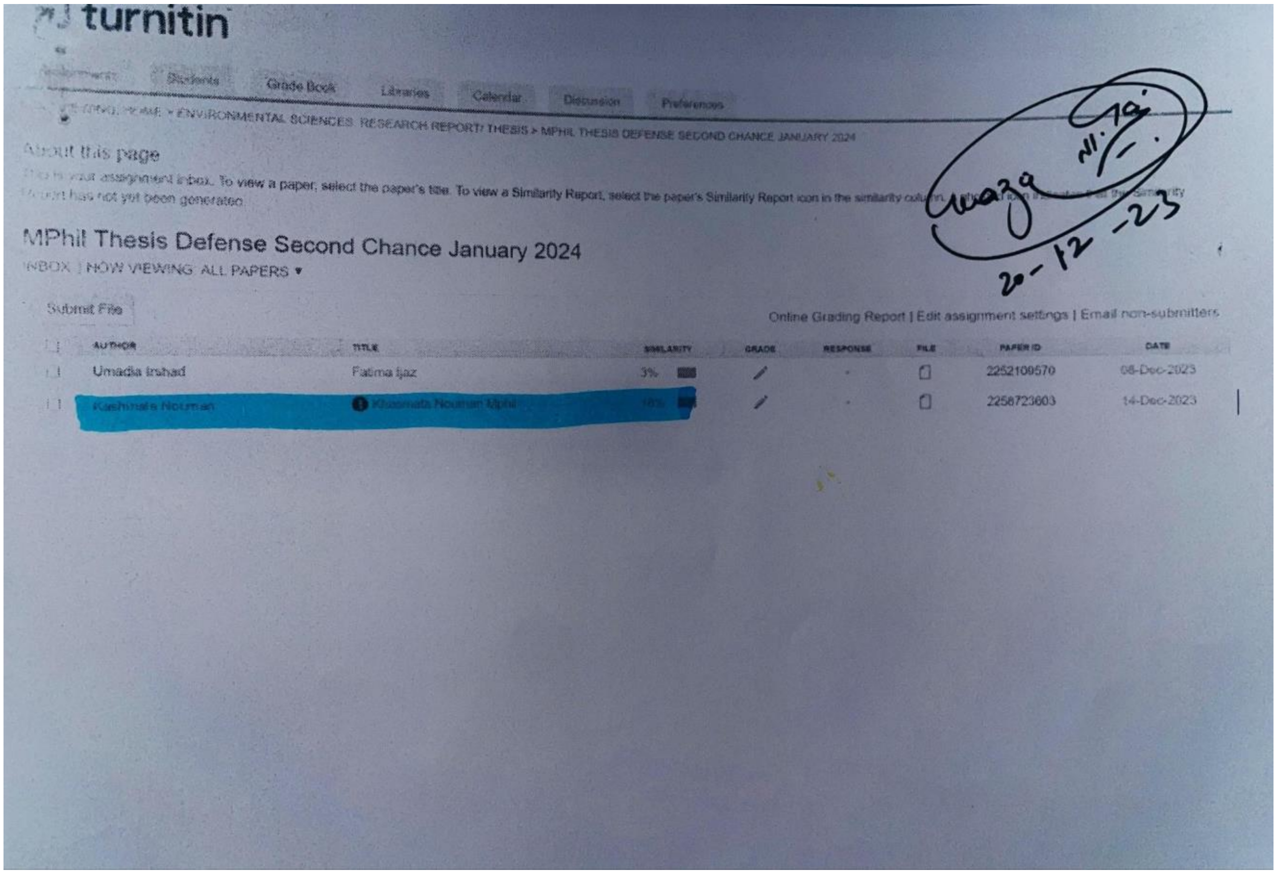
Sample 10 Lemon

Sample 11,12,13 Peach, Grapes, Pear

Sample 14,16 Pineapple and Papaya

Sample 15 Red Cherry

Sample 17 Lychee



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