ECOLOGICAL AND HUMAN HEALTH RISK ASSESSMENTS BASED ON HEAVY METAL AND PESTICIDE RESIDUES IN SOIL AND VEGETABLES AROUND LAKE ZIWAY, ETHIOPIA

PhD DISSERTATION

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HAWASSA UNIVERSITY, HAWASSA, ETHIOPIA

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This is to certify that the dissertation entitled "*ECOLOGICAL AND HUMAN HEALTH RISK ASSESSMENTS BASED ON HEAVY METAL AND PESTICIDE RESIDUES IN SOIL AND VEGETABLES AROUND LAKE ZIWAY, ETHIOPIA*" submitted in partial fulfilment of the requirements for the degree of **Doctor of Philosophy (PhD)** with specialization in Environmental Toxicology, to the Graduate Program of the Department of Biology, and has been carried out by **Asrat Fekadu Demsie ID. No. PhD ET/0003/11,** under our supervision. Therefore, we recommend that the student has fulfilled the requirements and hence hereby can submit the dissertation to the department.

1. **Girma Tilahun (Associate Professor)**
   Name of major advisor

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Signature Date

2. **Solomon Sorsa (Professor)**
   Name of co-advisor

___________________________ _____________________

Signature Date

DECLARATION

I hereby declare that this PhD dissertation is my original work and has not been presented for a degree in any other university, and all sources of material used for this dissertation have been duly acknowledged.

Name: Asrat Fekadu Demsie
Date: May 2024
Signature: _______________

DEDICATION

May this work serve as a memorial to all those who lost their lives to cancer, including my mother Fanayea Demsie.

BIOGRAPHICAL SKETCH

The author of this text is Asrat Fekadu and he was born on September 19, 1987, in Addis Ababa, Ethiopia. He attended Nesanet Chora Elementary and Junior Secondary School from 1992 to 1999 for his elementary education. For his secondary and preparatory education, he attended Werda 20 High School from 2000 to 2003. In 2003, he took the Ethiopian University Entrance Examination and joined Jimma University Ambo College in 2004, where he obtained a Diploma in Chemistry in 2005. After graduating with a Diploma, he worked as a laboratory technician at Hawassa College of Teachers' Education in 2006.

The author joined Hawassa University in 2007 to study BSc in Medical Laboratory Technology, which he completed in 2011. Soon, he rejoined same University to study Master of Science in Limnology, Fisheries, and Aquatic Ecotoxicology from 2012 to 2014, which he successfully completed. After completing his MSc, he became a lecturer at Hawassa College of Teachers' Education. In 2019, he returned to Hawassa University to pursue a PhD in Environmental Toxicology, and this dissertation is the result of his research.

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EXECUTIVE SUMMARY

The excessive use of pesticides can lead to harmful residues accumulating in vegetables, posing risks to human health. Therefore, regular monitoring and assessment of these potential health hazards are crucial. This study utilized the QuEChERS extraction method to analyze 15 composite samples (vegetables and soil). It employed an inductively coupled plasma optical emission spectrometer (ICP-OES) to detect heavy metal contamination in 18 composite samples of vegetables and soil. The findings revealed that some pesticide residues exceeded safety limits in tomatoes and onions. In tomatoes, α-endosulfan (0.58 mg/kg), β-BHC (beta-benzene hexachloride) (0.04 mg/kg), heptachlor (0.02 mg/kg), and Malathion (0.03 mg/kg) surpassed safety limits. Similarly, the average concentrations of heptachlor epoxide (0.04 mg/kg) and propargite (0.11 mg/kg) exceeded safety limits for onions. The study also evaluated potential health risks for adults and children, identifying both carcinogenic and non-carcinogenic risks. Non-carcinogenic health risk estimates indicated that onion heptachlor epoxide posed a systemic health risk for adult and child consumers with THQ (Target hazard quetient) > 1. Carcinogenic health risks (CHRs) revealed that heptachlor epoxide was present in levels exceeding acceptable limits (10^{-4}) for both adults and children, while the CHRs of tomatoes and onions surpassed acceptable limits only for children. Additionally, heavy metal contamination of vegetables presents a significant concern, especially in areas with prolonged irrigation. The excessive use of agrochemicals particularly impacts the central region of the Rift Valley in Ethiopia. In a study of a soil-vegetable system irrigated by Lake Ziway in Ethiopia, researchers analyzed the levels of nine heavy metals (As, Cd, Cr, Co, Cu, Hg, Ni, Pb, and Zn). The analysis revealed that the concentrations of lead (Pb), arsenic (As), mercury (Hg), and chromium (Cr) in all tomato and onion samples exceeded the thresholds set by the FAO/WHO. In addition, the average concentrations of Zn, Pb, Cd, and Hg in all soil samples under tomato and onion plants were found to be above the recommended levels. This poses significant health risks, including systemic and cancerous effects. Moreover, traditional farming methods in the region were found to pose a high ecological risk to non-target soil species due to the use of common pesticides. The study aimed to assess the ecological risks that pesticides could pose to soil biotas, such as earthworms, springtails, and nitrogen mineralization organisms. The evaluation was based on the use of toxicity exposure ratios (TERs) and risk quotient (RQ) methodologies to determine general and worst-case scenarios, respectively. Of the detected pesticides, α-BHC, heptachlor, fenthion, parathion, and propoxur were detected at a rate of 100%. The highest concentration of 119.9 μg/kg was found for p,p'-DDE. Fenthion and Chlorpyrifos methyl posed a chronic exposure risk to *F. candida* *($TER_{max}=0.86$)* and N mineralization organisms ($\mathrm{TER}_{\mathrm{max}}=1.2$), respectively. Non-target soil species are at high ecological risk (RQs > 1) due to Alpha-endosulfan, which contributes to more than 90% of the risk than the other pesticides. The ecological risk assessment (ERA) reported that the overall pesticide mixture in soil poses a high ecological risk $\sum RQ=5.3$ in both scenarios. Conventional farming practices in the study area put soil organisms at risk. Therefore, it is crucial to establish effective monitoring protocols and raise awareness among stakeholders to ensure the preservation of the environment and the population's well-being. Furthermore, replacing harmful pesticides with low-risk alternatives is recommended to mitigate these risks. Urgent policies for awareness and surveillance are necessary to protect public health within and beyond the research field.

LIST OF ABBREVIATIONS AND ACRONYMS

AF	Assessment Factor
BCF	Bioconcentration Factor
CA	Concentration Addition
CEC	Cation Exchange Capacity
CERV	Central Ethiopian Rift Valley
EC	European Commission
EC50	50% Effective Concentration
EDI	Estimated Daily Intake
ERA	Ecological Risk Assessment
ERI	Ecological Risk Index
GC-MS	Gas Chromatography-Mass Spectrometry
HI	Hazard Index
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IDF	International Dairy Federation
MPL	Maximum Permissible Limit
MRL	Maximum Residue Limit
NCHR	Non Carcinogenic Health Risk
NOEC	No Observed Effect Concentration
OECD	Organization for Economic Cooperation and Development
OM	Organic Matter
PCA	Principal Component Analysis
PNEC	Predicted No Effect Concentration
RQ	Risk Quotient
SPSS	Statistical Package for Social Sciences
TCR	Target Cancer Risk
TERs	Toxicity-Exposure Ratio
THQ	Target Hazard Quotient
USEPA	United States Environmental Protection Agency

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CHAPTER ONE

1. GENERAL INTRODUCTION

1.1. Background and Justification of the Study

The world's population is expected to reach 10 billion by 2050, resulting in a 50% increase in demand for agricultural products compared to 2013 (FAO, 2017). To meet the growing population's needs, the United Nations Food and Agriculture Organization (FAO, 2018) has suggested a 54% increase in vegetable production and a 56% increase in cereal production between 2012 and 2050 (FAO, 2018). However, the misuse of agricultural chemicals, such as pesticides and fertilizers, is a significant concern, particularly in developing countries where it is widespread (Parven *et al*., 2021; Qin *et al*., 2021). This raises concerns for consumers since even trace amounts of pesticide residues in vegetables can pose a health risk to humans (Beyene Negatu *et al*., 2021).

Chemical pesticides and fertilizers are commonly used in agriculture to control pests and increase crop yields. However, studies conducted by Barau *et al.* (2018) and Usman *et al.* (2020) have found that the excessive use of these chemicals has led to the contamination of the environment with heavy metal residues that exceeded permissible limits. This poses a significant threat to human health and the environment.

For instance, copper-containing fungicides like copper sulfate (also known as Bordeaux mixture), copper oxychloride, lead-containing insecticides like lead arsenate, and copper-containing insecticides such as copper acetoarsenite were found to contain high concentrations of heavy metals in their active ingredients (Rashid *et al*., 2023). Heavy metals: Copper (Cu), Arsenic (As), Lead (Pb), Mercury (Hg), chromium (Cr), Zinc (Zn), Aluminum (Al), Lithium (Li), Barium (Ba), Boron (B), and Titanium (Ti) are frequently present in Fertilizers (Benson, 2014; Salem et al., 2020) and pesticide products' active ingredients, as reported by Lewis *et al.*(2016). Furthermore, some heavy metal elements may contaminate pesticide products during the manufacturing process, while others may be intentionally added as Nano-pesticides for greater efficacy, as pointed out by Priyanka *et al.*(2020).

In the Ethiopian Rift Valley, agriculture is estimated to account for more than 75% of the entire land in the Lake Ziway basin (Awdenegest Moges *et al.*, 2023). The population in this area heavily relies on fertilizers, mainly urea and DAP (Hayal Desta *et al.*, 2015; Dessie Tibebe, 2017). According to the findings, urea and DAP are the primary sources of HM in agricultural soils (Benson, 2014; Salem *et al.*, 2020). On the other hand, heavy metals are natural elements present in the soil. However, human activities have disrupted their balance and caused changes in their biochemical and geochemical cycles (Bawa, 2023). Previous studies have shown that phosphate fertilizers tend to have high levels of heavy metal (HM) contaminants. For instance, superphosphate fertilizers might contain Cd, Co, Cu, Pb, Zn, Cr, and Ni (Wei *et al.*, 2020; Rashid *et al.*, 2023). Moreover, P fertilizers have been observed to increase the concentration of Cd in the soil over time (Gambuoe & Wieczorek, 2012; Bawa, 2023).

As literature showed, synthetic pesticides were first used in the 1950s in Ethiopia to manage desert locusts and armyworms (MoANR, 2016), while mineral fertilizers were introduced in the late 1960s (PAN-Ethiopia, 2020). However, the use of both pesticides and fertilizers remained minimal until 1995 when an agricultural intensification policy was introduced, leading to a significant increase in consumption (Tadesse Amera & Asferachew Abate, 2008; Rashid *et al*., 2013). According to the FAO (2017), there has been a steady increase in agricultural pesticide and fertilizer use in Ethiopia (as shown in Figure 1.1). This increase is mainly due to the expansion of large-scale horticulture and floriculture investments by foreign and domestic investors in the country (Berhan Mellese, 2016).

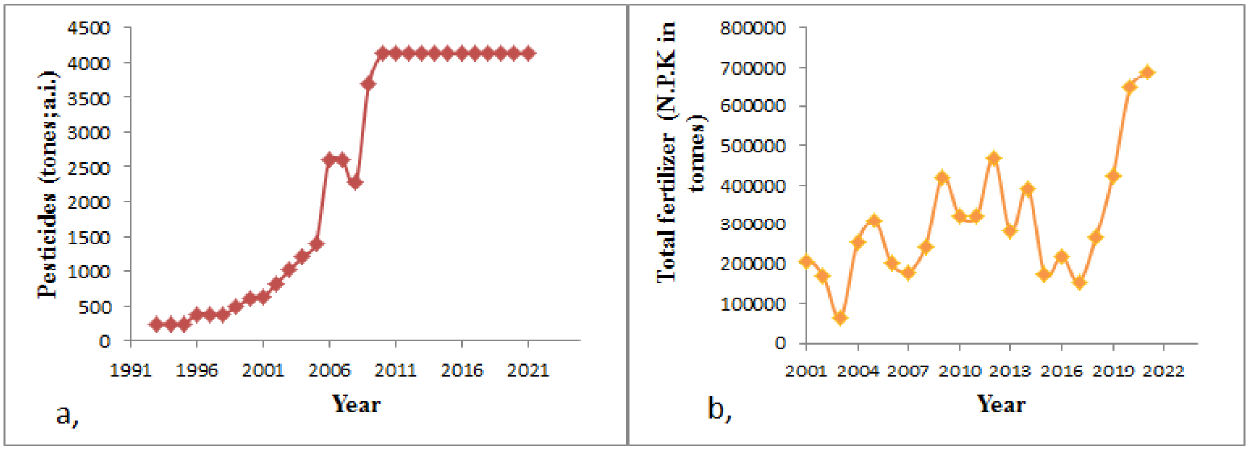

Figure 1-1 Pesticides use in weight of active ingredients in tones/year (a) and mineral fertilizers in tones/year (b) in Ethiopia. Graphs generated using FAO data (https://www.fao.org/faostat/en/#data/RFN)

Ethiopia is a country situated near the equator, where agriculture heavily relies on synthetic pesticides and fertilizers to enhance soil fertility and prevent crop losses. However, it is crucial to monitor the levels of pesticide residue in crops and the environment to ensure they do not exceed the safety limits. Despite implementing good agricultural practices (GAPs), some residues may continue to exist. Developed countries have established pesticide compliance audits (OECD, 2012), but developing countries, including Ethiopia, often lack the necessary resources and experience to enforce legislation effectively (FAO, 2017).

Although Ethiopia has ratified international conventions and agreements related to pesticides, including the Rotterdam, Stockholm, Basel, and Bamako conventions, as well as the FAO code of conduct on pesticide distribution and use, there is still a significant gap in the implementation of these conventions. Ethiopia has not yet established its maximum residue limit (MRL) for monitoring pesticide use, so it relies on the Codex Alimentarius Commission or FAO/WHO limit as a reference since it is a member country. This means that vegetable products can only be exported to nearby countries (Somalia, Djibouti, Saudi Arabia and UAE) since the European Union has set more stringent MRLs than the Codex Alimentarius Commission. One of the main reasons for this is the inability to prove that pesticide use is compliant with GAP and that the MRLs are within the required limits. This poses a constraint for Ethiopia's access to the EU market (CBI, 2020).

The European Union (EU) has recently updated its policy regarding the MRLs for certain pesticides allowed on horticulture imports. The new policy sets significantly lower permissible limits at 0.01 milligrams per kilogram (mg/kg), as reported by the Food Business Africa (2019). This is much lower than the international standard MRL level of 2.0 mg/kg (CBI, 2020). As a result, it is crucial to conduct inspections for MRL and risk assessment to meet this requirement and to supply the demand for organic fruits and vegetables.

Concerning the registration, distribution, and application of pesticides, Ethiopia has regulations that govern. However, there are concerns about the effectiveness of these policies at both the national and local levels due to insufficient implementation and a lack of legal instruments, as highlighted by Belay Tizazu *et al*. (2016). Previous research has also shown that the uncontrolled use of pesticides over an extended period has had adverse effects on both the soil and vegetables in the Central Ethiopian Rift Valley (CERV) area (Kumelachew Mulu *et al*., 2020; Lemessa Bente *et al*., 2021). This has led to the accumulation of heavy metals in them. Unfortunately, there is a lack of available data in the region, particularly on the ecological and human health risks, especially for children and adults residing on the irrigated agricultural farms in the area.

This investigation aimed to measure the presence of heavy metals and pesticides in the soil-vegetable system. It also evaluated the potential ecological and human health hazards, both carcinogenic and non-carcinogenic, to adults and children who consume contaminated tomatoes and onions. Furthermore, this analysis intends to ensure the safety of people, including adults and children, residing in the study area and beyond.

1.2 Statement of the problem

In the CERV, there has been a considerable increase in the irrigation of farmlands around Lake Koka and Lake Ziway, thanks to favorable climatic and socio-economic conditions. Lake Ziway, the largest lake in the CRV, provides water to irrigate nearby farmlands all year round, but there is a concern that untreated or inadequately treated urban and industrial wastewater may be reaching these farmlands. To promote a safe and sustainable environment that is protected from the harmful effects of pesticides and hazardous chemicals, the Pesticides Action Network International-UK and Pesticide Action Nexus Ethiopia (PANE) have partnered. Their objective is to promote collaboration among the government, non-governmental organizations, civil society interest groups, and urban and rural communities to reduce pesticide use and implement ecologically friendly pest and production management practices nationwide.

Despite their efforts, smallholder farmers in the Ziway area are still using 18 out of the 28 highly hazardous pesticides (HHPs) identified by PAN-UK (2017). These HHPs pose acute human toxicity, chronic human health, and environmental risks. Additionally, out of the 409 registered pesticides in 2016, 236 (58%) are considered HHPs and listed under the 2019 PAN HHPs list, as reported by PANE in 2020. Furthermore, there have been very few studies conducted to examine the pollution levels of farm soils, irrigation water, vegetables, and fruits grown in irrigated farmlands around Lake Ziway (Tolera Seda *et al*., 2019; Hailu Reta & Leta Danno, 2020; Leta Danno & Hailu Reta, 2021).

1.3 Objectives of the Study

1.3.1 General Objectives

The general objective of the study was to determine the ecological and human health risks based on heavy metal and pesticide residues in soil and vegetables around lake Ziway, Ethiopia.

1.3.2 Specific Objectives

This research paper aimed to achieve the following specific objectives:

1. To assess pesticide residues and associated public health risks in vegetables from irrigated farms adjacent to Lake Ziway, Ethiopia (Chapter III).
2. To assess the potential human health risk associated with heavy metals in the soil–vegetable system irrigated by Lake Ziway, Ethiopia (Chapter IV).
3. To evaluate the potential ecological risk in irrigated horticultural farms near Lake Ziway, Central Ethiopian Rift Valley Region (Chapter V).

1.3.3 Research Questions

The aim of this study was to assess the levels of heavy metal and pesticide residues in the soil and vegetables from farms near Lake Ziway in Ethiopia. Additionally, the research aimed to investigate the potential environmental and human health risks associated with these contaminants. Specifically, the study sought to address the following questions:

1. What is the level of pesticide residues in vegetables and associated public health risks in vegetables from irrigated farms in the study area?
2. What is the level of heavy metals in irrigated soil-vegetables System and associated public health risks in vegetables from irrigated farms in the study area?
3. What is the potential ecological risk due to the contaminant in the study area?

1.4 Scope and limitations of the study

The study was conducted on three irrigated farmlands located between Meki and Ziway in three villages: Abenea-Girmama, Wellibulla, and Girrissa. These farmlands are situated adjacent to the western side of Lake Ziway in the CRV basin of Ethiopia. These are sites where vegetables are grown in a large field with a large number of pesticide users and near Lake Ziway fresh water. However, the study has some limitations. The number of sample sites and samples was limited due to the lack of resources to cover the full cost of the study.

1.5 General description of the study area

The study area is situated near Lake Ziway, along the international highway to Moyale (Kenya) (Fig 1.2). It is 130- 150 km to South of Addis Ababa. Lake Ziway is the largest freshwater lake in CERVR, with a surface area of 434 km^2. It has a maximum depth of 8.9 m, making it the shallowest. The lake is home to numerous hippopotamuses, commercially important fish species, and indigenous bird species that nest on the five islands and the lake's shoreline. The Ziway catchment covers an area of approximately 7300 km^2, located between 07^{0}57' N and 08^{0}30' N latitude and 38^{0}E to 39^{0}30' longitude, as reported by Hughes & Hughes (1992) (Fig 1.2). As per Hayal Desta *et al*. (2017), there have been recent changes in land use and land cover in the Lake

Ziway region. Agricultural and settlement areas have expanded from 57% in 1973 to 75% in 2014, at the cost of forests, which were reduced from 26.16% to 6.63%. The climate in the area ranges from semi-arid to arid, with an average annual rainfall of 700 mm, with an elevation of 1,643-1,655 m above sea level (Mulugeta Musie *et al.*, 2020). The maximum temperature during the short rainy season ranges from 25 to 29 °C (locally known as Belg) and the peak temperature during the rainy season (known as Kiremt) ranges from 22 to 26°C (Kumelachew Mulu *et al.*, 2020).The irrigated farm's soil type is sandy loam, and the main crops cultivated are onion, tomato, cabbage, and green pepper, with maize and beans also widespread in the area.

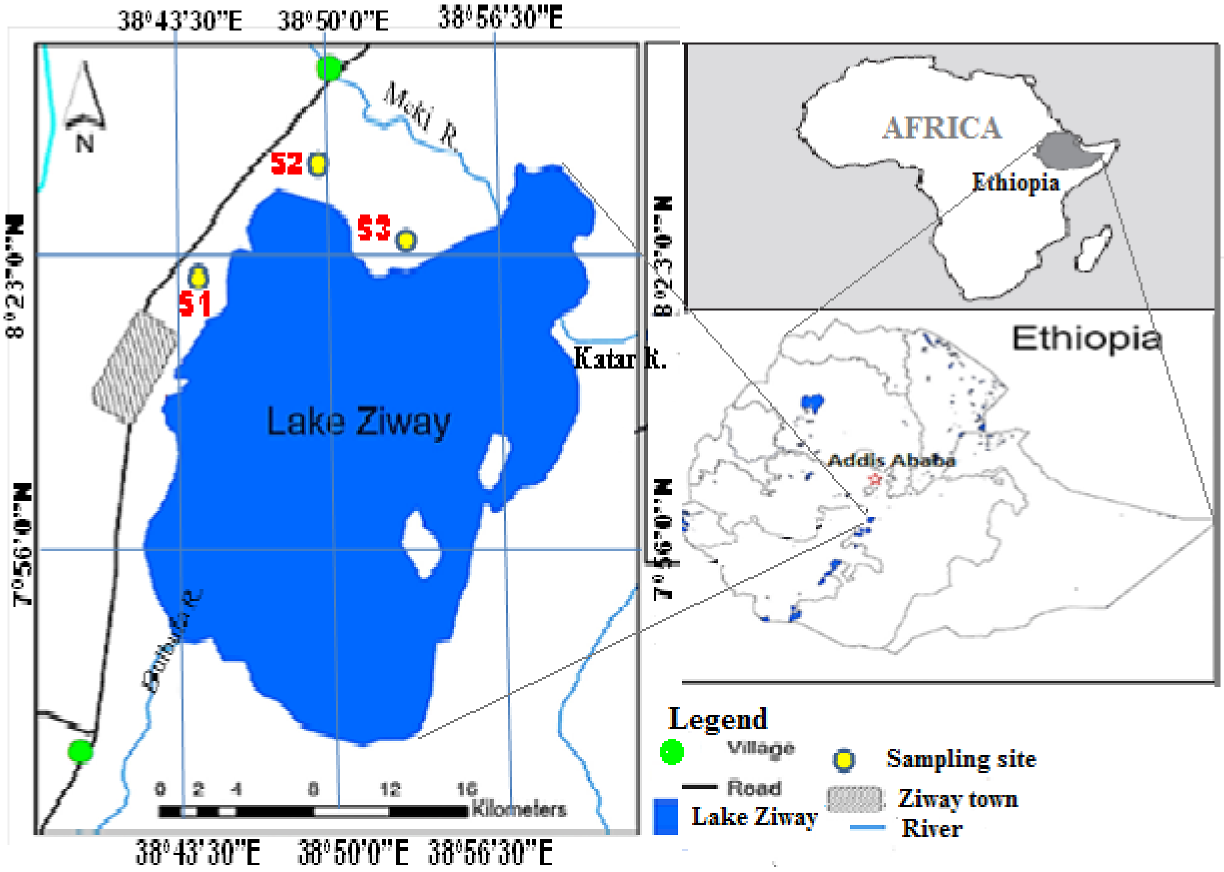

Figure 1-2 Lake Ziway and the location of the three sampling sites

1.6 Dissertation Structure

This dissertation consists of six chapters, which are listed as follows:

Chapter 1 presents the background and justification of the study, including the problem statement, objectives, research questions, scope and limitations, general description of the study area, and dissertation structure.

Chapter 2 presents a literature review that includes the definition of pesticides and heavy metals, the classification of pesticides, and the discussion of pesticides and fertilizers as sources of heavy metals. It also covers the exposure of humans to pesticides and heavy metals, as well as the associated health risks from pesticide residues and heavy metals.

Chapter 3 focuses on the presence of pesticide residues in vegetables that are grown in farms irrigated by Lake Ziway in the Rift Valley, Ethiopia. The objective of the study was to determine the potential hazards of pesticide residues found in tomatoes (*Lycopersicon esculentum* L.) and onions (*Allium cepa* var. aggregatum) to human health. The samples underwent analysis for pesticide concentrations and were compared to the EU-MRL standards.

To assess the risks associated with consuming these vegetables, target hazard quotients (THQs), hazard index (HI), and target cancer risks (TCRs) were used. The study's findings provide significant insights into the levels of pesticide residues in vegetables grown in farms that rely on Lake Ziway for irrigation and the potential risks these residues may pose to human health.

Part of this chapter has been published in the Journal of Food Quality in publisher of Wiley/Hindawi, under the title "**Pesticide Residues and Associated Public Health Risks in**

Vegetables from Irrigated Farms Adjacent to Rift Valley Lake Ziway, Ethiopia". (https://doi.org/10.1155/2024/5516159)

Chapter 4 focuses on assessing potential human health risks associated with heavy metals in the soil-vegetable system irrigated using Lake Ziway in the Rift Valley of Ethiopia. This chapter presents findings from a study that analyzed heavy metal concentrations in tomatoes and onions grown in irrigated farms around Lake Ziway. The levels of heavy metals detected were compared to FAO/WHO standards. The study used indices such as THQs, HI, and TCRs to determine the associated health risks for adults and children who consume these vegetables. The results provide baseline information on heavy metal levels in vegetables and the potential health risks associated with their consumption from the irrigated farms around Lake Ziway.

Part of this chapter has been published in the Journal of **Analytical Letters** in the Taylor and Francis publisher (www.tandfonline.com/journals/lanl20) under the title of "Assessment of Potential Human Health Risk Associated with Heavy Metals in Soil-Vegetable System Irrigated by Rift Valley Lake Ziway, Ethiopia." https://doi.org/10.1080/00032719.2024.2330487 .

Chapter 5 focuses on the level of pesticide residues in soil and the ecological risk assessment of pesticides on soil biota around Lake Ziway, Ethiopia. The study examines the concentration of pesticide residues in irrigated soil and the ecological risks of pesticides to the soil biota, including earthworms, enchytraeids, springtails, mites, and nitrogen mineralization microorganisms, which were assessed using toxicity exposure ratios (TERs) and risk quotient (RQ) methods.

Part of this chapter has been submitted to the Journal of Toxicology under the title, "**Level of pesticide residues in soil and ecological risk on soil biota in irrigated vegetable farms near Lake Ziway, Ethiopia**." It is currently under review.

Chapter 6 provides an overall summary of the study and suggests recommendations based on the findings.

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CHAPTER TWO

2. LITERATURE REVIEW

2.1. Definition and concept of Heavy metals (HM) and Pesticide

2.1.1. Heavy Metals

The term "Heavy Metals (HM)" refers to naturally occurring elements with an atomic number greater than 20 and an elemental density greater than 5 g / cm^3, according to the definition proposed by Ali & Kha (2019). Metalloids are typically excluded from this category since they are generally less dense, lustrous, and hard than metals (**https://www.meadmetals.com**). However, in the present day, the term "HM" is often used to refer to both metals and metalloids associated with contamination and potential toxicity, regardless of their atomic mass or density (Aprile & De Bellis, 2020; Briffa *et al*., 2020). Therefore, the most common heavy metals found in the environment include lead (Pb), nickel (Ni), chromium (Cr), cadmium (Cd), arsenic (As), mercury (Hg), zinc (Zn), and copper (Cu) (Bakshi *et al*., 2018; Nkwunonwo *et al*., 2020). According to this study, arsenic (As) is classified as a heavy metal and is considered a metalloid. Additionally, any metal with a potential negative health effect or environmental impact may be termed a heavy metal, such as Cobalt (Co), Chromium (Cr), Lithium (Li), and even Iron (Fe).

Heavy metals have not only been known for their high density but most importantly for their adverse effects to the ecosystem and living organisms (Engwa *et al*., 2019). For example, Gall *et al*. (2015) and, Harguinteguy *et al*. (2016) have been reported heavy metals mercury (Hg), cadmium (Cd), arsenic (As) and lead (Pb) induce severe toxicity to living organisms even at low applied levels. Thus, they have been included in the top 20 list of dangerous substances by the United States Environmental Protection Agency and the Agency for Toxic Substances and

Disease Registry (ATSDR) (ATSDR, 2007; Rai *et al*., 2019). Moreover, those metals classically represent the “dark side of chemistry” due to their toxic effects already at low concentrations (Koller & Saleh, 2018). On the other hand, some heavy metals such as manganese (Mn), zinc (Zn), chromium (Cr), copper (Cu), iron (Fe) and nickel (Ni) are physiologically essential for living organisms as trace elements (TEs), but when present in excessive concentrations they may have harmful effects on microorganisms, animals, plants and humans (Antoniadis *et al*., 2017; Shahid *et al*., 2015). For instance, in the human body, these heavy metals are transported and compartmentalized into body cells and tissues binding to proteins, and nucleic acids destroying these macromolecules and disrupting their cellular functions, causing mutation, mimic hormones thereby disrupting the endocrine and reproductive system and ultimately lead to cancer (Järup, 2003).

2.1.1. Pesticides

Pesticides are chemical or natural compounds used to control pests in different fields such as agriculture, aquaculture, forestry, and food production (Akashe *et al*., 2018; Pathak *et al*., 2022). The United States Environmental Protection Agency (USEPA) defines pesticides as "any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest". The term pesticide encompasses a wide range of chemicals, including herbicides, fungicides, and substances used to control pests in addition to insecticides. Additionally, the World Health Organization (WHO) defines pesticides as substances used as growth regulators, defoliants, drying agents, fruit thinning agents, or to prevent the premature fall of fruit. This term also encompasses substances applied to crops before or after harvest to prevent deterioration during storage and transportation. Furthermore, pesticides include synergistic and detoxifying products when they are essential to the pesticide's satisfactory performance, according to the FAO.

Good Agricultural Practices (GAP) and regulations on pesticide usage are meant to help farmers produce crops using fewer agrochemicals, which in turn reduces pesticide residues in the final product (Inonda *et al*., 2015; Kılıç *et al*., 2020). However, these practices are not commonly followed in agricultural activities in developing countries (Dinede *et al*., 2023), leading to pesticide residues in the soil and the final product. The term "pesticide residues" refers to any remaining pesticide-active ingredients that may remain on or inside the food after being applied to crops (Njoku *et al.*, 2017). These residues may include any substance or combination of substances that result from the use of pesticides, such as degradation and conversion products, metabolites, reaction products, and impurities. According to the definition by WHO (2016), all these substances are considered toxicologically significant.

Pesticides in agricultural products are a major concern for consumers due to potential health risks and exposure to pesticide toxicity categorized into acute (short-term exposure) and chronic (long-term exposure) toxicity. The toxic effects of pesticide residues can be divided into two major categories, as Anderson & Meade (2014) reported. Acute effects include abdominal pain, headache, nausea, vomiting, diarrhea, and other similar symptoms. Long-term effects can lead to serious health problems such as cancer, depression, neurological deficits, genetic disorders, neurodevelopmental delays, endocrine disruption, respiratory distress, and immune system impact (Beyene Negatu *et al*., 2021).

2.2 Sources of Heavy metals and Pesticides in the environment

Heavy metals and pesticides are at the top of the list of environmental contaminants threatening nature (Alengebawy *et al.*, 2021). Its residues in the environment emanate from natural as well as anthropogenic sources (Alengebawy *et al.*, 2021; Ali & Khan, 2019; Meena & Mishra, 2020; Naccarato *et al.*, 2020; Rashid *et al.*, 2023). However, human activities are the primary sources and routes of distribution for heavy metals and pesticides in the environment. Therefore, the following sections provide detailed explanations of the various sources of heavy metals and pesticides in the environment.

2.2.1 Natural sources of HMs and pesticides

Heavy metals are naturally occurring elements found in the earth's crust, which persist in the environment because they cannot be degraded or destroyed (Ming-Ho, 2005). The primary sources of heavy metals are the weathering of metal-bearing rocks, volcanic eruptions, sea-salt sprays, forest fires, and biogenic sources (Ali & Khan, 2019; Masindi & Muedi, 2018). Pesticides also have natural sources, such as minerals, plants, or animals (Egwu *et al.*, 2019; Meena & Mishra, 2020). These organic pesticides break down relatively quickly due to weather or soil microbes. Examples of organic pesticides include diatomaceous earth (fossilized water microbes), neem oil (a tree oil extract), or pyrethrins (an extract from chrysanthemums) (Nnamonu & Onekutu, 2015). Among the natural sources of heavy metals, igneous and sedimentary rocks are considered to be the most common (Alengebawy *et al.*, 2021). Of the 92 natural elements, about 30 metals and metalloids are potentially toxic to humans, such as Be, B, Li, Al, Ti, V, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Mo, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, W, Pt, Au, Hg, Pb, and Bi (Aprile & De Bellis, 2020).

2.2.2 Anthropogenic Sources of Heavy Metals and Pesticides

Human activities such as agriculture, industry, application of sewage-sludge, and solid waste disposals are the primary sources of heavy metals and pesticides that are detrimental to the environment. These activities result in the buildup of toxic chemicals and heavy metals, which present a substantial environmental hazard (Das *et al*., 2021; Jiao *et al*., 2015). This section will briefly discuss some major anthropogenic sources of heavy metals and pesticides in the environment.

2.2.2.1 Agricultural activities

A. Irrigation with wastewater

Reusing wastewater is gaining global attention as an effective solution for addressing water scarcity (Contreras *et al*., 2017; Mishra & Bharagava, 2016). However, using wastewater for irrigation poses risks to human health and the environment due to residual pesticides, drugs, and chemicals that can end up on plant surfaces, be absorbed by crops, or contaminate the soil (Naik, 2014). Irrigation with wastewater and sewage water is a common practice in many developing countries, including Ethiopia. Previous studies reveal that Ethiopian farmers, particularly in urban areas, have been irrigating their crop plants with contaminated river water that contains high levels of toxic metals and pesticide residues (Mulate Zerihun *et al*., 2022; Bekele Bahiru, 2021; Samuel Bekele *et al*., 2021).

The effects of long-term wastewater irrigation on trace elements (TEs) content in soils under vegetable cultivation have been studied extensively in many rivers. For instance, the Akaki River in Addis Ababa was assessed extensively. Minbale Aschale *et al.* (2016) found toxic elements in farmland soil, including As, Cd, Cr, Co, Cu, Fe, Pb, Ni, and Zn, exceeding safety limits for vegetables. Kumelachew Mulu *et al.* (2020) reported pesticide concentrations exceeding safety limits for vegetables. Trace metals were also found in soil, vegetables, and fruits (Hayal Desta *et al*., 2017; Minbale Aschale *et al*., 2016).

B. Use of agrochemicals

Agricultural practices such as using fertilizers, pesticides, composts, and manure are common to increase agricultural yield. However, they can also increase the concentration of trace elements (TEs) and pesticide residues in the soil-vegetable system, which can be harmful to health. For example, phosphate-based fertilizers like Triple Super Phosphate (TSP) and Di-ammonium Phosphate (DAP) are widely used because phosphorous is an essential nutrient for plant growth (Gupta *et al*., 2014). However, these fertilizers can contain pollutants like chromium, cadmium, cobalt, lead, copper, zinc, and nickel (Rashid *et al*., 2023), which can be toxic. Similarly, fertilizers containing copper sulphate, iron sulphate, and zinc sulphate can also be contaminated with heavy metals like lead (Atafar *et al*., 2010).

In the Ethiopian Rift Valley, it has been reported that over 75% of the total land in the Lake Ziway catchment is used for agriculture. The people in this area rely heavily on fertilizers, with urea and DAP being the most commonly used types (Dessie Tibebe, 2017; Hayal Desta *et al*., 2015). According to the literature, urea and DAP are the primary sources of Hm in agricultural soils, as shown in Table 2.1.

The use of manures and compost is a common practice in agricultural crop production. However, these materials often contain high concentrations of harmful contaminants such as copper (Cu), zinc (Zn), cadmium (Cd), nickel (Ni), chromium (Cr), arsenic (As), lead (Pb), and mercury (Hg). Several studies, including Zhang *et al.* (2020) have reported on this issue. In addition, some studies have confirmed that Zn, Cu, As, and Cd are artificially added to commercial feed to promote animal growth and improve disease resistance (Rashid *et al.*, 2023). However, animals can not digest these heavy metal (HM) elements and discharge them through manure (Jensen *et al.*, 2016). Since HM is not degradable, it is not decomposed during the composting process (Lopes *et al.*, 2011). Therefore, long-term repeated application of fertilizers and compost can cause HM elements to accumulate to toxic levels in agricultural soils (Yang *et al.*, 2018; Zhou & Wang, 2019). This can affect crop health and productivity.

Table 2: 1 Some of heavy metals content in chemical fertilizer

Chemical fertilizers	Heavy metals (mg/kg)						References
	As	Cd	Cr	Cu	Ni	Pb	
Phosphate Fertilizers							
DAP	-	1.18	3.40	0.87	2.64	ND	(Salem *et al.*, 2020)
	2.80	7.90	-	-	-	2.10	(AlKhader, 2015)
SSP	0.0012	2.59	-	7.80	5.26	6.65	(Benson, 2014)
	-	-	0.053	0.101	-	-	(Murtadha, 2016)
	5.50	6.10	-	-	-	2.20	(AlKhader, 2015)
	8.00	3.10	33.00	10.00	11.00	9.90	(Murray & Graeme, 2013)
Rock phosphate	-	-	0.29	1.02	0.19	-	(Murtadha, 2016)
MAP	43.00	0.50	-	-	-	1.80	(AlKhader, 2015)
Nitrogen fertilizers							
Urea	0.0013	2.67	-	3.49	5.87	7.46	(Benson, 2014)
	-	ND	0.15	ND	0.26	ND	(Salem *et al.*, 2020)
	<1	<0.1	<1.00	1.00	<1.00	0.30	(Murray & Graeme, 2013)
Urea phosphate	13.74	2.76	-	-	-	0.40	(AlKhader, 2015)
Ammonium nitrate	<1	<0.1	<1	12.00	<1	0.2	(Murray & Graeme, 2013)
Potassium fertilizers							
MOP	-	0.01	0.29	1.17	0.55	1.31	(Gambuoe & Wieczorek, 2012)
	<1	<0.1	1.00	1.00	<1.00	0.40	(Murray & Graeme, 2013)
Potassium nitrate	<1	<0.1	<1	1.00	<1	0.3	

DAP= Di-ammonium Phosphate, SSP= (Single super phosphate), MAP= (mono-ammonium phosphate), MOP= (Muriate of Potash)

Pesticides may contain HM elements in their active ingredients. Some of the HM elements commonly found in pesticide products include Cu, As, Pb, Hg, Cr, Zn, Al, Li, Ba, B, and Ti (Lewis *et al*., 2016). In the past, many fungicides and insecticides used in agriculture had significant levels of heavy metal elements in their active ingredients. For instance, fungicides such as copper sulphate or Bordeaux mixture and copper oxychloride, and insecticides like lead arsenate and copper acetoarsenite were found to have high levels of HM elements (Rashid *et al*., 2023).

Furthermore, using obsolete pesticides in developing countries can result in pesticide residues remaining in the soil, which can be harmful to health. For instance, DDT was widely used in agriculture but has been banned in most countries since it is a persistent organic pollutant. However, some developing countries still use it (Devi *et al*., 2022). Therefore, it is essential to be aware of the potential health risks associated with the use of certain fertilizers and pesticides.

2.2.2.2 Industrial activities

Industrial activity is thought to be a significant source of environmental contamination (He *et al*., 2005). The industrial sources of heavy metals and pesticides include mineral mining in the earth's crust, mineral processing, energy generation, waste disposal, and the floriculture industry (Masindi & Muedi, 2018; Tchounwou *et al*., 2012). The floriculture industry is the primary source of pesticides and heavy metals in the current research area's environment; hence the following sections focus on the floriculture industry, mineral processing, and waste management.

In 2022, the Sustainable Floristry Network (SFN) released a report stating that the flower industry is contributing to the release of pesticides and other harmful chemicals into the environment. This is due to the incorrect use of pesticides, which can include using the wrong dose or chemicals, unsafe application (such as a lack of personal protective equipment), or using the chemicals at the wrong time during the crop's growing cycle. For example, a recent research by Yohannes Gelaye (2022) highlighted the Ethiopian floriculture industry's lack of suitable waste disposal technology and worker safety equipment. As a result, the chemicals, plastics, and corrugated irons that are used in farms are carelessly disposed of, causing pollution in the environment. Additionally, pesticides, plastics, and fertilizers are also freely discharged into water bodies and terrestrial land, leading to health risks, aquatic life hazards, and soil, water, and air pollution.

The land near the industrial area is vulnerable to trace metals contamination due to the discharge of untreated/poorly treated effluent and disposal of solid waste in the area. The TEs are deposited into the soil at different distances depending on wind velocity and particle size (Ogunkunle & Fatoba, 2014). Moreover, each industrial activity is usually associated with some specific metals depending on its product. For instance, cement industries contribute to high levels of Cd, Cr, Cu, Pb, and Zn in the atmosphere while Ni, Co, Pb, and Cu are used as catalysts, modifiers, and dryers (Janik *et al*., 2010). Tannery activity released higher concentration of Cr, and traces of Ni, Fe, and Zn (Nigam *et al*., 2022). Ni contamination in the environment is primarily caused by manufacturing processes such as batteries, alloys, printing, metal coating, smelting, waste incineration, fossil fuel combustion, power generation, and car emissions (Jadaa & Mohammed, 2023). Lead (Pb) is primarily released into the environment through electroplating, smelting, painting, dye manufacturing, plastics, fabrics, yachts, printing, Pb-contained tubes, and preservative materials (Zheng *et al*., 2017; Wani *et al*., 2015).

2.2.2.3 Application of Sewage-Sludge-Solid waste disposal

The sewage sludge that comes from urban and industrial waste can be heavily contaminated with heavy metals, such as As, Cd, Cr, Cu, Pb, Hg, Ni, Mo, Zn, and others (Rashid *et al*., 2023).. Similarly, solid waste disposal through landfills, open dumps, and sanitary landfills is an important source of heavy metal release into the soil (Ali & Khan, 2019). This also includes electronic waste, used batteries, painting waste, and electroplating waste, which increase the total element (TE) content in dumpsites. According to Nakhaei *et al*. (2015), leachate is produced in association with rainfall by the slow leaching of trace elements from solid waste dumpsites. This leachate infiltrates the soil and can result in the movement of these trace elements into the groundwater. As a result, soils become contaminated with TEs that contain cadmium Cd, Cr, Cu, Fe, Pb, Mn, and Zn.

2.2.2.4 Other source of pesticides Contamination

Pesticide contamination can occur through a variety of processes, including manufacture, storage, shipping, field application, warehousing, and human misuse. Unfortunately, other catastrophes have occurred around the world, including India (1986), Italy (1976), Germany (1953), and Ethiopia (2017) (Saud AL-Ahmadi, 2019). According to reports, approximately 50,000 tons of expired pesticides are presently dispersed across already susceptible territory in Sub-Saharan Africa (Hendery, 2018). This is important since pesticides can contaminate food, water, soil, and air, causing a variety of health concerns such as headaches, sleepiness, fertility troubles, and even fatal illnesses. Children, pregnant women, and farmers are the most vulnerable populations, with hundreds of thousands of deaths reported each year due to pesticide exposure (Hendery, 2018). Pesticides can boost crop yields, but it is not worth sacrificing human life for a surplus of crops.

2.3 Transport and fate of heavy metals and pesticides in the Environment

The transport and fate of heavy metals in soil are determined by physical processes associated with fertilizers and insecticides. Unlike organic substances, heavy metals cannot be broken down chemically. Heavy metal loss from an application location is caused by soil erosion from runoff, leaching, volatilization, and harvested plant parts (Kumar *et al*., 2023).

Heavy metals' behavior in soil is heavily influenced by their chemical form and metal speciation. Heavy metals penetrate the soil and undergo fast reactions for the initial few minutes or hours, followed by slower adsorption reactions that continue several days or years. These interactions produce a variety of chemical forms with varied bioavailability, mobility, and toxicity (Wuana & Okieimen, 2011). Several variables influence the distribution of heavy metals in soil, including mineral precipitation and dissolution, ion exchange, sorption and decomposition, water complexation, biological immobilization and mobilization, and plant absorption. While free ion species are typically the most bioavailable and hazardous forms of heavy metals, this is not always the case. Organic forms of mercury, such as methylmercury, are more hazardous than free ionic species because they can cross biological membranes such as the blood-brain barrier and the placental barrier (Hong *et al*., 2012). In addition, the toxicity of several heavy metals is determined by their oxidation state. For example, Cr (VI) is a hazardous carcinogen to living creatures and is highly mobile in soil, whereas Cr (III) is not poisonous to plants and is required for animal feeding. As a result, it is critical to convert the Cr (VI) combination into a more stable Cr (III) complex in organic materials and soil reducers (Mishra & Bharagava, 2016).

Pesticides used on plants can have harmful effects on the environment. These chemicals can be disposed of in the soil and can move within the soil through water by transport or degradation. As a result of pesticide breakdown, new compounds are generated in the environment. They can move from target locations to non-vegetated areas through leaching, adsorption, spray drift, volatilization, and runoff, depending on their behavior (Dad *et al*., 2022) (Fig 2.1).

According to the literature of Mahmood *et al*. (2016) and Saud AL-Ahmadi (2019), pesticides can also enter the atmosphere through application drift, post-application vapor losses, or wind erosion of pesticide-treated soil. Moreover, photodegradation can transport pesticides long distances before being removed by atmospheric wet and dry deposition at the earth's surface.

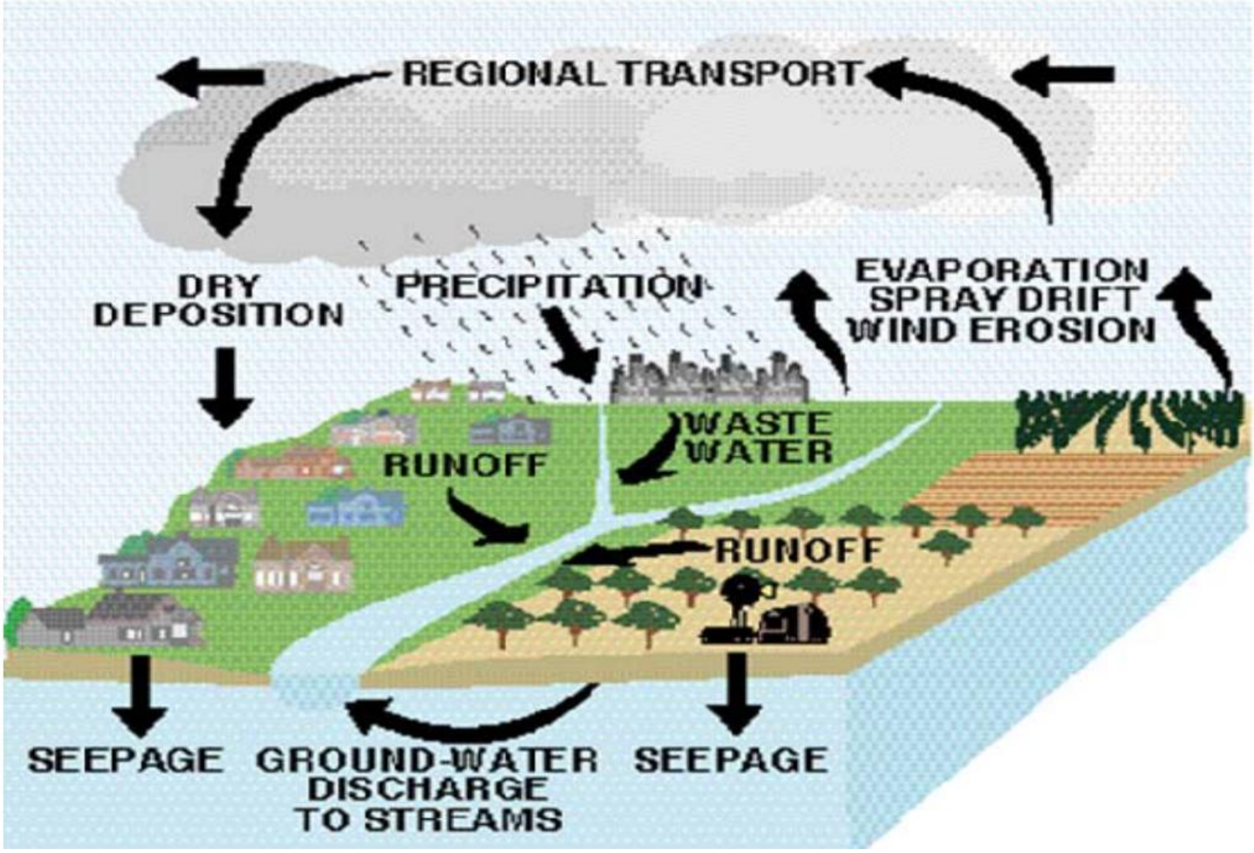

Figure 2: 1Pathway/Transport of pesticides in the environment (Dad *et al*., 2022)

The fate of soil pesticides is affected by a variety of factors, including mobility and persistence. Pesticide persistence refers to a pesticide's ability to maintain molecular integrity as well as chemical, physical, and functional qualities after being discharged into the soil over time. The term "half-life time" (t1/2) is commonly used to estimate pesticide lifespan, or the time required for pesticides to decay to half their initial concentration in soil (Curran, 2016). A pesticide's half-life is usually greater than 100 days, whereas non-permanent pesticides have a half-life of fewer than 30 days. As a result, moderately persistent insecticides remain active for 30 to 100 days (Gavrilescu, 2005).

2.4 Effect of heavy metals and pesticide residues to the environment

2.4.1 Effect of heavy metals to living organisms and the environment

Heavy metal contamination is a huge global health hazard that affects plants, animals, and the ecosystem in general. Numerous extensive investigations have concluded that heavy metals cause substantial adverse effects to bacteria, humans, and plants. They can be very harmful to the development and structure of plant cells, producing protein denaturation and DNA damage that leads to oxidative stress. Furthermore, heavy metals can enter the food chain after being absorbed by plants. These metals establish stable inorganic interactions with organic molecules in the soil, affecting critical soil qualities such as porosity, particle size distribution, color, and pH (Zhang *et al.*, 2023).

Exposure to concentrations beyond the prescribed limits can lead to health impacts that can be chronic, acute, mutagenic, or carcinogenic, depending on the heavy metal and the amount of exposure. The World Health Organization (WHO) and the United States Environmental

Protection Agency (USEPA) have defined acceptable limits for various heavy metals in drinking water, soil, and plants. Table 2.2 presents the limits and effects of continuous exposure to various contaminants on human health, vegetable growth, and soil quality.

Although heavy metal contamination has been found to have negative impacts on soil, plants, and human health, it is also crucial to study its effects on beneficial microorganisms. This is essential for sustainable crop production since these microorganisms, such as bacteria, fungi, actinomycetes, and others, are vital components of crop productivity. They perform various functions in soil fertility and crop health, such as breaking down organic matter to release nutrients, recycling plant nutrients, fixing atmospheric nitrogen, producing hormones, enzymes, and secondary metabolites, degrading pesticides, controlling pathogens, and producing antibiotics (Mohamed *et al*., 2021).

According to the literature, certain HMs can encourage growth at low concentrations, but higher amounts can significantly limit the growth, diversity, and reproduction of soil microbial populations (Rashid *et al*., 2023). Such limitations can negatively impact crop health and productivity. Research has indicated that bacteria are more vulnerable to HM toxicity than other living organisms, including plants in the same environment. However, the toxicity level of HMs to different microbial groups varies depending on the toxicity level of the HM components and their bioavailability in the soil (Abdu *et al*., 2017).

Heavy metal contamination poses a significant threat to global food safety, according to studies by Nkwunonwo *et al*. (2020) and Rai *et al*. (2019). In Ethiopia, this problem is severe, with research indicating that the concentration of heavy metals in soil and vegetables exceeds recommended limits. Investigations conducted in areas like Mojo and Koka have revealed that certain heavy metals, including As, Pb, Cd, Zn, Cu, Hg, and Cr, are present in soil and vegetables at levels that surpass safety thresholds established by international standards.

The As, Pb, Cd, Cr, and Hg were found above the safety level in vegetables such as tomatoes and cabbage from Mojo and Koka Area. The hazard quatient (HQ) that indicates the non-carcinogenic risk due to As and Hg contamination of tomato is greater than unity, while for cabbage, the HQ is less than one for As, Hg, and Co. This finding suggests that commercial veggies in the area may pose a non-carcinogenic risk to consumers. Furthermore, the risk of cancer owing to As, Cd, Hg, and Ni was high (Leta Danno & Hailu Reta, 2021; Hailu Reta & Leta Danno ,2020).

Mulate Zerihun *et al*. (2022) also found that soil concentrations of Fe, Mn, Zn, and Cr were higher in the Central Rift Valley region than in other countries. In the research area, the average daily consumption of Pb, Fe, Zn, and Cu was higher than the WHO/FAO maximum acceptable level. The non-carcinogenic risk (HQ) for Pb, Fe, Zn, Mn, and Cu, as well as the combined effect (HI), surpassed one.

Extensive research has demonstrated that excessive consumption of heavy metals can have a significant impact on human health, surpassing recommended dietary intake levels. These metals can result in various toxicological consequences, jeopardizing food quality and safety and increasing the likelihood of kidney and liver failure, infertility, cancer, nervous breakdown, leukemia, mental illness, and other toxicity-related issues (Ali & Khan, 2019). These findings have been meticulously investigated and documented (Dong et al., 2011). These studies suggest that heavy metal contamination is a significant food safety concern in Ethiopia. The accumulation of heavy metals in several vegetables exceeds the permissible threshold set by organizations such as the FAO and WHO. As a result, future toxicity assessments and food chain safety precautions are recommended, especially as industrial and human activities expand, posing a greater risk of heavy metal dangers, notably non-carcinogenic and carcinogenic risks.

According to the literature reviewed, the findings of the ecological risk assessment indicate that the presence of heavy metals, namely Cadmium (Cd), Lead (Pb), and Mercury (Hg), as well as the usage of pesticides, can potentially pose a significant risk to the surrounding ecosystem. In Table 2.3 of the review, the heavy metal concentrations in tomato and onion samples obtained from Ethiopia are presented.

Table 2: 2 Recommended limits for some heavy metals in potable water, vegetables, and soil, and their effects on human health, vegetables, and soil

Hm	**Chronic health limit**			**Effects on**	**References**
As	water	WHO	EPA	HH**:** Carcinogenecity (lung, urinary and skin cancer); blackfoot disease (arsenicosis), genotoxicity, cardiovascular disease, neurobehavioral effects in children.	(Jadaa & Mohammed, 2023; Nurchi *et al*., 2020)
		(10 µg/L)	(10 µg/L)		
	Veg			Reduction in seed germination; decrease in seedling height; reduced leaf area and dry matter production; stunted growth; chlorosis; wilting. Increases chlorophyll-A and Chlorophyll-B content in onion leaf	(Miteva & Merakchiyska, 2002)
	Soil			Inhibits phosphatase and sulfatase	(Singh & Kalamdhad, 2011)
Cd	water	(3 µg/L)	(5µg/L)	HH: Carcinogenecity, embryogenecity, mutagenecity, teratogenecity, hyperglycemia, reduced immunopotency, anemia, renal dysfunction and liver damage and bone structure deformation, cadmium pneumonitis, *itai-itai* disease (Cd poisoning)	(Ayangbenro & Babalola, 2017)
	Veg			Resulting in less photosynthetic carbon absorption interferes with the regulation of the guard cell(affect water status)	(Bakshi *et al*., 2018)
	Soil			Reduce the soil nitrogen and sulphur availability for crop	
Cr	water	50 µg/L	100µg/L	Carcinogenicity, skin ulcer, gastrointestinal tract diseases, convulsions, kidney & liver damage, lung cancer	(Jadaa & Mohammed, 2023)
	Veg			Decreases plant nutrients, inhibits the germination process and reduces plant biomass	(Rubiya, *et al*., 2018)
	Soil			Negative effects on microbial cell metabolism	(Shun-hong, *et al*., 2009)
Hg	water	1 µg/L	2 µg/L	Brain damage, heart, kidney and lung disease, permanent damage to central nervous system, brain damage in fetus, Minamata disease	(Li *et al*., 2018)
	Veg			decrease in photosynthetic rate, increases the rate of oxidizing enzymes	(Chakraborty & Choudhury, 2023)
	Soil			Abnormalities in the metabolic function of organisms	(Akanchise *et al*., 2020)
Ni	water	70 µg/L	70µg/L	HH: Increased risk of cancer (lung, nasal), kidney failure,	(Ayangbenro & Babalola, 2017)

				and cardiovascular diseases	
	Veg			Chlorosis and necrosis in different plant species, impairment of nutrient balance, phytotoxic , inhibits the germination of seed	(Asati *et al*., 2016)
	Soil	35mg/kg		growth inhibition in plant, resulting in chlorosis, induces necrosis and causes wilting,	(Hayyat *et al*., 2020)
Pb	Water	10 µg/L	15 µg/L	HH: Affect kidney, liver, bone and brain. Encephalopathy in children	(Jordao *et al*., 2006; Verma & Dwivedi, 2013)
	Veg			Reduction in plant growth causes cellular malformation, decreased chlorophyll biosynthesis, hormonal imbalance, and increased production of reactive oxygen species (ROS)	(Tang *et al*., 2017)
	Soil			Decreases the acid phosphatase, catalase, invertase and urease Decreases the phosphorous availability in soil. Disrupts the balance of water, enzymes, and minerals	(Singh & Kalamdhad, 2011)
Zn	Water	3000	5000	HH: Muscular pain and intestinal haemorrhage	(Jordao *et al*., 2006)
	Veg			Phytotoxic and potentially harmful to crop production Reduces the shoot growth and inhibits root growth	(Balkhair & Ashraf, 2016; Rubiya, et al., 2018; Yao et al., 2003)
	Soil			Phytotoxic and can directly affect soil fertility Decrease the microbial biomass N Decreases the phosphorous availability in soil	(Balkhair & Ashraf, 2016; Yao *et al*., 2003)

HH: Human health; Veg : Vegetables

Table 2: 3 Mean heavy metal concentrations in various locations of Ethiopia.

Vegetable	**Study area**	**Name of heavy metals**	**Value of heavy metals in vegetables(mg/kg)**	**Authors**	**Remark**
Tomato	Eastern Industrial Zone in Dukem	Cr, Cd and Pb	2.97, 2.20 and 4.60 respectively	(Dagne Bekele & Endale Teju, 2019)	Above the recommended limit of both WHO
Tomato	Eastern Industrial Zone in Dukem	Zn,Fe and Cu	45.63, 358.17and 10.20 respectively	(Dagne Bekele & Endale Teju, 2019)	
Tomato	Gonder City	Pb, Cr, Cd, Cu, Ni, Mn and Zn	5.95,2.43,5.8,2.01 24.61,13.88 & 2.42 respectively	(Banchamlak Tegegne *et al*., 2021)	Cr, Cd & Pb are above safe limit
Onion			ND,3.93,6.66,2.15 19.15,9.25 &3.94 Respectively		Cr & Cd are above safe limit
Onion	Akaki	Cd, Cr, Cu, Zn& Ni	0.018,2.81,5.24, 15.4 &0.44 respectively	(Fisseha Itanna, 1998)	Cr is Above safe limit
Tomato	Arbamnich(KRA)	Cd, Cr, Pb, Zn, Cu & Ni	0.43,1.84,0.28,13.65, 24.23&26.89 Respectively	(Abrham & Gholap, 2021)	Cd is Above safe limit
	Arbaminch(ATSHCA)		0.27,1.52,0.16,10.23, 19.56&24.45 Respectively		
Tomato	Ziway	Cd, Cr, Pb &Cu	0.025,0.32,0.48 & 0.39 Respectively	(Mulat Anagaw e*t al*., 2019)	Pb is above safe limit
Tomato	Dukem	Cu, Fe, Zn	10.20, 358.17, 45.62 respectively	(Dagne Bekele *et al*., 2019)	Cu,Fe,Zn is above safe limit

2.4.2 Effect of pesticide residues to living organisms and the environment

Pesticides play a crucial role in agriculture as they help protect crops from harmful pests and increase yields. They are commonly employed through manual spraying or via trucks and airplanes. By using pesticides, farmers ensure that their crops are healthy and abundant, which in turn helps to feed the world's growing population. However, there have been reports of poisoning among farmers, rural workers, and their families during the administration of these chemicals, which has raised concerns about their safety. As a result, WHO has classified pesticides into five categories based on their potential risks to humans from accidental exposure. These categories are Class Ia: Extremely hazardous (for example, parathion, dieldrin), Class Ib: Highly dangerous (e.g., eldrin, dichlorvos), Class II: Somewhat harmful (e.g., DDT, chlordane), Class III: Slightly dangerous (for example, Malathion), and Class IV: Unlikely to cause an acute danger in routine usage (for example, carbendazim) (Saud AL-Ahmadi, 2019).

Research indicates that most pesticides have broad effects, harming non-target organisms as well as the intended pests. Only about 1% of pesticides reach the intended organism, while the remaining pesticides contaminate the surrounding environment (Intisar *et al.*, 2022). In this section, we will explore the impact of pesticides on plants, aquatic species, microorganisms, humans, and the environment.

2.4.2.1 Effect of Pesticides on plants

Pesticides, when applied to plants, can cause damage to their defense mechanisms, growth, and development. One of the effects of pesticide use is the creation of reactive oxygen species (ROS), which results in oxidative stress in plants. This can lead to growth deficits and reduced efficiency of photosynthesis. In response to this toxicity, plants activate their antioxidative defense mechanisms, which include both antioxidant enzymes and antioxidants themselves (Sharma *et al*., 2018; Xie *et al*., 2016).

However, despite these defense mechanisms, oxidative stress can still harm plant proteins, chlorophyll pigments, and the efficiency of photosynthesis. This can disrupt the normal growth and development of plants, ultimately leading to a shortage of crops and disrupting their life cycle. For example, (Parween *et al*., 2016) reported that pesticides have a significant impact on plant growth, germination, development, metabolic pathways, yield, and some antioxidant enzymes. Overall, excessive and arbitrary use of pesticides on various crops can cause harm to beneficial microorganisms, honey bees, predators, birds, and small animals (Alengebawy *et al*., 2021).

2.4.2.2 Effects of Pesticides on aquatic organisms

Pesticides enter water through drift, runoff, soil leaching, or, in some situations, direct application, such as mosquito control. Pesticide-contaminated water presents a significant threat to aquatic life. It can harm aquatic vegetation, reduce dissolved oxygen levels in the water, and alter the physiological and behavioral patterns of fish populations (Mahmood *et al*., 2016). Pesticides are taken in by aquatic organisms in three ways: dermally (direct absorption through the skin), breathing (uptake through the gills during breathing), and orally (entry via contaminated water (Shefali *et al*., 2020). It can also affect the aquatic system in a variety of ways, including atmospheric precipitation. Various authors have reported the effects of pesticides. Numerous studies have demonstrated that even low levels of Malathion can have adverse effects on the population and composition of plankton and periphyton. Additionally, it can negatively impact the growth of frog tadpoles, as noted in a study conducted by (Relyea & Diecks, 2008). Similarly, Dimitrie & Sparling (2014) research in 2014 revealed that chlorpyrifos and endosulfans also have a significant impact on amphibians. It is worth mentioning that these studies have shown that exposure to pesticides, even at low levels, can have severe consequences on the aquatic ecosystem and its inhabitants. The use of pesticides in aquatic ecosystems can result in their accumulation and spread to higher trophic levels, ultimately leading to potential health risks for humans through ingestion or other means.

Furthermore, consuming aquatic products or crops that are contaminated with pesticides can have harmful effects on the top predators in the food chain, namely human beings. Pesticides used on crops can expose humans to harmful chemicals both directly and indirectly, leading to problems with the skin, eyes, mouth, and respiratory tract. These acute reactions can result in headaches, irritation, vomiting, sneezing, and skin rashes, and the severity of the symptoms depends on the concentration and duration of exposure (Pathak *et al*., 2022).

2.4.2.3 Effects Pesticides on soil microorganisms

Microorganisms like bacteria, algae, actinomycetes, protozoa, and microfauna are present in soil. They play a crucial role in breaking down waste and converting hazardous chemicals into simpler compounds, which ultimately helps in reducing risks in the soil. The use of pesticides can have adverse effects on the soil's characteristics and microorganisms. These pesticides can interact with the soil and its native microbes through various mechanisms like degradation, transport, and adsorption/desorption, affecting the diversity of microbes, enzymatic activity, and metabolic processes (Muñoz-Leoz *et al*., 2011; Yadav & N.L., 2017).

2.4.2.4 Effects of Pesticides on human

Pesticides can harm human health in various ways. According to (Mahmood *et al*., 2016), pesticides can enter the body through inhalation of contaminated air, dust, and vapors, ingestion of contaminated food and water, or skin contact. The most common way people are affected is by consuming foods contaminated with pesticides. Although the body can eliminate pesticides through the kidneys, bile, and secretory glands, prolonged exposure to fruits and vegetables grown in pesticide-contaminated soil and water can increase the concentration of toxins in the body.

Pesticide exposure can have both acute and chronic effects on human health. Acute effects include symptoms such as headaches, skin irritation, and gastrointestinal issues, among others. In some rare cases, acute exposure can even lead to death. In contrast, chronic effects are often more severe and can take years to manifest. These effects can cause damage to multiple organs in the body, such as the brain, lungs, heart, and reproductive system, and can result in conditions such as cancer, asthma, and diabetes (Calaf, 2021; Kalyabina *et al*., 2021).

2.5 The need for ecological and human health risk assessment of contaminant

The need for ecological and human health risk assessment is to ensuring public safety as it determines the maximum allowable levels of contaminants that can exist in a given area without posing a threat to human health. It involves a standardized approach for evaluating and documenting the potential health risks associated with exposure to environmental pollutants, leaving no room for ambiguity. The global demand for food products that are safe, non-toxic, and nutritious is increasing. To achieve this, it is necessary to follow good agricultural practice (GAP) and safe post-harvest processing techniques. Sustainable agricultural practices cannot be achieved solely through scientific expertise, as farmers' knowledge of combating pest problems should also be given proper importance. The growing demand for organic and pesticide-independent food ingredients is the main driving force behind the development of safer pesticides for agricultural practices (Meena & Mishra, 2020).

Although pesticides are effective in controlling harmful insects, the potential dangers associated with their use outweigh the benefits. Nonselective pesticides can damage non-targeted plants and animals, as well as the intended ones. Moreover, with continuous use, some pests may develop genetic resistance to pesticides (Kumar, 2016). To limit pesticide use and reduce its negative effects, registration is a crucial aspect of pesticide management. It ensures that the pesticides sold in the market are authorized and used solely for their intended purpose. Additionally, it allows authorities to set rules on pesticide pricing, packaging, labeling, safety, and advertising to safeguard the interests of the users (FAO/WHO, 2021).

Ecological risk assessment (ERA) is used to evaluate and assess the potential adverse effects of pesticide use in agriculture on non-target organisms. It involves identifying potential exposure pathways that may lead to environmental contamination and ecological impacts. ERA provides a scientific basis for decision-making and risk management strategies to mitigate the hazards of pesticides in the ecosystem (EPA, 2022).

The risk assessment process involves four steps: hazard identification, exposure assessment, toxicity assessment, and risk characterization. Hazard identification involves investigating the presence of chemicals in vegetables and soil, their concentrations, and spatial distribution. Exposure assessment measures the intensity, frequency, and duration of human exposure to environmental contaminants. Toxicity assessment estimates the toxicity due to exposure levels of chemicals using the Cancer Slope Factor (CSF) and the Reference Oral Dose (RfDo) indices. Risk characterization predicts potential health risks of the population in the study area using hazard quotient (HQ), hazard index (HI), and target cancer risk (TCR) based on the USEPA (2019) established approaches. To analyze ecological health risk, different environmental indices were used to evaluate soil pollution; including the Toxic exposure risk (TER) approach assesses species-specific exposure risks to individual pesticide compounds, with trigger values for chronic and acute exposure. However, regional studies show pesticides are mostly detected as mixtures in arable soil, requiring consideration of ecological risks. The RQ-based assessment uses the concentration-addition method to assess ecological risks of exposure to multiple pesticide mixtures in study locations (Mu *et al*., 2023). Uncertainties arise due to assumptions, models, and data. This is especially true when applying laboratory data to field conditions or estimating pesticide exposure for non-target organisms (Dirikumo, 2023).

Efforts have been made to address environmental contamination and its toxic effects in developed countries since the publication of Rachel Carson's report on Silent Spring in 1962. Nevertheless, there is still a lot of work that needs to be done, particularly in developing countries like Ethiopia. To enhance pest management, it is imperative to develop new chemicals, improve pesticide formulations, and create better application devices like bio-pesticides and biodegradable nano-pesticides (Meena & Mishra, 2020). The ultimate goal is to minimize environmental contamination and reduce the exposure of living organisms to toxic substances. Accordingly, ecological and human risk assessment of potentially toxic elements (PTEs) needed to be assessed to take the right measure for decision makers through conducting ecological and human health risk assessment.

In Ethiopia, there have been few laboratory investigations reported. One such investigation was conducted by Ashenafi Hayi *et al*. (2016), who found pesticides in tomatoes from Piasa atekelet tera. The pesticides detected were heptachlor, aldrin, endosulfan, and DDT, but none of them exceeded international maximum residue limit (MRL) values. In 2020, Loha et al. reported the presence of pesticides in tomatoes and onions from an irrigation site around Lake Ziway. The pesticides detected in tomatoes were profenofos, alpha and beta endosulfan, and metalaxyl, while in onions, the pesticides were profenofos, beta endosulfan, and λ-cyhalothrin. In both samples, the pesticides exceeded European MRL values (Kumelachew Mulu *et al*., 2020).

In 2017, Belay Tizazu *et al*. surveyed to evaluate the practices of smallholder vegetable farmers in the Central Rift Valley of Ethiopia regarding the buying and use of pesticides. The study was conducted from a practice perspective. The survey results showed that farmers were using pesticides in violation of the recommended guidelines. They were also storing pesticides unsafely, ignoring safety instructions and risks, not using protective gear when applying pesticides, and disposing of containers in an unsafe manner (Belay Tizazu *et al*., 2017).

In 2020, Yegrem reviewed the levels of pesticide residues found in fruits, vegetables, cereals, and legume food products in Ethiopia. The review suggested that the impact of pesticide residues could be reduced by taking certain measures such as the rational use of pesticides, promoting organic farming, exploiting natural and bio-pesticides, and properly implementing and amending pesticide-related laws (Lamesgen Yegrem, 2020).

Lemessa Bente *et al.* (2020) found that nutrients and trace metals have been increasing in concentration over time, with higher values observed at shoreline sites near floriculture farming. The lake's water quality has exceeded guideline values for drinking water and aquatic life, creating negative impacts on human health and the lake's ecosystem functions. The authors suggest that stakeholders and concerned bodies should take appropriate interventions to address these issues.

Moreover, protecting the environment and minimizing health risks associated with pesticide use in Ethiopia require action from all concerned bodies. Beyene Negatu *et al.* (2021) recommend improved institutional arrangements for the enforcement of regulations, increased awareness, and further intervention studies to reduce the high risks of pesticide misuse.

According to a study conducted by Midekesa Chala (2021), farmers in the surveyed areas are misusing pesticides by applying them without discretion, storing them unsafely, ignoring safety instructions, and not disposing of containers properly. Another study done by (Lemessa Bente *et al.*, 2021) assessed the levels of pesticides in water and sediment samples from Lake Ziway, revealing that more than half of the water samples contained malathion, dimethoate, metalaxyl, diazinon, chlorpyrifos, fenitrothion, and endosulfan. Meanwhile, sediment samples frequently detected diazinon, α-cypermethrin, and endosulfan. The majority of the pesticides detected in the lake's water showed a potential acute risk (RQ > 1), particularly chlorpyrifos, λ-cyhalothrin, and α-cypermethrin insecticides. The authors recommended taking immediate intervention measures, including training smallholder farmers on pesticide safety and usage, and implementing improved effluent management mechanisms by floriculture farms, to reduce pollution.

Literature reports indicate that most of the pesticide data reported in the Central Rift Valley of Ethiopia, particularly around Lake Ziway, focuses on water bodies located within agricultural watersheds. However, there is still a lack of published data on the irrigation farmlands of Ethiopian water bodies located within agricultural watersheds. Furthermore, in the present study area, the likelihood of the occurrence of the risk may be increased due to the ever-increasing industrial and anthropogenic activities. Therefore, the authors suggest conducting future toxicology assessments and implementing food chain safety measures, as this study could help fill this gap in the region.

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CHAPTER THREE

3. PESTICIDE RESIDUES AND ASSOCIATED PUBLIC HEALTH RISKS IN VEGETABLES FROM IRRIGATED FARMS ADJACENT TO LAKE ZIWAY, ETHIOPIA

ABSTRACT: The excessive use of pesticides has led to the accumulation of harmful residues in vegetables, necessitating monitoring to evaluate the risks to human health.This article presents the levels of 35 pesticide residues in 15 composite vegetable samples from irrigated farmlands adjacent to Lake Ziway using the QuEChERS extraction method (Quick, Easy, Cheap, Effective, Rugged, and Safe) and then analyzed using GC-MS. The study also estimated the health risks of consuming contaminated vegetables in children and adults, including carcinogenic and non-carcinogenic risks. The predominant pesticide residues found in tomatoes were α-endosulfan (0.58 mg/kg), β-BHC (0.04 mg/kg), heptachlor (0.02 mg / kg), and malathion (0.03 mg/kg), all of which were above the safety limits. Similarly, the mean concentration of heptachlor epoxide (0.04 mg/kg) and propargite (0.11 mg / kg) were higher than the allowed levels of the safety limits for onions. The concentration of pesticide residues detected in 10.6% and 7.9% of tomato and onion samples was above the maximum residual limits of the European Commission (EU-MRLs), respectively. Non-carcinogenic health risk estimates show that onion heptachlor epoxide had THQ > 1, indicating the possibility of systemic health risk in both adults and children consumers. The carcinogenic health risk (CHRs) showed that heptachlor epoxide for adults and children, while only heptachlor in children had CHR > acceptable limit (10^{-4}) for tomato and onion. Therefore, it is critical to raise awareness among stakeholders while simultaneously implementing sound monitoring policy actions to protect the ecosystem and the health of the population in the study area and beyond.

3.1. INTRODUCTION

Pesticides are natural or synthetic substances that are often used to control plant pests, weeds, and diseases (Sharma *et al*., 2019). They are critical in modern agriculture; without them, up to 50% of crops in tropical warm-climate zones could be destroyed (FAO, 2019). The agroclimatic conditions of the Ethiopian rift valley, particularly around Lake Ziway, are suitable for the production of fruits and vegetable production; however, the area is highly affected by infestation of pests during vegetable production and storage, which significantly reduces the yield and quality of agricultural products (Pesticide Action Nexus Ethiopia) (PAN-Ethiopia, 2020). Therefore, the application of pesticides is mandatory in modern agriculture because it significantly reduces yield losses and maintains the quality of fruit and vegetables by controlling the infestation of pests (Meftaul *et al*., 2020).

Pesticide application is more severe in the Ethiopian rift valley than in other Ethiopian areas. Several studies have found that farmers overuse pesticides in their vegetable fields every other day, or even every day, due to a lack of knowledge and the lack of available sustainable alternatives (Tadesse Amera & Asferachew Abate, 2008; Belay Tizazu *et al*., 2016, 2017; Mekuria Teshome *et al*., 2021). Furthermore, reports revealed widespread use of pesticides in Ethiopia's central rift valley, also poor pesticide management during storage, application and empty container handling (Belay Tizazu *et al*., 2017; Beyene Negatu *et al*., 2021; Mekuria Teshome *et al*., 2021). Furthermore, after pesticide application, farmers and farm workers in the region reported symptoms of acute poisoning: headache, nausea, and vomiting, in addition to using empty containers for food and beverage storage (PAN-Ethiopia, 2020).

Pesticide residues in fresh fruits and vegetables pose serious health risks to consumers (Jallow *et al*., 2017). As a result, the identification and quantifying of pesticides in the food matrix is becoming a public concern (Villaverde *et al*., 2020). Although a previous study conducted by Kumelachew Mulu *et al.* (2020) found metalaxyl, λ-cyhalothrin, p,p′-DDT, p,p′-DDE, and α and β-endosulfan pesticides in vegetables grown on irrigated farmland surrounding Lake Ziway, only profenofos residues exceeded EU MRL in tomato and onion, with widespread cultivation and sale in nearby cities, including the capital, Addis Ababa. However, no research has been conducted on the health risks associated with the consumption of pesticide-contaminated vegetables on the irrigated farmlands of the Ethiopian rift valley, particularly in the Ziway district. Thus, more research is needed to determine the actual scenario of pesticide residues present in vegetables grown by irrigation in Ethiopia's rift valley's Ziway district, as well as the risks to consumer health. The current study aims to determine the concentration of 35 pesticide residues in tomatoes and onions grown on irrigated farmlands adjacent to Lake Ziway. The pesticides chosen for this study are commonly applied to manage pests at various stages of vegetable production in irrigated farmlands near Lake Ziway; in particular, those pesticides formulated by Adami Tulu Pesticide Processing Share Company located in the Central Rift Valley of Ethiopia (PAN-Ethiopia, 2020). This study has raised public awareness and is helping policymakers take necessary steps to reduce human health risks.

3.1. MATERIALS AND METHODS

3.1.1. Study Design and Period

In a cross-sectional laboratory-based study, the concentration and type of pesticide residues in tomato (*Lycopersicon esculentum* L.), and onion (*Allium cepa* var. aggregatum) from three irrigated farmlands adjacent to Lake Ziway were examined.

The samples were collected during the rainy season in late August 2021. It is worth mentioning that pesticide contamination is considerably higher during the wet season compared to the dry season (Nguyen *et al*., 2022). As described by Nguyen *et al*., this is due to the fact that pesticides from various sources can be washed into existing ones, leading to increased contamination levels.

3.1.2. Sampling Site Selection and Sample Collection

Three sample sites (S1-S3) were chosen from three villages: Abenea-Girmama, Wellibulla, and Girrissa, based on intensive and extensive irrigation activities, proximity to pesticide stores, and proximity to a water source (Lake Ziway). Additionally, each site is approximately 1 hectare in size and has been in cultivation for more than 20 years. Tomato (*Lycopersicon esculentum* L) (n=9) and onion (*Allium cepa* var. aggregatum) (n=6) the samples were collected with the permission of the farmers of the three irrigated farms. From each site, seven subsamples were collected in triplicates. The sample (roughly 1 kg for each type) was taken using the zigzag method with 1m apart and homogenized to represent the bulk samples. Fifteen composite vegetable samples (tomatoes and onions) were collected in triplicates from three and two sampling sites, respectively. The sample was individually packed in ziplock polyethylene bags, labeled, and brought to the laboratory in an insulated icebox, then stored in the dark at 4 °C until further analysis.

3.1.3. Chemicals and reagents used

All the 35 standards (99% purity) used were obtained from Sigma-Aldrich (St. Louis, USA) and include the following:

- 16 organochlorine pesticides (Aldrin, α-BHC, β-BHC, chlordane, dieldrin, endrin, α-endosulfan, β-endosulfan, heptachlor, heptachlor epoxide, hexachlorobenzene, lindane, methoxychlor, 4,4-DDD, 4.4-DDE, and 4,4-DDT);

- 11 organophosphate pesticides (bromophos-ethyl, chlorpyrifosmethyl, diazinon, ethion, famphur, fenitrothion, fenthion, malathion, parathion, profenofos, thionazin);
- 2 pyrethroids [cypermethrin (Zeta), cyfluthrin];
- 2 carbamates (bendiocarb, propoxur) and 4 other pesticides (dichlorobenzonitrile, propargite, piperonyl butoxide, indoxacarb).

All reagents and solvents used for extraction and cleaning of the samples, including acetonitrile, acetic acid, magnesium sulfate, sodium acetate, and primary secondary amine (PSA) were of analytical grade and offered from BDH (British Drug Houses).

3.1.4. Sample preparation, extraction and clean-up of samples

3.1.4.1. Sample preparation

Each tomato and onion sample was chopped using a stainless steel knife and then blended to obtain a homogenous composite. After each sample was chopped, the chopping board and blender were washed to avoid cross-contamination. The homogenous composite samples were stored in labelled bags and kept refrigerated at 4°C until further analysis.

3.1.4.2. Extraction and clean-up of samples

The quick easy cheap effective rugged and safe extraction method (QuEChERS) was used for the extraction of pesticides in vegetable samples as indicated in the Association of Official Analytical Chemists (AOAC) Method 2007.01 with slight modifications (AOAC, 2007). Method optimization with its basic steps of the experimental procedure was done as described in (Romniou *et al.*, 2022). Fifteen (15) g of homogenized sample matrices weighed in a 50 ml Teflon tube and 15 ml of Acetonitrile (MeCN) containing 1% Acetic acid, 6 g of anhydrous MgSO4 and 1.5 g of NaAc were added and the sample was shaken for 1 minute with Vortex (IKA® Vortex Geniw3) to facilitate contact between the solvent and the sample before centrifuged at 4000 rpm for 5 minutes (Eppendorf 5804 R, Hamburg, Germany). To clean the extract, the upper organic layer 4 ml was taken into a dispersive solid phase extraction tube (d-SPE) containing 150 mg MgSO4 and 50 mg PSA. The extracted sample was agitated for 30 seconds before being centrifuged for 5 minutes at 4000 rpm. A 4 ml supernatant was filtered through a 0.45μm PTFE filter (polytetrafluoroethylene polymer) and transferred to clean GC vials for further analysis.

3.1.5. Quality control and Pesticides instrumental analysis method

3.1.5.1. Pesticides standard solution preparation methods

Standard pesticide stock solutions of the 35 target pesticides were prepared separately in acetonitrile (MeCN) using a method of Nisha *et al* (2021) at a concentration of 1000 mg/L. Then working solutions of 0.1, 0.2, 0.5, 1, 2, 3, and 5 mg/L in MeCN were prepared. The matrix-matched standard for the preparation of the calibration curve was made by adding multiple standard working solutions to the blank extracts of both matrices separately (Nisha *et al*., 2021) and kept in the dark at -20 ° C.

3.1.5.2. Analysis performance method evaluation

To create calibration curves for peak area versus pesticide concentrations, standard working solutions were made by dissolving required volumes of stock solution in acetone (9:1, v/v). The resulting standard working solutions were utilized to generate calibration curves as a function of peak area versus pesticide concentrations. Organochlorines, organophosphates concentrations ranged from 10 to 50 μg/kg, while, pyrethroids, carbamates, organosulfite and other agrochemicals ranged from 15 to 50 μg/kg. The analytical performance of these solutions was tested for linearity (expressed as a correlation coefficient), accuracy (represented as relative standard deviation of repeatability), and mean recovery / reliability (as a measure of trueness). Table 3.1

summarizes the results of these tests. Before conducting the real analysis, we validated the method as described by (Jigar, 2022). The validation results met the SANTE/12682/2019 guidelines with LOQ set at 0.01mg/kg for all analytes.

3.1.5.3. Limits of Detection (LOD) and Quantification (LOQ)

The LOD and LOQ were calculated using the International Conference on Harmonization (ICH, 2005) suggested guidelines (LOD = 3.3 x δ /m and LOQ = 10 x δ /m), based on the standard deviation of the response and the slope of the calibration curves, where m is the slope of the calibration curve, and δ is the standard deviation. The standard deviation of the result was used as the standard deviation of the y-intercepts of the regression lines (Table 3.1).

Table3: 1 Method validation parameter’s results in vegetable pesticide residue analysis

Pesticides	**Conc, before spike(µg/kg)**	**Spike (µg/kg)**	**Conc. after spiking (µg/kg)**	**%Recovery**	**%RSD**	**Linearity (r^2)**	**LOD(µg/kg)**	**LOQ(µg/kg)**
Aldrin	0.2	50	50.74	101.2	11.6	0.9952	0.008	0.025
alpha BHC	1.26	30	27.9	89	1.53	0.9986	0.005	0.014
alpha-Endosulfan	0.11	15	15.18	100.5	2.7	0.9978	0.006	0.019
Bendiocarb	0.1	15	14.83	98.2	6.73	0.9945	0.018	0.053
Beta BHC	0.07	10	11.35	**112.8**	1.63	0.999	0.004	0.011
Beta-Endosulfan	0.02	50	52.21	104.4	11.2	0.9972	0.006	0.017
Bromophos-Ethyl	0.01	50	44.69	89.4	5.31	0.9981	0.002	0.006
Chlordane	0.15	50	53.32	106.3	1.92	0.9977	0.006	0.017
Chloropyrs-Methyl	0.01	30	25.6	85.3	5.59	0.9987	0.002	0.005
Cyfluthrin	10.26	50	50.56	80.6	3.14	0.9982	0.005	0.015
Cypermethrin (Zeta	2.1	50	50.29	96.4	4.13	0.9927	0.018	0.0562
p,p’-DDD	0.02	50	53.15	106.3	11.2	0.9954	0.008	0.245
p,p’-DDE	0.01	50	37.92	**75.8**	10.23	0.9961	0.008	0.025
p,p’-DDT	0.05	50	48.87	97.6	6.73	0.9937	0.009	0.029
Dieldrin	0.02	50	45.98	92	6.65	0.9977	0.009	0.02812
Diazinon	0.02	50	47.17	94.3	4.49	0.998	0.003	0.009
Dichlobenil	0.03	30	27.4	91.2	4.13	0.9972	0.004	0.011
Endrin	0.03	50	50.22	100.4	3.41	0.9995	0.006	0.01945
Ethion	0.03	30	28.42	94.7	5.96	0.9962	0.003	0.008
Famphur	0.71	30	31.05	101.1	2.11	0.9989	0.002	0.006

Fenitrothion	0.18	30	33.46	110.9	5.76	0.9982	0.003	0.009
Fenthion	0.3	30	31.57	104.2	5.12	0.9987	0.002	0.006
Heptachlor	0.01	15	12.1	80.6	10.26	0.9978	0.006	0.017
Heptachlor epoxide	0.01	50	54.45	108.9	6.97	0.9983	0.005	0.015
Hexachlorobenzene	0.01	15	12.04	80.2	10.62	0.9906	0.006	0.018
Indoxacarb	0.01	30	28.42	94.7	14.64	0.9969	0.004	0.012
Lindane	0.02	10	10.64	106.2	9.45	0.9966	0.014	0.04159
Malathion	0.01	50	52.4	104.8	4.48	0.9974	0.013	0.03799
Methoxychlor	0.01	50	51.6	103.2	8.26	0.9969	0.005	0.016
Parathion	0.01	50	48.87	97.7	10.3	0.996	0.004	0.013
Pipronyl Butoxide	0.12	50	48.07	95.9	8.24	0.9963	0.007	0.02203
Profenofos	0.04	30	27.55	91.7	8.44	0.9991	0.002	0.006
Propargite	0.05	50	41.89	83.7	6.38	0.9963	0.007	0.02203
Propoxur	0.02	30	27.96	93.1	8.42	0.9987	0.002	0.007
Thionazin	0.01	10	7.7	76.9	13.83	0.9957	0.004	0.013

Note: Value in Bold indicate the upper and lower limit

3.1.5.4. Instrumental pesticide analysis

Gas Chromatography-Mass Spectrometry (GC-MS) (Agilent 7890B Turbo MSD 5977A, Agilent, Santa Clara, USA) was used to determine levels of pesticide residue. GC-MS equipped with triple quadruple MS operated in electron impact (EI) mode, Triple-Axis HED EM employed as a detector, and an HP-5 MS 30 m × 0.32 mm × 0.25 µm column (Agilent, Santa Clara, USA). The injection volume was 2µL in splitless mode at 180°C, with helium used as a carrier gas at a flow rate of 1.2 ml/min. The oven temperature started at 60 ° C and remained at this temperature for 1 min, increasing to 120 ° C at 40°Cmin-1 for a ramp rate of 2.5 min and then to 310 ° C at a ramp of 5 ° Cmin-1, holding at 300 ° C for 40.5 minutes. All instrumental analyzes were performed at the Bless Agri-Food Laboratory, which is an approved laboratory of the Ethiopian National Accreditation Office (ENAO) (FA: T0030).

3.1.6. Potential Risk Assessment Method

A previously described model proposed by USEPA (2010) assessed the carcinogenic and non-carcinogenic risks of identifying pesticides to adults and children in the monitored region.

3.1.6.1.Non-Carcinogenic Risk (NCR)/Hazard Quotient

The target hazard quotient (THQ) and the hazard index (HI) were used to evaluate non-carcinogenic health risks based on the results of the pesticide analysis and the exposure assumptions, according to the US Environmental Protection Agency (USEPA, 2011). THQ is calculated by comparing the Chronic Daily Intake (CDI) with the Reference Dose (RFD) (IRIS, 2009) using Equation 1.

$$\mathbf{THQ} = \frac{\mathbf{CDI}}{\mathbf{RFD}} \qquad (1)$$

Equation 2, where THQ is the target hazard quotient, CDI is the chronic daily intake, and RFD is the oral reference dose obtained from the integrated risk information system, was used to calculate the CDI of pesticide-contaminated vegetables (Razzaghi *et al.*, 2018).

$$\mathbf{CDI} = \frac{C_{veg} x IR_i x EF_i x ED_i}{BW_i x\ AT} \qquad (2)$$

Where C_{veg} is the concentration of pesticides (mg/kg) in vegetables (mean and 95% confidence interval detected concentrations); IR is the ingestion rate of vegetable food for adults and children, which is 240 g/person/day and 160 g/person/day, respectively, according to Ethiopian Food Based Dietary Guidelines (EFBDG, 2022); EF_i is the frequency of exposure (365 days/year for both age groups that eat vegetables seven times a week to 52 days/year for people who eat (for children and adults is between 15kg and 60 kg, respectively); ED_i, the duration of exposure (for children and adults is 6 and 65 years, respectively) (WHO 2015); BW_i, the default average body weight used by FAO/WHO (for children and adults is between 15kg and 60 kg, respectively); AT is the average exposure time for non-carcinogens (365 days/year x ED) (children and adults are 2190 and 23,725 days, respectively) (Kumar *et al.*, 2013).

The HI of a pesticide mixture was calculated by the sum of THQ for each component (Equation 3). According to the USEPA (2019), HI < 1 indicates no appreciable risk of adverse health effects, while HI > 1 indicates a chance of non-cancer effects.

$$\mathbf{HI} = \sum_{i=1}^{n} THQ_i \qquad (3)$$

3.1.6.2.Target Carcinogenic risk (TCR)

The possible target cancer risk to the population due to the intake of specific potentially cancer-causing pesticides was assessed using Equation (4). The TCR was estimated for adults and children based on their lifetime exposure to pesticides in this study (USEPA, 2010).

$$\mathbf{TCR} = CDI\ x\ \mathbf{CSF}\ x\ \mathbf{ADAF} \qquad (4)$$

In this equation (4), CSF is the cancer slope factor for carcinogenic pesticides in vegetables (mg/kg/day), the probability that a single substance increases the risk of cancer through an oral exposure pathway, and ADAF is an age-dependent adjustment factor (for children three and adults is 1) (USEPA, 2011). CSF (mg/kg/d) for targeted pesticides: Heptachlorepoxide = 9.1; Heptachlor = 4.5; Hexachlorobenzene=1.6; and not available for α-Endosulfan, Malathion, and Propargite. If TCR < 10^{-6}, cancer risks are considered negligible; however, if CR >10^{-4}, cancer risks are considered unacceptable by most international regulatory agencies (USEPA, 2002). Acceptable risk limits for carcinogens range from 10^{-4} (where a person's lifetime risk of developing cancer is 1 in 10,000) to 10^{-6}(risk of developing cancer over a human lifetime is 1 in 1,000,000) (USEPA, 2002).

3.1.7. Data analysis

Data were analyzed using SPSS software version 26.0. We compared the average concentration of pesticide residues in different samples to the maximum permissible limits (MPL) using a one-sample t-test to assess the statistical significance of the sample pesticide residues with respect to the trading standards established by international agencies (e.g. the EU standards) to ensure that residues are regulated in the global food trade.

3.2.Results and Discussion

3.2.1. Method validation result

Ensuring the safety of pesticide use requires analyzing residues in food particularly vegetables, which pose a significant challenge to public health (Khan *et al.*, 2011). Table 3.1 shows the validation results that satisfied the SANTE/12682/2019 guidelines. The calibration curves for a collection of 35 pesticide standards, including isomers and degradation products, have a correlation coefficient (r^2) greater than 0.9906. The average recovery for both vegetables was between 75 and 113%, within the analytical range permitted (Dinede *et al.*, 2023). The LOD and LOQ for the pesticides tested ranged from 0.002 to 0.018µg/kg and 0.005 to 0.245µg/kg, respectively. The average relative standard deviation (% RSD) is less than 10%. These results indicate that the technique is accurate since most of the collected pesticides were within the allowed analytical range (70-120%) and precise, as the percentage RSD < 20 (Dinede *et al.*, 2023).

3.2.2. Pesticide residues concentration in vegetables

Following validation of the QuEChERS method, the concentrations of pesticide residues in fifteen composite samples of tomatoes and onions were determined. The results show that 22 (62.9%) pesticide residues were detected in both vegetables, with 21 (60%) and 20 (57.1%) pesticide residues detected in tomato and onion, respectively (Tables 3.2 and 3. 3), while the concentrations of the remaining 14 pesticides in tomato and 15 in onion were found to be below the detection limit: In tomatoes 8 Organochlorines (α-endosulfan, Chlordane,4-4(DDT, DDD, and DDE), Dieldrin, Lindane, and Methoxychlor), 2 Carbamates (Bendiocarb, indoxacarb), 1Benzodioxole (pipronyl butoxide) and 3pyrethroids (cyfluthrin, cypermethrin, and deltamethrin), similarly in onion 10(Aldrin, β-endosulfan, Chlordane,4-4(DDT, DDD, and DDE), Dieldrin, lindane, Hexachlorobenzene, and methoxychlor);1(Bendiocarb);1(Pipronyl butoxide), and 3(Cyfluthrin, Cypermethrin, and Deltamethrin), respectively.

3.2.2.1.Pesticide residues concentrations in tomatoes

As shown in Table 3.2, five pesticide residues in tomatoes exceeded the default EU-MRL 0.01mg/kg standards. Only food items with pesticide residues exceeding the default EU-MRL of 0.01mg/kg were considered for substantial pollution and food safety concerns. The mean residue of β-BHC in tomatoes was 0.024mg/kg, which was twice that of EU-MRL (0.01mg/kg) and Codex Alimentarius (FAO/WHO) (0.01mg/kg). A sample t-test revealed statistically significant differences ($P<0.05$) between the mean β-BHC content of tomatoes and the Codex Alimentarius and EU MRL standards (see Table 3.2). As a result, eating tomatoes in the current study area may be unsafe due to β-BHC contamination.

The mean concentration of heptachlor was found to be higher than EU-MRL (0.01mg/kg), while the difference was not statistically significant ($p>0.05$) (Table 3.2). This indicates that the average heptachlor concentration was close to the acceptable standard of EU-MRL. According to the Agency for Toxic Substances and Diseases Registry (ATSDR, 2005), heptachlor can accumulate in the soil and be passed on to

Table3: 2 Concentration (mg/kg) of pesticide residues in tomato samples collected from irrigated farmlands near Lake Ziway (n=9).

Category	Pesticides detected	Lowest value	Highest value	Mean ±SD	EU MRL	Mean-difference (Mean-EUMRL)	P=value. Sig.(2-tailed)
OC	α-BHC	0.002	0.005	0.003±0.001	0.01	-0.0066	≤ 0.001
	β –BHC	0.0001	**0.04**	**0.024±0.005**	0.01	0.0139	**0.034**
	Hept-epoxide	0.0001	0.01	0.005±0.003	0.01	-0.0063	0.024
	Heptachlor	0.01	**0.02**	**0.012±0.005**	0.01	0.0017	0.468
	α-Endosulfan	0.003	**0.63**	**0.331±0.220**	0.05	0.3225	**0.003**
	Aldrin	0.0004	0.01	0.003±0.003	0.01	-0.0069	0.015
	Hexachlorobenze	0.000	0.**152**	0.001±0.0005	0.01	-0.009	0.025
OP	Bromopho-Ethyl	0.000	0.003	0.001±0.001	0.01	-0.0086	≤ 0.001
	Chloropy-Methyl	0.0002	0.003	0.001±0.0007	0.01	-0.0089	≤ 0.001
	Diazinon	0.0000	0.001	0.0004 ±0.0004	0.01	-0.0095	≤ 0.001
	Ethion	0.0001	0.001	0.001±0.0004	0.01	-0.0092	≤ 0.001
	Famphur	0.0006	0.003	0.001±0.001	0.01	-0.0085	≤ 0.001
	Fenitrothion	0.000	0.003	0.001±0.001	0.01	-0.0090	≤ 0.001
	Fenthion	0.001	0.003	0.002±0.001	0.01	-0.0081	≤ 0.001
	Malathion	0.008	**0.048**	**0.02±0.02**	0.02	0.0112	0.304
	Parathion	0.0005	0.004	0.001±0.0001	0.05	-0.0087	≤ 0.001
	Profenofos	0.0004	0.002	0.001±0.0006	10	-9.9996	≤ 0.001
	Thionazin	0.0002	0.0005	0.0002±0.0001	0.01	-0.0099	0.014
C	Propoxur	0.01	0.038	0.023±0.00001	0.05	-0.0275	≤ 0.001
OS	Propargite	0.001	**0.792**	**0.032±0.012**	0.01	0.0221	0.162
NA	Dichlobenil	0.0002	0.002	0.001±0.0003	0.01	-0.0089	≤ 0.001

Note: OC=Organo chlorine, OP=Organo phosphate, C=Carbamate, OS= Organosulfite, NA=Not Assigned, values in bold indicate the conc. Above acceptable EU-MRL

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-vegetables. The mean residue concentrations of α-endosulfan (0.331 mg/kg) were six times higher than the EU-MRL limit of 0.05mg/kg but less than the FAO/WHO standard of 0.5mg/kg. The difference in mean concentrations of α-endosulfan and EU-MRL was statistically significant ($p<0.05$). Therefore, the tomato in the current study may be unsafe to consume because of α-endosulfan contamination. In this particular study, the highest concentration of α-Endosulfan recorded was similar to the findings of Sheikh *et al.* (2013) in tomato samples from the Pakistani Sindh market, where the values ranged from null to 0.68 mg/kg. The average concentration of this study is also consistent with the results of Essumang *et al.* (2008) from Ghana (0.3 mg/kg) and Mahugija *et al.* (2017) from Tanzania (0.3 mg/kg). However, the current finding was higher than the results of López-Dávila *et al.* (2021) (0.01 mg/kg) from Cuba, Oyeyiola *et al.* (2017) (0.0016 mg/kg) from Nigeria, and Kumelachew Mulu *et al.* (2020) (0.006

mg/kg) from Ethiopia. The difference in results may be due to the difference in research settings. Nonetheless, the high concentration of endosulfan in tomatoes in this study could be attributed to the hyper accumulating nature of tomatoes as stated by (Kumar *et al.*, 2013).

Malathion residues were in concentrations ranging from less than the detection limit to 0.048 mg/kg (Table 3.2). The average recorded malathion concentration was 0.02 mg/kg, comparable to EU-MRL but less than FAO/WHO Codex Alimentarius (0.5mg/kg). Consuming tomatoes according to the FAO/WHO standard could be safe with regard to Malathion residues. This finding was comparable to the data obtained by (Akoto *et al.*, 2015) from Ghana (0.027 ± 0.021 mg/kg). The residual concentrations of propargite were determined to be 0.154mg/kg, higher than the EU-MRL limit of 0.01 mg / kg, but less than the Codex Alimentarius standard (FAO/WHO, 2011) of 2mg/kg. According to FAO / WHO standards, the tomatoes at the current study site were safe in terms of contamination by propargite residues. This result was comparable to the 0.06mg/kg reported by Marrez *et al.* (2021) from Egypt. Generally, the order of pesticide residues in tomatoes was the following order: α-Endosulfan > Propargite > β-BHC > malathion > heptachlor (Table 3.2).

3.2.2.2. Pesticide residues concentration in onions

As shown in Table 3.3, the present results indicated that the levels of heptachlor epoxide (0.023 ± 0.014mg/kg) and propargite (0.042±0.025mg/kg) in onions were higher than the maximum residue limit (MRL) of (0.01mg/kg) suggested by the European Union, while the remaining were detected below the EU-MRL standards. The concentration of identified heptachlor epoxide and propargite residues in onion exceeded the EU-MRL twice and five times, respectively. But the difference was not statistically significant (p>0.05). As a result, onion in the present study area was safe for human consumption with respect to heptachlor epoxide and propargite residue contamination.

Table3: 3 Concentration (mg/kg) of pesticide residues in onion samples collected from irrigated farmlands in the vicinity of Lake Ziway (n=6).

Category	Pesticides detected	Lowest value	Highest Value	Mean ± SD	EU MRL	Mean-difference (Mean-EUMRL)	P=Value Sig.(2tailed)
OC	α-BHC	0.002	0.005	0.004±0.001	0.01	-0.0065	≤ 0.001
	β -BHC	0.0001	0.01	0.001±0.002	0.01	-0.0086	≤ 0.001
	Hepta-epoxide	0.006	**0.038**	**0.023±0.014**	**0.01**	**0.0132**	0.069
	Hepta chlor	0.0004	0.01	0.003±0.004	0.01	-0.0017	0.083
	α-Endosulfan	0.001	0.003	0.002±0.001	0.1	-0.0473	≤ 0.001
OP	Bromoph-Ethyl	0.00004	0.003	0.0004±0.0004	0.01	-0.0097	≤ 0.001
	Chlorop-Methyl	0.0002	0.001	0.0005±0.0002	0.01	-0.0095	≤ 0.001
	Diazinon	0.00004	0.0012	0.0001±0.001	0.05	-0.0099	0.005
	Ethion	0.0004	0.001	0.0007±0.0004	0.02	-0.0093	0.017
	Famphur	0.0001	0.001	0.0009±0.0003	0.01	-0.0091	≤ 0.001
	Fenitrothion	0.0002	0.0005	0.0003±0.0001	0.01	-0.0097	≤ 0.001
	Fenthion	0.001	0.003	0.002±0.0005	0.01	-0.0082	≤ 0.001
	Malathion	0.001	**0.02**	**0.016+0.007**	0.02	**0.0059**	0.440
	Parathion	0.001	0.001	0.001±0.0003	0.05	-0.0091	≤ 0.001
	Profenofos	0.0002	0.001	0.001±0.0002	0.02	-0.0194	≤ 0.001
	Thionazin	0.00001	0.001	0.0003±0.0001	0.01	-0.0097	≤ 0.001
C	Indoxacarb	0.0003	0.004	0.003±0.002	0.02	-0.0170	0.006
	Propoxur	0.01	0.025	0.02±0.01	0.05	-0.0345	≤ 0.001
OS	Propargite	**0.0004**	**0.112**	**0.042±0.025**	0.01	0.0321	0.295
NA	Diclobenil	0.0001	0.001	0.001±0.0003	0.01	-0.0091	≤ 0.001

Note: OC=Organo-chlorine, OP=Organo phosphate, C=Carbamate, OS= Organosulfite, NA=Not Assigned, values in bold indicate the conc. above acceptable EU-MRL.

3.2.3. Comparison of pesticide residue with the MRL set by International Authorities

The pesticide residues in tomato and onion were compared with the corresponding MRLs of each pesticide and indicated in Appendixes (Tables S1 & S2). Ethiopia does not have a national MRL for any pesticide but relies on Codex (Gumataw Abebe & Issmat Kassem, 2018). However, due to the lack of available data on the present pesticides tested, we consider the MRL set by the EU. The current study found residues in 71.4% and 73.8% of the tomato and onion samples, respectively. Only 10.6% and 7.9% of the tomato and onion samples respectively exceeded the EU's maximum residue limit (MRL), (see Annex 1 and 2). According to this study the use of pesticides in the study area is excessive. Additionally, the detected pesticides that exceeded the Maximum Residue Limit (MRL) were out-dated. The levels of heptachlor and heptachlor epoxide surpassed the MRL and banned by the Stockholm Convention. Despite being a signatory to the Stockholm Agreement, Ethiopia continues to use obsolete chemicals in agriculture. Although Ethiopia has ratified the Basel, Stockholm, and Rotterdam Conventions, the laws and regulations regarding hazardous chemicals and environmental protection are still insufficient to prevent the unauthorized use of out-dated chemicals (UNEPA, 2019). Overall, pesticide concentrations that exceed the MPL may have acute or chronic health consequences if consumed regularly. Pesticides, for example, have been documented to cause nausea, dizziness, vomiting, migraines, stomach discomfort, rashes, and even death (McCauley *et al.*, 2006). Pesticides have a wide range of long-term health effects, including respiratory and cognitive difficulties, cancer, diabetes, cardiovascular disease, neurological diseases such as Parkinson's disease, autism, infertility, congenital birth defects, and DNA damage (Alavanja, 2004; Kisby *et al.*, 2009; Ledda *et al.*, 2021).

3.2.4. Potential Health Risks from Vegetable Consumption

3.2.4.1.Target Hazard Quotient (THQ)

Tables 3:4 and 3:5 show the THQ results for the research areas for those who consume tomatoes and onions one to seven times a week. THQ was estimated using only residue concentrations greater than or equal to the EU-MRL standard. The THQ values for α-endosulfan, heptachlor, malathion, and propargite residues in adults ranged from 0.0003 to 0.12, while in children they varied from 0.001 to 0.32 (Table 3.5). THQ values less than one (THQ<1) were reported in both cases, indicating that consuming tomatoes from current research sites can pose negligible non-carcinogenic health risks to adults and children. This result was comparable to that of Oyeyiola *et al*. (2017) from Nigeria for these pesticide residues (HQ<1). Likewise, THQ levels in onion for residues of heptachlor, malathion, and propargite ranged from 0.001 to 0.08 for adults and 0.002 to 0.21 for children (Table 3:5). This result finds THQ values less than one (THQ<1), showing that onions consumed at study sites may not cause non-carcinogenic health risks to children and adults. The THQ values for onion heptachlor epoxide ranged from 0.44 to 12.3 for adults and 4.69 to 32.82 for children, showing that onion consumption at study sites may pose non-carcinogenic health risks for both adults and children.

Regarding the site, the estimated THQ levels in onion for heptachlor epoxide were higher than one (THQ>1) for all exposure periods for adults and children at Site 2, while at Site 1 adults were exposed more than three days a week and children were exposed two days a week.

Table3: 4 Target Hazard Quotient (THQ) and Hazard Index (HI) of pesticide residues from consumption of tomatoes produced in the study sites at different levels (days per week) of exposure

Sites	**Levels of Exposure d/w**	**Target Hazard Quotient (THQ)**								**Hazard Index(HI)**	
		α-Endosulfan		**Heptachlor**		**Malathion**		**Propargite**			
		A	C	A	C	A	C	A	C	A	C
S1	1	0.016	0.044	0.017	0.046	0.0003	0.001	-	-	0.034	0.090
	2	0.033	0.088	0.034	0.091	0.001	0.002	-	-	0.068	0.181
	3	0.049	0.131	0.051	0.137	0.001	0.002	-	-	0.102	0.271
	5	0.082	0.219	0.086	0.229	0.001	0.004	-	-	0.169	0.451
	7	0.115	0.307	0.120	0.320	0.002	0.005	-	-	0.237	0.632
S2	1	0.008	0.020	-	-	-	-	0.002	0.004	0.009	0.024
	2	0.015	0.040	-	-	-	-	0.003	0.008	0.018	0.048
	3	0.023	0.060	-	-	-	-	0.005	0.012	0.027	0.072
	5	0.038	0.101	-	-	-	-	0.008	0.020	0.045	0.121
	7	0.053	0.141	-	-	-	-	0.011	0.028	0.063	0.169
S3	1	0.010	0.026	0.011	0.030	0.001	0.002	0.000	0.001	0.023	0.060
	2	0.020	0.053	0.023	0.061	0.002	0.005	0.001	0.002	0.045	0.120
	3	0.030	0.079	0.034	0.091	0.003	0.007	0.001	0.003	0.068	0.180
	5	0.049	0.132	0.057	0.152	0.004	0.012	0.002	0.005	0.113	0.301
	7	0.069	0.185	0.080	0.213	0.006	0.017	0.002	0.006	0.158	0.421

Note: Values in bold (>1) indicate potential non-carcinogenic health risk for humans. A=Adult, C= Children

3.2.4.2.Hazard Index (HI)

The estimated hazard index was shown in Tables 3:5 and 3:6 as the sum of THQ for tomato and onion consumption at the sample sites one to seven times per week. The HI values obtained from tomato consumption at all three sites were less than unity (HI<1). The findings indicate that the consumption of all pesticide residues evaluated in this study through the consumption of tomatoes at the given exposure levels from each site poses potentially insignificant non-carcinogenic health hazards (Fig 3.1a). The HI values obtained from onion consumption were higher than 1 for children from sites 1 and 2 and adults from site 2 (Fig 3. 1b). Therefore, farmers' families around the study areas and other individuals who consume this vegetable regularly are more vulnerable to pesticide toxicities. This result is in line with earlier epidemiological research (Faustman *et a*l., 2000), which showed that pesticide exposure can have a greater impact on children compared to adults.

Table3: 5 Target Hazard Quotient (THQ) and Hazard Index (HI) of pesticide residues from consumption of onion produced in the study sites at different levels (days per week) of exposure

Sites	**Levels of Exposure d/w**	**Target Hazard Quotient (THQ)**								**Hazard Index(HI)**	
		Hept-epoxide		Heptachlor		Malathion		Propargite			
		A	C	A	C	A	C	A	C	A	C
S1	1	0.440	1.172	-	-	-	-	0.001	0.003	0.441	**1.175**
	2	0.879	**2.344**	-	-	-	-	0.002	0.006	0.881	**2.350**
	3	**1.319**	**3.516**	-	-	-	-	0.003	0.009	**1.322**	**3.526**
	5	**2.198**	**5.861**	-	-	-	-	0.006	0.015	**2.204**	**5.876**
	7	**3.077**	**8.205**	-	-	-	-	0.008	0.021	**3.085**	**8.226**
S2	1	**1.758**	**4.689**	0.011	0.030	0.001	0.002	0.003	0.008	**1.773**	**4.729**
	2	**3.516**	**9.377**	0.023	0.061	0.001	0.003	0.006	0.017	**3.547**	**9.458**
	3	**5.275**	**14.066**	0.034	0.091	0.002	0.005	0.009	0.025	**5.320**	**14.187**
	5	**8.791**	**23.443**	0.057	0.152	0.003	0.008	0.016	0.042	**8.867**	**23.645**
	7	**12.308**	**32.821**	0.080	0.213	0.004	0.011	0.022	0.059	**12.414**	**33.103**

Note: Values in bold (>1) indicate potential non-carcinogenic health risks for humans. A= Adult, C=Children

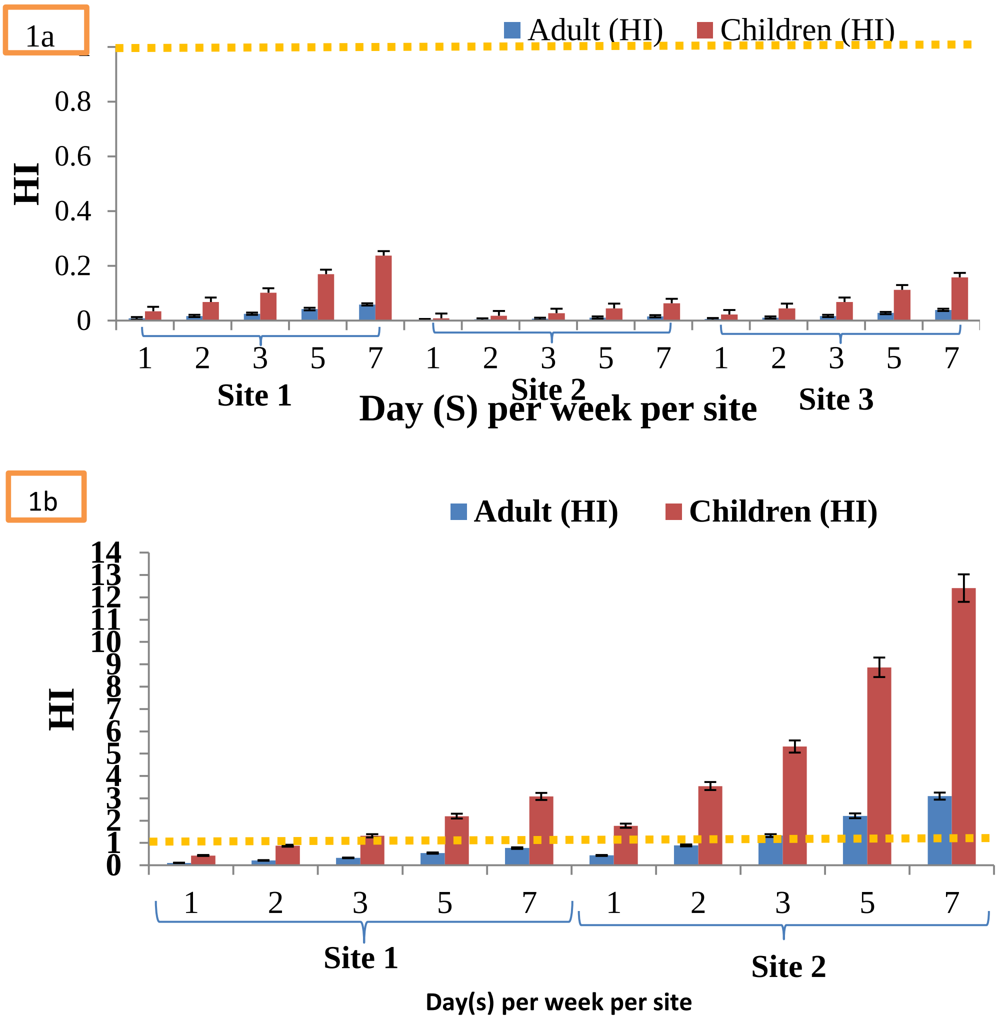

Figure 3: 1 None-carcinogenic risk (HI) due to consuming contaminated tomatoes (a) and onions (b)

3.2.4.3.Carcinogenic Health Risks (CHRs)

According to the Registry of Toxic Substances and Diseases (ATSDR, 2005), heptachlor has been classified as a probable human carcinogen by the EPA and the International Agency for Research on Cancer (IARC). Additionally, the EPA has categorized heptachlor epoxide as a possible human carcinogen. Tables 3:7 and 3:8 summarize the Cancer Hazard Ratios (CHRs) associated with the consumption of tomatoes and onions from one to seven times a week.

The highest CHR value obtained for a seven-day exposure to heptachlor through tomato consumption was 2.16E-03 for tomato intake from site 1 (Table 3.6), indicating that two cancer cases occur per 1000 children individuals. The lowest value was 5.20E-05 for onion consumption from site 2 (Table 3.7) for adults with one exposure per week, suggesting that approximately three cancer cases occur per 100,000 adult individuals (Fig 3.2a).Similarly, for heptachlor epoxide, the highest CHR value was 1.16E-02 from Site 2 for children to seven-day exposure per week, which means that one cancer case occurs every 100 children individual, the lowest was 5.2E-05 from Site 1 for adults to once exposure per week (5 cancer cases per 100,000 adult individuals) (Fig 3.2b). The study revealed that the cancer health risk (CHR) for heptachlor were within the acceptable range ($<10^{-4}$) for a dose of 2 days per week or less for site 1when it comes tomato consumption, and 3 days per week or less for sites 2 and 3 with respect to adults consumption tomatoes and onions, respectively. This indicates that as this level of exposure there is no possible risk of developing cancer from ingesting heptachlor residues from tomato consumption for adults.

On the other hand, the CHR values for heptachlor exceeded the acceptable limit ($>10^{-4}$) in the case of children who consumed tomatoes and onions at all levels of exposure per week. Furthermore, for adults, the CHR values were exceeded the acceptable limit at site 1 with respect to tomato consumption of 3 days per week or more, and at site 3 for tomato consumption of more than 5 days per week (Table 3. 6). Therefore, it is reasonable to conclude that children at all levels of exposure and adults who consume tomatoes more than 3 days per week may face a potential risk of developing cancer in the study area and beyond.

Table3: 6 Carcinogenic risks (CR) of heptachlor due to consumption of tomato from the study sites

Levels of Exposure (d/w)	Site 1		Site 3	
	A	C	A	C
1	3.86E-05	3.09E-04	2.6E-05	2.06E-04
2	7.71E-05	6.17E-04	5.1E-05	4.11E-04
3	1.54E-04	9.26E-04	7.7E-05	6.17E-04
5	3.09E-04	**1.54E-03**	1.29E-04	**1.03E-03**
7	2.70E-04	**2.16E-03**	1.80E-04	**1.44E-03**

Note: Values in bold indicate TCR above acceptable limit (10^{-4}), A=Adult, C=Children

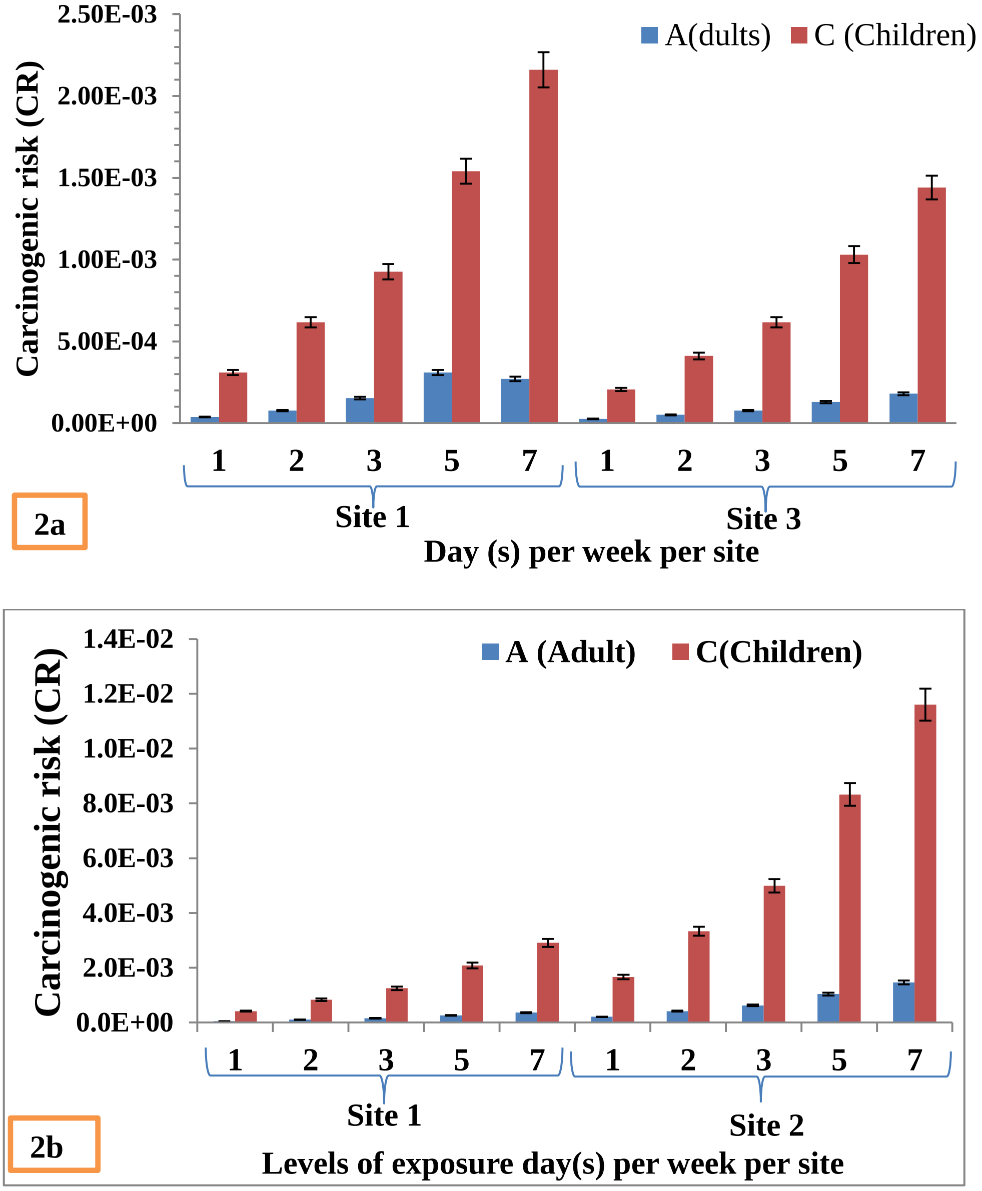

Figure 3: 2 Carcinogenic risk (CR) due to consuming tomato (a) and onion (b)

The CHR values for heptachlor epoxide for all levels of exposure to children from sites

1 and 2, and for adults exposure of two or more days of consumption per week from site1 and at all levels of exposure from site 2 were higher than the permissible limit ($>10^{-4}$) (Table 3:7). Therefore, it is possible to conclude that individuals, both children and adults, who ingest heptachlor epoxide through onions, a component of the residents' diet in the research area, may face significant cancer risks.

In summary, the results of this study showed that the dietary intake of heptachlor and heptachlor epoxide at average exposure levels would create the possibility of developing cancer in children through the consumption of the investigated vegetables. Furthermore, this finding is consistent with previous research indicating that children appear to be particularly vulnerable to heptachlor and heptachlor epoxide poisoning (ATSDR, 2005). Thus, immediate measures such as reducing exposure or substituting the toxic pesticides with less toxic pesticides needed to be taken to control and minimize heptachlor and heptachlor epoxide exposure through vegetable consumption in the research region.

Table3: 7 Carcinogenic risks (CR) of pesticides due to consumption of onion per sites

Levels of Exposure (d/W)	**Site 1**		**Site 2**		**Site 2**	
	Hept-epoxide		**Hept-epoxide**		**Heptachlor**	
	A	**C**	**A**	**C**	**A**	**C**
1	5.20E-05	4.16E-04	2.08E-04	**1.66E-03**	2.57E-05	2.06E-04
2	1.04E-04	8.32E-04	4.16E-04	**3.33E-03**	5.14E-05	4.11E-04
3	1.56E-04	**1.25E-03**	**6.24E-04**	**4.99E-03**	7.71E-05	6.17E-04
5	2.60E-04	**2.08E-03**	**1.04E-03**	**8.32E-03**	1.29E-04	**1.03E-03**
7	3.64E-04	**2.91E-03**	**1.46E-03**	**1.16E-02**	1.80E-04	**1.44E-03**

Note: Values in bold indicate TCR above acceptable limit (10^{-4}*), A=Adult, C=Children*

3.3. Conclusion

This study found that the consumption of tomatoes and onions from all study sites at varying levels (days per week) of exposure could be safe from the non - carcinogenic risk of the toxicities of α-endosulfan, heptachlor, malathion, and propargite residues for adults and children. Concerning the carcinogenic risk, the consumption of tomatoes and onions from all study sites at varying degrees of exposure (days per week) may be safer in terms of residual heptachlor toxicities for adults and children (consuming < 3 days per week). The carcinogenic risk of onion heptachlor epoxide was estimated to be 1.46 $x10^{-3}$g / kg/day, which implies that the cancer risk of heptachlor epoxide in an adult is 1.46 per 1,000 individuals continuously exposed. In children, the risk was estimated to be 1.16 $x10^{-2}$g / kg/day (1.16 per 100 individuals), with a threat multiplied by 10. The findings suggest that farmers and their families, as well as those who consume vegetables grown on soils contaminated by pesticides regularly, are the most vulnerable risk group whose health must be protected. Therefore, it is critical to raise awareness among stakeholders while simultaneously implementing sound monitoring policy actions to protect the ecosystem and the health of the population.

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CHAPTER FOUR

4. ASSESSMENT OF POTENTIAL HUMAN HEALTH RISK ASSOCIATED WITH HEAVY METALS IN SOIL – VEGETABLE SYSTEM IRRIGATED BY RIFT VALLEY LAKE ZIWAY, ETHIOPIA

ABSTRACT: Heavy metal contamination of vegetables is a major concern, especially in areas where irrigation has been used for a long time. The Central Ethiopian Rift Valley Region is highly affected by the heavy use of agrochemicals throughout the year. Although some studies have been conducted on the concentration and level of heavy metal pollution, no attention has been paid to their impact on human health. This study analyzed the concentration of nine heavy metals (As, Cd, Cr, Co, Cu, Hg, Ni, Pb, and Zn) in a soil-vegetable system (tomatoes and onions) irrigated using Lake Ziway, Ethiopia. An inductively coupled plasma optical emission spectrometer (ICP-OES) was used to test the heavy metal contamination. Moreover, the study determined the health risks associated with consuming contaminated vegetables by employing major indices, including non-carcinogenic and carcinogenic risks. The results showed that the mean concentration of Pb, As, Hg, and Cr in all tomato and onion samples and the average Zn, Pb, Cd, and Hg levels in all soil samples under tomato and onion plants exceeded the FAO/WHO threshold limit. Non-carcinogenic health risk estimates showed that As, Pb, Hg, and Co for children and Pb and Co for adults had THQ values greater than 1, indicating the possibility of systemic health risks. Carcinogenic health risk showed that Ni posed a risk of developing cancer for both adults and children, with values ranging from 10^{-3} to 10^{-1}. In addition, children are likely to have a higher cancer risk due to exposure to As and Cr. Therefore, it is crucial to raise awareness among stakeholders and implement effective monitoring policies with a sense of urgency to safeguard public health both within and beyond the study area.

4.1. INTRODUCTION

Vegetables have numerous health benefits as they contain high levels of antioxidants, minerals, and vitamins (Manwani *et al.*, 2022). However, consumers are becoming increasingly worried about the vegetables grown using various agrochemicals on irrigation farms. Due to water scarcity and market demand, untreated wastewater and hazardous agrochemicals are used to increase horticultural products (Ngugi *et al*., 2022). Moreover, the long-term usage of partially treated or untreated wastewater could result in the accumulation of heavy metals in the soil (Elgallal *et al*., 2016). This could be a potential threat to human health as heavy metals can be transferred through the food chain (Yang *et al*., 2018).

Research conducted globally has revealed an alarming increase in health concerns related to consuming irrigated vegetables that are contaminated with heavy metal deposition (Jabeen & Aslam, 2018; Jibrin *et al*., 2022). Various hazardous heavy metals, such as lead (Pb), arsenic (As), mercury (Hg), and cadmium (Cd), are considered probable carcinogens and have been linked to the development of various diseases, including cardiovascular, renal, nervous system, infertility, blood, and bone disease (Järup, 2003). This comprehensive study has mainly focused on the harmful effects of heavy metals on human health, particularly in children and adults (Yang *et al*., 2018; Ashraf *et al*., 2021). The situation is similar in Ethiopia, as indicated by previous studies (Samuel Bekele *et al*., 2021; Yohannes Gelaye & Sintayehu Musie, 2023).

Recent studies conducted in Ethiopia have found that vegetables irrigated with contaminated water have high levels of heavy metals. Consuming such vegetables can pose serious health risks, but there is limited research on the extent of these risks for adults and children. For example, Mulat Anagaw *et al.* (2019) conducted a study on the levels of heavy metals in tomatoes grown near and far from an industrial site in Ethiopia's Rift Valley. Buzuayehu Abebe (2017) focused only on onions, soil, and irrigation water. Additionally, three other studies were conducted on the Ethiopian rift (Hailu Reta & Leta Danno, 2020; Leta Danno & Hailu Reta, 2021; Samuel Bekele *et* *al*., 2021), but they primarily focused on adult health concerns and did not assess the effects of cabbage, tomato, and potato products on children.

The purpose of this study was to analyze the levels of nine different heavy metals - As, Pb, Cd, Cr, Co, Cu, Ni, Hg, and Zn in the soil – vegetable system and assess the potential health risks, both carcinogenic and non-carcinogenic, to adults and children through consumption of the contaminated tomatoes and onions. Additionally, the goal of this analysis is to ensure the safety of people, including adults and children, who live in the study area and beyond.

4.2. MATERIALS AND METHODS

4.2.1. Study design and period

In a cross-sectional laboratory study, the concentration of heavy metals in tomato (*Lycopersicon esculentum* L.) and onion (*Allium cepa* var. *aggregatum*), and the soil beneath it from three irrigated farmlands adjacent to Lake Ziway were examined. The samples were collected during the rainy season in late August 2021. It is worth mentioning that heavy metal contamination is considerably lower during the wet season compared to the dry season (Ahmed *et al*., 2019). As described by the authors, this is due to the dilution of water by rainfall, the lower absorption of heavy metals from diluted irrigation water, and heavy metal absorption from low- concentrated irrigation water and/or soil.

4.2.2. Samples and sampling procedure

Eighteen soil samples and 18 vegetable samples were collected purposely from three irrigated farm sites (S1-S3) in three villages: Abenea-Girmama (S1), Wellibulla (S2), and Girrissa (S3) adjacent to Lake Ziway. These are sites where vegetables are grown in a large field with many pesticide users and near Lake Ziway fresh water. Composite surface soil samples at 0-20 cm depth using a steeliness steel auger in a zigzag pattern following the procedure described by Mondal (2020) collected under tomato (*Lycopersicon esculentum* L.) and onion (*Allium cepa* var. aggregatum) plants grown on farmlands. During the same time, tomato (n=9) and onion (n=9) samples were collected in their consumption stages from the spot where the soil was collected. Each sample was packed separately in ziplock polyethylene bags, labeled, and transported to the laboratory in an insulated icebox, stored in the dark at 4 °C until ready for preparation.

Soil samples were air dried, cleaned by removing visible traces of leaves and other waste materials, homogenized ground / crushed, and sieved through a mesh size of 2mm before being stored in clean and airtight polyethylene bags until further analysis. Vegetable samples (tomatoes and onions) were washed with double distilled water, oven-dried (60°C), ground to a fine powder with an acid-washed mortar and pestle, and stored in airtight polyethylene bags at 4 °C until further analysis.

4.2.3. Chemical and reagents

The reagents and chemicals used in laboratory work were all analytical grade: Deionized water, Nitric acid (69% HNO_3, Merck, France), 37% HCl (Fine Chem. Industries Mumbai, France), extra pure hydrogen peroxide (30% H2O2, Scharlau, European Union), sodium hydroxide (Merck, Germany) and standard stock solutions such as $Cd(NO3)_2$, $Pb(NO3)_2$, $Cu(NO3)_2$, $CoCl_2{\cdot}6H2O$, $Cr(NO_3)_2$, $Hg(NO_3)_2{\cdot}H_2O$, As_2O_3, $Ni(NO_3)_2$ and $Zn(NO_3)_2.6H_2O$ (99.99%, Merck, Germany). All closed containers, polyethylene flasks, and plastic containers were soaked in 10% (v/v) HNO_3, freshly prepared using high-purity water, for at least 24hr and finally washed with deionized water. Subsequently, all materials were dried at 50 ° C and stored in clean air.

4.2.4. Soil and vegetable Samples digestion

The soil samples were digested using the wet digestion method (US Environmental Protection Agency 3050B method) with slight modifications (USEPA, 1996). Optimization of the method with its basic steps of the experimental procedure was carried out as described by Mulat Anagaw *et al*. (2019) and vegetable samples were digested using the method of the Association of Official Analytical Chemists (AOAC, 2000), and the wet digestion optimization procedure was carried out as described by Biset Asrade & Gebremariam Ketema (2023). After digestion, each soil and vegetable sample was properly cooled, filtered through Whatman No. 42 filter paper, diluted to a final volume of 20 and 50ml, respectively, using double distilled water, and then stored in a glass container until further analysis. The concentrations of heavy metals (As, Pb, Cd, Cr, Co, Cu, Ni, Hg, and Zn) from soil and vegetable-digested solutions were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES: ARCOSFHS12, USA) in the agricultural laboratory of HORTICOOP ETHIOPIA, Debre Zeit.

4.2.5. Physico-chemical analysis of soil

Hydrometer methods Bouyoucos (1962) were used to examine the distribution of soil particle size and the name of the textural class was derived from the USDA textural triangle system described by Rowell (1994). The pH of soils in water suspension was measured following the Van Reeuwijk (1992) method using a potentiometric method with a glass-calomel combination electrode in a 1:2.5 (soil: liquid ratio). Electrical conductivity (EC) was measured from a soil-to-water suspension of 1:2.5 using a conductivity meter. The wet digestion method developed by Walkley & Black (1934) was used to determine the organic carbon (OC) content of the soil. The percentage of soil organic matter (OM) was calculated by multiplying the percent of soil OC by 1.724, assuming that the OM is composed of 58 % OC (De Brogniez et al., 2015). Cation exchange capacity (CEC) was determined using sodium acetate and ammonium acetate solutions, as described by Loring & Rantala (1992).

4.2.6. Quality Control and Instrumental Analysis

A. Standard Solution Preparation Methods

Calibration and standard solution preparation procedures have an impact on the quality of findings from heavy metal investigations utilizing an optimal standard mode of operating conditions of ICP-OES in the appendix (Table 4.1). A standard solution (1000 mg/L) containing the analytical grades of As, Pb, Cd, Cr, Co, Cu, Ni, Hg, and Zn was used in the corresponding salts. Standard stock solutions 1000 mg L^{-1} were prepared from metals nitrate salts prepared in 3% HNO_3. The working standard solutions of the selected metals were freshly prepared from the intermediate standard solutions (100 mg L^{-1}) that was obtained by diluting the stock standard solutions with 0.5% HNO_3. Finally, the equipment was calibrated using a nine-point calibration curve is constructed using the standard concentration of metals and the intensity values of each metal (Table 4:2).

Table 4: 1 linear regression equations and the coefficient of determination (r^2) of each heavy metal in the study area

HM	Concentration of standards solution (mgL^{-1})	Regression equation (Y = mx + b)	(r^2)	Wavelength (nm)
As	0,0.06,0.13,0.19,0.64,1.28,1.92,2.56,3.2	y =9089.3x+1428.3	0.997	189.98
Pb	0,0.06,0.11,0.17,0.56,1.12,1.68,2.24,2.8	y=4519x-60.79	0.999	220.353
Cd	0,0.03,0.06,0.08,0.28,0.56,0.84,1.12,1.4	y=172592x+3742.3	0.999	206.502
Cr	0,0.03,0.6, 0.08,0.28,0.56,0.84,1.12,1.4	y=42073x+4087.1	0.994	205.560
Co	0,0.03,0.6, 0.08,0.28,0.56,0.84,1.12,1.4	y=55955x+4791.4	0.996	228.165
Cu	0,0.06,0.11,0.17,0.56,1.12,1.68,2.24,2.8	y=71162x+13399	0.994	213.598
Hg	0,0.06,0.13,0.19,0.64,1.28,1.92,2.56,3.2	y=22633x+1143.5	0.999	194.164
Ni	0,0.03,0.06,0.08,0.28,0.56,0.84,1.12,1.4	y=41219x+5708.1	0.989	231.604
Zn	0,0.06,0.11,0.17,0.56,1.12,1.68,2.24,2.8	y=119311x+4007.1	0.999	206.2

B. Method detection and quantification

The detection limit of the method (MDL) is defined as the minimum concentration measured of chemicals that can be reported with 99% confidence that the concentration measured is different from the method's blank results (USEPA, 2016). Six blank samples were digested following the same procedure as the samples and each of the samples was determined for the elements of interest by ICP-OES. The standard deviation (SD) of the six blanks for each element was calculated and multiplied by three (LOD = $3SD_b$) to determine the detection limit of the method (Demisew Jemaneh & Chandravanshi, 2021). The limit of quantification (LOQ) is the smallest quantity of analyte that can be measured with acceptable precision and accuracy and is described as ten times the standard deviation of the blank (LOQ= $10*SD_b$). The MDL values obtained were compared with the instrument detection limit and found to be higher in all cases (Table 4:3).

Table 4: 2 Method detection limits for vegetable and soil sample analysis

Metals	Vegetable sample		Soil sample		IDL(mg/L)
	MDL(mg/L)	LOQ(mg/L)	MDL(mg/L)	LOQ(mg/L)	
As	0.120	0.400	0.211	0.702	0.008
Pb	0.113	0.378	0.099	0.329	0.004
Zn	0.069	0.230	0.131	0.437	0.0006
Cd	0.035	0.115	0.035	0.118	0.0004
Hg	0.113	0.376	0.116	0.388	0.003
Cu	0.216	0.720	0.290	0.967	0.006
Ni	0.179	0.597	0.177	0.590	0.002
Co	0.112	0.373	0.113	0.378	0.003
Cr	0.126	0.421	0.119	0.398	0.001

IDL= (Instrument Detection Limit)

C. Precision and accuracy

The precision and accuracy of the analytical method used in the analysis of heavy metals in vegetable and soil samples were validated using the spike recovery analysis method, the data presented in Table appendix (Tables 4.3 to 4.5). As can be observed from the data, the spike recovery falls within the typically acceptable range of 71-118% for good recovery, validating the accuracy and reliability of the methods used for metal-level analysis. The reduced percentage of values found for relative standard deviation (% RSD) (<12%) indicated that the approach used was precise enough for the analysis of heavy metals in the samples.

4.2.7. Bio-concentration factor (BCF)

The BCF was calculated as given in Eq. (1):

$$BCF = C_{plant}/C_{soil} \tag{1}$$

where C_{plant} and C_{soil} are the heavy metal concentrations in plant and soil extracts on a dry weight basis, respectively. BCF > 1 shows that the plant is a hyperaccumulator species (Zhang *et al*., 2002).

4.2.8. Human health Risk Assessment

4.2.8.1. Non-carcinogenic health risk

A. Estimated Daily dietary intake (EDI)

EDI refers to the amount of heavy metals in vegetables that can be consumed daily over a lifetime without presenting a considerable /noticeable risk to health. Daily dietary intake of various heavy metals such as As, Co, Cr, Cu, Hg, Ni, Pb, and Zn from vegetables was estimated using Equation (2):

$$EDI = C \times IR \times Ef \times ED \times Cf / BW \times AT \tag{2}$$

where C is the concentration of metals in vegetables (mg/kg dry weight); IR is the ingestion rate of a vegetable per day (0.240 kg/person/day) and 0.160 kg/person/day, respectively, obtained from Ethiopian Food-Based Dietary Guidelines (EFBDG, 2022);

EF is the exposure frequency (365 days per year); ED is the duration of exposure, which is 6 and 65 years, respectively (WHO, 2015); Cf is the concentration conversion factor for fresh to dry vegetable weight, which is 0.085 (Leta Danno & Hailu Reta, 2021). BW stands for average body weight, which for children is 15 kg and for adults is 60 kg (FAO/WHO, 2011). AT is the average exposure time (365 days per year1 ED), which is 2,190 days for children and 23,725 days for adults, respectively. RfD or (Df) is an oral reference dose of heavy metal.

B. Target hazard quotient (THQ)

THQ was evaluated according to the USEPA (1989) using Equation 3.

$$THQ = EDI / RfD \qquad (\mathbf{3})$$

Where THQ is a non-cancer hazard quotient, RfD is the oral reference dose of heavy metal. RfD values (mg/kg/day) for As, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn are 0.0003, 0.001, 0.0003, 0.003, 0.04, 0.0003, 0.02, 0.0035, and 0.3, respectively (USEPA, 2019). $THQ > 1$ indicates a risk of non-carcinogenic health risk, while $THQ \leq 1$ indicates no possible health risk (USEPA, 2002).

C. Hazard index (HI)

HI was determined using Equation (4) (Ashraf et al., 2021):

$$HI = \sum THQi = THQAs + THQPb + THQZn + THQHg + \ldots + THQCr \qquad (4)$$

If the HI value < 1.0, the metals under consideration had no discernible effect on health. An HI value > 1 indicates potential health problems. HI > 10 indicates a serious chronic health risk (IRIS, 2009).

D. ***Target Cancer Risk (TCR)***

The TCR was estimated using Equation (5) for adults and children based on their lifetime exposure to heavy metals in this study (USEPA, 2012).

$$TCR = EDI \times CSF \times ADAF \qquad (\mathbf{5})$$

Where CSF is the cancer slope factor for carcinogenic heavy metals in vegetables (1.5 mg/kg/day) for As, 1.7 (Ni), 0.5 (Cr), 15 (Cd), and 0.0085 mg /kg /day for Pb (USEPA, 2010). The USEPA has not published the CSF values for Cu, Co, Hg, or Zn. Thus, the cancer risks associated with these heavy metals remain uncertain. ADAF is an age-dependent adjustment factor (for children and adults, 3 and 1, respectively) (USEPA, 2012). The acceptable range of the TCR value is between 1×10^{-6} - 1×10^{-4}, if the TCR threshold value is below 1×10^{-6}, it is accepted that there are no significant risks to human health, and if the TCR threshold value exceeds 1×10^{-4} indicates a potential lifetime carcinogenic risk (USEPA, 2015).

4.2.9. Data Analysis

The obtained data from the experimental investigation was analyzed using the Statistical Package for Social Sciences (SPSS, Version 26.0). We compared the average amount of heavy metals found in different samples to the maximum permissible limits (MPL) using a one-sample t-test. We conducted statistical tests at a 5% confidence level ($p<0.05$) to evaluate the presence of heavy metals in vegetables in the study area. We utilized a multivariate analysis to speculate the origin of the heavy metals.

4.3.RESULTS AND DISCUSSION

4.3.1. Physicochemical properties of soil samples

Table 4.4 summarizes the physicochemical properties of soil samples obtained from onion and tomato cultivation in irrigated farmlands near Lake Ziway. Soil texture varies from sandy loam to sandy clay loam, with 25%-26% clay, 49%-58% silt and 17%-25% sand. This finding is consistent with the report of (Kiflu Alemayehu et al., 2016),who reported that the soil texture of the Ethiopian rift valley is predominantly sandy loam, with silt to clay. Furthermore, the present result is consistent with (Mesfin Hundessa, 2020), which discovered that the soil texture of Meki and Adamitulu in the central rift valley of Ethiopia's sandy loam is dominant. The pH values of the soil analyzed in the study area ranged between 7.56 and 7.65. This suggests that the soil is slightly alkaline and saline, which is comparable with the findings reported by (Mesfin Hundessa, 2020) 7.7 to 7.8. Furthermore, the observation of white stains on the surface soil provides clear evidence of soil salinity.

The amount of Soil Organic Matter (SOM) in the research area ranges from 7.06% to 14.46%, which is higher than the 3.4% requirement set by Teagasc (Agricultural Development Agency) (Spink *et al*., 2010). Soils with more than 3.4% OM are beneficial to agriculture and produce well. Therefore, there is no need to increase OM in the soil. These results are higher than those of Musefa Redi & Israel Bekele (2019) (2.4%) from the same site, Hailu Reta & Leta Danno (2020) (2.13 %) from the Mojo area, and Leta Danno & Hailu Reta (2021) (2.3 %) from the Koka areas of central Ethiopia. However, they are lower than the report of Balkhair & Ashraf (2016) (44.9%) from the western region of Saudi Arabia. The differences in research settings may contribute to the disparity in results but changes in nutritional status over shorter periods: seasonal drying may occur at the same site Turner *et al*. (2015).The CEC of the soil samples in the study area was higher. This result may be due to the relatively high content of the OM. Furthermore, the clay texture also contributed to the higher value of CEC. Usually, the CEC of the soil increases with the pH of the soil, as a result of the increasing negative load of organic matter and clay minerals (Streat & Nair, 1992).This result was consistent with the report of Yirgaalem Weldegebriel *et al*. (2012) (50.2 cmol (+) /kg) from Akaki irrigated vegetable farms in Addis Ababa. And comparable to Hailu Reta & Leta Danno (2020) (42.78 and 43.08 cmol (+) /kg) from the Mojo irrigated farm.

Table 4: 3 Physicochemical characteristics of soil samples from irrigated farmlands around Lake Ziway in Ethiopia

Physicochemical parameters		Tomato farmland	Onion farmland
pH(1:2.5)		7.56±0.15	7.65±0.07
Electrical Conductivity (dSm-1)		2.46±0.49	1.64±0.21
Organic Carbon (%)		4.1±0.68*	8.39±1.65*
Organic matter (%)		7.06±1.16*	14.46+2.85*
CEC (cmolc/kg)		47.47±7.22	50.4±14.71
Soil Texture	%Sand	25	17
	%Clay	26	25
	%Silt	49	58
Texture Class		**Sandy loam**	**Sand clay loam**

*statically significant between and among the group (p<0.05)

4.3.2. Concentrations of heavy metals in soil and vegetables

4.3.2. 1. Concentration of heavy metals in soil samples

Table 4:4 summarizes the concentrations of heavy metals in soil samples from irrigated tomato and onion farms in the study region. Nine heavy metals were identified in the soil samples analyzed. The average concentrations of all heavy metals in the soil sample were higher for onion cultivation than for tomato production. The level of heavy metals in tomato soil is generally followed in the following order: Zn > Pb > Cr > Cu > Ni > As > Co > Hg > Cd. Similarly, the same sequence is observed in the onion soil samples, except that Ni appears before Cu. The average concentration of heavy metals varies considerably between the three sampling sites ($p < 0.05$). Heavy metal concentrations were higher in soil samples from tomato farms at site 1, followed by site 2, and lowest in soil samples from site 3. Similarly, soil samples from onion farms followed the highest at site 2, followed by site 1, and the lowest at site 3. The result indicates that the soil of the two farms at Site 1 and Site 2 was relatively more contaminated with heavy metals, while the soil at Site 3 was relatively less contaminated. Heavy metal levels in the soil of the two plants are almost of the same order, with Zn and Pb suggesting higher levels and Co, Hg, and Cd indicating lower levels. Among the metals detected in soils from tomato and onion farmlands, the concentrations of Pb, Zn, Cd, and Hg exceeded the reference levels for agricultural soils set by FAO/ WHO (1993), which were 10, 50, 0.3, and 0.3 mg/kg, respectively, for all selected sites except Pb from site 3 for onion farmlands, Zn from sites 2 and 3 for tomato farmlands, and site 3 for onion farmlands (Table 4:4). Compared to our report, recent studies in the central rift valley of the Mojo area found higher concentrations of Cd (4.76-5.3 mg/kg), Co (14.93-15.13 mg/kg), Hg (6.26-7.3 mg / kg) and Zn (93.7-98.9 mg/kg) than in the current study in tomato soil samples (Hailu Reta & Leta Danno, 2020). The discrepancy in the results might be attributed to various sources of pollution other than the sampling season.

A high concentration of Cd, Hg, Pb, and Zn in the soil above the regulatory limits may indicate the existence of human activities that cause these metals to occur. Similar studies conducted by (Mahurpawar, 2015) and (Sankhla *et al.*, 2016) have revealed that the high levels of Cd, Hg, Pb, and Zn detected in the soil of the current study area may be attributed to the use of chemical and metal-based pesticides and fertilizers. These pollutants may have also been caused by atmospheric deposition as the study area was adjacent to Ethiopia's busiest main roads and highways to Kenya. Additionally, it is worth noting that these heavy metals are common pollutants in industrial and urbanized areas (Egbueri, 2020; Egbueri & Unigwe, 2020; Egbueri *et al.*, 2022).

Table 4: 4 Heavy metal Concentrations in soil samples collected from irrigated farmlands around Lake Ziway, Ethiopia (n=9).

Heavy metals	**Concentrations of heavy metals in soil Samples(mg/kg)**						***FAO/WHO References Con. in soil**
	Under tomato Cultivation			**Under onion Cultivation**			
	S1	**S2**	**S3**	**S1**	**S2**	**S3**	
As	5.68 ± 1.99^{a}	4.02 ± 0.14^{a}	1.37 ± 0.44^{b}	5.48 ± 0.14^{a}	7.63 ± 0.89^{a}	1.27 ± 0.07^{b}	14
Pb	**22.13 ± 6.02^{a}**	**14.39 ± 0.81^{b}**	**10.06 ± 0.03^{c}**	**16.52 ± 1.56^{b}**	**28.58 ± 2.89^{a}**	6.66 ± 1.29^{c}	10
Zn	**68.66 ± 10.24^{a}**	49.00 ± 4.12^{b}	15.89 ± 1.14^{b}	**56.08 ± 1.61^{b}**	**72.34 ± 6.12^{a}**	30.78 ± 0.99^{c}	50
Cd	**1.18 ± 0.48^{a}**	**0.71 ± 0.26^{a}**	**0.32 ± 0.03^{b}**	**1.01 ± 0.27^{a}**	**1.76 ± 0.01^{a}**	**0.42 ± 0.14^{b}**	0.3

Hg	**1.97±0.55^{a}**	**1.82±0.56^{a}**	**0.38±0.05^{b}**	**1.96±0.19^{a}**	**2.66±0.47^{a}**	**0.58±0.03^{b}**	0.3
Cu	7.19±1.85^{a}	7.54±0.42^{a}	2.53±0.05^{b}	9.76±0.62^{a}	7.01±1.52^{a}	3.28±0.56^{b}	20
Ni	6.62±0.19^{a}	3.69±0.75^{a}	0.81±0.07^{b}	5.68±0.22^{a}	13.17±0.85^{a}	1.55±0.62^{b}	50
Co	2.37±1.68^{a}	1.86±0.41^{b}	0.78±0.06^{c}	2.11±0.58^{b}	4.66±1.12^{a}	0.64±0.12^{c}	8
Cr	10.16±1.51^{a}	5.87±1.42^{b}	2.39±0.29^{c}	9.94±1.53^{b}	13.18±0.14^{a}	3.37±0.39^{c}	100
Total. S	13.99±3.30^{a}	9.88±1.23^{a}	3.84±0.37^{b}	12.06±0.63^{a}	16.78±1.91^{a}	5.39±0.44^{b}	

NB: Values in bold are those values above the reference limit; References concentration of Heavy Metals in unpolluted Soil (FAO / WHO, 1993; FAO/WHO, 2002)

4.3.2.2 Concentration of heavy metals in vegetable samples

Table 4:5 summarizes the concentrations of heavy metals in tomato and onion samples collected from irrigated farmland in the research area. The levels of heavy metals in the tomato samples were arranged in the following order: Pb > Zn > Cu > Ni > Cr > Co > As > Hg. Similarly, the concentration in onion samples was Pb > Zn > Cu > Cr > Co > Ni > Hg > As. Of the metals detected in tomato and onion farms, the average concentrations of As (0.6 mg /kg and 0.49 mg/kg), Pb (25.69 mg/kg and 27.25 mg / kg) and Hg (0.43 mg/kg and 0.64 mg / kg) exceeded the (FAO / WHO, 1993; FAO/WHO, 2002) MPL of 0.1, 0.3, and 0.03 mg/kg, respectively. Additionally, the average concentration of Cr (2.56 mg/kg) in the tomato sample exceeded FAO/WHO MPL (2.3 mg/kg) at site 1. Although Alemayehu Washe *et al.* (2018) reported a higher concentration of Cd in tomatoes and onions in the sample area of the Ziway flowering industry (0.475 mg/kg and 0.391 mg/kg, respectively), the detection limit of the two vegetable samples in the current study was still below. This is related to the soil pH of current studies (7.5 to 6.65) (see Table 4.4) because a lower pH reduces the solubility and availability of plant Cd absorption (Akinola & Mendes, 2008). When soil pH is low, plant cadmium absorption increases (FAO/WHO, 1995).

Lead was detected at higher concentrations in both vegetable samples, ranging from 20.6 mg/kg to 32.5 mg/kg. The mean level of Pb in tomato was 25.7 mg/kg and 27.1

mg/kg in onion (Table 4.6), both of which were higher than the FAO/WHO acceptable limit of 0.3 mg/kg. This suggests that the consumption of these veggies may pose a health risk to consumers due to Pb poisoning. The concentration of Pb in the current study was higher than in previous studies on tomato and onion in the CRV area of Ethiopia by Hailu Reta & Leta Danno (2020) Pb in tomato (3.63 mg/kg) from Mojo, Alemayehu Washe *et al.* (2018) Pb in tomato (0.08-0.51 mg/kg) and onion (1.03-1.67 mg/kg) from Ziway around the area of the floriculture industry and Buzuayehu Abebe (2017) Pb in tomato (0.23 mg/kg) and for onion (0.4-0.48 mg/kg) from Meki irrigation area. In contrast, the Pb levels in the current study are consistent with those found in a similar study in the southern Ethiopian rift valley in the Arba-Minch area (Awoke Guadie *et al.*, 2021), which ranged from 2-23 mg/kg, and in Algeria (Cherfi *et al.*, 2014), which ranged from 12.33 to 39.33 mg/kg. As the research region was adjacent to the main Ethio-Kenyan highway, this result could be attributed to the excessive use of inorganic fertilizers and pesticides (Mulat Anagaw *et al.*, 2019), wastewater irrigation, and air deposition (Eid *et al.*, 2017).

Arsenic and Hg concentrations in tomatoes and onions samples ranged from 0.45 mg/kg to 0.74 mg/kg and 0.4 mg/kg to 0.67 mg/kg, respectively (Figure 4). Average concentrations of As (0.6 mg/kg and 0.49 mg/kg) and Hg (0.43 mg/kg and 0.63 mg/kg) in tomatoes and onions are higher than the FAO / WHO recommendations of 0.1 mg/kg and 0.03 mg/kg, respectively. Accordingly, consumption of these vegetables may pose a health risk to consumers due to As and Hg poisoning. This result is lower than the previous report on CRV in Ethiopia by Hailu Reta & Leta Danno (2020) from the Koka area (1.93 and 3.43 mg/kg) for As and Hg concentrations in tomatoes, and Leta Danno & Hailu Reta (2021) from the Mojo area for As and Hg concentrations in tomatoes

(1.03 and 3.26 mg/kg), respectively. Similarly, Ashraf *et al.* (2021) from Pakistan for As and Hg in tomatoes (1.75 and 2.15 mg/kg), respectively. The difference in As and Hg tomatoes may be related to soil organic matter (SOM), which is three times higher than previous Mojo and Koka reports, so high OM concentrations remain on the soil surface (Yu *et al*., 2018). Based on the laboratory report, it has been identified that As, Hg and Pb are the prevalent heavy metal contaminants in the study area. The excessive occurrence of these heavy metals in the vegetables of the study area may be due to the excessive use of agrochemicals, wastewater irrigation, and air deposition.

Chronic-level ingestion of these toxic metals can have undesirable impacts on humans. Chronic exposure to arsenic can cause several health problems: bronchitis, skin irritation, bone marrow suppression, anemia, liver enlargement, and bladder and lung cancers (Kapaj *et al*., 2006; Shen *et al*., 2013). Similarly, Hg can cause damage to the nervous system, protoplasm poisoning, skin and eye corrosion, dermatitis, and kidney damage (Tsai *et al*., 2017; C. Zhang *et al*., 2020). Lastly, Pb can lead to anemia, brain damage, anorexia, malaise, loss of appetite, liver and gastrointestinal damage, and mental retardation in children (Boskabady *et al*., 2016; Mazumdar *et al*., 2011).

The concentrations of Zn, Cu, Ni and Co were detected within the FAO / WHO guidelines (Table 4. 6), which indicated that both vegetables in the current study were safe due to heavy metal contamination. This result is consistent with those reported in the CRV area of Ethiopia by Leta Danno & Hailu Reta (2021) for tomato from the Koka area (Zn= 18.2 mg/kg, Cu =10.9 mg/kg, Ni=1.33 mg/kg, Co=0.46 mg/kg); from the Mojo area by Hailu Reta & Leta Danno (2020) (Zn=24.5 mg/kg, Ni=1.86 mg/kg, Co=0.63 mg/kg, but Cu=16.3 mg/kg is twice higher than this study),however, lower than the report of Washe *et al*. (2018) sampled tomato and onion from the Ziway floriculture industry area (Zn= 31.2-40.5, Ni= 17.2-34.5), while Co (0.13- 1.39) and Cu (2-3.29 mg/kg). The discrepancy of the result could be related to the study setting, because the floriculture industry requires the extensive use of agrochemicals (fertilizers and pesticides) (PANNA, 2002).

Table 4: 5 Heavy metal concentrations (mg/kg) in onion and tomato samples collected from irrigated farmlands, around Lake, Ziway (n=9).

Heavy metals	Tomato			Onion			FAO/WHO MPL
	S1	S2	S3	S1	S2	S3	
As	**0.53±0.1**	**0.54±0.07**	**0.74±0.2**	**0.45±0.03**	**0.52±0.15**	**0.51±0.15**	0.1
Pb	**26.18±3.18**	**25.42±3.87**	**25.46±4.37**	**26.78±1.05**	**27.48±4.42**	**27.5±4.4**	0.3
Zn	12.95±2.32	14.58±4.73	12.98±2.69	13.2±1.64	22.56±9.81	22.99±9.23	60
Cd	ND	ND	ND	ND	ND	ND	0.2
Hg	**0.4±0.14**	**0.42±0.16**	**0.48±0.18**	**0.58±0.09**	**0.67±0.31**	**0.43±.11**	0.03
Cu	7.02±5.13	3.7±2.01	9.16±5.22	1.67±0.41	2.43±0.18	2.32±0.37	40
Ni	5.76±3.58	2.16±0.79	6.49±2.71	1.49±0.74	1.22±0.17	0.22±0.22	10
Co	1.8±0.1	1.79±0.15	2.04±0.21	1.58±0.09	1.56±0.04	1.55±0.05	10
Cr	**2.73±0.08**	2.24±0.15	1.12±1.12	2.08±0.19	2.08±0.23	2.04±026	2.3

Note: Values in bold are those above the maximum permissible limit (MPL) in the diet of humans according to the (FAO / WHO 1993;2011) standards; and ND = Not Detected

4.3.3 Comparison with previous studies

Table 4:6 compares the Hms of the irrigated vegetables found in this study with the heavy metals of the irrigated vegetables found in previous studies. Concentrations of Pb, Cr, and Co concentrations were higher than those of irrigated vegetable samples collected from Ethiopia (Koka, Mojo, and Ziway areas) (Alemayehu Washe *et al*., 2018; Hailu Reta & Leta Danno, 2020; Leta Danno & Hailu Reta, 2021) and other countries such as Bauchi, Northern Nigeria (Barau *et al*., 2018), Jhansi, India (Gupta *et al*., 2022) and Kasur, Pakistan (Ashraf *et al*., 2021). The present study did not detect Cd concentrations, but other studies have been reported in Ethiopia and other countries (Buzuayehu Abebe, 2017; Alemayehu Washe *et al*., 2018; Mulat Anagaw *et al*., 2019 Hailu Reta & Leta Danno, 2020; Leta Danno & Hailu Reta, 2021). The discrepancy in the results could be attributed to the soil nature of the irrigated farmlands, as the soil in the current study area had a slightly basic pH (7.56 to 7.65) (Table 4.4), which reduces the solubility and availability of Cd uptake by plants (Akinola *et al*., 2008). Furthermore, when soil pH is low, vegetable Cd uptake increases (FAO/WHO, 1995). Aschalew Tadesse (2016) report for onion (Nill) was consistent with the present levels of Cd. Similarly, studies in Lebanon and Jordan, Karachi City in southern Pakistan, and Ethiopia around Arba Minch City (Al-Chaarani *et al*., 2009; Tolera Seda *et al*., 2019) found Cd levels in onions and tomatoes below the FAO / WHO allowed range of 0.2 mg/kg.

Table 4: 6 Comparison of heavy metals concentration (mg/kg dw) in vegetables with previous studies.

Sample type	Point of sample collection	Levels of metals (mg/kg dry weight)									References
		As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn	
O	Vicinity of highway	0.49	ND	1.57	2.08	2.05	0.54	1.36	**27.13**	17.88	**Present study**
T		0.6	ND	**1.88**	**2.56**	6.63	0.43	3.49	25.69	12.57	
O	Waste-water irrigation	-	ND	-	0.08	-	-	-	0.23	-	(Buzuayehu Abebe, 2017)
T	Industrial area	-	0.01-0.03	-	0.11-0.32	0.16-0.39	-	-	0.4-0.48	-	(Mulat Anagaw et al., 2019)
T	Waste-water irrigation	**1.93**	**0.56**	0.63	1.49	**16.27**	**3.43**	1.86	3.63	24.5	(Hailu Reta & Leta Danno, 2020)
T	Waste-water irrigation	**1.03**	**0.5**	0.46	0.9	10.9	**3.26**	1.33	2.63	18.16	(Leta Danno & Hailu Reta, 2021)
O	Industrial area	-	0.26-0.39	0.13-0.23	1.22-3.01	2-2.1		**23.65-34.46**	1.03-1.67	31.2-40.53	(Alemayehu Washe et al., 2018)
T		-	**0.44-0.48**	0.28-1.39	1.22-1.36	2.6-3.29		**17.15-21.65**	0.08-0.51	**33.3-34.78**	
O	Fresh water irrigation	0.02	0.11	-	0.02	-	-	-	0.79	4.70	Barau *et al*. 2018
T		0.08	0.27	-	0.02	-	-	-	0.79	4.19	
O	Vicinity of highway	-	0.13	0.32	-	6.25	-	0.54	0.66	23.94	Gupta *et al*. 2022
T		-	0.14	0.22	-	4.77	-	0.89	0.46	16.77	
T	Industrial area	1.75	0.44	0.66	1.44	12.45	2.15	2.35	2.84	22.67	Ashraf *et al*. 2021
MPL		0.1	0.2	50	1.3	10.0-40	0.01	10	0.1-0.3	50	FAO/WHO 2011

ND = Not Detected; O=Onion; T=Tomat

4.3.4 Bio-concentration Factor (BCF) analysis

BCF represents the path of heavy metal deposits from the soil to the edibles of plants (Sharma *et al*., 2018). The calculated BCF values of heavy metals in tomatoes are observed in Fig 4.1 with the following sequence: Pb (1.65), Ni (1.30), Cu (1.15), Co (1.12), Cr (0.33), Hg (0.31), Zn (0.30), and As (0.16). Also, Pb (0.88), Co (0.63), Hg (0.37), Zn (0.37), Cu (0.32), Cr (0.23), Ni (0.14) and As (0.01) are the onion ratios. The calculated BCF values for tomato Pb, Ni, Cu, and Co, as well as Pb for onion were above 1, indicating that the absorption rate of heavy metals in vegetables was higher than in soil. BCF values for other heavy metals are ranged from 0.1 to 0.63, and vegetables are moderately accumulated. This result shows that these four heavy metals require special attention and could pose a risk to consumers.

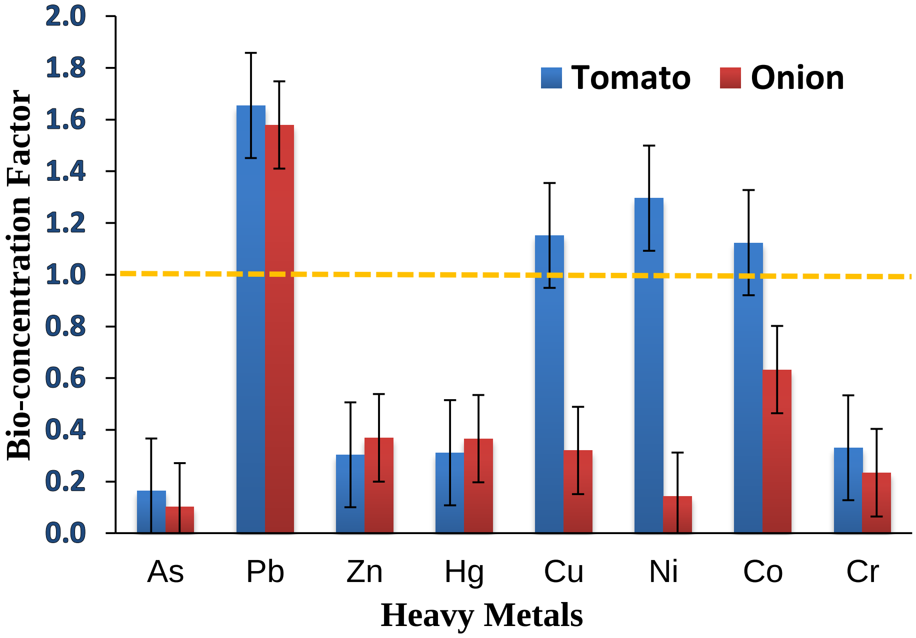

Figure 4: 1 BCF for tomato and onion samples.

4.3.5 Potential Human Health Risk Assessment

4.3.5.1 Estimated Daily Intake (EDI) Assessment

EDI is calculated on the basis of the average concentration of each metal in vegetables and the corresponding consumption rate. The formula used to calculate EDI is by Eq. (2), and the results are shown in Table 4:7. These values were compared with reference values to assess their impact on human health. According to the New York State Department of Health (NYSDOH), a ratio of EDI/Df less than or equal to Df (oral reference dose) indicates minimal health risks, and a ratio of 1 to 5 times higher than Df is associated with low health risks. The ratio between 5 and 10 times higher than Df is a moderate risk to health and 10 times higher than Df is considered a high risk to health (McGrath et al., 2001). Analysis showed that both adults and children have high values of Pb and Co EDI. Regarding the ratio (EDI/Df), we conclude that vegetable metals such as As and Hg are 1 to 5 times higher than Df in adults and children, so the health risks of using these vegetables grown in the region are low, and Co and Cr are also low in adults and children, respectively. Metals in Zn, Cu, and Ni in vegetables are < Df, so both consumers should take the lowest health risk. The Pb concentration is 5 to 10 times higher and poses a moderate health risk to adults using vegetables, but the proportion to children is >10 times higher than Df, so children using these vegetables grown in this study area are at high risk of health. This high level of Pb in children is consistent with the report by Health Canada (2011) that Pb exposure in children is generally high and decreases with age. The results of the current study are consistent with those of (Ashraf *et al.* (2021) from Pakistan who investigated the presence of As, Co, Hg, and Ni in the consumption of adult and child tomatoes. In the current study, the total daily intake of certain metals estimated by adults decreased in the following order: Pb > Zn > Ni > Cu > Cr > Co > Hg > As. Similarly, in children, the decreasing sequence is Pb > Zn > Cu > Ni > Cr > Co > As > Hg. High concentrations of Pb and Co in daily intake cause accumulation of these heavy metals, causing damage to various organs and functions, including oxidative stress, bone damage, neurological disorders, immune system damage, and cancer (Boskabady *et al*., 2016; Leyssens *et al*., 2017).

Table 4: 7. The EDI of Hms in mg/day/kg body weight from consumption of contaminated tomato and onion.

Heavy metals	EDI Values (mg/day/kg body weight)				TEDI Tomato and Onion	
	Tomato		Onion			
	Adult	Children	Adult	Children	Adult	Children
As	2.04E-04	5.44E-04	1.80E-04	4.81E-04	3.84E-04	6.61E-04
Pb	8.73E-03	2.33E-02	8.99E-03	2.40E-02	1.77E-02	4.73E-02
Zn	4.20E-03	1.12E-02	6.10E-03	1.63E-02	1.03E-02	2.75E-02
Hg	1.46E-04	3.90E-04	1.84E-04	4.90E-04	3.30E-04	8.80E-04
Cu	2.25E-03	6.01E-03	1.04E-03	2.77E-03	3.29E-03	8.78E-03
Ni	4.45E-03	2.97E-03	2.30E-03	1.53E-03	6.75E-03	4.50E-03
Co	6.39E-04	1.70E-03	5.68E-04	1.51E-03	1.21E-03	3.21E-03
Cr	8.70E-04	2.32E-03	7.34E-04	1.96E-03	1.61E-03	4.26E-03

Total Estimated Daily Intake (TEDI)

4.3.5.2 Non carcinogenic health risk (NCHR) assessment

The possible NCHRs associated with consuming vegetables that contain heavy metals were assessed using two indices, THQ and HI. The results of THQ and HI for adults and children, calculated using equations (3) and (4), are presented in Table 4:8. The THQ index evaluates the health risks of individual heavy metals, whereas the HI index estimates the combined health risks of multiple heavy metals. These indices are commonly used by the United States Environmental Protection Agency (USEPA) to evaluate the non-carcinogenic health hazards of consuming vegetables.

Scientific reports have revealed that if the HI (hazard index) value is greater than 1, the non-carcinogenic health risk associated with consuming a specific element is above the safe limit. Conversely, if the HI value is less than 1, the health risk is within the safe limit (Ukah *et al*., 2019; USEPA, 2019; Egbueri, 2020). The THQ values for Zn, Cu, Ni, and Cr were found to be less than one in individual vegetables such as tomatoes or onions, both for adults and children. Similarly, the value for the sum of individual metals (GTHQ) for Zn, Cu, and Ni was also less than one for adults and children who ate both vegetables (Table 4:9). This suggests that there is no non-carcinogenic risk associated with the consumption of these vegetables for adults and children. Studies conducted in Ethiopia by Hailu Reta & Leta Danno (2020) and Leta Danno & Hailu Reta (2021) found that the metals zinc (Zn), copper (Cu), nickel (Ni), and chromium (Cr) in adults posed a minimal or no non-cancer risk (THQ value <1). Similarly, a study from Pakistan in 2021 by Ashraf *et al.* (2021) reported comparable findings for individuals, including children, who consume only tomatoes. Additionally, a study from India in 2022 by Gupta *et al.* (2022) reported similar results for individuals consuming both tomatoes and onions.

Table 4: 8 Non-carcinogenic risk of heavy metals from ingestion of contaminated tomatoes and onions collected from Irrigated farmlands around Lake Ziway.

Risk indicator	Hm (mg/Kg)	Tomato		Onion		GTHQ	
		Adult	Children	Adult	Children	Adult	Children
THQ	As	0.68	**1.81**	0.6	**1.6**	**1.28**	**3.41**
	Pb	**2.5**	**6.65**	**2.57**	**6.85**	**5.07**	**13.5**
	Zn	0.01	0.04	0.02	0.05	0.03	0.09
	Hg	0.49	**1.3**	0.61	**1.63**	**1.1**	**2.93**
	Cu	0.06	0.15	0.03	0.07	0.09	0.22
	Ni	0.22	0.15	0.11	0.08	0.33	0.23
	Co	**2.13**	**5.68**	**1.89**	**5.05**	**4.02**	**10.73**
	Cr	0.29	0.77	0.24	0.65	0.53	**1.42**
HI	$\sum$= THQ_n	**6.**38	**16.56**	**6.08**	**15.99**	12.45	32.53

Note: Values in bold are indicates potential non-carcinogenic risk; GTHQ is the sum of individual metals, Target Hazard Quotient (THQ) for every vegetable, HI is hazard index

The study found that adults and children who consumed tomatoes or onions had THQ values for Pb and Co greater than one. Similarly, for those who consumed both vegetables, the GTHQ values for Pb, Co, and As were also greater than one, indicating potential non-carcinogenic risks associated with consuming these vegetables. These findings differ from previous studies conducted in Ethiopia (Hailu Reta & Leta Danno, 2020; Leta Danno & Hailu Reta, 2021) and India Gupta *et al.* (2022), which reported no non-carcinogenic risk for vegetable consumption in both age groups. The high use of metal-containing agrochemicals (pesticides and fertilizers) in the study area, as well as the location of the study area near the main Ethio-Kenya highway, could explain this discrepancy, as suggested by Dagne Bekele *et al.* (2019).

The THQ values for As and Hg were found to be greater than one only for children who ate individual vegetables (either tomatoes or onions). Similarly, the value of GTHQ for Cr is also greater than that for children (Table 4:9). This suggests that children are likely to be at risk of non-carcinogenic risk due to exposure to As and Hg from consuming one of the vegetables and due to exposure to Cr for consuming both of the vegetables. Regarding As and Hg, the findings of the present study are consistent with those of Pakistan (Ashraf *et al.*, 2021) for the consumption of tomatoes. However, it is in total disagreement with that (no carcinogenic risk) reported from Ethiopia by Hailu Reta & Leta Danno (2020) and Leta Danno & Hailu Reta (2021). The observed discrepancy in the result may be related to the difference in the setting of the study area and the source of heavy metals.

In general, the present THQ values for adults for Co, Cr, Cu, Ni, Pb, and Zn are notably lower than the recent findings by Mulate Zerihun *et al.* (2022) in the central rift area of Ethiopia at the Melkassa Agricultural Research Center. Zerihun *et al*. reported values of (128, 326.8), (5089.2, 10990.8), (101.8, 242.8), (179.4, 171.6), (1256.7, 1760), and (530.2, 146.7) for Co, Cr, Cu, Ni, Pb, and Zn, respectively, for tomato and onion. This disparity in the results may be attributed to variations in the sources of heavy metals. The authors noted that the study area is home to numerous industries, including medium-sized leather and textile factories, plastic factories, edible oil factories, and other related industries (Mulate Zerihun *et al*., 2022). On the other hand, the THQ and HI values of both vegetables (Table 4:9) are higher (more than double in most cases) for children than for adults, indicating that children are more likely to suffer from non-carcinogenic risks than adults. Furthermore, the

THQ mean values show that Pb poses the highest non-carcinogenic risk for adults and children in the study area.

The present study showed that the HI values for vegetables grown in the study area exceeded the safe limit of 1. The study also revealed that adults and children who consumed tomatoes and onions had HI values of 6.4 and 6.1 and 16.6 and 16, respectively. This indicates that residents of Ziway irrigated areas are at risk of health problems. Children are three times more likely to face potential health risks than adults. However, exceeding a risk score of 1 does not necessarily mean that adverse health effects will occur. It only suggests the likelihood of potential health risks. Regarding the relative contributions of each metal (Pb, Co, As, Hg, Cr, Ni, Cu, and Zn) to HI, the study found that they contributed as follows: Pb (42.3%), Co (31.1%), As (10.1%), Hg (9.9%), Cr (3.9%), Ni (1.8%), Cu (0.5%), and Zn (0.3%). Therefore, the main elements that contributed to the potential non-carcinogenic health risks of vegetable consumption for residents in the study area were Pb and Co.

4.3.5.3 Target Cancer Risk (TCR) Assessment

The target cancer risk (TCR) associated with consuming vegetables contaminated with heavy metals was estimated as the incremental threat of an individual developing cancer over a lifetime, resulting from exposure to a potential carcinogen (Ukah *et al.*, 2019). The TCR of the carcinogenic metals (As, Cr, Ni, and Pb) was calculated using the equation (5). According to Bawa (2023), the New York State Department of Health (NYSDOH) classified TCR as follows: a value below 10^{-6} indicates a minimum risk of carcinogenesis; a value between 10^{-5} and 10^{-3} indicates a moderate risk of cancer; and a value between 10^{-3} and 10^{-1} indicates a high risk of cancer.

Figure 4:2 summarizes the carcinogenic health risk of heavy metals using TCR for adults and children living in irrigated areas around Lake Ziway. The TCR values of the metals studied in the study area ranged from 10^{-5} to 10^{-2}, indicating a moderate to high cancer risk for residents. In children and adults, a TCR of Ni values from 10^{-3} to 10^{-1} was recorded, and a similar values of Cr and As was determined only in children who consumed tomatoes and onions produced in the study area (Figure 4:2). According to the NYSDOH risk classification, these results indicate that exposure to Ni increases the risk of cancer in both age groups, while exposure to Cr and As increases the risk of cancer in children. Similar findings (TCR=10^{-3} to 10^{-2}) have been reported in Pakistan on the presence of metals (Ni and As) in adults and children that eat only tomatoes (Ashraf *et al.*, 2021). In India Gupta *et al.* (2022), similar results were reported for those who consumed Ni contaminated tomatoes and onions. However, this study showed higher metal contamination levels than similar studies in Ethiopia (Hailu Reta & Leta Danno, 2020; Leta Danno & Hailu Reta, 2021), with moderate risk for adults. The difference in results may be related to the source of heavy metals.

The TCR for Pb ranges from 10^{-5} to 10^{-3} for both age groups, and the same values for Cr and As were recorded only for adults eating vegetables (Figure4:2). These results clearly indicate that both age groups have a moderate risk of cancer due to exposure to Pb and that only children may have a moderate risk of cancer due to the consumption of vegetables in the study area contaminated with Cr and As. Although age groups have not been identified or explained, the results of the present study (moderate cancer risk) are consistent with the report for As, Cr and Ni by Hailu Reta & Leta Danno (2020) from the Ethiopian Mojo and Leta Danno & Hailu Reta (2021) from the Ethiopian Koka reagion of the rift valley for tomatoes for people consuming tomatoes contaminated with these metals from the areas.

The disparity in the result might be related to the source of heavy metals. Furthermore, very recently, Lemessa *et al.*(2022) for tomato collected from the Bole Lemi industry area in Ethiopia, and Mao *et al.*(2023) from China also reported moderate cancer risk due to consumption of Cr-contaminated tomato for both adults and children. The results of this study indicate that children in the study area are more susceptible to cancer risk than adults. Among the carcinogens identified in the area, the contribution rates of the four heavy metals to TCR were Ni with the highest risk (84.6 to 90.3%), followed by Cr (5.2-7.9%), As (3.6-5.8%) and Pb (0.9-1.6%) for adults. Similarly, for children, the contribution rates of the four heavy metals to TCR were Ni (57.8-69.6%) > Cr (16-21.8%) > As (11.3-16%) > Pb (2.7-4.5%). In general, regular tests of vegetables irrigated in the study area are recommended to assess the potential health risks of toxic substances to consumers.

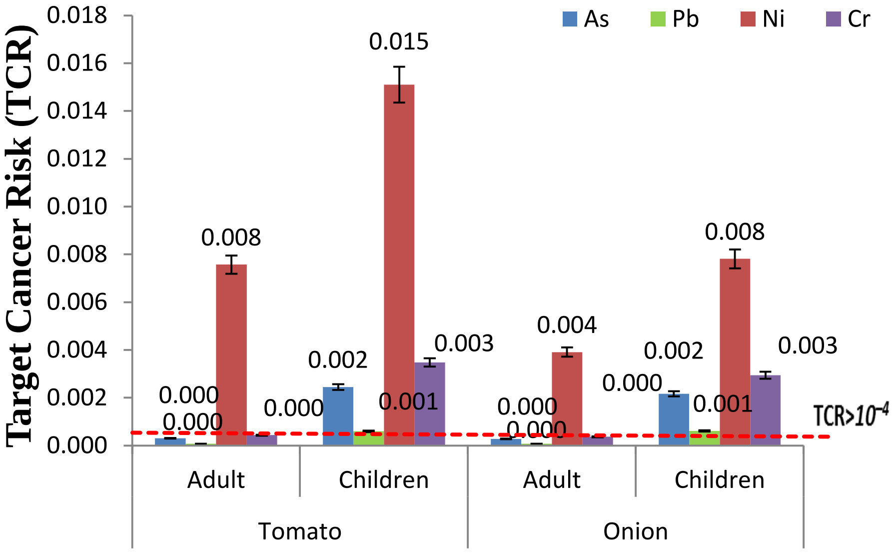

Figure 4: 2 Estimated target cancer risk of chosen heavy metals for vegetable diet.

4.3.6 Heavy metals source apportionment

Correlation as part of the multivariate analysis is employed to study the source and route of heavy metals in vegetables. The study used Pearson's correlation coefficient to determine the relationship between various heavy metals. The results are presented in Table 4.9. The study found that some pairs of heavy metals have a very significant positive correlation in vegetables, such as Cu-Co (0.82), Cu-Cr (0.78) and As-Co (0.75), and are $p<0.001$. Co-Cr ($r = 0.68$), As-Cu ($r = 0.64$), Pb-Hg ($r = 0.62$) and As-Cr (0.56) also showed moderate positive correlations at $p<0.05$. There is a clear positive correlation between these metals, indicating that these metals come from the same source.

The above-mentioned arguments are supported by the principal component analysis (PCA) with varimax rotation method to assume the source of these metals in vegetables. The results show that PCA reduces the initial dimensions of the data set to three components, resulting in 81.26 % of data variations. The first principal component (PC-1) explained 42.1% of the total variation and load of Co (0.92), Cu (0.91), As (0.85) and Cr (0.84), indicating that the highest load of these heavy metals would come from the same source. As suggested by Bayissa and Gebeyehu (2021), these heavy metals can contribute to the composition due to the accumulation of irrigated water (Cd, As, Cr, Cu) in the soil of the current study area, as well as the accumulation of heavy metals (Cd, As, Cr) in the catchment area. The contribution of PC-2 was 23.83 % to the overall difference with the high positive loadings of Pb (0.91) and Hg (0.87) (Table 4:10). These two heavy metals may have the same source. According to a study by Huang *et al.* in 2015, heavy metals found in vegetables can be attributed to agricultural practices such as the use of pesticides and fertilizers. Additionally, heavy metal pollution from Pb and Hg can be caused by roads, road dust, traffic activity, and major highways in the area of study. In Table 4.11, it is shown that PC-3 contributes 15.32% of the overall variation in Zn positive loading (0.89). The origin of these heavy metals may be mixed (both natural and anthropogenic) in the study area, as indicated in Figure 4.3. While the first two components of heavy metals (PC1 and PC2) may result from human activities, the third component (PC3) may have a mixed source.

Table 4: 9 Correlation matrixe between heavy metals in vegetables

	As	Pb	Zn	Hg	Cu	Ni	Co	Cr
As	1							
Pb	0.337	1						
Zn	0.188	-0.017	1					
Hg	0.107	**.618****	-0.086	1				
Cu	**.638****	-0.244	-0.046	-0.269	1			
Ni	0.155	-0.169	-0.213	-0.28	.494*	1		
Co	**.751****	-0.159	0.079	-0.185	**.824****	0.367	1	
Cr	**.559***	0.226	-0.129	0.077	**.783****	0.396	**.679****	1

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

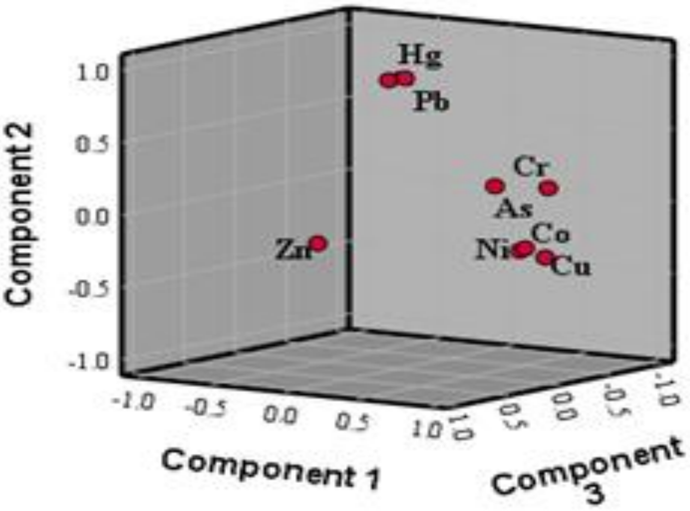

Figure 4: 3The component plot in rotated space for heavy metals

Table 4: 10 Rotated component matrix for selected metals in vegetables

Heavy metals	PC1	PC2	PC3
As	**0.845**	0.274	0.257
Pb	0.069	**0.908**	0.028
Zn	0.084	-0.106	**0.903**
Hg	-0.083	**0.871**	-0.031
Cu	**0.906**	-0.272	-0.146
Ni	0.453	-0.329	-0.542
Co	**0.915**	-0.177	0.061
Cr	**0.844**	0.185	-0.264
Eigenvalue	3.368	1.907	1.226
Variability (%)	42.102	23.834	15.321
Cumulative (%)	42.102	65.936	81.257

Note: PC = principal component

4.4 CONCLUSION

The findings of this study, besides estimating the level of heavy metals, have pointed out the human health risks emanating from consuming contaminated vegetables neglected in other studies conducted in the central Ethiopian Rift Valley Region. As to the severity of contamination, As, Pb, and Hg in tomato and onion samples obtained from farms irrigated around Lake Ziway exceed the recommended limits of FAO/WHO. Furthermore, soil samples collected beneath the irrigated vegetables had an excess of Cd, Hg, Pb, and Zn, which exceeded the allowed limits. The BCF values of Pb, Ni, Cu and Co in tomatoes, as well as Pb in onions, were greater than 1, indicating a higher uptake of heavy metals in vegetables compared to soil. The daily intake of Pb for children due to tomato and onion consumption was found to be ten times higher than the oral reference dose of heavy metals, indicating high health risks for children who consume these vegetables from the study area. The THQ for Cu, Cr, Ni, and Zn in individual vegetables was found to be less than one. However, for Pb and Co, it could pose a non-carcinogenic risk to both adults and children because the THQ values were >1. The cumulative non-carcinogenic effects of multiple metals estimated by the health index (HI) for tomato (HI= 6.38, 16.56) and onion (HI= 6.08, 15.99) for adults and children, respectively was >1, indicating a potential non-carcinogenic risk to the public. The TCR was measured for Ni values ranging from 10^{-3} to 10^{-1} for both children and adults. Similar values were also determined for As and Cr in children only who consume tomatoes and onions produced in the study area. This indicates that both age groups are at higher risk of developing cancer due to exposure to Ni, and only children are likely to have higher cancer risk due to exposure to As and Cr. The PCA analysis showed that human activities have had a significant impact on the current concentration of heavy metals in research areas. Therefore, it is strongly suggested to regularly monitor soil and vegetable crops in the research region to avoid further accumulations that may pose substantial non-carcinogenic and carcinogenic health risks to consumers of these vegetables in the research region and beyond.

4.5 References

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CHAPTER FIVE

5. LEVEL OF PESTICIDE RESIDUES IN SOIL AND ECOLOGICAL RISK ON SOIL BIOTA IN IRRIGATED VEGETABLE FARMS NEAR LAKE ZIWAY, ETHIOPIA

ABSTRACT: Pesticides are widely used in agriculture, but they can contaminate the soil, which can hurt soil health and biodiversity. However, there is a lack of research on the toxicity and exposure risks of pesticides on soil biota in Ethiopia, where pesticides are heavily used. To address this issue, a study was conducted during the rainy season in August 2021, analyzing the presence of 35 pesticides in three fields of an irrigated farm near Lake Ziway, Ethiopia. The study aimed to assess the ecological risks posed by pesticides to soil biotas, such as earthworms, springtails, and nitrogen mineralization microbes. The evaluation was based on toxicity exposure ratios (TERs) and risk quotient (RQ) methodologies to determine general and worst-case scenarios, respectively. Of the detected pesticides, α-BHC, heptachlor, fenthion, parathion, and propoxur were detected at a rate of 100%. The highest concentration of 119.9 μg/kg was found for p,p'-DDE. Fenthion and Chlorpyrifos methyl posed an acute exposure risk to *F. candida* and N-fixing organisms, respectively, with TERs exceeding the trigger value. Non-target soil species (earthworms, springtails, and N-fixing organisms) are at high ecological risk (RQs > 1) due to Alpha-endosulfan, which contributes to more than 90% of the risk than the other pesticides. The ecological risk assessment (ERA) reported that the overall pesticide mixture in soil poses a high ecological risk ∑RQ=5.3 in both scenarios. Conventional farming practices in the study area put soil organisms at risk. Therefore, to mitigate this risk, it is recommended to replace hazardous pesticides with low-risk alternatives.

5.1. INTRODUCTION

Pesticides are vital in contemporary agriculture, safeguarding crops, boosting yields, and enhancing produce quality. Nevertheless, their widespread application worldwide has resulted in the current pesticides and their by-products being one of the primary sources of potentially harmful substances intentionally introduced into various environmental compartments (Vašíčková *et al.*, 2019). As a result, this presents a noteworthy hazard to both human populations and the environment**.**

Pesticide environmental risk assessments are common in developed countries such as North America, Europe, Japan, and Australia (Bhandari *et al.*, 2021; Daam, *et al.*, 2019). However, in many developing countries, clear requirements and adequate implementation are lacking, which can lead to increased pesticide use and potential environmental risks (Qin *et al.*, 2021). Ethiopia is similar to other developing countries in this regard (Berhan Mellese *et al.*, 2023). For example, Ethiopia's use of pesticides has increased to improve crop production and meet the food demand of the population. According to the FAO report of 2023, agricultural use of pesticides increased by 4% in 2021, 11% in the past decade, and doubled since 1990, totaling 3.5 million tons (FAO, 2023). Ethiopia uses 0.22kg of pesticides per hectare of agricultural land, accounting for half of Africa's total pesticide application per arable area per year (FAO/WHO, 2021). Furthermore, the extensive use of pesticides in Ethiopia, coupled with the unsafe handling practices of farmers (Belay Tizazu *et al.*, 2017; Lemessa Bente *et al.*, 2021), endangers biodiversity, especially aquatic and soil habitats.

In Ethiopia, there is a lack of model-based risk assessments for the safety of humans, and aquatic and terrestrial environments. There are only a few studies available, such as the one conducted by (Lemessa Bente *et al.*, 2021), which examined the levels of 19 pesticides (insecticides and fungicides) and nutrients in Lake Ziway water and sediment samples to estimate the ecological risk of pesticides in this lake. However, the sources of pesticides (vegetables and soil beneath) were not investigated. Another study conducted by Kumelachew Mulu *et al.* (2020) focused on just seven pesticides found in tomatoes, onions, and surface water; but they did not evaluate the level of pesticides in the soils beneath the vegetables. It is important to examine irrigated soil as pesticides can remain in the soil for years or decades after application, providing information on pesticide distribution and accumulation in the different compartments of irrigated farmlands. Moreover, more than half (236/436) of the pesticides registered in Ethiopia are classified as highly hazardous (Elsai Mati *et al*., 2024).

Furthermore, Berhan Mellese *et al*. (2023) conducted a study that revealed a significant percentage of pesticides evaluated posed high acute and chronic risks to fish and aquatic invertebrates through model-based analysis. However, the study relied on predicted concentrations rather than measured concentrations, which Bhandari *et al*. (2021) argued could lead to less accurate risk estimates. Despite the importance of improving our understanding of pesticide use, there remains a lack of comprehensive data on residue levels in irrigation-based vegetable cultivation in the Ethiopian Rift Valley.

Ranking pesticides based on various quantitative criteria is crucial for long-term pollution control and risk mitigation (Mu *et al*., 2023; Sang *et al*., 2022). Thus, the present study endeavors to accomplish two goals: (1) to explore the presence of pesticides in the soil of an irrigated farm near Lake Ziway; and (2) to evaluate the ecological hazards that single pesticides and pesticide mixtures present to soil biota. The results of the study can guide future risk reduction actions and contribute to a more sustainable regional pesticide management plan.

5.2. MATERIALS AND METHODS

5.2.1 Study Design and Period

A laboratory-based cross-sectional study technique was used to detect the type and concentration of targeted pesticide residues in soil under vegetable rotation of tomato and onion from three irrigated farmlands near Lake Ziway. The samples were collected in late August 2021, during the rainy season. It is important to note that pesticide contamination is considerably higher during the wet season as compared to the dry season (Nguyen *et al.*, 2022). According to the authors, this is due to pesticides from multiple sources being washed into existing ones, resulting in higher contamination levels.

5.2.2 Chemicals and reagents used

All of the chemicals, reagents, and solvents utilized for both sample extraction and cleaning were listed in Chapter 3, section 3.2.3.

5.2.3 Sampling site selection and collection

5.2.3.1 Sampling site selection and Sample collection

The sample site selection was done following a similar procedure in Chapter 3, section 3.2.2. Fifteen composite surface soil samples at 0-20 cm depth using a steel steel auger in a zigzag pattern following the procedure described by Mondal (2020) were collected under vegetable (tomato onion rotation) growing irrigated farmlands. In each sampling field, soil samples were taken from 6 to 7 points as sub-samples in the field and then mixed into one composite sample. Each sample was packed in ziplock polyethylene bags separately, labeled, and transported to the laboratory (Bless Agri Food Laboratory Services, Legetafo Legedadi, Addis Ababa, Ethiopia) in an insulated icebox, stored in the dark at -20°C deep freeze refrigerator until ready for preparation and analysis.

5.2.3.2 Sample preparation, Extraction and clean-up

Soil samples were air dried, cleaned by removing visible traces of leaves and other waste materials, homogenized (ground / crushed, and sieved through a mesh size of 2mm before being stored in clean and airtight polyethylene bags until further analysis. The QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method was used to extract pesticides in soil samples as indicated in the AOAC Official Method 2007.01 with slight modifications (AOAC, 2007). Ten grams of the sieved soil sample was weighed into a cleaned test tube and mixed with 15g anhydrous magnesium sulfate; 20 ml of acetonitrile was added. The mixture was shaken for 20 minutes and allowed to stand for 2 hours. After centrifuging the mixture at 3000 rpm for 10 minutes, the clear supernatant was transferred into a 50 ml test tube for clean-up (AOAC, 2007).

An aliquot of the organic phase (8 mL) was cleaned-up by a dispersive solid-phase extraction (d-SPE) tube containing 150 mg of anhydrous $MgSO_4$ for the removal of residual water, 50 mg primary secondary amine (PSA) for adsorbing organic acids, pigments, and other polar impurities from the sample and shaked for 30 sec before being centrifuged for 1 minute at 2000 rpm. Following clean-up, extracts were acidified by adding a small amount (< 1 ml) of formic acid to improve the storage stability of certain base-sensitive pesticides. A fraction of 2 ml of the extracted aliquot was evaporated in the TurboVap at 50 ° C using N_2 gas under a 10 psi pressure. Toluene was used to reconstitute the residues for the GC-MS analysis. The resulting extract can be immediately used for GC-based determinative analysis. An internal standard was used for quantification, and it was added directly before being injected into the GC-MS apparatus. Using GC-MS, the method validated 35 pesticides. Pesticide residues were detected and confirmed in the samples using GC-MS.

5.2.3.3 Pesticides Quality Control and Instrumental Analysis Method

A pesticide standard solution was prepared and validated using method validation, and the limits of detection (LOD) and quantification (LOQ) were determined through the same procedure outlined in Chapter 3, Section 3.2.5.

5.2.4 Ecological risk assessment

5.2.4.1 Risk assessment

The evaluation includes environmental exposure, risk assessments, and risk characteristics. Two methods were used to evaluate environmental risk: toxicity exposure ratios (TER) for each species as specified in EC (2002) and risk quotients (RQ) for each sampled location. The risk of the residue combination found in these areas was assessed using the concentration additive (CA) technique, which combined all of the risks of the mixture's components.

To evaluate toxicity, ecotoxicological data was collected from various sources such as the pesticide properties database (PPDB) (*https://sitem.herts.ac.uk/aeru/ppdb/*), the ECOTOX knowledge base (*https://cfpub.epa.gov/ecotox/search.cfm*) and basic literature search on the Web of Science Core Collection and Scopus databases. The search terms used were: (i) pesticide, soil, and “toxic”, (ii) Pesticide, soil, and organism.

5.2.4.2 Toxicity exposure ratio (TER)

TER is a widely used measure for assessing ecological risk (EC, 2002). It is calculated using specific pesticide toxicity data and measured pesticide concentrations (MCs) for certain soil species (according to equation 5.1). By considering the average and maximum values of observed concentrations, TERs can indicate the potential acute and chronic exposure risks associated with particular pesticides. This method can generate species-specific results based on toxicity data and measured pesticide concentrations.

$$\boldsymbol{TER}_{speces}=\frac{\boldsymbol{NOEC_{species}\ or\ LC50_{species}}}{\boldsymbol{MC_{min}}} \qquad \textbf{(5.1)}$$

Where $NOEC_{species}$ and $LC50_{species}$ represent the no observed effect concentration (mg/kg) and 50% lethal concentration (mg/kg) for certain pesticides and soil species. MC_{mean} and MC_{max} represent the mean and maximum values of measured pesticide concentrations, respectively. Species-specific NOEC and LC50 were derived from the Pesticide Properties Database database (PPDB, 2024) and presented in Table 3.

General and worst scenarios (Mu et al., 2023) are generated by assuming that the MC input is at an average and maximum concentration (Bhandari et al., 2021). In this study, three species as indicators of pesticide exposure risk were selected: earthworms (*Eisenia fetida*), springtails (*Folsomia candida*), and nitrogen-fixing organisms, have been selected as indicators of pesticide exposure risk (OECD, 2000). EC (2002) defined 10 and 5 cutoff values (trigger point) for acute and chronic exposure risk, respectively. If the calculated TER exceeds the trigger value, the risk of exposure to a specific species may be considered negligible. TER values of ≥10 or ≥5, which are acceptable trigger point values for acute and chronic exposure, respectively, indicated an acceptable risk for the organisms (Bhandari *et al*., 2021).

The risk quotient for pesticides i (RQi) is a risk indice for a single pesticide that was computed using equation (5.2).

$$RQ_i = \frac{MC_{soil}}{PNEC_{mss}} \qquad (5.2)$$

Where MC_s is the measured pesticide content in the soil and $PNEC_{mss}$ is the predicted no-effect concentration for the most sensitive species. $PNEC_{mss}$ is determined as the ratio of the most sensitive species' endpoints (LC50, EC50, and NOEC) to the assessment factor (AF). The AF can be set to 10, 50, 100, or 1000, depending on the available toxicity data (Mu et al., 2023; Vašíčková et al., 2019). In summary, (1) the AF is defined as 1000 if at least one LC_{50} is accessible at a single ecological level; (2) the AF is defined as 100 if long-term assays are available; and (3) an AF of 50 or 10 is given when two or more NOECs are available. Toxicity data, AF, and calculated $PNEC_{mss}$ are obtained from the PPDB.

The risk quotient was classified into four risk levels: negligible risk ($RQ < 0.01$), lower risk ($0.01 \leq RQ < 0.1$), moderate risk ($0.1 \leq RQ < 1$), and high risk ($RQ \geq 1$) (Bhandari *et al.*, 2021; Vašíčková *et al.*, 2019).

5.2.4.3 Ecological risks due to pesticide mixtures

The ecological risks of pesticide mixtures on soil biota were analyzed using the risk quotient (RQ_{mix}) approach, which quantifies mixture risk quotients through concentration addition using equations (5.3).

$$\sum \boldsymbol{RQ}_{\boldsymbol{mix}} = \sum_{i=1}^{n} \boldsymbol{RQ}_{\boldsymbol{i}} = \sum_{i=1}^{n} \frac{MC_i}{PNEC_i} \qquad \textbf{(5. 3)}$$

Where, the $\sum RQ_{mix}$ represents the entire ecological risk of the mixture for a specific location. The risk ratios were classified into four levels: negligible risk ($\sum RQ_{mix} < 0.01$), moderate risk ($0.01 \leq \sum RQ_{mix} < 0.1$), medium risk ($0.1 \leq \sum RQ_{mix} < 1$), and high risk ($\sum RQ_{mix} > 1$) (Mu et al., 2023; Vašíčková *et al.*, 2019).

To calculate the risk contribution of a component i to the mixture risk, divide the RQi of the pesticide at the monitored locality by the total risk quotient ($\sum RQmix$) at the site (Equation (5.4)).

$$\textbf{Contribution}\ \% = \left(\frac{\mathbf{RQ_i}}{\sum \mathbf{RQ_{mix}}}\right) \qquad \textbf{(5.4)}$$

Where, RQi = Risk quotient of a pesticide i; RQmix = Risk quotient of pesticide mixtures

5.2.5 Data analysis

Data were analyzed using SPSS software version 26.0. Descriptive analysis was performed for pesticide residues in the soil. A one-way analysis of variance (ANOVA) was employed to assess whether there is a significant difference ($p < 0.05$) in the concentrations of pesticide residues in soil samples from various sampling sites. Subsequently, the average concentration of pesticide residues in the samples was compared to the maximum permissible limits (MPL) set by FAO/WHO using criteria referenced or a sample t-test. All statistical tests were carried out with a confidence level of $p < 0.05$.

5.3 Results and Discussion

5.3.1 Concentration of pesticide residues in soil

Table 5.1 displays the occurrence and concentration of pesticide residues in the soil of selected farms. Out of all the soil samples examined, 47% of them had multiple types of pesticide residues. On average, each sample had 7 different types of pesticides detected in it. The five most frequently detected pesticide residues in the soil were α-BHC, heptachlor, fenthion, parathion, and propoxur, all of which had a detection rate of 100% apendex (Table 5).

Of the targeted 35 pesticides, 24 (68.6%) were detected in the soil samples. Among the detected pesticide residues, 6 (25%) pesticides were found to be within the maximum permissible limits (MPLs), while five pesticide residues (20.8%) exceeded the MPL. The remaining 13(37.1%) pesticide residues had no MPLs. The study found that organophosphate (Ops) (41.7%) was the most common pesticide found in the soil samples, followed by organochlorine (OCs) (37.5%), carbamate (C) (8.3%), and Os (4.2%) (Fig 5.1 a). This suggests that organophosphates were the most frequently used insecticide in the region. These findings are consistent with earlier studies conducted in the area by (Elsai

Mati et al. (2024), Shiferaw Ayele et al. (2022), Lemessa Bente et al. (2021), and (Mekuria Teshome et al. (2022). The authors state that pesticides, particularly OPs and OCs, are widely used in both small- and large-scale agricultural activities and pose a significant threat to the ecological balance of nearby bodies of water, including Lake Ziway. Similarly, Leonel et al. (2021) showed that half of all pesticides used globally are OPs.

Based on classifications from the World Health Organization, the majority of detected pesticides (54.2%) were moderately hazardous (Class II), followed by slightly hazardous (Class III) pesticides at 20.8%. However, highly hazardous (Class Ia and Ib) and obsolete pesticides were also detected, each accounting for 8.3%, while those unlikely to present an acute hazard (Class U) accounted for 4.3%.

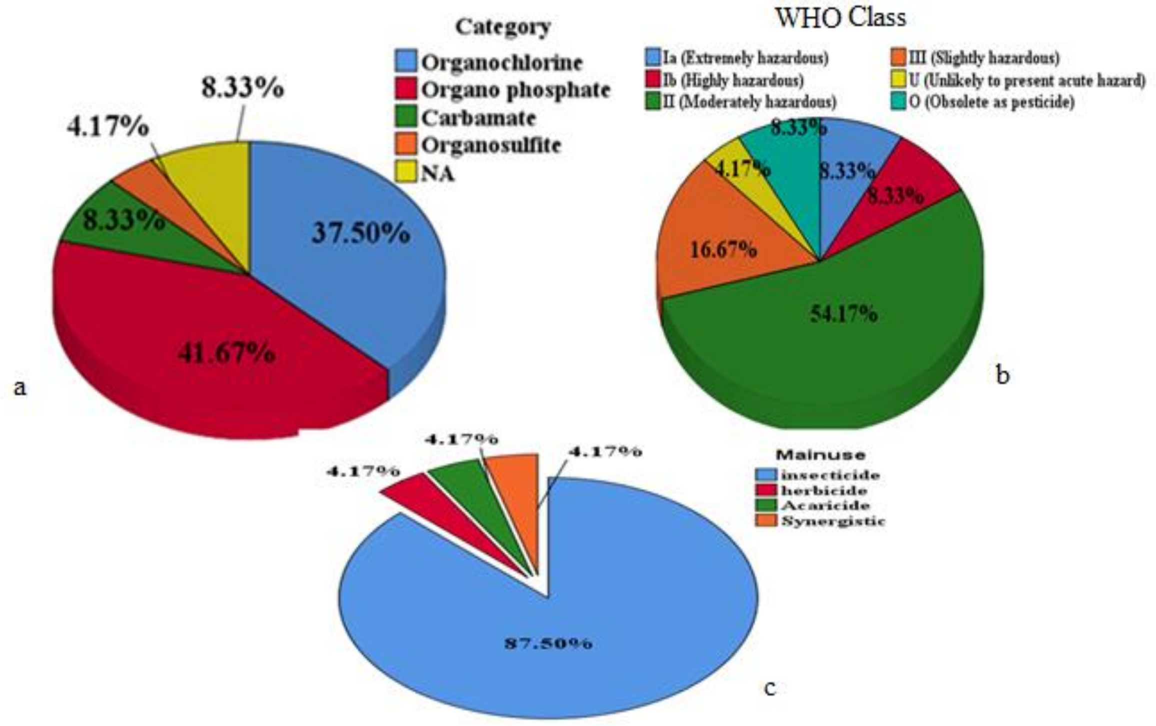

Figure5: 1 Pesticides residues category (a) and WHO classification (b), Main use (c)

These results indicate that over 70% of the pesticides used in the study area were from slightly hazardous to moderately hazardous. Still, it's worth noting that extremely hazardous and obsolete pesticides were also detected, which could threaten humans and the environment. Insecticides were the most commonly used type of pesticide (87.5%), suggesting a high level of insect infestation in the study area. These findings are consistent with a report from the United States Environmental Protection Agency (USEPA) that indicates the widespread use of insecticides for agricultural, public health, industrial, and household purposes, such as controlling roaches and termites (USEPA, 2024).

Table 5: 1 Concentration of pesticide residues in soil (µg/kg) samples collected from irrigated farmlands, around Lake, Ziwa

Pesticides Category	Pesticides detected	Main use	WHO Class	Lowest value	Highest value	Mean ± SD	FAO/WHO MPL	Mean-difference (mean-EU-MRL)	*P* = Value sig. (2 tailed)
OC	α-BHC	I	II	1.5	7.38	3.66±0.44	7.4^{ATSDR}	-3.73793	≤ 0.001
	β -BHC	I	II	BDL	5.36	1.10±0.35	6^{ATSDR}	-4.899253	≤ 0.001
	Hepta chlor	I	O	BDL	4.74	1.80±0.36	30	-28.253493	≤ 0.001
	Heptachlor epoxide	I	O	0.9	**31.65**	6.59±2.32	30	-23.41239	≤ 0.001
	α-Endosulfan	I	II	BDL	**69.68**	11.7±5.88	20	-8.29714	0.18
	4,4-DDE	I	II	BDL	119.94	37.48±10.22	1000	-962.520013	≤ 0.001
	4,4-DDD	I	II	BDL	18.51	4.22±1.58	2000	-1995.78222	≤ 0.001
	4,4-DDT	I	II	BDL	**20.68**	4.02±**1.77**	20	3.02299	0.110
	Hexachlorobenzene	I	Ia	BDL	38.53	7.87±3.71			
OP	Bromophos-Ethyl	I	Ib	0.06	2.73	0.79±0.21			
	Chloropyrifos-Methyl	I	III	BDL	**86.94**	6±5.78	30	-4.99558	**0.402**
	Diazinon	I	II	BDL	0.58	0.09±0.05			
	Ethion	I	II	BDL	3.17	0.94±0.32			
	Famphur	I	Ib	BDL	0.89	0.49±0.09			
	Fenitrothion	I	II	BDL	0.93	0.21±0.07			
	Fenthion	I/L	II	1.18	83.39	8.02±5.4			
	Malathion	I	III	BDL	**89.29**	**38.35±8.26**	20^{EU}	18.35419	**0.043354**
	Parathion	I	Ia	0.43	4.38	1.97±0.33			
	Profenofos	I	II	BDL	0.74	0.32±0.07	50^{USEPA}	-49.67542	< 0.001
NA	Pipronyl Butoxide	SY	U	BDL	46.07	7.04±3.88			
	Dichlobenil	H	III	BDL	4.3	2.2±0.38			
C	Propoxur	I	II	4.79	49.99	23.94±3.49			
	Indoxacarb	I	II	BDL	6.25	2±0.68			
OS	Propargite	AC	III	BDL	93.49	21.91±6.97			

C=Carbamate, OC= Organo chlorine, Os= Organosulfite, Na=Not assigned; BDL = Below Detection Limit; EU means European Union; USEPA means United States Environmental Protection Agency,I= insecticide, L= larvicide, SY= Synergist,H=Herbicide, AC= acaricid

Table 5:1 depicts the list of common pesticides found in soil samples, which include p,p'-DDE, propagate, malathion, chloropyrifos-methyl, fenthion, α-endosulfan, heptachlor epoxide, o,p'-DDT, propoxur, ..., and Diazinon. The concentration of p,p'-DDE in soil-samples ranged from BDL to 86.9 µg/kg, with a mean concentration of 37.48 ± 10.22 µg/kg. The soil samples had the highest concentration of p,p'-DDE.

A paired samples t-test revealed significant variations in the concentrations of p,p'-DDE and p,p'-DDD ($t = 3.643$, $p = 0.003$, 14 degrees of freedom), as well as p,p'-DDE, and p,p'-DDT ($t = 3.635$, $p = 0.003$, 14 df) across all of the examined sites. This indicates that p,p'-DDE is a highly degraded metabolite in the area. Reports indicate that DDE is a significant metabolite of DDT, formed through aerobic transformation in the environment (ATSDR, 2007).

The concentrations of three chemicals - p,p'-DDT, p,p'-DDE, and p,p'-DDD - exhibited significant correlations. The correlation coefficient ranged from 0.63 to 0.64, with a p-value of less than 0.05 and 14 degrees of freedom, indicating a likely common origin. To assess the presence or historical context of contamination, we can utilize the ratio of (p,p'-DDE + p,p'-DDD) to p,p'-DDT. A ratio greater than 1 suggests extensive transformation of DDT into DDE and DDD, indicating a degradation process rather than new DDT accumulation. Conversely, a ratio less than 1 suggests recent use or exposure to DDT in its original form with minimal degradation.

The ratio of (p, p'-DDE + p,p'-DDD)/p,p'-DDT) was found to be 10.37, indicating that there had been no recent input or usage of DDT in the region. This result was consistent with recent studies conducted in the area by Mekuria Teshome *et al.* (2022), Shiferaw Ayele *et* al. (2022), and Elsai Mati et al. (2024). The current results of DDT and its metabolites (DDD and DDE) in agricultural soil are similar to the findings reported by Westbom et al. (2008) in the upper Awash farm soils of Ethiopia. However, the results are lower than those reported by Kihampa & Mato (2009) in Tanzanian soil (DDT: 42,760 µg/kg, DDD: 92,500 µg/kg, and DDE: 20,840 µg/kg). The difference in the results could be due to different settings.

The level of malathion residue active ingredient was found in the range of BDL to 84.9 µg/kg and the average concentration (27.07 ± 7.69 µg/kg) exceeded the EU (2007) standard limit of 20 µg/kg, and this difference was statistically significant ($P<0.005$). This result was lower than the report of Joko et al. (2017) (360 µg/kg) from Indonesia.

5.3.2 Ecoogical risk assessment

Data on the acute mortality LC50 for *E. fetida* was available for only 50% of the 24 detected pesticides. On the other hand, only 16.7% had NOEC data available. One-third (33.3%) of the assessed pesticides had data on no significant adverse effect (NOSAE) of soil organisms, while 20.8% had chronic effects. However, it is worth noting that 45.8% of the pesticides were not analyzed due to a lack of toxicity data (Table 5:2).

Table 5: 2 Toxicity levels (measured in mg/kg) of the soil sample on *Eisenia fetida* (earthworms), *Folsomia candida* (springtails), and soil microorganisms (effect on nitrogen mineralization).

Pesticides	Fereq. detec (%)	MEC_{max}	MEC_{min}	*E.fetida* LC50	*E.fetida* NOEC	*F. candida* NOEC	N/C mineralization	PNEC AF	PNECmss
α-Endosulfan	47	0.070	0.015	14				1000	0.014
4,4-DDT	33	0.021	0.005	1000	280	176		50	5.6
chlorpyrifos-me	87	0.087	0.011	182	12.5	0.075	1	10	1.25
Diazinon	20	0.014	0.002	65			80	100	0.65
Fenitrothion	60	0.093	0.012	231	25		10	10	2.5
Fenthion	100	0.083	0.013	375			0.01	100	3.75
HCB	80	0.039	0.010	1000				1000	1
Indoxacarb	40	0.006	0.002	625	29.2	125	0.5	10	2.92
Malathion	53	0.085	0.026	306			12.6	10	30.6
Profenofos	67	0.001	0.000			50	250	50	1
Propargite	60	0.293	0.055	378			12.8	100	3.78
Dichlobenil	87	0.004	0.002	135		33.8		100	1.35
Propoxur	100	0.049	0.025	1000				1000	1

5.3.2.1 Risk assessment of single pesticides using TERs

Table 5:3 shows the toxicity exposure ratio (TER) for both a general scenario (GS) and a worst-case scenario (WS). The results revealed that all the pesticides examined in soil samples had insignificant acute and chronic effects on *E. fetida*, and *F. candida under chronic*, and N fixing organisms under both scenarios, with the exceptions of Chlorpy-methyl under the worst-case scenario for *F. candida* (TERmax=0.86) and Fenthion for N fixing organisms (TERmax=1.2). This indicates that the calculated TER_{max} for these two pesticides was under the EC (2002) trigger value of 10 for acute toxicity. However, the toxic exposure value for chronic toxicity (TERmin=6.8, and 7.9) for *F. candida* and N fixing organisms was almost at the trigger value of 5 for chronic toxicity. This could be a result of their continuous exposure to chlorpyrifos-methyl (EC, 2011). Previous reports have demonstrated that *F. candida* is highly vulnerable to pesticides and is one of the most susceptible organisms among soil invertebrates (Fountain & Hopkin, 2005). Therefore, the local pesticide application patterns might have led to negative effects on *F. candida* and N fixing organisms' communities, such as a decrease in microbial populations. The present results of chlorpyrifos-methyl are consistent with previous studies conducted by Merga *et al*. (2020) on sediment and Berhan Mellese *et al.* (2023) on soil. These studies have reported that chlorpyrifos is highly toxic to all soil biota, posing both acute and chronic risks. Similarly, USEPA (2010) has also reported that Chlorpyrifos is one of the most acutely and chronically toxic pesticides for soil organisms. Moreover, a recent report by Mu *et al*. (2023) from North China has shown evidence of chronic exposure risks to soil biota from chlorpyrifos.

5.3.2.2 Risk assessment of pesticide mixtures by RQ

The study assessed the ecological risk of pesticides mixture under both general and worst-case scenarios, as shown in Table 5:4. The results indicated that alpha endosulfan posed a high risk (RQs > 1) in both scenarios as individual pesticides for soil biota in the study region. Morover, this pesticide contributes 94% of the risk than the other pesticides. The present risk indice of alpha endosulfan is related with our earlier research on pesticide residues in vegetables, which showed that endosulfan levels exceeded the EU's maximum permitted limit (Demsie *et al*., 2024). The result indicates that the endosulfan may not only affect soil biota but also tomato plants, and potentially reach humans through the food chain in the study area. This could be attributed to the persistent nature of endosulfan residues in the environment (Milesi *et al*., 2020), which can adversely affect non-target organisms, including humans (Sathishkumar *et al*., 2021). The results of the present study confirm those of a prior investigation carried out in a similar region (Merga *et al*., 2021). The preceding study exposed that endosulfan poses an imminent risk to the environment, with a risk quotient (RQ>1) that is elevated in both dry and rainy seasons.

Table 5: 3 TERmax and TERmean calculated based on the selected species and single pesticides in top soil. Trigger value: 10 for acute risk 5

Pesticides	**MEC_{max}**	**MEC_{mean}**	***E.fetida***	***E.fetida***	***F. candida***	**N Minera lization**	***E. fetida acute***		***F. candida chronic***		**Nitrogen**	
	mg/kg	**mg/kg**	**LC50**	**NOEC**	**NOEC**		TERmax	TERmean	TERmax	TERmean	TERmax	TERmean
α-Endosulfan	0.0697	0.0153	14				200.91	913.45				
4,4-DDT	0.0207	0.0051	1000	280	176		48363.15	55293.83	8511.914	34756.12		
chlorpyrifos-me	0.0869	0.0111	182	12.5	0.075	1	2093.31	1129.88	**0.86263**	6.7793	11.5017	90.39037
Diazinon	0.0135	0.0017	65			80	4810.36	37179.64			5920.444	45759.55
Fenitrothion	0.0928	0.0117	231	25		10	2488.532	2134.43			107.7287	853.7709
Fenthion	0.0834	0.0127	375			0.1	4497.115	29467.64			**1.199231**	7.858037
HCB	0.0385	0.0098	1000				25956.56	102154.4		1000		
Indoxacarb	0.0063	0.0023	625	29.2	125	0.5	99928.05	12887.35				
Malathion	0.0849	0.0259	306			12.6	3603.922	11812.1			148.3968	486.3804
Profenofos	0.0013	0.0005			50	250			37108.51	105771.1	185542.5	528855.7
Propargite	0.2933	0.0547	278			12.8	947.9869	5078.41			43.64832	233.826
Dichlobenil	0.0043	0.0022	135		33.8		31385.13	62169.19	7857.91	15565.32		
Propoxur	0.049	0.025	1000				20004.761	39111.53265				

Note: Value in bold in dicated TERbelow trigger value or *indicated risk*

The study found that certain pesticides, namely Chloropyrifosmethyl, Hexachlorobenzene, propargite, and propoxer, posed low individual risks ($0.01 \leq RQ < 0.1$) in both scenarios for soil biota in the study region. Diazinon, Fenitrothion, and Fenthion had a lower risk only in the worst-case scenario. However, 4,4-DDT, Indoxacarb, Malathion, Profenofos, and Dichlobenil were found to have negligible individual risks ($RQ < 0.01$) in the study area. These pesticides contributed less than 10% overall (as indicated in Table 5). The study conducted in the area indicated a high ecological risk $\sum RQ=5.3$ due to the overall pesticide mixture, in both scenarios.

Table 5: 4. Risk Quetient (RQ) for sample soil biota

Pesticides	RQ(Ws)	RQ(Gs)	%Cont(Ws)
α-Endosulfan	**4.977**	**1.095**	93.7
4,4-DDT	0.004	0.001	0.07
Chloropyrifos-me	0.070	0.009	1.21
Diazinon	0.021	0.003	0.36
Fenitrothion	0.037	0.005	0.65
Fenthion	0.022	0.003	0.40
Hexachlorobenzene	0.039	0.010	0.75
Indoxacarb	0.002	0.001	0.04
Malathion	0.003	0.001	0.06
Profenofos	0.001	0.000	0.03
Propargite	0.078	0.014	1.42
Dichlobenil	0.003	0.002	0.07
Propoxur	0.050	0.026	1.17
$\sum_i \boldsymbol{RQ}$	**5.306**	**1.169**	

Note: RQ values in bold indicated high risk

The primary pesticide found in the area was alpha-endosulfan, followed by propargite and propoxur, which pose a high ecological risk to non-target soil species. Similar results were reported in a previous study conducted in the same area (Lemessa Bente et al., 2021). To maintain soil quality and reduce risks associated with pesticide exposure, it is vital to develop specific integrated crop protection strategies for the area. These strategies may include introducing natural pest enemies, establishing trap crops, and applying mulches in multiple colors (Seidenglanz *et al*., 2022).

5.4 Conclusions

This study evaluates the presence and concentration of pesticide residues in the irrigated soil of selected farms around Lake Ziway, Ethiopia. The study assesses the ecological risks to soil biota posed by single pesticides and mixtures at sampled locations using TERs and the RQ method. Out of the 35 targeted pesticide residues, 24 (68.6%) were detected in the soil samples. Only 5 (20.8%) of these pesticides were detected above the Maximum Permissible Limit (MPL). Organophosphate (41.7%) was the dominant pesticide followed by organochlorine (37.5%) in the soil samples. The majority (75%) of detected pesticides was classified as moderately hazardous (Class II) and slightly hazardous (Class III) pesticides, but extremely hazardous and obsolete pesticides were also detected, which could pose a threat to humans and the environment.

The highest concentration detected was p,p'-DDE, followed by propagate, malathion, Chlorpyrifos-Methyl, Fenthion, α-endosulfan, Heptachlor epoxide, o,p'-DDT, propoxur, and Diazinon. The ratio of (p,p'-DDE + p,p'-DDD)/p,p'-DDT was found to be 10.37, indicating that there had been no recent input or usage of DDT in the region.

Chlorpyrifos-methyl and Fenthion pose chronic exposure risks to soil biota such as F. candida and for N/C mineralization organisms. Alpha-endosulfan posed a high risk (RQs > 1) in both scenarios for soil biota in the study region. Chloropyrifos-methyl, Hexachlorobenzene, propargite, and propoxur posed low individual risks ($0.01 \leq RQ < 0.1$)

in both scenarios for soil biota in the study region. The overall pesticide mixture risk indicated a high ecological risk ($\sum_i RQ > 1$) in the study area in both scenarios. The dominant pesticide was alpha-endosulfan followed by propargite and propoxur. Several studies have highlighted the absence of risk assessments as a significant issue affecting environmental monitoring and management efforts. The current environmental policies and regulations in Ethiopia are inadequate in reducing pollution levels and risks in large-scale catchments. This poses a threat to both human health and the environment. Therefore, it is necessary to conduct risk assessments, exposure, and toxicity investigations to prioritize hazards in guidelines and standards. Informed decisions for risk mitigation can be made based on investigation findings.

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CHAPTER SIX

6. GENERAL CONCLUSIONS AND RECOMMENDATIONS

Excessive use of pesticides can lead to harmful residues in vegetables, which poses a risk to human health. Our study found that specific vegetables, such as tomatoes and onions, contained pesticide residues that exceeded safety limits. We also assessed the potential health risks for adults and children, as well as the ecological risks to soil organisms. Therefore, our findings highlight the need for specific actions to address these challenges.

6.1 GENERAL CONCLUSIONS

According to this study, consuming tomatoes and onions from various sources with varying levels of exposure to toxicities such as α-endosulfan, heptachlor, malathion, and propargite residues poses no non-carcinogenic risks to both adults and children. However, there is a carcinogenic risk associated with onion heptachlor epoxide, estimated at 1.46 x 10-3g/kg/day in adults and 1.16 x 10-2g/kg/day in children. This translates to a cancer risk of 1.46 per 1,000 continuously exposed adults and 1.16 per 100 continuously exposed children. The study highlights that farmers and their families, as well as those who regularly consume vegetables cultivated with pesticide contamination are the most vulnerable risk group and their health should be prioritized.

The findings highlight the human health risks emanating from consuming contaminated vegetables neglected in other studies conducted in the central Ethiopian Rift valley Region. The daily intake of heavy metals in tomatoes and onions was found to be ten times higher than the oral reference dose of heavy metals, indicating high health risks for children who consume these vegetables from the study area. The concentration of heavy metals in tomato and onion samples exceeded the recommended limits of FAO/WHO, and soil samples collected beneath the irrigated vegetables had an excess of Cd, Hg, Pb, and Zn. The cumulative non-carcinogenic effects of multiple metals estimated by the health index (HI) for tomato and onion were >1, indicating a potential non-carcinogenic risk to the public. The PCA analysis showed that human activities have had a significant impact on the current concentration of heavy metals in research areas. Regular monitoring of soil and vegetable crops in the research region is strongly suggested to avoid further accumulations that may pose substantial non-carcinogenic and carcinogenic health risks to consumers of these vegetables.

The study also evaluates the presence and concentration of pesticide residues in the irrigated soil of selected farms around Lake Ziway, Ethiopia. Out of 35 targeted pesticide residues, 24 (68.6%) were detected in the soil samples, with organophosphate (41.7%) being the dominant pesticide. Chlorpyrifos-methyl and Fenthion pose acute exposure risks to soil biota, while alpha-endosulfan posed a high ecological risk.The study highlights the need for risk assessments and improved environmental policies to reduce pollution levels and risks in large-scale catchments.

6.2 RECOMMENDATIONS

Based on the specific findings of the study and the general conclusions outlined above, I recommend some actions that could lead to positive changes in the current agrochemical utilization in the irrigated farming sites around Lake Ziway:

1. Educate farmers about the negative impacts of excessive and toxic pesticide use, as well as inappropriate handling practices, on their vegetable products, health, and the environment. Train them to replace hazardous pesticides with low-risk alternatives to mitigate these risks.
2. Strictly enforce laws and regulations at all levels to ensure compliance and prevent any violations by government authorities.

3. Create urgent awareness and monitoring policies must be put in place to safeguard public health within and beyond the study area.
4. Encourage communities to eat assorted diet to avoid excessive pesticide exposure from a small range of food items. They should not consume vegetables as frequently as three or more days a week.
5. Conduct quantitative and qualitative studies regarding pesticide residues and toxic metal accumulation in people who work in irrigated farmland, particularly in the assumed risk groups, such as farmers and their children. This should take into account their sex and the amount of exposure at the site and food items consumed by the people. This would enable public health interventions to be carried out meaningfully.

7. **Appendices**

Table Annex 3.1: Pesticide residues concentration (µg/kg) in tomatoes samples collected from irrigated farmlands in the vicinity of Lake Ziway

Site		**α-BHC**	**β -BHC**	**H-epoxy**	**H-chlor**	**α-Endo**	**Aldrin**	**HCB**	**Bro-E**	**Chlor**	**Diazin**	**Ethion**	**Famp**	**Fenitro**	**Fenthion**
S1 (Abunea-Germama)	**R1**	1.75	BDL	7.32	14.02	BDL	BDL	1.01	1.98	1.66	BDL	BDL	2.60	2.86	2.71
	R2	5.04	42.06	BDL	12.99	518.49	BDL	1.70	0.38	0.69	BDL	0.65	BDL	0.16	1.70
	R3	3.75	32.87	3.41	18.22	630.52	BDL	BDL	0.80	1.12	BDL	1.14	1.26	0.74	1.95
S2 (Wellibulla)	**R1**	2.24	BDL	BDL	BDL	189.04	0.39	BDL	3.29	2.60	1.19	BDL	2.90	2.39	2.70
	R2	3.91	23.71	BDL	BDL	402.77	1.20	BDL	1.05	0.34	0.07	BDL	0.79	0.06	1.33
	R3	2.90	7.79	BDL	BDL	200.34	BDL	BDL	0.96	1.12	0.05	BDL	1.47	0.69	1.93
S3 Guirissa	**R1**	2.13	20.81	BDL	7.27	258.49	5.87	BDL	0.14	0.51	0.48	BDL	0.65	0.18	1.43
	R2	3.91	33.84	0.12	BDL	626.12	4.87	BDL	0.06	0.20	BDL	0.21	1.01	0.04	1.44
	R3	5.24	6.26	4.12	6.86	153.99	BDL	BDL	1.66	1.04	0.44	1.12	1.65	1.69	2.14
EU-MRL		10	10	10	10	50	10	10	10	10	10	10	10	10	10
Total detected		9	8	5	5	9	5	2	9	9	5	4	8	9	9
%(+ve) Sample		100	88.9	55.6	55.6	100.0	55.6	22.2	100	100	55.6	44.4	88.9	100	100
Sa >EU-MRL		0	5	0	3	8	0	0	0	0	0	0	0	0	0
%(>EU-MRL)		0	55.6	0.0	33.3	88.9	0.0	0	0	0	0	0	0	0	0

Annex 3.1: Continued.

Site		**Malathion**	**Parathion**	**Profenofos**	**Thionazin**	**Propargite**	**Propoxur**	**Dichlobenil**
S1 (Abunea-Germama**)**	R1	14.156	3.62	BDL	0.02	BDL	8.75	0.02
	R2	BDL	1.52	0.53	0.46	BDL	30.88	1.34
	R3	7.6837	1.16	0.58	BDL	BDL	14.18	1.24
S2 (Wellibulla)	R1	BDL	0.51	1.71	BDL	50.15	16.60	BDL
	R2	BDL	0.56	1.42	BDL	BDL	36.05	BDL
	R3	BDL	0.45	0.37	BDL	55.35	17.79	BDL
S3 (Guirissa)	R1	47.75	1.16	0.77	BDL	10.02	16.53	1.26
	R2	15.16	0.72	1.64	BDL	BDL	38.46	0.51
	R3	BDL	1.66	ND	BDL	13.01	23.43	2.36
EU-MRL		20	50	10000	10	10	50	10
Total detected		4	9	7	2	4	9	6
Sample >EU-MRL		1	0	0	0	4	0	0
%(+ve) Sample		44.44	100	77.78	22.22	44.44	100.00	66.67
%(>EU-MRL)		11.11	0	0.00	0.00	44.44	0.00	0.00

Annex 3.2: Pesticides concentration (µg/kg) in onion samples collected from irrigated farmlands in the vicinity of Lake Ziway

Site		α-BHC	β -BHC	Hepta-epoxide	Hepta chlor	α-Endosulfan	Bromophos-Ethyl	Chloropyrifos-Methyl	Diazinon	Thionazin	Ethion	Famphur
S1	R1	3.56	5.45	13.73	BDL	1.50	0.55	0.80	0.19	BDL	BDL	1.45
	R2	BDL	1.32	5.74	BDL	3.35	BDL	0.23	0.04	0.26	BDL	BDL
	R3	3.02	BDL	13.17	BDL	3.35	0.09	0.44	BDL	0.38	BDL	0.73
S2	R1	2.25	0.48	37.55	BDL	BDL	0.04	0.25	BDL	0.01	BDL	0.74
	R2	5.46	0.90	31.23	8.02	BDL	0.40	0.60	BDL	0.30	0.94	0.93
	R3	3.02	0.09	37.55	8.48	BDL	0.09	0.44	BDL	0.39	0.43	0.73
EU-MRL		10	10	10	10	100	10	10	50	10	20	10
Total detected		6	6	6	3	3	5	6	2	5	2	5
Sample >EU-MRL		0	0	5	0	0	0	0	0	0	0	0
%(+ve) Sample		100	100	100	50	33.33	83.33	100	33.33	83.33	33.33	83.33333
%(>EU-MRL)		0	0	83.3	0	0	0	0	0	0	0	0

Annex 3.2: Continued

Site		**Fenitrothion**	**Fenthion**	**Malathion**	**Parathion**	**Profenofos**	**PBO**	**Propargite**	**Propoxur**	**Indoxacarb**	**Dichlobenil**
S1 (Abunea-Germama)	R1	0.46	1.80	BDL	1.29	0.82	BDL	45.75	8.61	BDL	BDL
	R2	0.30	2.75	BDL	1.05	0.54	BDL	BDL	12.73	BDL	0.10
	R3	0.40	1.63	BDL	0.60	0.82	BDL	29.77	25.15	BDL	1.10
S2 (Wellibulla)	R1	0.16	1.50	11.02	1.19	0.64	BDL	BDL	7.42	0.29	1.09
	R2	0.25	1.45	20.74	0.73	0.23	BDL	112.36	13.74	4.30	BDL
	R3	0.40	1.63	BDL	0.60	0.82	BDL	112.36	25.15	4.30	1.10
EU-MRL		10	10.00	20.00	50.00	20.00	0	10.00	50.00	20.00	10.00
Sample detected		6.00	6.00	2.00	6.00	6.00	0	5.00	6.00	3.00	4.00
Sample >EU-MRL		0.00	0.00	1.00	0.00	0.00	0	4.00	0.00	0.00	0.00
%(+ve) Sample		100	100.00	33.33	100.00	100.00	0	83.33	100.00	50.00	66.67

Table **Appendix 4.1**: Optimal ICP-OES operating conditions for analysis of metal in soil and vegetable samples

Instrument parameter	**Conditions**
Plasma power	1400W
Pump Speed	30rpm
Coolant Flow	13 L/min
Auxiliary Flow	0.8 L/min
Nebulizer Flow	0.73 L min-1
Optic Temperature	15.05℃ (14.0-16.0)
Flow light tube	0.90 L/min (0.8-1.8)
Nebulizer Pressure	1.96 bar (2.0-4.0)
Main Argon Pressure	6.75 bar (6.0-8.0)
Replicates	3

Table Appendix 4.2: Percentage recovery values of the method used for tomato sample digestion (n = 3)

Heavy metals	Concentration before spiking (M± SDs) (mg/kg)	Amount spiked (mg/kg)	Concentration after spiking (M± SD) (mg/kg)	% Recovery	% RSD
As	0.438 ± 0.034	1	1.353 ± 0.032	91.57	7.79
Pb	0.288 ± 0.01	1	1.29 ± 0.005	100.3	3.3
Zn	0.135 ± 0.001	1	1.18 ± 0.007	104.57	1.23
Cd	0.001 ± 0.0001	1	0.953 ± 0.032	95.24	11.1
Hg	0.634 ± 0.007	1	1.545 ± 0.056	91.13	1.05
Cu	0.146 ± 0.006	1	1.159 ± 0.067	101.3	4.17
Ni	0.245 ± 0.005	1	1.17 ± 0.034	92.8	2.16
Co	0.162 ± 0.002	1	1.15 ± 0.036	99.13	1.5
Cr	0.287 ± 0.003	1	1.257 ± 0.047	97	1.12

RSD= Relative Standard Deviation; M=Mean concentration; SD=Standard Division

Tabl3 Appendix 4.3: Percentage recovery values of the method used for onion sample digestion (n = 3)

Heavy metals	Concentration before spiking (M± SDs) (mg/kg)	Amount spiked (mg/kg)	Concentration after spiking (M± SD) (mg/kg)	% Recovery	% RSD
As	0.018±0.001	1	1.147±0.012	112.9	6.29
Pb	0.028±0.002	1	1.053±0.021	71.8	1.14
Zn	0.727±0.049	1	1.70±0.292	106	5.6
Cd	0.001±5.8-05	1	0.947±0.05	94.57	5.97
Hg	0.029±0.002	1	1.057±0.031	102.77	6.9
Cu	0.087±0.006	1	1.083±0.057	99.67	6.35
Ni	0.047±0.006	1	0.903±0.05	85.67	12.37
Co	0.063±0.002	1	1.09±0.061	102.73	3.32
Cr	0.087±0.003	1	1.04±0.044	95.27	6.68

RSD= Relative Standard Deviation; M=Mean concentration; SD=Standard Division

Table Appendix 4.4: Percentage recovery values of the method used for soil sample digestion (n = 3)

Heavy metals	Concentration before spiking (M± SDs) (mg/kg)	Amount spiked (mg/kg)	Concentration after spiking (M± SD) (mg/kg)	% Recovery	% RSD
As	0.105 ± 0.004	1	1.248 ± 0.002	114.3	4.15
Pb	0.207 ± 0.008	1	1.209 ± 0.002	100.2	3.94
Zn	0.142 ± 0.007	1	1.217± 0.09	107.47	4.62
Cd	0.032 ± 0.002	1	1.087± 0.015	105.5	6.57
Hg	0.042 ± 0.001	1	1.223± 0.011	118.1	2.38
Cu	0.343 ± 0.021	1	1.463± 0.032	112	6.06
Ni	0.147 ± 0.015	1	1.16 ± 0.03	101.7	10.4
Co	0.553 ± 0.021	1	1.727± 0.015	117.3	3.76
Cr	0.283+0.011	1	1.337±0.015	105.3	4.1

RSD= Relative Standard Deviation; M=Mean concentration; SD=Standard Division