LEVELS AND POSSIBLE RISKS OF HEAVY METALS IN THE LOWER OMO RIVER AND DELTA (L. TURKANA) IN SOUTHERN ETHIOPIA, INCLUDING AN ASSESSMENT OF SOME OTHER WATER QUALITY FACTORS

PhD DISSERTATION

BY

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HAWASSA UNIVERSITY
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A DISSERTATION SUBMITTED TO THE COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCE, DEPARTMENT OF BIOLOGY, SCHOOLOF GRADUATE STUDIES HAWASSA UNIVERSITY HAWASSA, ETHIOPIA INPARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN ENVIRONMENTAL TOXICOLOGY

Advisors: 1. Major advisor: Girma Tilahun Yimer (PhD, Associate Professor)

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Hawassa University

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SCHOOL OF GRADUATE STUDIES

HAWASSA UNIVERSITY

ADVISORS' APPROVAL SHEET

This is to certify that the PhD Thesis entitled "Pollution in Lower Omo River and Delta Lake (L. Turkana), Southern Ethiopia : Levels and Possible Risks of Heavy Metals including an Assessment of Some Other Water Quality Factors " submitted in partial fulfillment of the requirements for the PhD in Environmental Toxicology, the Graduate Program of the Department of Biology and has been carried out by Abiy Andemo Kotacho, Id. No PhDEnTo/0002/11, under our supervision. Therefore I/we recommend that the student has fulfilled the requirements and hence hereby can submit the PhD Thesis to the department.

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2. Co- advisorSolomon Sorsa Sota (Professor)

Signature ________________________________ Date ___________________________

DECLARATION

I here declare that this PhD dissertation is my own original work and has not been presented for a degree in any other University either in part or as a whole. All sources of materials used for this dissertation have been duly acknowledged.

Name: Abiy Andemo Kotacho

Signature ______________________________ Date_____________________________

This thesis has been submitted for examination with our approval as university supervisors

1. Major advisor: Girma Tilahun Yimer (PhD, Associate Professor)

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BIOGRAPHICAL SKETCH

Abiy Andemo is a PhD student in Environmental Toxicology at Hawassa University, College of Natural and Computational Science since Dec/2019. He received a bachelor's degree in Chemistry from Mekelle University and a bachelor's degree in Civil engineering from Infolink University College. He received a master's degree in Environmental Science and Technology from Jimma University. He is interested in Environmental Toxicology, Ecotoxicology, Environmental Engineering, and Wastewater Engineering, Human health Risk Assessment, Environmental Risk Assessment, Water Treatment, Wastewater Treatment, and Waste Water Management.

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LIST OF ABBREVIATIONS AND ACRONYMS

ADD	Average daily dose
ANOVA	Analysis of Variance
AT	Average exposure time
BAF	Bio-Accumulation Factor
BCF	Bio-Concentration Factor
CD	Contamination Degree
CDI	Chronic daily intake
CF	Contamination Factor
Cm	Mean concentration of metals
CR	Carcinogenic risk
CRI	Comprehensive risk index
$CSF_{ingestion}$	Oral carcinogenic slope factor
ED	Exposure duration
EF	Exposure frequency
EPA	Environmental Protection Authority
ERi	Potential Ecological Risk Factor
ET	*E*xposure time
FAAS	Flame Atomic Absorption Spectroscopy
FAO	Food and Agricultural Organization
HI	Hazard index

Igeo	Geo Accumulation
IR	Ingestion rate
KP	Dermal permeability coefficient
MCD	Modified Contamination Degree
NTU	Nephelometric Turbidity unit
PLI	Pollution Load Index
RfD	Reference dose
RI	Risk index factor
SA	Skin area available
SPSS	Statistical Package for Social Sciences
TCR	target carcinogenic risks
THQ	Non carcinogenic health risk
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

Contents

LIST OF TABLES

List of Figures

GENERAL ABSTRACT

Heavy metal concentrations in water and sediments can be biomagnifyied and impact human health through consuming of contaminated water or fish. Human activities in the Omo River and Delta have caused increased heavy metal levels in the freshwater ecosystem, adversely affecting the freshwater quality. Studies have shown higher levels of heavy metals in Lake Turkana freshwater ecosystem including in the fish tissues and water on the Kenyan side, but information gaps exist on the Ethiopian side. Commercially exploited fish species, such as Lates *niloticus (*Nile perch*) and Oreochromis niloticus (*Nile tilapia*),* may accumulate heavy metals from the freshwater, leading to health risks in humans. Apparently, no study has been reported on the water quality status of the freshwater ecosystem of the Lower Omo Basin especially with respect to heavy metals. Therefore, the current study aimed to investigate the levels and possible risks of the nine heavy metals (Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) including an assessment of some other water quality factors from from the Lower Omo River and Delta (L. Turkana) in southern Ethiopia. Surface water, surface sediment, irrigated soil, and two fish species (*L. niloticus* and O. *niloticus*) of the freshwater ecosystems were examined for heavy metals.

The study was carried out at the Lower Omo River Basin near Omorate town and the Omo Delta where River Omo joins Lake Turkana. To assess the levels of heavy metals and the water quality from this freshwater ecosystem, thirty sampling points were taken of which 15 sampling points were designed to represent the River water and 15 the Delta. About 120 fish samples of each of the two fish species *(L. niloticus* and *O. niloticus*) were taken. Liver and muscle tissues of the two fish species were analyzed for heavy metals. Sediment samples were also taken from the same sites where the water samples were collected. Soil samples were collected from the vicinity of Lower Omo River where irrigation is intensively used. The levels of heavy metals in water; fish tissues, sediment, and soil samples were analyzed with Flame Atomic Absorption Spectrometer (FAAS**,** novAA400p). The other water quality parameters were analyzed using the standard methods for each parameter as described in the protocol or guidelines APHA (2017). The analysis was carried out at Arbaminch university in the laboratories of chemistry, water and environmental engineering.

The eight heavy metals (Mn, Zn, Cu, Co, Cr, Pb, Ni, and Fe) were detected in the different environmental compartments of the freshwater ecosystem from Lower Omo River and Delta. Accordingly, the mean values of the measured heavy metals detected in the River waterin mg/L were 0.439, 0.1, 0.168 , 0.393, 0.318 , 0.007 , 8.926, and 0.06 whereas the respective values for Delta were 0.43, 0.118 , 0.166 , 0.382 , 0.338 , 0.008, 8.684 and 0.064 for Mn, Zn, Cu, Cr, Pb, Ni, Fe, and Co respectively. Both the River and Delta water had mean levels of lead (Pb), manganese (Mn), Cobalt (Co), and chromium (Cr) that exceeded WHO's permissible limits for water. The target hazard quotient (THQ) value greater than 1 was examined for Cr, Pb, and Mn both in children and adults through ingestion and dermal route from the River and Delta Water. The CRs for both children and adults via ingestion of the River and Delta water followed the order Cr > Pb. According to the CRI value, both the River and Delta water could be classified as high environmental risk in terms of the detected heavy metals heavy metal levels under consideration.

In terms of heavy metal levels of freshwater fish, the Pb level in muscle tissues ranged from 0.597mg kg-1 to 0.890mg kg-1, with a greater value in the Omo Delta sample, which could be attributable to the water character of the Omo River and the Delta. The mean Pb levels in the muscle tissue of *O. niloticus* in the Omo River and the Delta were above the FAO/WHO recommended limits in the human diet. The high values of Pb could be due to intensive anthropogenic activities like use of agrochemicals (pesticides and fertilizers), petrol from fishing boats that contain lead, Car washing, gas/fuel station, solid wastes, and effluents from factories. It’s also possible that heavy rains carried the wastes down; contributing to the greater heavy metal levels of the study area.

The target hazard quotient (THQ) and hazard index (HI) indices were used to assess the noncarcinogenic health hazards associated with the detected heavy metals in children and adults who consumed *L. Niloticus* and *O. niloticus* muscle from the Lower Omo River and Delta. In all of the samples tested, the THQs for heavy metals in fish muscle consumed by adults and children were less than one. However, the Hazard Index (HI) for the detected heavy metals for children was larger than one. Pb had the highest THQ levels in both L. niloticus and O. niloticus, while Fe and Ni had the lowest values in O. niloticus muscle and L. niloticus muscle, respectively.

In terms of sediment pollution, the mean concentrations of the detected heavy metals in mg/kg in the sediments of River and Delta Lake were respectively 2.947 and 2.904 for (Mn), 0.801 and 0.809 for (Zn), 0.278 and 0.278 for (Cu), 0.437 and 0.434 for (Cr), 0.054 and 0.058 for (Pb), 0.009 and 0.008 for (Ni), 19.553 and 19.515 for (Fe), and 0.236 and 0.223 for (Co). The order of the mean values of the detected heavy metals in the river sediment were Fe > Mn > Zn > Cr > Cu > Co > Pb > Ni, but in the Delta Lake, the order was Fe > Mn > Zn > Co > Cu >Pb > Cr > Ni. The mean pollution liad index (PLI) values of heavy metals in sediment revealed low metal contamination of the sediment (PLI < 1.0). Thus, the study highlighted the importance of monitoring heavy metal levels in sediments to ensure the safety of the freshwater ecosystem.

Regarding the heavy metal level in soil, the mean values of the measured heavy metals in mg/kg in the soil irrigated by the lower Omo River were 4.4 for Mn, 1.142 for Zn, 0.2 for Cu, 0.43 for Cr, 0.424 for Pb, 0.004 for Ni, 23.5 for Fe, and 0.588 for Co. The order of the typical concentrations of heavy metals in soil were Fe > Mn > Zn > Co > Cr > Cu > Ni. The EI results for the detected heavy metals in the soil irrigated by the Lower Omo River in decreasing order were: Fe > Cu > Mn > Pb > Co > Zn > Cr > Ni. Except for Fe, the CFvalue showed a low level of contamination which was less than one.

Concerning the other water quality factors, the mean BOD_5 levels in the upstream and downstream of this study were 16.268±1.47 mg/L and 16.28 ±1.133 mg/L, respectively. The COD value of the

river, which is upstream, was higher at 376.06 ± 130.45 mg/L than that of the Lake, which is downstream, at 136.00 ± 41.52 mg/L. Fluoride ion levels in the river were 0.89 ±0.0135, while those in the Lake were 2.026 ±0.064 mg/l on average. The phosphate ($PO4^{-3}$) concentrations in the River and Lake (Delta) were 1.866 ± 0.625 mg/L and 5.108 ± 0.975 mg/L, respectively. The mean NH_3 readings of the River and Lake were 0.54 ±0.361 and 1.354 ± 0.655, respectively. The higher values of the water quality factors could be due to anthropogenic activities such as agrochemical use, and domestic wastes. The finding of the water quality index (WQI) also revealed that the water quality status was poor and unsuitable for drinking particularly in the Omo Delta.The Delta Lake's WQI value was found to be 142.47, which was beyond the threshold value for water quality index and Unsuitable fordrinking.

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CHAPTER ONE

GENERAL INTRODUCTION

1.1. Background

Heavy metals in the freshwater ecosystems and other environmental compartments are of global concern due to their bioaccumulation, biomagnifications and toxic effect to the environment and human health (Solomon *et al*., 2016; Zepeng *et al*., 2018). They find their way into the water bodies through anthropogenic impacts such as, agricultural activities, urbanization and industrial development (Abdullah and Ahmad, 2016). Poor water quality is mainly the result of high levels of heavy metals and changes in the physicochemical properties of water(Anweting *et al*., 2024).The toxicity of metals may depend on the physical and chemical characteristics of water. Thus, the physicochemical properties of water also indicate the quality of water (Anweting *et al*., 2024).

Heavy metals in the aquatic environment have the potential to bioaccumulate in a variety of aquatic organisms, particularly in fish (Manal *et al*., 2014). If ingested by humans, these metals might then enter the human metabolism, accumulate over time and pose major health risks (Yılmaz *et al*., 2005; Ahmed *et al*., 2021).Various Studies have indicated that high levels of heavy metals in water, fish, sediments and soil may be biomagnified along the food chains (Ahmed *et al.*, 2021) which could finally affect human health through consumption of the metal polluted water or fish or both (Edward *et al.*, 2013**;** Mbuthia, 2015).Fish consumption and ingestion of water can be a significant source of human exposure to a variety of heavy metals, concentrating substantial levels of some heavy metals (Mbuthia, 2015).

The increase in industrial activities, agricultural activities, and urbanization in Africa has led to a massive increase of heavy metals in freshwater ecosystem and also alter the physicochemical quality of the freshwater (Asrafuzzaman *et al.*, 2011). Despite the importance of ensuring the quality of freshwater, less attention has been given to water quality monitoring in developing countries such as Ethiopia (Maschal and Truye, 2018). Ethiopian freshwater ecosystem has been reported to have high concentration of heavy metals, in water, fish, sediment and soil (Samuel *et al.*, 2020).In Ethiopia, pollution of freshwater ecosystem by heavy metals is growing due to discharge of wastes from factories without being treated (Tamiru *et al.*, 2022**)**, agrochemicals containing heavy metals and urbanization (Sorsa *et al.*, 2016).Various studies in Ethiopia also revealed that high concentration of heavy metals occurred in different human diets such as fish, vegetables and fruits (Samuel *et al.*, 2020; Davit *et al.*, 2023). Accordingly, occurrence of Cr, Pd, Cd, Cu, and Co in fish tissue (Gure *et al.*, 2019); Cr, Co, Fe, Ni, Cu, Zn, As, Se, Pb and Hg in fish muscle (Samuel *et al.*, 2020**);** As, Cd, Cr, Zn, and Fe in fish muscle (Kindie *et al*,2021); Pb, Cd, Cu, Zn, Co and Ni in vegetable and fruit (Bahiru *et al.*, 2019; Gebeyehu and Bayissa, 2020) and Cr, Mn, Cu, Zn, Cd, and Pb in milk (Akele *et al.*, 2017) have been reported in different parts of the country.

The Lower Omo River and Delta are the fresh waters in the East African Rift Valley which is mainly used for various domestic uses, agriculture (irrigation), livestock, industries, and also supports a variety of fish populations, providing subsistence food to the local communities, as well as, a source of income. It is a vital resource of East African freshwater ecosystem in general and southern Ethiopia in particular comprising of various fish species in it (Wakjira and Getahun, 2017).The fish community of Lower Omo River and its Delta Lake comprises of about 31 species (Wakjira and Getahun, 2017) with *O.niloticus* and *L.niloticus*being the predominant species that contribute more to the commercial fishery. However, in Ethiopia, River monitoring is not sufficiently extensive to give the data required for managing the quality of the freshwater ecosystem (Zinabu *et al.*, 2019).

Owing to the anthropogenic activities on the catchment of Lower Omo River basin, the water quality of the River may be impaired due to the high concentrations of dissolved organic and inorganic substances such as heavy metals and, sulphate, nitrates, and chlorine. These human activities could alter physicochemical properties of the River and the Delta Lake water. They could change the pH of water, increase water turbidity, decrease biological oxygen demand (BOD), increase total dissolved solids and heavy metals. Thus, this dissertation aimed to investigate the levels and possible risks of heavy metals including an assessment of some other water quality factors from the freshwater ecosystem of Lower Omo River and Delta Lake in southern Ethiopia.

1.2 Statement of the problem

Globally, anthropogenic activities, notably fast urbanization, industrialization, extensive use of agrochemicals, and unrelenting population growth, have resulted in the deterioration of the water quality of freshwater bodies (Singh *et al.*, 2018). People across the world are at risk as a result of unfavorable changes in the physical, chemical, and biological properties of fresh water. High levels of pollutants such as heavy metals and other water quality factors in the freshwater ecosystems may make the water unsuitable for recreation, swimming/ bathing, drinking and fishing (Tibebe *et al*., 2019).The physicochemical water quality characteristics of the freshwater are influenced principally by anthropogenic factors (Saturday *et al.*, 2021). Heavy metals are one of the major contaminating agents of the freshwater ecosystem and food supply (Manal *et al*., 2014) and are serious threat to both aquatic organisms such as fish and humans (Sorsa *et al.*, 2016**)**.

In recent years, human activities have intensified in the Lower Omo River(Lotic) and the Omo delta (Lentic) (USEPA, 2010, Wakjira and Getahun, 2017).These activities have threatened the quality of the water bodies (Ojwang *et al*., 2010, Avery, 2012), which have been linked to the presence of heavy metals and other water quality factors in the freshwater ecosystem. Studies have also shown that fish tissues from Lake Turkana, which is located close to the Omo delta, contain higher levels of heavy metals (Magu *et al*., 2016, Christof *et al*., 2017) on the Kenyan side . However, there was information gap on the Ethiopian side.

The Lower Omo River Basin, which includes the Lower Omo River and Delta Lake, is the most significant supplies of water for human activities and home for a variety of fish species. The major commercially exploited fish species in Lower Omo River and Delta Lake include *Lates niloticus* and *Oreochromis niloticus*, which form a vital food source to the local community and different parts of the country. These fish species form important routes of human exposure to a variety of heavy metals through food chain and may accumulate the heavy metals from the freshwater. Consumption of heavy metal contaminated fish can lead to various health (Mbuthia, 2015). Thus; assessment of human health risk from heavy metal exposure via fish muscle was a vital issue which has not been addressed so far.

In spite of all the above serious environmental concerns in the freshwater ecosystem, to the best of our knowledge, no study has been reported on the level of heavy metals and associated human health and ecological risks. However, some studies have been performed on the concentrationsof elements in fish tissue from Lake Turkana on the Kenyan side (Magu *et al*., 2016, Christof *et al*., 2017), which is the point where the southernmost tip of the Omo River extends into it. Therefore, it is crucial to determine the concentrations of heavy metals in fish tissues from the lower Omo

River (Lotic) and the Omo delta (Lentic) for environmental and public health concerns. Thus, the current study aimed to determine the levels of heavy metals present in water, commonly consumed fish spices (*L. niloticus* and *O. niloticus*), sediment, soil and the physicochemical water quality factors from the lower Omo River (Lotic) and the Omo delta (Lentic). The study also evaluated human health risk, and ecological risks.

1.3 Objectives

1.3.1 General objective

The main objective of this study is to investigate the levels and possible risks of heavy metals including an assessment of some other water quality factors from the freshwater ecosystem of Lower Omo River and Delta in southern Ethiopia.

1.3.2 Specific objectives

1) To determine the heavy metal levels and associated human health risks in the Lower Omo River and Delta.
2) To evaluate levels of heavy metals in freshwater fish (L. niloticus and O. niloticus) and associated human health risk from the Lower Omo River and Delta
3) To assess the heavy metal levels and ecological risk in the surface sediments of Lower Omo River and Delta
4) To determine heavy metal pollution level and associated ecological risk in the Lower Omo River's irrigated soil.
5) To determine the physichechemical water quality factors and to evaluate the overall water quality status of Lower Omo River and Delta using WQI

1.4 Research questions

1.4.1What are the heavy metal levels in Lower Omo River and Delta water, and do they create a concern to human health?

1.4.2. What are the heavy metal levels in fish tissues from Omo River and Delta Lake, and do they constitute a human health risk?

1.4.3. What are the heavy metal levels in surface sediments of the freshwater and in the lower Omo River's irrigated soil, and do they pose an ecological risk?

1.4.4. What are the features of physicochemical water quality factors and current water quality status of the Lower Omo River and Delta?

1.5 Scope of the study

This study mainly included the following points:

- The Lower Omo River near Omorate Town and the Omo Delta Lake adjacent to Lake Turkana.
- The four environmental compartments including water, fish, sediment, and soil from the Lower Omo River and Omo Delta
- The liver muscle tissues of *L.niloticus* and *O.niloticus*
- The nine heavy metals such as Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn
- The physicochemical water quality factors and water quality
- Human and ecological risk assessments

1.6 Limitations of the study

This dissertation has been carried out with some limitations. The limitations of the present study include the nonconsideration of heavy metals such as arsenic, mercury etc due to financial constrains. The study was also limited in addressing seasonal effects due to the arid nature of the study area where there was no rainfall during the study period (between June and September 2022).The study area was also inaccesssibile which limited the researcher in adrresing various environmental concerns.

1.7 Significance of the study

This study is vital in providing first hand information on the pollution levels of heavy metals and the water quality status of the lower Omo River basin including the risk assessments as a first-hand information. The outcome of this study will therefore help different government offices and policy makers like the Ministry of Health and Water, and Environmental Agencies to generate guidelines for sustaining the social, ecological, and economic benefits of human and wildlife health. The study also serves as a base line source of data for further study. Moreover, this study has provided possible suggestions and recommendations on existing level of Heavy metal and physico-chemical parameter in order to improve the current condition of the water sector and find a way to solve the problems.

1.8 Structure of the Thesis

Chapter One: General Introduction

This chapter presentthe abstract, background of the study, statement of the problem, objectives, scope of the study, limitations, significance, and structure of the dissertation.

Chapter Two: Literature review

This chapter mainly reviews about characteristics of heavy metals including their Source, distribution, and various factors affecting the distribution of heavy metals in the environment. The toxic effects of heavy metals in freshwater ecosystems such as effects on Fish and on humans were reviewed in this chapter. Reviews of ecological and human risk assessment associated with heavy metal exposure were also included in this chapter. Finally, the water quality parameters (physical, chemical, and biological) and Phytochemical treatment for coagulation and disinfection were reviewed in this chapter.

Chapter Three: Heavy Metal Levels in Omo River and Delta and Associated Human Health Risk in Southern Ethiopia.

This chapter presents pollution levels of heavy metals from the Lower Omo River and Delta Lake water, health risk due to ingestion and dermal exposure to heavy metals and Suitability of the water bodies for drinking and irrigation purposes.

This paper has been publication in the journal of Applied Sciences $ Environmental Management (JASEM) as Pollution Level of Heavy Metals and Risk Implications from the Lower Omo River: East African Fresh Water in the Semiarid Region of Southern Ethiopia

Chapter Four: Levels of Heavy Metal in Fish of Omo River and Omo Delta in Southern Ethiopia and Associated Human Health Risk

This chapter includes level of heavy metals from the freshwater fish species namely *L. niloticus and O. niloticus* from Lower Omo River and Delta. The liver and muscle tissues of the two fish species was analyzed for nine heavy metals. The health risk assessment of heavy metals via consumption of fish muscle was also addressed in this chapter. In this chapter two papers have been published.

The first paper has been published in the in the journal of Environ Health Insights (Sage) as ‘Level of Heavy Metals in Fish and Associated Human Health Risk from the Omo Delta in Southern Ethiopia: A First-Hand Report. *EnvironmentalHealth Insights*. 18: 1–11. doi: 10.1177/11786302241238180’and the second paper has been published in the in the journal of PeerJ as ‘Heavy metal levels and human health risk implications associated with fish consumption from the lower Omo river (Lotic) and Omo delta lake (Lentic), Ethiopia: DOI 10.7717/peerj.17216.

Chapter Five: Heavy metals concentrations in surface sediments of Lower Omo River and Omo Delta in Southern Ethiopia and associated Ecological risk assessment

This chapter deals with the pollution levels of nine heavy metals from the surface sediment of Lower Omo River and Omo Delta. The chapter also presents ecological risk of the heavy metals from the sediments of both water bodies. This paper is under review in the Journal of Environmental health insights (Sage)

Chapter Six: Assessment of heavy metal levels of irrigated soil in the vicinity lower Omo River and ecological risk

This chapter deals with the pollution level of soil with nine heavy metals which was being irrigated from lower Omo River and the associated ecological risk.

Chapter Seven: Evaluating Water Quality of Lower Omo River and the Delta Lake, Southern Ethiopia.

This chapter includes about 22 water quality factors and evaluates the water quality using WQI. This paper has been published in the journal of Applied Science & Environmental Management (JASEM)as 'Evaluating Water Quality of Lower Omo River and the Ethiopian part of Lake Turkana, Southern Ethiopia. *J. Appl. Sci. Environ. Manage.* 28 (1) 187-194. https://www.ajol.info/index.php/jasem https://www.bioline.org.br/ja*''*

Chapter Eight: General Conclusion and Recommendation

This chapter deals with the comprehensive conclusion and recommendation of each chapter in this dissertation.

1.9 Materials and methods

1.9.1 Description of the study area

The Omo-Turkana Basin extends over a sizable area in southwestern Ethiopia and Northern Kenya (Feibel, 2011; Velpuri *et al*., 2012). The 760 km long river flows south before reaching Lake Turkana in the lowlands at an altitude of 365 meters (CSA, 2017, Wakjira and Getahun, 2017). It passes through Omorate town, where domestic, municipal, and industrial waste from the town and its vicinities, including agrochemicals, flows into the river. It drains south from Ethiopia's wet highlands to arid lowlands terminating in the Omo delta on Lake Turkana, where its lower portion is found in the eastern arm of the East African Great Rift Valley. The samples of the present were collected between June and September 2022 for the study area described below.

Table 1.1 Geographic coordinates of the sites in the Lower Omo River and Delta Lake.

The samples were collected between June and September 2022 for the study

Sites	River Coordinates	Delta Coordinates
1	4°47'50.42"N 36° 1'39.35"E	4°27'42.60"N 36°3'14.42"E
2	4°47'58.93"N36° 1'47.64"E	4°27'44.34"N 36° 3'52.53"E
3	4°48'9.96"N 36° 1'58.54"E	4°28'27.88"N 36° 4'40.73"E
4	4°48'6.72"N36° 2'10.00"E	4°28'59.88"N 36° 5'20.88"E
5	4°47'54.23"N36° 2'6.47"E	4°29'30.61"N 36° 6'35.87"E
6	4°47'39.92"N 36° 2'10.28"E	4°30'43.60"N 36° 6'13.60"E
7	4°47'34.76"N 36° 2'21.82"E	4°30'46.21"N 36°7'16.45"E
8	4°47'39.03"N 36° 2'34.90"E	4°30'30.30"N 36° 7'59.41"E
9	4°47'46.56"N36° 2'43.05"E	4°30'8.11"N 36° 8'43.33"E
10	4°47'58.71"N36° 2'49.75"E	4°30'0.29"N 36° 9'53.50"E
11	4°48'13.85"N 36° 2'52.73"E	4°29'8.49"N 36° 8'50.77"E
12	4°48'27.16"N 36° 2'52.48"E	4°28'25.92"N 36° 8'48.33"E
13	4°48'42.03"N 36° 2'54.62"E	4°27'47.30"N 36° 9'40.06"E
14	4°48'58.74"N 36° 3'2.92"E	4°27'33.41"N 36° 8'1.15"E
15	4°49'17.44"N36° 3'5.48"E	4°27'54.98"N36° 6'50.51"E

The Lower Omo River (Lotic) is located in southern Ethiopia, is one of the countries' most important river systems , covering an area of approximately 79,000 km^2 (CSA, 2017). It starts at an altitude of 2,200 m above sea level (a.s.l) and flows through the Eastern Arm of the Great Rift Valley of East Africa before finally ending in Lake Turkana at an altitude of 365 m (a.s.l.) (Wakjira and Getahun, 2017).The water and sediment samples were taken from fifteen(15) sampling sites of the River as presented in figure 1.1. The fish samples were taken from the five sampling sites of the River which were commonly used sites for fish trapping by local fishermen as presented in figure 1.2.

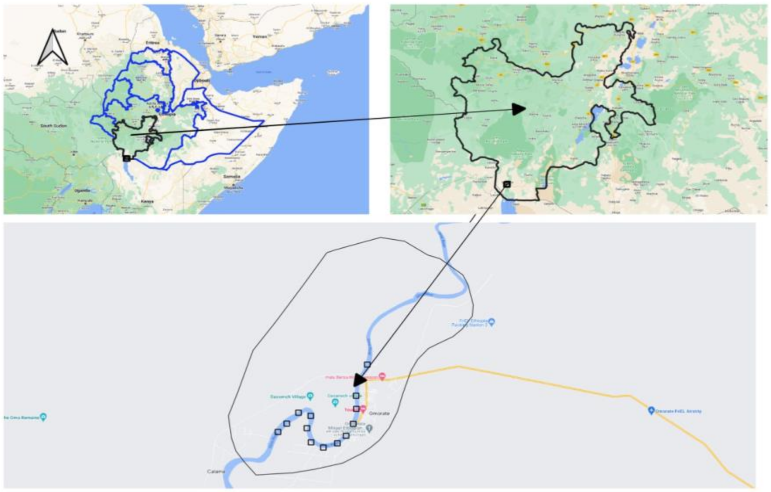

Figure 1.1Map of the study site in the Lower Omo River (water, fish and sediment samples)

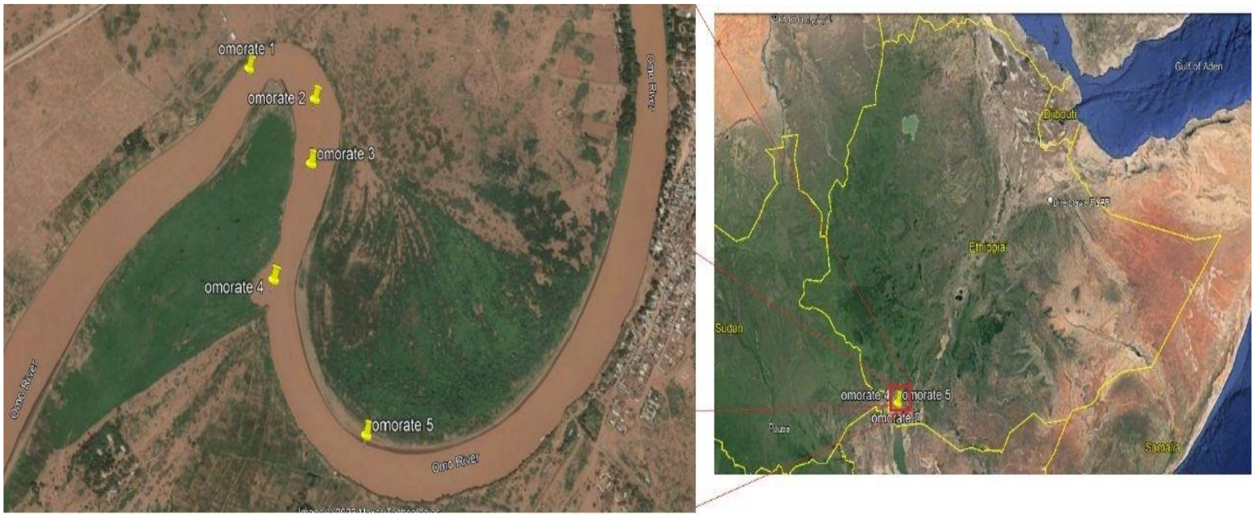

Figure 1.2 Map of the study site for fish sampling from the Lower Omo River

The Omo Delta (Lentic), situated in the Eastern Arm of the Great Rift Valley, is approximately 50 kilometers from Omorate Town in the downstream direction (Figure 1.2). It forms a Bird’s Foot

Delta with an area of 98 km^2(Wakjira and Getahun, 2017) and lies across the Ethiopia-Kenya border in southern Ethiopia lowlands. The Omo Delta starts at an altitude of 2,200 meters above sea level (a.s.l) and flows in its lower portion (Omo Delta) at an altitude that ends Lake Turkana (Wakjira and Getahun, 2017).The Omo Delta is almost 820 km South of Addis Ababa, the capital city, and 508km from the regional city of Hawassa. The water, fish and sediment samples were taken from the same point of fifteen sampling sites as presented in figure 1.3.

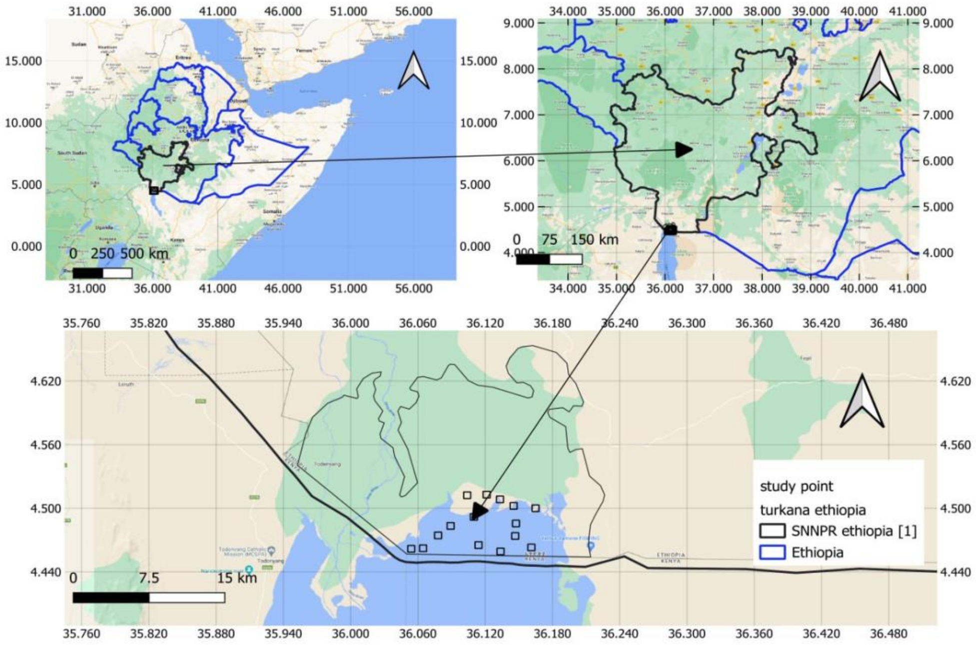

Figure 1.3 Map of the study site in the Delta Lake (water, fish, and sediment samples)

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CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Freshwater is a limited resource that is necessary for industry, agriculture, and the survival of human and animal life. It is essential to the creation of freshwater flows locally, the global water cycle, and the robustness and health of other ecosystems (Stephen *et al*., 2011; Matthews, 2022; Teshome, 2020). A portion of the aquatic ecosystems on Earth are known as freshwater ecosystems. They consist of marshes, rivers, streams, and springs, as well as lakes and ponds. They can be compared to marine habitats, which often contain more than 1% salt. Lakes, reservoirs, and rivers that are surface freshwaters are among of the planet's most heavily modified ecosystems **(**Stephen *et al*., 2011).

Special classes of naturally occurring elements known as heavy metals are non-biodegradable and have a lengthy half-life in the environment. If they surpass a certain threshold, they could have detrimental effects on one's health (Kanamarlapudi *et al*. 2018). Pollution of the fresh water ecosystem with these heavy metals is a worldwide problem because of their environmental persistence, bioaccumulation, and biomagnifications in food chains and toxicity of these elements to plants, animals, and human health (Kok *et al*., 2015; Mensoor & Said, 2018)**.** According to various studies done on lakes and rivers, they have become common pollutants that have detrimental effects on the ecosystem and human health (Arantes *et al*., 2016; Ali *et al*., 2019). They are considered as critical contaminants of aquatic ecosystems due to their ability being deposited in suspended particulate matter and sediments that can be a long-term source of contamination and high bioaccumulation potential in food chains (Luo *et al*., 2010; Beyene, 2014).

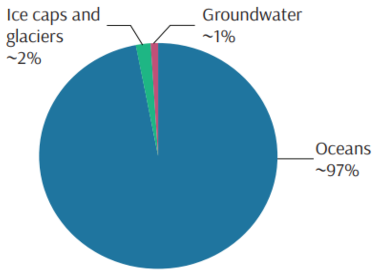
2.2 Freshwater ecosystems and their characteristics

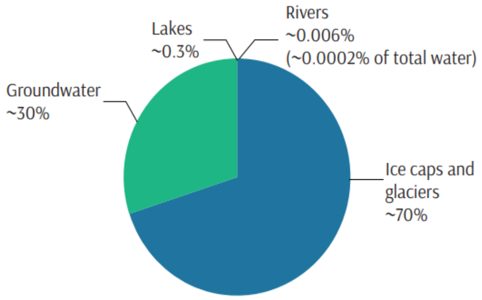
A biological habitat made up of both biotic and abiotic elements is called an ecosystem (Stephen, 2011). Terrestrial ecosystems are categorized as either aquatic or land-based (Matthews, 2015). Aquatic habitats are divided into freshwater and marine water types according to the quality of the water involved (Wrona & Reist, 2013; Matthews, 2015). Lakes, ponds, rivers, streams, and wetlands are examples of freshwater ecosystems (Stephen R *et al*., 2011). They can be compared to marine habitats, which often contain more than 1% salt. According to Stephen *et al*. (2011), surface freshwater ecosystems like lakes, reservoirs, and rivers are some of the most drastically changed places on the planet.

There are two types of water ecosystems: lotic ecosystems commonly referred to as riverine habitats, and lentic ecosystems, sometimes known as lacustrine ecosystems or still water ecosystems. The differences in water residence time and flow velocity distinguish the two categories of freshwater habitats known as lentic and lotic ecosystems. In lotic ecosystems, the average duration of water residency is two weeks, whereas in lentic ecosystems, it is 10 years (Huang *et al.*, 2020). All flowing bodies of water, such as rivers, springs, and streams, are considered to be part of the lotic ecosystems (Vincent & Laybourn, 2008; Salim *et al*., 2009; Koki *et al.,* 2015). The habitat of aquatic organisms is actively controlled by nearly all Physico-chemicalparameters, including temperature, light, pH, dissolved gases, dissolved salts in water, turbidity, alkalinity, depth, and areal distribution.

Fresh water accounts for around 3% of the total water on the earth's surface (salinity < 0.5 parts per thousand). However, only 0.01% of this is available, with two-thirds of the earth's surface covered by water. Only a small percentage of the 3% of global fresh water is available as a habitat for living species on Earth's surface (Koki *et al*., 2015). The majority of the Earth's freshwater is frozen in polar ice caps and glaciers (about 70%) or buried beneath as groundwater (30%). Lakes and rivers account for only approximately 0.3% of all fresh water. Rivers (including streams) account for only 0.0002% of global water volume. Overall, available freshwater ecosystems cover around 0.8% of the Earth's surface(Hitt *et al*., 2015). Global composition and availability of fresh water is presented in Figures 1 and 2.

Regrettably, even this small portion of fresh water is under pressure due to anthropogenic sources and rapid growth in population and industrial activities (FAO, 2011; Enaam, 2013; Yong, *et al*., 2017). Freshwater ecosystems are home to approximately 126,000 species. Apart from being an important home for biodiversity; these aquatic ecosystems provide supporting livelihoods and wellbeing of billions of people (Matthew, 2016; UN, 2017; Jiang *et al*., 2017; Gokce, 2019). Fish are a key constituent of the fresh water ecosystems. Contamination in natural fresh water ecosystems is often too low to cause mortality but sufficient to interfere with normal functioning. Alteration of complex, naturally occurring fish behaviors such as foraging and aggression are ecologically relevant indicators of toxicity and ideal for assessing sub lethal impacts (Magellan *et al.,* 2014).





Figurre 2.1A. Global composition of fresh water   Figure 1B. Global availability of fresh water (Hitt *et al.*, 2015)

2.2.1 Physical characteristics of freshwater ecosystem

Table 2.1. Physical characteristics of River ecosystem (Hitt *et al.,* 2015)

River ecosystem (Lotic)	**Lake ecosystem (Lentic)**
▪ The current velocity in running waters depends on gradient and substrates, with the wind having minimal influence. ▪ Downstream movement is primarily determined by drainage basin characteristics, with stream patterns determining soil erosion hazards**.**	▪ Lake stratification occurs due to density differences from heating, affecting water mixing and circulation patterns. ▪ Strong winds cause uniform temperature ▪ Temperature differences cause stratification into epilimnion, hypolimnion, and thermocline. ▪ Water movement is strongly influenced by wind patterns and temperature.
▪ **Light penetration in running waters is influenced by turbidity, particle scattering, and water absorption.**	▪ The growth depth of rooted Macrophytes and attached algae on suitable substrates is largely determined by the spectral composition and intensity of light there.

2.2.2. **Chemical characteristics freshwater ecosystems**

Table 2.2 Chemical characteristics of River (Lotic) and Lake Ecosystem (Hitt *et al*., 2015)

River ecosystem (Lotic)	Lake ecosystem (Lentic)
○ Oxygen is the most abundant and important dissolved gas in running waters, with high concentrations due to turbulence and mixing. Low concentrations indicate organic pollution. Oxygen content is scarce due to constant water turbulence and air contact. ○ The amount of oxygen present is related to the current, the water temperature, and the presence of respiring plants and animals. ○ The carbon dioxide content of the running water tends to be scarce due to the constant turbulence of water and its frequent contact with air.	○ The oxygen content of a lake is influenced by air contact, water circulation, and oxygen production and consumption. ○ It varies due to thermal stratification, primary production and respiration equilibrium, lake productivity, and bottom sediment anoxia. ○ pH management is influenced by free carbon dioxide, and consistent values are maintained across well-mixed waters.

○ River dissolved solids content varies from source to mouth, with rainfall impacting the amount. Substratum rocks and soil characteristics influence solids content(Maitland, 1990)	○ Lake stratification and water intake influence dissolved solids, while phytoplankton and nutrients' depletion can affect algal composition and output, influenced by the catchment area and water intake.

2.2.3. Biological characteristics freshwater ecosystems

Table 2.3 Biological characteristics of Rivers (Lotic) and Lake ecosystems (Hitt *et al.*, 2015)

River ecosystem (Lotic environments)	Lake ecosystem (Lentic environments)
○ The current is more pronounced at the surface than in the bottom substrate. Hence, the bottom substrate conditions are similar to lentic habitats. ○ In riffles and pools, the plankton exhibits the characteristics similar to lentic ecosystem. ○ The fishes are highly adopted to resist water currents. Since the dissolved oxygen levels are high throughout the water column due to water turbulence, the fishes are distributed from surface to bottom substrate and often among the rocks (Moss, 1998).	○ The nutritional condition of the water has a significant impact on the species composition of communities of all those kinds. ○ Benthic habitat is connected to the lake's substrate, whereas pelagic habitat is found in open water distant from the impact of the shore or bottom substrate. ○ The phytoplankton and zooplankton communities of plankton live in areas with high light intensity, which are the littoral zone and the pelagic zone's surface layer. ○ A portion of the zooplankton also lives in the benthic zone, where they eat debris.

2.3 Freshwater ecosystems and potential pollutants (source and distribution)

2.3.1 Sources of heavy metal pollution in freshwater ecosystem (Point and non point source)

Freshwater ecosystem encounters many threats from point and non-point pollution sources (Tsegaye and Tadele, 2018). Yohannes and Elias (2017) on their study have also reported that river and water reservoirs quality can be affected by pollution from point and non-point sources. According to Naggar *et al.* (2018), Point sources are identifiable locations (such as a factory, often with a pipe or channel leading from them) that discharge directly into a body of surface water.

Non-point or diffuse sources on the other hand are those where pollution arises over a wide area and it is often difficult to locate the exact place of origin and also difficult to manage and control (Naggar *et al.* (2018). These may include fertilizer or pesticide that has been widely spread may be washed from a field by rain into a river or stream at many places, or seep into groundwater; urban and industrial runoff and erosion associated with construction; mining (Loague & Corwin, 2006**).** Runoff is generally associated with non point source pollution, as water is emptied into streams or rivers after accumulating contaminants from different points (USEPA, 2020).

According to Sorsa *et al.* (2016), higher concentrations of Cu, Zn, Cr and Ni were detected at the Dore Baffena site from Lake Hawassa as the result of non-point source of pollution, especially surface run-off, from nearby agricultural fields that use fertilizers and pesticides. Agricultural fertilizer and biocides (pesticides, herbicides, preservatives) are known to contain Cd, Hg, Pb, Al, As, Cr, Cu, Mn, Ni and Zn and it is likely that these metals get introduced in to the aquatic environment (Biney *et al*. 1994) via surface run off. The study by Yirgu (2011) in Lake Hawassa with Cu concentrations of 0.005 mg/L and 0.003 mg/L at Dorie and Tikur Wuha sites respectively, and 0.003 mg/L of Pb at Tikur Wuha site. The higher concentration of the Cu at Dorie site could be the contribution of the non-point sources of pollutions, especially from agricultural fields that might be used copper containing fertilizer and pesticides.

A. Natural source of heavy metals

Sources of heavy metals in the environment can be natural or geogenic (Peters *et al.,* 2019**)**. Russi *et al. (*2013) noted that the natural or geological sources of heavy metals in the environment include weathering of metal-bearing rocks and volcanic eruptions. Heavy metals are natural constituents of rocks and soils and enter the environment as a consequence of weathering and erosion (Khalil and Ghorab, 2018). The main natural sources of metals in waters include chemical weathering of minerals and soil leaching (Bouraie *et al*., 2010; Baby *et al*., 2011; Naggar *et al*., 2018). Metals also occur in small amounts naturally and may enter into aquatic system through leaching of rocks, airborne dust, forest fires and vegetation (Ogoyi *et al*., 2011).The finding by Cullen and Maldonado (2013) showed that the weathering of rocks releases cadmium to soils and aquatic systems. This process plays a significant role in the global cadmium cycle, but only rarely results in elevated concentrations in any environmental compartment (UNEP, 2010).

B. Anthropogenic source of heavy metals

Anthropogenic sources include industry, agriculture, mining, and domestic effluents. Environmental contamination and human exposure of heavy metals often emanate from anthropogenic sources such industrial, agricultural runoff, domestic, mining, urbanization can increase the metal concentrations in the environment to higher than background levels *(*Naggar *et al.,* 2018; Gokce, 2019). Different studies have indicated in their study that aquatic ecosystems are contaminated by heavy metals from different sources including effluents from mining operations**,** different industrial effluents, domestic sewage, and agricultural run-off, are a major source of pollution of surface water (Russi *et al*., 2013; Afzal *et al.*,2018).

C. Industrial sources

Industrial effluent can give rise to higher concentrations of the metals relative to the normal background values (*Beyene, 2014)*. According to Sorsa *et al*. (2015), the major problem associated with textile processing effluents is presence of heavy metal ions, which arise from material used in the dyeing process or in a considerably high amount, from metal containing dye. The finding in this study from Hawassa textile factory showed that four heavy metals (Cu; 0.52 and 0.47 mg/L , Mn; 0.42 mg/L and 0.19 mg/L , Zn; 0.372 and 0.103 mg/L), and Cr; 0.093 mg/L and 0.076 mg/L) were detected in effluent of the factory at two different sites namely, site one which was 500m far from the Biological Lagoons and site two which was at downstream, about 1.5 km away from site one respectively. Thus textile factories are considered as one of the major sources from industrial activities. Zinabu and Pearce (2003) studied concentrations of heavy metals and related trace elements in some Ethiopian rift valley Lakes and their inflows and indicated in their study finding that the textile effluent, Ceramic effluent and soft drink factory contains different heavy metals in the textile effluent in their way to Lake.

A study byTian *et al*. (2013) has reported that combustion of fossil fuels in industries, homes, and transportation is an anthropogenic source of heavy metals. Vehicle traffic is among the major anthropogenic sources of heavy metals such as Cr, Zn, Cd, and Pb. Thus, metals discharged from industrial effluents, and sewage runoff by rapid urbanization is of concern as contaminants of freshwater ecosystem from anthropogenic sources **(**Yonglong *et al*., 2017). According to Tsegaye and Tadele (2018), a higher levels of Zn (17.4 mg/L), (8.77 mg/L) and (7.50 mg/L) at different points were recorded due to storm water draining from vehicle oil, grease and lubricants spill on roads, vehicle repairing and washing areas into the Lake during rainfall.

Ogoyi *et al*. (2011) studied determination of heavy metal content in water, sediment and microalgae from Lake Victoria, East Africa. The pollution sources to the Lake Victoria included a number of industries such as shipping, mining, breweries, tanning, and agro-processing factories. Yeshiwas (2017) has reported in his study thatwaste water from the industries of mining, electroplating, paint or chemical laboratories often contains high concentrations of heavy metals, including cadmium (Cd), copper (Cu) and lead (Pb). Metals are constantly released in aquatic systems from anthropic sources such as, electronic waste, anthropic accidents; navigation traffic

(Gheorghe *et al*., 2016). As stated byFisseha (2003), the Ethiopian metal tools factory is the major source of pollution of rivers which is used to irrigate part of vegetable farms. In addition to that the author reported that waste from garage and gas station discharged into rivers. This had impact on concentration of heavy metals such as Cu, Zn, Pb, Cd and Cr were exceeding the maximum limits recommended by FAO/WHO in the vegetables produced by irrigating these contaminated rivers *(*Yeshiwas, 2017).

Salim *et al*. (2019) reported that Sources of As and Cr contamination are predominately associated with anthropogenic activities arising from disposal of industrial wastes, sewage discharge and combustion of fuels. Tilahun (2018) has also indicated in his report that the wide spread industrial production of perfumes, batteries, oils and fats, cement-making, quarrying (especially limestone), and brick-making, sewage effluents, high ways or motor boat traffic, mine and smelting operations, consider main sources of lead in the environment.

D. Agricultral source of heavy metals

Pesticides and chemical fertilizers contain varying amounts of heavy metals, depending on their source. As indicated by Nagajyoti (2010) commercial inorganic fertilizers, particularly phosphate fertilizers can potentially contribute to the global transport of heavy metals**.** Heavy metals added to agricultural soils through inorganic fertilizers may leach into water bodies andcontaminate it (Ali *et al*., 2019). Since commercial chemical fertilizers are usually not purified enough during the manufacturing processes, they usually contain heavy metals as impurities (Chandrajith, 2009). Much of the phosphate fertilizers in the world are commercially produced from phosphate rocks that contain the mineral apatite [Ca_5(PO4)3OH,F,Cl]. Due to their geological and mineralogical nature, phosphate rocks contain different environmentally hazardous elements including Cr, Cd, Pb, Hg, (Atafar *et al*., 2010). A high correlation has been reported between concentrations of metals such as Cr, Ni, Cd, Pb and content of phosphate in fertilizers (Grant and Sheppar, 2009).

Wang *et al.* (2017) noted that application of chemical fertilizers leads to increase in the concentrations of potentially toxic heavy metals in agricultural soilsandthen enter the freshwater ecosystem The addition of toxic heavy metals from long-term application of phosphate fertilizers to agricultural soils and their subsequent transfer to the aquatic ecosystem and human food chain is a matter of great concern with respect to human health, especially in case of low-quality phosphate fertilizers containing elevated levels of heavy metals (Ukpabi *et al.,* 2012). Anthropogenic increasesin Cd concentrations are also caused by excessive application of chemical fertilizers (Wang *et al*., 2017). According to the study in the aquatic ecosystems of Egypt byNaggar *et al*.(2018)**,** As, Cd, Cu, Hg and Zn are five metals with most potential impact that enter the environment in elevated concentrations as a consequence of agricultural activity. In their study Salim *et al*. (2019) also indicated that Sources of As and Cr contamination are predominately associated with anthropogenic activities arising from the applications of fertilizers and pesticide.

2.3.2. Factors affecting distribution of heavy metals (HMs) in freshwater ecosystems

Metals are partitioned among the various aquatic environmental compartments (water, suspended solids, sediments and biota) and can occur in dissolved, particulates or complex form (Islam *et al.,*2018**)**. Once introduced into the aquatic environment, metals are redistributed through the water column, accumulated in sediments or consumed by biota. Naggar *et al*. (2018**)** indicated that heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota, which generally exist in low levels in water and attain considerable concentration in sediments and biota (Ali *et al.,* 2019**).**Once discharged into the environment, the behavior and fate of polluting substances will be determined by the combined effects of different variables such as the compound's physico chemical properties, river hydrologyand hydrochemistry (Kucuksezgin *et al*., 2008; Islam *et al*., 2018; Islam and Ahmed, 2018).

Due to desorption and remobilization process of metals, the sediments constitute a long-term source of contamination to the food chain (Gheorghe *et al*., 2016). The distribution of metals within sediments and their surrounding water is dynamic. Sediment solids can hold up more metal than an equivalent volume of water (Ermias *et al*., 2015). Hence, sediments as a sensitive reference to monitor pollutants in the environment can provide extensive information on changes in aquatic and watershed ecology (Liang *et al*., 2015)**.** The study by Sorsa *et al*. (2015) noted in their finding that higher distribution of heavy metals were found in sediments than in water of lake. According to this study finding, Cd and Pb were detected in sediment samples but not in waste water and Macrophytes samples. The distribution of heavy metal in the samples collected and analyzed generally followed the order: sediment > wastewater. Haile *et al*.(2015) studied analysis of selected metals in edible fish and bottom sediment from Lake Hawassa and found that the distribution of metals in sediment samples were higher than those of fish samples.

Heavy metals may enter the body of an organism directly from the abiotic environment, i.e., water, sediments, and soil or may enter the organism body from its food/prey. For example, heavy metals may enter the fish body directly from water or sediments through the fish gills/skin or from the fish food/prey through its alimentary canal. The concentration of a heavy metal may increase or decrease along successive trophic levels in a food chain (Jiang *et al*., 2017). The retention of heavy metals in the body of an organism depends on many factors such as the speciation of the metal concerned and the physiological mechanisms developed by the organism for the regulation, homeostasis, and detoxification of the heavy metal. Methylated forms of heavy metals such as Hg are accumulated in biota to a greater extent and therefore biomagnified in food chains due to their (Yong. *et al*., 2017). Different heavy metals have different half lives in different species (Naggar *et al*., 2018**).**

According to Nigussie *et al*. (2010), the correlation among metals in *Oreochromis niloticus*, sediment and water samples of Lakes Hawassa and Ziway revealed that the distribution of the eight metals in the bile, intestine, scale, spleen and sediment varied and most of the elements in water samples occurred at lower level relative to the sediment. Rajeshkumar and Li (2018) studied the distribution of the heavy metals Cr, Cu, Cd, and Pb in various tissues of freshwater fish during summer and winter seasons were significantly different. Accordingly, the distributions of Pb, Cu and Cr in *C. carpio* during summer and winter were in the order gill > kidney> intestine > liver > muscle, while the concentration of Cd indicated the sequence of kidney > gill > muscle > liver > intestine during summer and kidney > gill > intestine > liver > muscle during winter seasons (Rajeshkumar and Li, 2018).Sorsa *et al.* (2016) studied the relationships between concentrations of five heavy metals and body size in the two *L. intermedius* morphotypes from Lake Hawassa. Accordingly, the highest concentrations of heavy metals were detected in large-sized fish than in medium and small-sized fish. Thus, the result of the finding in general indicated that distribution of heavy metals in fish varied according to differences in fish spices and size.

A. Factors affecting distribution of heavy metals in freshwater

Heavy metals are of high environmental significance since they are not removed from water as a result of self-purification, but accumulate in reservoirs and enter the food chain (Rajaei *et al.*, 2012; Sun . *et al.,* 2013). Water reservoirs are collectors of all materials spread by human activities. HMs penetrates into water resrviors via atmosphere, drainage, soil waters and soil erosion (Sun. *et al.,* 2013). Bouraie *et al.* (2010) noted that given heavy metals, concentrations were higher during winter closure period, which is due to smaller amounts of discharging water and the elements adsorb and precipitate on the sediment particles resulting from low pH values and microbial activity. Nábělkováa and Komínková (2006) conducted a study on the distribution of heavy metals in freshwater ecosystem of a small Stream impacted by urban drainage in which their concentrations in water can be increased during occasional events (heavy rain especially), but because of strong ability of heavy metals to bind into solid phase (sediment, suspended solids) it is only for a short period of time (Nwani *et al.*, 2009). Concentrations of HMs in sediment of this study decreased because of washing out of sediment or remobilization of pollutants *(Mensoor and Said, 2018; Naggar et al., 2018).*

Kucuksezgin *et al*. (2008) studied the distribution of heavy metals in water, particulate matter and sediments of Gediz River (Eastern Aegean) and reported that the water quality parameters such as dissolved oxygen,p_H, temperature, BOD_5, COD and particle matter clearly influence the distribution of pollutants and affect their fate in the aquatic system. The pH values were measured as 5.8–8.3 in the sampling stations. The lowest p_H values were found during winter period due to rainfall and the river water was well oxygenated in the winter period. The COD values were generally higher in summer and fall in periods due to less rainfall than winter and spring (Kucuksezgin *et al*.,2008; Rajeshkumar and Li, 2018).

Nwani *et al*. (2009) had reported that rain water infiltrates the soil and underlying geologic formations, dissolve metals causing them to seep into aquifers and finally to the river and lakes thus increasing their concentration. The fall in p_H during the rainy season may have also resulted to higher concentrations of these metals during the rainy season as solubility of the metals increase with increasing acidity (Ochieng *et al.,* 2007; Roberto *et al.,* 2008; Naggar *et al*., 2018). This indicates that when p_H falls, metals solubility increases and the metals particles become more mobile.

B. Factors affecting Distribution of Heavy Metals in Sediments

Contamination of sediments with heavy metals is an environmentally important issue with consequences for aquatic life and human health (Bouraie *et al.,* 2010). Sediment poses one of the worst environmental problems in ecosystems, acting as sinks and sources of contaminants in aquatic systems (Njogu *et al.,* 2011; Mensoor and Said, 2018. Contaminants are not necessarily fixed permanently by the sediments, and under changing environmental conditions, they may be released to the water column by various processes of remobilization (Naggar *et al.*, 2018). Thus, in aquatic systems, sediments may be both a carrier and possible source of pollutants **(**Zahra *et al.,* 2014; Naggar *et al.*, 2018)**.** The adsorption, and subsequent concentrations of heavy metals in sediments are affected by many physicochemical factors such as temperature, hydrodynamic conditions, redox state, content of organic matter and microbes, salinity, and particle size (Mansouri *et al*.,2012; Zahra *et al.,* 2014).

According to Azadi *et al.* (2018), distribution of heavy metals in sediments is affected by chemical composition of the sediments, grain size, and content of total organic matter (TOM). An important determinant of metal bioavailability in sediments is p_H. A lowering in pH increases the competition between metal ions and H^+ for binding sites in sediments and may result in dissolution of metal complexes, thereby releasing free metal ions into the water column (Nowrouzi *et al.,* 2014**)**. Generally the element mobilization in the sediment environment is dependent on physicochemical changes in the water at the sediment–water interface; the precipitation of heavy metal elements in the form of insoluble hydroxides, oxides and carbonates (Bouraie *et al.* , 2010; Alloway,2013; Decena *et al.*,2018).

According toHuang *et al.* (2020)study report**,** Sediment samples presented to be more polluted than soil samples, possibly due to long time sedimentation, fewer disturbances compared to the soil as well as plant uptakes. Sequential extraction analyses show that each metal prefers different geochemical fraction for binding in sediment (Decena *et al.*, 2018). Copper binds mostly into organic matter, zinc into carbonates and lead prefers residual fraction. Zinc has the highest tendency to release from sediment to water, because it is bound in the second most available fraction (Nábělkováa and Komínková, 2006**).** On the contrary, lead was the least available and leachable, because it bound the most firmly in residual fraction. Remobilization of copper from sediment to water can be dependent on the amount of organic matter in sediment. The highest values of Kd were measured in sampling site where the highest amount of organic matter in sediment was determined which proves the fact that the presence of organic matter in sediment is important for binding of heavy metals (Decena *et al.*, 2018; Huang *et al.*, 2020).

A study by Bouraie *et al.* (2010) has indicated that the highest concentrations of most of the elements were observed during winter closure period (in low flow conditions). This phenomenon may be attributed to the increase in organic matter concentrations which facilitate settling of Fe to the sediment during hot seasons and the low element concentrations may be attributed to the mobilization of Fe from sediment to water (Bao *et al.*, 2015). Many heavy metals concentrations in sediment, especially in the fine-grained sediment, which acts as a transport agent in the water column, are at least three orders of magnitude higher than the same metals in surrounding water (Bouraie *et al.*, 2010; Decena *et al*., 2018).

C. Factors affecting distribution of heavy metals in Fish

The aquatic organism takes heavy metals through the body surface, gills and food (Rajeshkumar and Xiaoyu, 2018). A study byRajeshkumar and Xiaoyu (2018) have also addressed the two main ways by which heavy metals enter the aquatic food chain are by direct consumption of water and food through the digestive tract and non-dietary routes across permeable membranes such as the muscle and gills. Man, at the end of food chain suffers from the results of an enrichment having taken place at each trophic level, where less is excreted than ingested (Baby *et al*., 2010). Therefore levels in fish usually reflect levels found in sediment and water of the particular aquatic environment from which they are sourced (Nhiwatiwa *et al*., 2011; Annabi *et al*., 2013)**.** Fish have the ability to accumulate heavy metals in their tissues by absorption along gill surface, liver, kidney, and gut tract wall to higher levels than environmental concentration (Zakaria *et al*, 2016). Differences in accumulation of heavy metals by organisms could be as a result of differences in assimilation, egestion or both (Egila *et al*., 2011). Fish are relatively situated at the top of the aquatic food chain; therefore, they normally can accumulate heavy metals from food, water and sediments (Zhao s *et al*., 2012).

Mensoor and Said (2018) on their study have reported that the accumulation of heavy metals in fresh water fish depends on many factors. These factors can be either environmental (water chemistry, salinity, temperature, bioavailability of metals in the water column, metal types, and levels of contamination) and biological or fish characteristics including species, size, age, gender, sexual maturity, body physiology, and feeding habits (Ali *et al*., 2019). Water chemistry directly affects the accumulation of heavy metal in fish (Georgieva *et al*., 2014)**.** Sediment is also know to be an important factor of heavy metal accumulation in fish, as it is considered as the major source of contaminants for bottom dwelling and bottom feeding aquatic organisms (Annabi *et al*., 2013). Ecological needs, sex, size, seasonal changes and moult of aquatic animals were also found to affect metal accumulation in their tissues (Yılmaz *et al*., 2010; Georgieva *et al*., 2014).

When comparing the accumulation of heavy metals in fishes of both marine and freshwater biomes, it can be observed that freshwater fishes tend to accumulate heavy metals in their organs more than marine fishes (Baby *et al.,* 2010). The reason for such a difference between the two biomes is that freshwater fishes tend to lose salts and gain water. On the other hand, marine fishes tend to gain salts and lose water. Consequently, freshwater fishes are more exposed and vulnerable to heavy metal pollution (Nikinmaa, 2014; Donati, 2018).

The comparatively higher heavy metal accumulation in metabolically active tissues of fish such as liver and gills is generally explained by the induction/occurrence of metal binding proteins called metallothioneins (MTs**)** in the tissues upon exposure to heavy metals (Rahman *et al.*,2012). The liver is often used as a reference for analysis of tissue damage caused by environmental toxic compounds (Arantes *et al.,* 2016**;** Mensoor and Said, 2018).Fish gills have been found as the target tissue for accumulation and elimination of heavy metals. Although fish muscles are the tissue of poor heavy metal accumulation, they are important from the view point of consumption by humans (Kumar *et al.,* 2010; Mensoor and Said, 2018). Different studies revealed that the bioaccumulation of heavy metals in the gills and livers of fishes are higher than the concentrations of heavy metals in the muscles of fish (Mohammadi M *et al.,* 2011; Olsson *et al.,* 2013; Mensoor and Said, 2018). This is partly because the gill is naturally endowed with physiological and anatomical properties which must have maximized the absorption efficiency of the heavy metals from the aqueous phase (Eneji etal., 2011; Fafioye *et al.,* 2017). *Various studies also* addressed that gill is the organ that accumulates the highest concentration of metals since it is a metabolically active part, being a dominant site of gas exchange and muscle does not act as an active tissue in the accumulation of metals (Eneji *et al*., 2011; Adefemi *et al*., 2014; Olusola and Festus, 2015).It was also reported that cadmium accumulates in tissues of carp Cyprinus carpio in following order: kidney> Liver> Gills (Kumar *et al.,* 2005; Okocha and Adedeji, 2011). Generally, metabolically active tissues such as gills, liver, and kidneys have higher accumulations of heavy metals than other tissues such as skin and muscles (Rajeshkumar and Xiaoyu *et al*., 2018).

A number of studies (Yu *et al*., 2012; Jayaprakash *et al*., 2015) showed that the bioaccumulation of heavy metal in fish muscle is significantly correlated with fish species. The variation in the level of heavy metals among different species depends upon its feeding habit, age, size and length of the fish and their habitats (Rajeshkumar *et al*., 2018). As it has been reported by Arantes *et al*. (2016), Concentrations of Hg and Cd increased in accordance to fish size, whilst no significant concentration and size relationship was found for other metals, indicating that accumulation of Pb, Zn, and Cr in is not necessarily related to age. The muscles exhibited high levels of Hg contamination, and the Hg levels were also positively correlated to body weight, confirming the theory of bioaccumulation from continuous exposure to the metal (Seixas *et al.*, 2012).The levels of heavy metal in fish also vary with respect to different aquatic environments (Mensoor and Said, 2018). Bioaccumulation was prone to be strongest in carnivorous species (*P. fluvidraco*), followed by omnivorous (*C. carpio*) species, and it tended to be stronger in bottom-living fish than that in pelagic fish (Peters *et al.*, 2019). A fish that is a specific feeder will concentrate high levels of heavy metals than a fish that has a generalized feeding habit (Mbuthia, 2015).

Rajeshkumar and Xiaoyu *et al.* (2018)determined the level of Cd, Cr, Cu and Pb bioaccumulation in kidney, liver, gill, intestine and muscle of *C. carpio* and *P. fluvidraco* during summer and winter seasons. The periodic difference of heavy metals concentration from the fish farm revealed the following order, summer > autumn >winter > spring. The seasonal variation of metals in the fish species might be due to physicochemical and biotic factors of the lake, which influences the bioavailability of heavy metals (Afshan *et al*., 2013; Rosso *et al*., 2013). Moreover, the affinity for metal absorption from contaminated water and food may be different in relation to ecological needs, metabolism and the contamination gradients of water, food and sediment, salinity, temperature and interacting agents (Ebenezer *et al.*, 2015; Fafioye *et al.*, 2017).

2.4 Toxic effects of heavy metals in freshwater ecosystem

Toxicity refers to the property of a chemical to affect survival, growth, and reproduction of an organism (Zakaria *et al*., 2016). The exposure to some heavy metals has been associated with adverse health effects (Arantes *al.*, 2016). Some essential metals can damage human health at relatively high exposure levels, and nonessential metals are toxic at even very low concentrations (Debelius *et al.*, 2011; Yared Beyene, 2014).Certain heavy metals have been reported to be carcinogenic, mutagenic, and/or teratogenic to different species depending on dose and duration of exposure (Yang *et al*., 2020). According to Huang *et al*. (2020), heavy metals, even at low concentrations, have increasingly caused health concerns due to their hazardous bioaccumulation ability through the food chains. Most of these non-degradable toxic elements, such as Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Nickel (Ni), Lead (Pb), and Zinc (Zn), are listed as priority pollutants to be controlled by the EPA (Chen *et al*., 2015).

Tilahun (2018) indicated in his study that metal toxicity varies between organisms as the rate of uptake of metals affect the toxicity of the metal itself. The toxicity of metals is often explained on the basis of their ability to cause the generation of oxygen and nitrogen based reactants (Ali *et al*., 2019). Iron, chromium, aluminum, copper, vanadium and cobalt (Co) undergo redox cycling reactions thereby permitting massive free radical production (Tilahun, 2018). Mercury, Cadmium and Nickel have the ability to deplete the important endogenous antioxidant glutathione, and also to bind to sulfhydryl groups on proteins (Debelius *et al*., 2011; Ali *et al*., 2019). According to Ahmed *et al*. (2013), heavy metals are extremely toxic to aquatic organisms even at very low concentrations. These elements can cause significant histopathological alterations in tissues of aquatic organisms such as fish (Debelius *et al*., 2011).

Ali *et al.* (2019) reported that bioaccumulation of toxic heavy metals in biota of the riverine ecosystems may have adverse effects on animals and humans. Higher levels of heavy metals in biota can have negative effects on the ecological health of aquatic animal species and may contribute to declines in their populations (Malik and Maurya, 2014**).** Accumulation of potentially toxic heavy metals in biota causes a potential health threat to their consumers including humans (Luo *et al*., 2014). Oluyemi &Olabanji (2011)on their study have reported that heavy metal contamination may devastate impacts on the ecological balance of natural water bodies including the loss of aquatic diversity. Baby *et al*. (2010) indicated that ecosystem contamination from heavy metal pollution may damage aquatic organisms at the cellular level and possibly affect the ecological balance**.** Cadmium (Cd) has been considered as one of the factors likely responsible for the decline in populations of freshwater mussels due to its high toxicity, bioaccumulation potential, and transfer through food chains (Oluyemi &Olabanji, 2011; Ahmed *et al*.,2013). Heavy metals affect all groups of organisms and ecosystem processes, including microbialactivities (Naggar *et al*.,2018; Ali *et al*., 2020).The main threats to human well-being are associated with lead, arsenic, cadmium and mercury which are being targeted by international legislative bodies (Baby *et al*.,2010).

Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans (Baby *et al*., 2010).It has been shownby Ali and Khan

(2018) that growing human foods in heavy metal contaminated media lead to bioaccumulation of these elements in the human food chains from where these elements ultimately reach the human body. Ingestion of heavy metals through food and drinking water is a major exposure source for human(Baby *et al*., 2010).

2.4.1 Effects of heavy metals on water quality

Water quality is determined by its biological and physicochemical characteristics. Water can become unfit for human consumption due to changes in characteristics including pH, temperature, and essential and non-essential trace metal concentrations (Ternes *et al*.., 2015). Water degradation can occur as a result of dissolved harmful heavy metals, rendering the water unsuitable for human consumption. Water quality is heavily influenced by physicochemical parameters such as pH, temperature, conductivity, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), minerals, hardness, chloride ion, nitrates, fluoride ion, and heavy metal concentration (Bisimwa *et al*., 2022). Oluyemi &Olabanji (2011)on their study have reported that heavy metal contamination may devastate impacts on the ecological balance of natural water bodies including the loss of aquatic diversity.

2.4.2 Toxic effects of heavy metals (HMS) on fish and other biota

The accumulation of HMs in the tissues causes significant biochemical, physiological, and histological changes in fish and other freshwater fauna (Rascio *et al*., 2015). They can affect the individual growth rates, physiological functions, mortality and reproduction in fish (Afshan *et al*., 2013). Ali *et al*. (2019) noted that fishes are suitable indicators of heavy metal contamination and are extensively used to evaluate the health of aquatic ecosystem since they are of different sizes and occupy different tropic levels. Metals in the aquatic environment accumulate in the food chain and lead to ecological damage as well as human health risks after eating such aquatic organism

(Mensoor & Said, 2018). It has been observed that both humans as well as animals are contaminated by heavy metals. They are poisoning us and animals from environmental pollution of water, and foods.

Datta *et al*.(2019) noted that the accumulation of metals such as arsenic affects a variety of physiological systems, including fish growth, reproduction, immune function, and enzyme activity. As significantly accumulated in specific organs, e.g., gill, liver, and intestine, and manipulated growth toxicity to fish (Liao *et al*. 2004; Tsai and Liao 2006; Kumari *et al*., 2018).Okocha and Adedeji (2011)had shown that in aquatic systems, cadmium is most readily absorbed by organisms directly from the water in its free ionic form Cd (II). Cadmium interacts with the calcium metabolism of animals. In fish it causes lack of calcium (hypocalcaemia), probably by inhibiting calcium uptake from the water (Niyogi *et al*., 2008). Effects of long-term exposure to Cd include larval mortality and temporary reduction in growth (Okocha and Adedeji, 2011).

In addition, some metals may decrease the plasticity of cardio respiratory responses, reducing the survival chance of the fish under hypoxic conditions, which has been frequently observed in their wild habitats (Vitek *et al*., 2007; Barletta *et al*., 2012; Monteiro *et al*., 2013). Heavy metals can also cause the mutuation of fish inner organs, disturb immune reactions, change blood parameters, and reduce an organism’s adaptation qualities, vitality, and resistance to diseases (Ngo *et al*., 2011; Mensoor and Said, 2018). Increased concentration of chromium exposure has been shown to affect both survival and growth rate of fish significantly (Farag *et al.*, 2006 Azmat *et al*., 2011). It has been reported that lower concentration of chromium at different pH values (0.2 mg/L at pH 6.5 and 2.0 mg/L at pH 7.8) induces mortality of embryo and mild problem in hatching (Muthulingam *et al*., 2017). Hyperactivity and erratic swimming of freshwater fish have been found to be the most phenomenons while exposed to chromium contaminated environment (Ahmed *et al*., 2013; Dhara *et al*., 2014; Bakish *et al*., 2016).

Kumari *et al*.(2018) indicated that exposure with heavy metals caused various abnormal behaviors in fish such as erratic movement, rapid movement of the opercula, jumping out of the test media, lateral swimming, and loss of equilibrium . The abnormal behaviors were caused by neurotoxin effects and by the irritation to the sensory system. Jumping and back and forth movements indicate avoidance reactions of the fish to As (Kumar and Benerjee 2012). Lateral swimming and loss of equilibrium may be due to the impairment of the nervous system (Akter *et al.,* 2008; Mosammat *et al*., 2008; Baldissarelli *et al.,* 2012).Davodpour *et al*. (2019) also noted that cadmium affected foraging behavior, resulting in lower success at catching prey. Peters *et al*. (2019)revealed thatLong term exposure to heavy metals like Mn can result in negative effects such as reduced breeding potential of adult fish and high mortality of fish species *(*Ebrahimi and Taherianfard, 2011).

Heavy metal pollution of freshwater ecosystems is toxic to animals, and human health (Kok *et al*., 2015; Arantes *et al*., 2016; Mensoor & Said, 2018; Ali *et al*., 2019).The major consequences are habitat degradation, water pollution, and the resultant deterioration of the aquatic ecosystem (Baye, 2016). Thus, the progressive and irreversible accumulation of heavy metals in various organs of creatures leads to metal related diseases in the long run because of their toxicity, thereby endangering the aquatic biota and other organisms including human being (Baby *et al*., 2010). According to Ahmed *et al*. (2013), heavy metals are extremely toxic to aquatic organisms even at very low concentrations. These elements can cause significant histopathological alterations in tissues of aquatic organisms (Debelius *et al*., 2011).

Ali *et al.* (2019) has also reported that bioaccumulation of toxic heavy metals in biota of the riverine ecosystems may have adverse effects on animals and humans. Higher levels of heavy metals in biota can have negative effects on the ecological health of aquatic animal species and may contribute to declines in their populations (Malik and Maurya, 2014**).** Accumulation of potentially toxic heavy metals in biota causes a potential health threat to their consumers including humans (Luo *et al*., 2014). Baby *et al.* (2010) indicated that ecosystem contamination from heavy metal pollution may damage aquatic organisms at the cellular level and possibly affect the ecological balance**.**Cd has been considered as one of the factors likely responsible for the decline in populations of freshwater mussels due to its high toxicity, bioaccumulation potential, and transfer through food chains (Ahmed *et al*., 2013;Oluyemi&Olabanji, 2011).Heavy metals affect all groups of organisms and ecosystem processes, including microbialactivities (Baby *et al*.,2011; Naggar *et al*.,2018; Ali *et al*., 2020).

2.4.3 Toxic effects of heavy metals on Humans

Humans may be exposed to toxic heavy metals through different food items such as fish, cereals and vegetables as they are omnivorous (Eqani *et al*., 2016). They are exposed to toxic heavy metals in the environment through different routes including ingestion, inhalation, and dermal absorption (Mensoor & Said, 2018**).** In humans, heavy metal accumulation has hazardous effects on the brain, liver, kidneys, lungs, and muscles(Dwivedi *et al*., 2015; Petera and Viraraghavanb, 2015; Afrin *et al*., 2016). Ali *et al*.(2019)showed that Contamination of the human food chains with toxic heavy metals poses a threat to human health. Certain examples from the twentieth century have shown that such contamination is serious human health issue. Minamata disease (MD) and itai-itai disease both in Japan were caused by consumption of Hg-contaminated fish and Cd-contaminated rice, respectively (Ali *et al.*, 2019).

Vrankovic *et al*. (2018) indicated that the heavy metals Cd, Pb, Hg, and As deplete the major antioxidants of cells, particularly antioxidants and enzymes having the thiol group (—SH) (Salman *et al*., 2011; Arantes *et al*., 2014).Such metals may increase the generation of reactive oxygen species (ROS) like hydroxyl radical ($HO^{\cdot}$), superoxide radical ($O2^{\cdot -}$), and hydrogen peroxide (H_2O_2**).** Increased generation of ROS can devastate the inherent antioxidant defenses of cells and lead to a condition called “oxidative stress’’ (Ercal *et al*., 2001; *Baby et al., 2010*). Heavy metals, including Cd, Pb, and Hg, are nephrotoxic; especially in the renal cortex (Wilk *et al*., 2017). Mercury toxicity largely depends on Hg speciation (Ebrahimpour *et al*., 2010).

Some of the heavy metals such as Cadmium and chromium due to their toxicity effects accumulate in some vital organs especially in the kidney and liver causing human cancer (Sobhanardakani & Kianpour, 2016; Vrankovic *et al*., 2018). Lead**(**Pb) and Cadmium (Cd) are also classified among the most toxic heavy metals which have no known biochemical benefits to animals and humans (Akoto *et al*., 2014: Mahmoud and Abdel, 2015). Cadmium is an environmental contaminant unique among metals because of its diverse toxic effects, extremely protracted biological half-life, low rate of excretion from the body and predominant storage in soft tissue (Mahmoud and Abdel-Mohsein, 2015). Malakootian *et al*.(2016)on their study have reported that contamination of fish by toxic heavy metals is considered as a risk for human health and has raised concerns about their consumption especially in more sensitive groups of human population such as women, children, and people at risk of diseases from other causes (Ali *et al*., 2019). Several adverse effects of heavy metals to human health include serious threats like renal failure, liver damage, cardiovascular diseases and even death (Rajeshkumar and Xiaoyu, 2018; Vrankovic *et al*., 2018).Human exposure to some of the heavy metals and associated health impacts are presented below.

Table 2.4 Human health effects of some heavy metals

Heavy metals	Human health Effects
Mn	Damage of lung, liver , and kidneys (Shekhawat *et al*., 2015)
Zn	Gastrointestinal disorders,Kidney &Liver abnormal functioning(Abolfazl and Maryam, 2012).
Cu	Abdominal disorders,metabolic activity abnormalities (Pretto *et al*., 2011)
Cr	Lung disorders (bronchitis, cancer), disorder in renal and reproductive system (Sanyal *et al*., 2017; Guo *et al*.**,**2020)
Cd	Osteo related problems,prostate cancer,lung cancer,renal dysfunction (Stuart *et al*., 2010;Tilahun, 2018)
Pb	Serious effect on mental health (Alzheimer s disesase) and nervous system,seizure, coma and death (Baby *et al*., 2010; Abolfazl and Maryam, 2012; ATSDR, 2020).
Ni	Allergies, bronchitis, and lung cancers (Witkowska *et al*., 2021)
Fe	Diarrhea, abdominal pain,dehydration & lethargy (Burden, 2016)
Co	irritate the skin, eyes, nose and throat(Pretto *et al*., 2011)

2.5 Risk of heavy metals to the environment

2.5.1 Ecological Risk

2.5.1.1 . Assessment of environmental risk of heavy metals from water

Heavy metals are the most dangerous contaminants because of their persistence, biomagnifications, and environmental toxicity (*Saleem et al., 2019*). Their accumulation in water resources can pose threats to human health and ecological security (*Kumar et al., 2017*).

A. Estimation of environmental risks using the risk index factor (RI)

The risk index factor (RI) resulting from the ingestion of heavy metals from water is used to estimate potential environmental risk. A risk index factor related to the presence of toxic heavy metals in water was proposed by Hakanson and calculated according to Hakanson (1980).

$$RI = \frac{Ti \times OC}{NOEC}$$

Where RI is the risk index factor; Ti is the toxicity coefficient of the metal; OC is the mean concentration of the metal; and NOEC is the maximum allowable concentration. The toxicity coefficients of the metals were 5 for Pb= Ni=Cu=Co, 1 for Zn =Mn, 10 for Fe, and 2 for Cr (Hakanson, 1980, Collins *et al*., 2019).

B. Comprehensive risk index (CRI) of water

The comprehensive risk index (CRI), which is the summation of the risk index factor (RI), was calculated according to the following equation (Hakanson, 1980).

$CRI = \sum RI$, where RI is the risk index factor for each metal

Table 2.5 Environmental risk of toxic metals in water using the risk index factor (Hakanson, 1980).

Range of Risk index Factor (Ri)	**Potential environmental danger**
$RI < 1$	No potential environmental danger
$1 \leq RI < 40$	Low possible environmental danger
$40 \leq RI < 80$	Modest possible environmental danger
$80 \leq RI < 160$	Considerable possible environmental danger
$160 \leq RI < 320$	Severe possible environmental danger
$RI \geq 320$	Very severe potential environmental danger

Table 2.6 Environmental risk classification by using comprehensive risk factors (Hakanson, 1980).

Range of comprehensive risk factor	Classification
$CRI < 60$	Low
$60 \leq CRI < 120$	Moderate
$120 \leq CRI < 240$	High
$CRI \geq 240$	Very High

2.5.1.2. Assessment of ecological risk of heavy Metals in sediments and soil

A. **Contamination factor (CF) and contamination degree (CD)**

Contamination Factor (CF) and Contamination Degree (CD) are primary indicators of metal pollution status of the subjected sediment. Contamination Degree is the summation of all CF values (Acharjee *et al*., 2022).

$$CF = \frac{\text{Cm (sample)}}{\text{Cm (background)}}$$

Where, the C_{sample} and $C_{background}$ are the measured and background concentration respectively. The background concentration are presented in Table (WHO,2017). The Contamination factors are graded into four classes as: CF< 1, low contamination load ; 1 <CF< 3, moderate contamination ; 3<CF< 6, considerable contamination; and CF> 6, very high contamination.

$$CD = \sum CF$$

Table 2.7 Description of contamination factor (CF) and contamination degree (CD)

Contamination Factor Ranges	Description	Contamination Degree	Description
CF< 1	low contamination	CD<8	Low degree of Contamination
1 <CF< 3	moderate contamination	8< CD<16	Moderate degree of Contamination
3<CF< 6	considerable contamination	16 < CD <32	Considerable degree of contamination
CF> 6	very high contamination	CD>32	Very high degree of Contamination

B. Pollution load index (PLI)

The PLI was used for evaluating mutual contamination effects of the eight heavy metals in the sediments of the present study and calculated as follow.

$$PLI = [CF_{Mn} \times CF_{Zn} \times CF_{Cr} \times CF_{Ni} \times CF_{Pb} \times CF_{Fe} \times CF_{Co} \times CF_{Cu}]^{1/n}$$

where CF denotes the contamination factor, and n is the considered number of metals. There are three discrete categories for pollution measurement with this index. Pollution status is indicative of no pollution when the PLI values are 0 ; the baseline degree of pollution when the PLI values are equal or less than 1; and the third category (when PLI is greater than 1) designates Progressive decline in terms of pollution of the sites (Acharjee *et al.*, 2022)

C.Potential ecological risk index from sediment or soil (RI)

This was formulated by Hakanson (1980) to quantify the level of ecological risk of heavy metals in sediment. The RI assesses the combined ecological and environmental toxicity to provide an overall evaluation of the potential risk of heavy metal pollution which is calculated as follow:

$$EI = T_i \times CF$$

$$RI = \sum EI$$

Where, EI is the individual potential risk, and Ti is the toxicity effect coefficient, with Values for Mn, Zn, Cu, Cr, Pb, Ni, Fe , and Co are 1, 1, 5, 2, 5, 5,1,and 5 (Tegn *et al.*, 2014).

2.5.2. Human health risk

2.5.2.1 Human health risk assessment from heavy metals in water

The human risk of contamination by heavy metals can increase due to direct ingestion and dermal absorption through the skin. The common exposure pathways to water that are used for determining human health risk include dermal absorption and ingestion (Rofhiwa *et al.*, 2021).The health risks for the heavy metals from water through oral ingestion and dermal absorption were estimated according United States Environmental Protection Agency (USEPA) risk assessment guideline (USEPA, 2004).To assess non cancer and cancer risks for humans (children and adults), the chronic daily intake (CDI) of HMs, which represents the lifetime average daily dose (LADD) of exposure to a contaminantwas used (USEPA, 2004; Bamuwuwamye *et al*., 2017). The CDI of the HMs in water via oral ingestion and dermal absorption was calculated by using the following equation (Govind *et al*., 20222; Ugwu *et al*., 2022):

$$\text{CDI}_{\text{ingestion}} = {}^{(\text{C x IR x EF x ED})}\big/_{(\text{BW x AT})}$$

$$\text{CDI}_{\text{dermal}} = {}^{(\text{C x EF x ED} \times \text{ET} \times \text{SA} \times \text{KP} \times \text{CF})}\big/_{(\text{BW x AT})}$$

Where: CDI is the chronic daily intake (mg/kg/day); C is mean concentration of heavy metal in the water (mg/L); IR is the ingestion rate per day (1 L/day for a child and 2.2 L/day for adult) (Bamuwuwamye *et al*., 2017; Ugwu *et al*., 2022); ED is the exposure duration (6 years for a child and 30 years for an adult) (WHO, 2015; Ahmad *et al*., 2023); EF is the exposure frequency (365 days/year);*ET* is exposure time (0.58 h/day for adults; 1 h/day for children (UNEPA, 2004); BW is average body weight (15 kg for a child and 60 kg for adult) (WHO, 2012) over the exposure period; *AT* is the average time representing the period over which exposure is averaged [(for carcinogens, AT=60×365=21900 days for both children and adults in Ethiopia; for non-carcinogens, AT=ED×365 which equals 2190 days and 10950 days for children and adults, respectively) (USEPA, 1989; USEPA, 2004)];SA is exposed skin area available for contact (18000 cm^2 for adults; 6600 cm^2 for children) (USEPA, 2004); KP is dermal permeability coefficient of heavy metal in water (cm/h)[Pb (0.004), Ni (0.001), Co (0.001), Cu (0.001), Zn (0.006), Mn (0.001), Fe (0.001), and Cr (0.001)] (UNEPA, 2004); CF is unit conversion factor (0.001L/cm3) (UNEPA, 2004; Bamuwuwamye *et al*., 2017; Govind *et al*., 20222).

A. Noncarcinogenic risk assessment (HQ and HI)

The noncancer risks of HMs in water were determined by using the hazard quotient (HQ) and hazard index (HI) according to equation 2. The hazard index (*HI*) is the overall potential for noncarcinogenic effects posed by multiple pollutants via ingestion or dermal pathways.

HQ Ingestion $= {}^{CDI\ ingestion}/_{RfD\ ingestion}$

HQ dermal $= {}^{CDI\ dermal}/_{RfD\ dermal}$

$HI = \sum HQ$

Where*HI* represents the overall potential for noncarcinogenic effects posed by more than one pollutant via ingestion or dermal pathway; HQ is the noncancer hazard quotient; CDI is the chronic daily intake (mg metal/kg/day); and RfD represents the chronic oral reference dose which is probably without a significant risk of harmful effects throughout life (Bamuwamye *et al*., 2015).The oral reference doses ($RfD_{ingestion}$) of Pb, Ni, Co, Cu, Zn, Mn, Fe, and Cr are 0.0035, 0.02,0.03, 0.04, 0.3 , 0.014 , 0.7, and 0.003 mg/kg/day (USEPA, 2004; USEPA, 2005; USEPA, 2016).The dermal reference doses (RfD_{dermal}) of Pb, Ni, Cu, Zn, Co, Mn, Fe, and Cr are 0.000525, 0.0054, 0.012, 0.06, 0.016, 0.00005, 0.14 and 0.000075 (USEPA, 2002; USEPA, 2005; USEPA, 1995; Akaninyen *et al*., 2022) mg/kg/day, respectively. The potential risk to human health posed by exposure to multiple HMs was measured by the hazard index (HI), which is the sum of all HQs calculated for each heavy metal. A value of HQ or HI < 1 indicates no significant no cancer risk; a value > 1 indicates significant no cancer risk, which increases with increasing HQ or HI (Govind *et al*., 20222; Ugwu *et al*., 2022).

B. Carcinogenic risk assessments (CR)

Cancer risk was calculated as the quotient ofthe CDI (mg/kg/day) and cancer slope factor (CSF) measured in mg/kg/day)$^{-1}$.In the present study, the *CR* was assessed for elements that are considered to be toxic to humans, Cr, Pb, and Ni. The carcinogenic risk (*CR*) associated with the ingestion pathway can be estimated using the following formula:

$\mathrm{CR}_{\text{ingestion}} = \mathrm{CDI}_{\text{ingestion}} \times \mathrm{CSF}_{\text{ingestion}}$

$\mathrm{CR}_{\text{dermal}} = \mathrm{CDI}_{\text{dermal}} \times \mathrm{CSF}_{\text{derma}}$

where $\mathrm{CR}_{\text{ingestion}}$ = carcinogenic risk (*CR*) associated with ingestion; CDI = chronic intake (mg/kg/BW/day); and $CSF_{ingestion}$ = the oral carcinogenic slope factor (mg/kg/day), which is 0.0085 for Pb, 0.5 for Cr and 1.7 for Ni.The total cancer risk as a result of exposure to multiple contaminants due to consumption of a particular type of water was assumed to be the sum of each metal cancer risk (∑CR). The United States Environmental Protection Agency (USEPA) suggested that a$CR < 10^{-6}$ indicates no carcinogenic risk to human health; a $CR > 1 \times 10^{-4}$ indicates a high risk of developing cancer; and a risk ranging from 1×10^{-6} to 1×10^{-4} represents an acceptable risk to human health (USEPA, 1989)

2.5.2.2. Human health risk assessments from heavy metals in fish muscle

A. Nocarcinogenic risks

. This is done by calculating target hazard quotient (THQ) and hazard index, which help to determine the likely hood of non-carcinogenic health hazards in humans. The THQ result assess the risk posed by a single heavy metals ,while HI results calculate the cumulative risk from all heavy metals found in fish muscle. Values of THQ and HI < 1 indicate that the risk of health effects is low, while values greater than 1.0 suggest that potential noncarcinogenic health hazards are likely to occur individuals who consumed fish muscle. The greater the THQ value is, the greater the possibility of risk to the exposed individuals (USEPA, 2011).The noncarcinogenic risk was assessed for both adults and children who ingested fish muscle from the lower Omo River and Omo Delta ,one to seven days per week. The THQ and HI were estimated using EPA guidelines(USEPA, 2011, USEPA, 2019)using equations below.

$$\mathrm{THQ} = \frac{(EF\times \mathrm{ED}\times \mathrm{IR}\times \mathrm{Cm})}{(\mathrm{RfD}\times \mathrm{WAB}\times \mathrm{AT})}10^{-3}$$

$$HI = \sum \mathrm{THQ}$$

Where: THQ is a non-carcinogenic health risk; the average life expectancy in Ethiopia is 65 years for adults and 6 years for children .ED is the exposure duration (USEPA, 2005, WHO, 2015);EF is the exposure frequency which is 365 days/year for people who eat fish muscle 7 times a week and 52 days/year for those who eat once a week (FAO, 2014), and IR is the average fish ingestion rate of an individual in a day (g/day/person) which is 30g for adults and 15g for children in Ethiopia (USDA, 2000, USEPA, 2005).The RfD is the oral reference dose which is the daily ingestion of a contaminant that is unlikely to cause health effects during a life time as defined by the USEPA (2003) in mg kg^{-1}/day which is 0.001for Cd, 0.003 (Cr) , and 0.03; 0.040 (Cu), 0.7, 0.020 (Ni), 0.14 (Mn), 0.0035 (Pb) and 0.30 (Zn);BW is the average body weight equivalent to 60 kg for adults and 21kg for children in Ethiopians (WHO, 2012);AT is the average exposure time for non-carcinogens which is 365 days/year x ED;Cm is the average concentration of heavy metals in fish muscles (mg/kg dry weight);WAB is the average body weight .

B.Carcinogenic risk (TCR)

The target carcinogenic risks (TCR) test estimates an individual’s possibility of developing cancer over a lifetime while exposed to a potential carcinogen and the acceptable risk levels for carcinogens range from 10^{-4} to 10^{-6} ‘(USEPA, 1989).The TCR was estimated using equation below.

$$\text{TCR} = \frac{(EF \times \text{ED} \times \text{Cm} \times \text{IR} \times \text{CSFO}) \times 10 - 3}{(\text{WB} \times \text{AT})}$$

where: TCR is the target cancer risk; CPSO is an oral carcinogenic slope factor in mg/kg/day with values include1.7 mg kg^{-1}/day for Ni, and 0.5 (Cr), 0.001(Cd) and 0.0085 for Pb(USEPA, 2010).

2.6. Physicochemical water quality parameters and evaluation of water quality using WQI

Water quality is characterized on the basis of water quality parameters (physical, chemical, and microbiological), and human health is at risk if values exceed the acceptable limits (Ruth *et al.*, 2021). Initially, WQI was developed by Horton (1965) in United States by selecting 10 most commonly used water quality variables like dissolved oxygen (DO), pH, coliforms, specific conductance, alkalinity and chloride etc. and has been widely applied and accepted in European, African and Asian countries (shweta *et al.*, 2013; Douglas *et al.*, 2015). The three main water quality factors are physical, chemical, and biological.

2.6.1 Some physical water quality parameters

Physical factors of water quality are measurable features of water that relate to its physical properties (Patil *et al.*, 2015). These factors provide essential insights on the physical state and condition of water, which can have a significant impact on its overall quality and utility .The Physical water quality factors include: electrical conductivity, salinity, total dissolved solids, turbidity, temperature, color, particle size (solids), depth, topography, geology, bathymetry, taste and odor and some of them are presented below (Stephen *et al*., 2011).

A. Temperature

Water temperature needs to be monitored regularly as outside tolerable temperature range, disease and stress will become more prevalent. Among the consequences of temperature changes are; photosynthetic activity, diffusion rate or gases, amount of oxygen that can be dissolved etc (Spellman, 2017). The importance of temperature in water quality is derived mainly from its relationship with other water quality parameters (Pathak *et al*.; 2015). Warm water holds less dissolved oxygen than cool water and may not contain enough dissolved oxygen for the survival of different species of aquatic life (Patil *et al*., 2015). Factors affecting water temperature include; air temperature, amount of shade, Soil erosion increasing turbidity, thermal pollution from human activities, unknown chemical reactions those were not previously occurring in the water. Effects of water temperature include: Solubility of dissolved oxygen; more gas can be dissolved in cold water than warm (Vijay S, 2016).

B. Turbidity

Turbidity is a measure of the cloudiness of water. Cloudiness is caused by suspended solids (mainly soil particles) and plankton (microscopic plants and animals) that are suspended in the water column (Patil *et al*., 2015).Higher turbidity levels are often associated with higher levels of viruses, parasites and some bacteria because they can sometimes attach themselves to the dirt in the water. Turbid water usually has more pathogens, so drinking it increases our chances of becoming sick. Turbidity blocks out the light needed by submerged aquatic vegetation. It also can raise surface water temperatures above normal because suspended particles near the surface facilitate the absorption of heat from sunlight (Patil *et al*., 2015).Nephelometers measure the intensity of light scattered by the suspended particles. The WHO Guideline for turbidity in drinking water is less than 5 NTU. The turbidity in excess of 5 NTU may be noticeable and consequently objectionable to the consumers (Adimasu, 2015).

C.Color

Water color is a good visual indicator of its quality. Natural elements such as dissolved organic matter and human activities such as industrial discharges or pollution can both have an impact(Tomar, 1999). Unusual or severe changes in water colour can indicate the presence of toxins or pollutants (APHA, 2017).

D. Electrical conductivity

Electrical conductivity assesses water's ability to conduct an electric current. It delivers information about the concentration of dissolved salts, minerals, and other compounds. It is an important measure for evaluating water quality since it might indicate the presence of pollutants or changes in salinity levels (Navneet Kumar *et al.,* 2010).

E.Total dissolved solids (TDS)

The total dissolved solids (TDS) are the combined concentration of inorganic and organic compounds dissolved in water. It contains minerals, salts, metals, and other dissolved particles. High TDS levels can alter the taste and usefulness of water for drinking, irrigation, and industrial applications (Adjovu *et al*., 2023).

F. Total suspended solids (TDS)

The concentration of total dissolved solids in water is the sum of positively charged cations and negatively charged anions. As a result, the total dissolved solids test offers a qualitative assessment of the concentration of dissolved ions (Colburn *et al*., 2016). TDS in drinking water originates from natural sources, sewage, urban runoff, industrial effluent, and chemicals used in the water treatment process (Boyd, 2015). A TDS of less than 50 mg/L should raise concerns about a potential corrosion problem; a TDS of more than 250 mg/L should raise concerns about hardness, iron, manganese, alkalinity, chloride, sulfate, nitrate, and general salt content; and a TDS of more than 500 mg/L should raise concerns about other salts. A total dissolved solids concentration of more than 1000 mg/L should raise concerns about the possibility of a man-made direct or salty water effect on the source (Omer, 2019).

Table 2.8 Classification of total dissolved solids

freshwater	0 to 1000 mg/L
Slightly Saline	1000 to 3000 mg/L
Moderately Saline	3000 to 10,000 mg/L
Very Saline	10,000 to 35,000 mg/L
Briny	> 35,000 mg/L

(Source, Lehr,J. *et al.*, 1980) "Domestic Water Treatment, New York, NY: McGraw-Hill Book Company.)

2.6.2 Some chemical water quality parameters

Chemical parameters of water quality are measurements of the different chemical components found in water. These indicate the chemical composition of water, including the presence of natural and anthropogenic pollutants. Monitoring and evaluating these factors helps in determining the appropriateness of water for various uses and identifying potential threats to human health and the environment. The chemical water parameters include pH, acidity, alkalinity, hardness, chlorine, and dissolved oxygen and some of them are presented below.

A. Heavy metals:

Heavy metals are naturally occurring elements with a high atomic weight and at least five times the density of water (Fergusson, 1990). Their numerous industrial, residential, and agricultural applications have resulted in widespread distribution in the environment, raising concerns about their possible impact on human health and the environment (Bradl *et al*., 2002). Their toxicity is determined by a variety of parameters, including the dose, route of exposure, chemical species, as well as the age, gender, genetics, and nutritional state of those exposed (Duffus *et al*., 2002).

B. pH

P_H is a measure of the relative amount of free hydrogen and hydroxyl ions in the water. Water that has more free hydrogen ions is acidic, whereas water that has more free hydroxyl ions is basic. Since pH can be affected by chemicals in the water, p_H is an important indicator of water that is changing chemically (Patil *et al*.2015). The p_H of water determines the solubility (amount that can be dissolved in the water) and biological availability (amount that can be utilized by aquatic life) of chemical constituents such as nutrients (phosphorus, nitrogen and carbon) and heavy metals (lead, copper, cadmium etc.) In case of heavy metals, the degree to which they are soluble determines their toxicity. Metals tend to be more toxic at lower p_H because they are more soluble **(**Okey *et al*., 2021). The pH was positively correlated with electrical conductance and total alkalinity (Patil *et al*.,2015). Very high pH (greater than 9.5) or very low pH (lower than 4.5) values are unsuitable for most aquatic organisms. Aquatic organisms are extremely sensitive to p_H levels below 5 and may die at these low pH values. High pH levels (9-14) can harm fish due to the fact that ammonia will turn to toxic ammonia at high pH (>9) (Manoj & Avinash, 2012).The pH for drinking water generally lies between 6.5 and 8.0 at 25°C (80° F). For effective disinfection with chlorine, the p_H should preferably be less than 8. The optimum range for chlorine disinfection is between p_H 5.5 and 7.5 **(**Okey *et al*., 2021**).**

C.Dissolved oxygen (DO)

The dissolved oxygen (DO) describes the concentration of oxygen molecule in the water and it depends on the temperature of the water and the biological demand of the system. The quantity of oxygen that the water can hold depends on the temperature, salinity and pressure of the water. Gas solubility increases with decreasing salinity. Fresh water holds more oxygen than saltwater (Otene and Alfred-Ockiya, 2019). Levels of dissolved oxygen vary depending on factors including water temperature, time of day, season, depth, altitude, and rate of flow. Water at higher temperatures and altitudes will have less dissolved oxygen. Dissolved oxygen reaches its peak during the day. At night, it decreases as photosynthesis has stopped (WHO, 2008).

Rapidly moving water, such as in a mountain stream or large river, tends to contain a lot of dissolved oxygen, whereas stagnant water contains less. Aquatic life can have a hard time in stagnant water that has a lot of rotting, organic material in it, especially in summer. Conditions may become especially serious during a period of hot, calm weather, resulting in the loss of many fish. Human factors that affect dissolved oxygen in streams include addition of oxygen consuming organic wastes such as sewage, addition of nutrients changing the flow of water, raising the water temperature and the addition of chemicals (Rao *et al*., 2013).Cooler water has a greater capacity to dissolve oxygen than warmer water **(**Patil *et al*., 2015**).** Human activities such as removal of shade or the release of warm water used in industrial processes can cause an increase in water temperature, resulting in lower dissolved oxygen capacity (Araoye , 2009).

D. Nutrients

Nitrogen and phosphorus are essential nutrients for plant growth. However, excessive nutrient levels, which are frequently caused by human activities such as agriculture or wastewater discharge, can result in Eutrophication. This process can result in toxic algal blooms, oxygen deprivation, and changes in the balance of aquatic ecosystems.

E. Water hardness

Water hardness is the mineral content of water. If water is considered hard, calcium or magnesium is most likely the cause. Groundwater is naturally harder than surface water because it is more exposed to minerals and ions (Rosborg & Kozisek, 2015). Ca2+ and Mg2+ are common cations found in hard water, and they enter water sources through leaching from minerals in aquifers (Otieno *et al*., 2012). Calcium-containing minerals include calcite and gypsum. Dolomite is common magnesium mineral (it also includes calcium). Rainwater and distilled water are soft because they contain very few of these ions (Mons *et al*., 2007).

F. Alkalinity

Alkalinity is significant when monitoring water quality since it dictates how much soda ash is required to neutralize the water. Water becomes alkaline when bicarbonate, hydroxide, and carbonate ions dissolve in it (Peters, 2980). Water with a very high alkalinity level suggests pollution. In general, water is alkaline due to the existence of a weak acid and a strong base, resulting in salt, often in the form of bicarbonate salt, which can cause major difficulties in water bodies. Hard drinking water contains an overabundance of Ca and Mg salt, which may have mild health benefits but can cause serious difficulties in home and industrial contexts. Thus, it is critical to examine the water quality in terms of hardness and alkalinity (Yehia *et al*., 2021).

2.6.3 Microbiological water quality

The other water quality is biological, containing bacteria, algae, nutrients, and viruses.The greatest risk to public health from microbes in water is associated with consumption of water which is polluted with human and animal excreta (WHO, 2017). Polluted water serves as a mechanism to transmit communicable diseases such as diarrhea, cholera, dysentery, typhoid and guinea worm infection (Berhanu and Dejene, 2015). Human excreta contain a variety of intestinal pathogens which cause diseases ranging from mild gastro-enteritis to the serious dysentery, cholera and typhoid (Tsega *et al*., 2013). Diseases transmitted by the fecal pathway include diarrheal disease, enteric infection, poliomyelitis, trachoma, and adenoviruses (Strickland 2000). The most predominant waterborne disease, diarrhea, has an estimated annual nearly 1.7 billion cases of childhood diarrheal disease every year globally and causes 525, 000 children under five deaths every year(WHO, 2017). According to the WHO microbiological guidelines (WHO 2017), coliform bacteria must not be detected in 100 ml samples of water for the water to be considered safe; their detection in water indicates pathogenic bacterial contamination (Chalchisa *et al*., 2017).Waterborne diseases are caused by the ingestion of water contaminated with human or animal excreta or urine containing pathogenic bacteria or viruses including cholera, typhoid, bacillary dysentery, adenoviruses, retroviruses, and other diseases (Duressa *et al*., 2019).

Eutrophication of the waters due to disposal of phosphate and nitrate from agriculture and wastewater, among others, favors algae and bacteria growth and can cause health risks (Benti *et al*.., 2015). Bacteria in waters can cause illnesses as typhoid (*Salmonella typhi*), cholera (*Vibrio cholerae*) and diarrhea. Fecal coliforms and streptococci indicate that wastes from humans or animals contaminate the water. Fecal streptococci are the most resistant group of bacteria, and are often analyzed together with total coliforms as an indication of a total bacteriological status. Coliform bacteria can be removed from the water by chlorination (WHO, 2000).

Table 2.9 Guideline value/ permissible limits/ for Microbial in drinking water (Borah *et al*, 2010).

Parameters	Unit	WHO Guideline Value	EPA standards
Total coliform	MPN/100 ml	0	0
Fecal coliform	MPN/100 ml	0	0
E.coli	MPN/100 ml	0	0

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CHAPTER THREE

Heavy metal levels and the associated health risks in Omo River and Delta water in Southern Ethiopia

Abstract

The Omo River flows through Omorate town, carrying domestic, municipal, and industrial refuse from the town and its surroundings, including agrochemicals. The purpose of this study was to evaluate the levels of heavy metals in the Lower Omo River basin (Lower Omo River and Omo Delta) ,and human health implications. The mean values of the measured heavy metals in the river water were 0.439 mg/L for Mn, 0.1 for Zn, 0.168 for Cu, 0.393 for Cr, 0.318 for Pb, 0.007 for Ni, 8.926 for Fe, and 0.06 for Co where as the respective values for Delta Lake water were 0.43 for Mn 0.118 for Zn, 0.166 for Cu, 0.382 for Cr, 0.338 for Pb, 0.008 for Pb, 8.684 for Fe and 0.064 for Co. The mean concentrations of heavy metals in the River and Lake water were in the order Fe > Mn > Cr > Pb > Cu > Zn > Co > Ni > Cd. Both river and lake water had mean levels of lead (Pb), manganese (Mn), and chromium (Cr) that exceeded WHO's permissible limits for water. The HPI value indicates that the fresh water bodies of the present were polluted. The hazard quotients (HQs) through oral ingestion and dermal exposure for both children and adults were in the order of Cr >Pb> Mn > Fe >Cu > Co > Ni > Zn. The HQ value greater than 1 was examined for Cr, Pb, and Mn both in children and adults through ingestion and dermal route from the River water. The CRs for both children and adults via ingestion of the River and Lake water followed the order Cr > Pb. According to CRI value, both the River and Lake water could be classified as very high environmental risk.

Keywords: Ecological risk, Human health risk, Heavy metals, Omo River

3.1 Introduction

Fresh water is essential for all living things (Abdullah and Ahmad, 2016). Heavy metal pollution in surface water is a global environmental and public health issue. The riverine environment is the most significant aspect for supporting human life (Divya *et al*., 2016). The water quality of rivers is highly important because rivers are generally used for domestic water supplies, agriculture (irrigation, and other human purposes (Andreea, 2018). However, its quality is threatened by ecological degradation and pollution (Mehjbeen and Nazura, 2017). Different organic and inorganic pollutants are released from natural and anthropogenic sources in aquatic systems (Pramita *et al*., 20211). Pollution of river water bodies may occur due to the discharge of domestic and industrial wastewater, chemicals used for agriculture, solid waste and drainage from the land surface **(**Mekonnen and Amsalu, 2018**).**The mobilization of these pollutants could alter the physicochemical properties of water, which may be toxic to aquatic life and humans through the food chain (Pramita *et al*., 2021). Among these pollutants, heavy metals play a major role in environmental pollution due to their toxic nature, bioaccumulation and biomagnifications in the food chain (Samuel *et al*., 2020; Pramita *et al*., 2021).

In developing countries, clean and safe water is a vital concern (Asrafuzzaman *et al*., 2011).Despite the importance of ensuring the quality of drinking water, less attention has been given to water quality monitoring in developing countries such as Ethiopia (FMOH, 2007**;** Mekonnen and Amsalu, 2018**).**The Omo River Basin is a vital resource for the people of southern Ethiopia (Tola *et al*., 2017; Wakjira and Getahun, 2017). Although the quality and pollution level of this freshwater caused by heavy metals has not been yet reported, it is a major source of water for domestic use, agriculture (irrigation), and livestock.

Recently, the lower Omo River has experienced rapid development of industry and intensive agriculture along the river and its catchments, especially on the upstream side of the Omo Delta (Tola *et al*., 2017; Wakjira and Getahun, 2017). Large-scale irrigation development, industry and land use changes in the upper and middle Omo Basin in recent years have already resulted in changes in the environment of the lower Omo River basin ecosystem (Ojwang *et al*., 2010). It has been inevitably altered by the rapid development of industry and agriculture in its catchment (Ojwang *et al*., 2010).

The developments of irrigation and agriculture in general in the Omo River basin have led to increased use of fertilizers and pesticides. Over 30% of the Upper Omo upstream inflow will be abstracted for irrigation (Avery, 2012).According to the results gained from other irrigation projects, large-scale irrigation development in the Lower Omo could have a significant effect on aquatic resources and water chemistry due to agrochemicals and increased nutrient levels, leading to the destruction of aquatic biota (Avery, 2012).Experience with similar projects has also indicated that proper amounts of fertilizers and pesticides are not being used, and as a result, excessive chemical runoff can occur (Gure *et al*., 2019). This improper use of agrochemicals may cause potential adverse impacts, including depreciation of downstream water quality, increased vulnerability of the ecosystem and harm to humans and livestock (Ojwang *et al*., 2010). Chemical contamination of the lower Omo could arise from human activities. These include chemicals from large-scale irrigation projects, from construction projects (hydroelectric dams), waste discharges from sugar factories and from oil spillage (Avery, 2012; Gure *et al*., 2019). Thus, the present study aims to determine the pollution level of heavy metals and the associated risks from the Lower Omo River.

3.2 Materials and Methods

3.2.1 Description of the study area

The present study was conducted in the freshwater ecosystem of Lower Omo River and Omo Delta as described in chapter one (section1.9.1)

3.2.2. Sample Collection

Water samples were collected from different river locations of fifteen sub sample sites with three sampling points on each subsite were collected, yielding a total of 45 samples from the River. The water samples were collected in high-quality, screw capped, high density; polypropylene bottles, each with 2 litter capacities. The water samples were acidified with 5% HNO_3 at the sampling point to keep the metals dissolved in solution or to prevent the water's heavy metals from decaying (Kang *et al*., 2020; Solaiman *et al*., 2021) and then placed in an ice box. On the same day, the collected samples were transported and stored in the Research Laboratory of Chemistry, Water Supply and Environmental Engineering, Arba Minch University of Water Technology Institute, Arba Minch, Ethiopia.

3.2.3 Sample preparation

The water samples were digested with a concentrated acid mixture of 65% HNO_3 (1ml) and 35% HCl (0.5 ml) on a thermostatic hot plate. According to the methods developed by the United States Environmental Protection Agency (USEPA) 3005, a 50 ml aliquot of well mixed water samples was digested in a beaker covered with a watch glass by adding 1 ml of concentrated (65%) HNO_3 and 0.5 ml of concentrated (35%) HCl and heated on a hot plate boiled until a clear solution was formed. The beaker was subsequently removed and cooled. After digestion and cooling**,** the samples were diluted with distilled water and filtered through Whatman filter paper for analysis (Dugasa and Endale, 2018; Ibrahim *et al*., 2018).

3.2.4 Sample analysis (heavy metal analysis)

The samples were analyzed for heavy metal content using flame atomic absorption spectrometer (GFAAS- novAA400p; Germany), and the concentrations of the heavy metals in the water samples were determined from a standard calibration curve. Analytical grade standards of each target heavy metal were used to construct calibration curves. Before real sample analysis, the instrument was calibrated by preparing a series of concentrations of the standard solutions for each analyte. Analysis of each heavy metal was carried out in triplicate. Values below the detection limits were reported as 'ND' (not detected). Analysis was carried out according to APHA protocol (APHA, 2017).

3.2.5 Water quality evaluation based on water quality indices

One of the most significant components of water quality monitoring programs was the evaluation of heavy metal pollution. Metals including Al, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn are classified as high priority metals under the Global Environment Monitoring System (GEMS) program (Alma *et al*., 2022). Nine heavy metals, including Cd, Cr, Cu, Fe, Mn, Ni, Co, Pb, and Zn, were examined in this study.

3.2.5.1 Heavy metal pollution index (HPI)

The heavy metal pollution index (HPI) is used to assess overall water quality based on heavy metal content (Mohan *et al*., 1996; Alma *et al*., 2022). The impact of specific heavy metals on overall water quality is examined using the heavy metal pollution index (HPI) (Taygi *et al*., 2013) and calculated according to the following equation (Mohan *et al*., 1996; Ahmed *et al*., 2023).

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.1)$$

$$\mathrm{Wi} = \frac{K}{Si} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.2)$$

$$\mathbf{K} = \frac{\mathbf{1}}{\Sigma(\frac{\mathbf{1}}{\mathbf{Vstandard}})} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.3)$$

$$\mathrm{Qi} = \frac{Mi-Ii}{(Si-Ii)} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.4)$$

Where HPI is the metal pollution index (Equations 3.1), Wi is the unit weighting of the ith heavy metal (Equation 3.2), K is the proportionality constant that is inversely proportional to the maximum permissible value (Si) of the heavy metals for drinking, livestock, and irrigation use that is calculated as presented in Equation (3.3), and Qi is the sub-index for the ith heavy metal (the individual quality rating for the ith heavy metal) calculated using Equations (3.4). Mi and Ii are the measured and ideal values of the ith parameter for heavy metals (mg/L). A value of HPI < 100 indicates low heavy metal contamination, while HPI > 100 indicates inappropriate water for ingestion (Mohan *et al.*, 1996; Elsiddig *et al.*, 2020; Tala *et al.*, 2023)

3.2.5.2 Metal index (MI)

The MI is a water quality indicator that measures overall pollution levels based on heavy metal concentrations in comparison to their corresponding maximum permissible values (MAC). It is used to assess the quality of water for various applications (Josephine *et al.*, 2021). The MI index categorizes water samples as drinkable (MI <1), at risk of drinking (MI = 1), or non-potable (MI > 1) and calculated using equation (3.5) (Jafarabadi *et al.*, 2017; Goher *et al.*, 2020; Ahmad *et al.*, 2023)

$$\mathrm{MI} = \sum_{i=1}^{n} \frac{Ci}{MAC} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.5)$$

Where MI is the metal index, Ci is the mean concentration of each heavy metal in the water sample, and MAC is the maximum allowable concentration for each heavy metal in the water sample. An MI < 1 indicates that the water is suitable for consumption. An MI >1 indicates that the water is unsuitable for domestic use (Caerio *et al*,.2005; Edet & Offiong 2002; Alma *et al*., 2022).

3.2.5.3. Heavy metal evaluation index (HEI)

Similar to MI, the heavy metal evaluation index (HEI) reflects the quality of water with respect to heavy metal concentrations (Edet and Offiong, 2002, Prabakaran *et al*., 2020). Unlike MI, HEI classifies the water quality as low, moderate and high.

$$\text{HEI}= \text{MI} = \sum_{i=1}^{n} \frac{Ci}{MAC} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.6)$$

Where C_i is the actual concentrations of trace element, and MAC_i is the maximum permissible concentration of trace elements. The classification of surface water quality based upon HEI is low (HEI<10), moderate (10–20), and high pollution (HEI >20) (Prasanna *et al*., 2012).

3.2.6Estimation of environmental risks using the risk index factor (RI)

The risk index factors (RI) and Comprehensive risk index (CRI) of water resulting from the heavy metals were used to estimate potential environmental risk. A risk index factor related to the presence of toxic heavy metals in water was proposed by Hakanson and was calculated according to Hakanson (1980).

$$\text{RI}= \frac{\text{Ti}\times\text{OC}}{NOEC} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.7)$$

$$\text{CRI} = \sum \text{RI} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.8)$$

Where RI is the risk index factor for each metal; Ti is the toxicity coefficient of the metal; OC is the mean concentration of the metal; and NOEC is the maximum allowable concentration and CRI is the comprehensive risk index. The toxicity coefficients of the metals were 5 for Pb= Ni=Cu=Co, 1 for Zn =Mn, 10 for Fe, and 2 for Cr (Hakanson, 1980, Collins *et al*., 2019).

Table 3.1Environmental risk of toxic metals in water and the risk index factor

Range of Risk index Factor (Ri)	Potential environmental danger
RI < 1	No potential environmental danger
1≤ RI < 40	Low possible environmental danger
40≤ RI <80	Modest possible environmental danger
80≤ RI < 160	Considerable possible environmental danger
160 ≤ RI < 320	Severe possible environmental danger
RI ≥ 320	Very severe potential environmental danger

Table 3.2*Environmental risk classification by using comprehensive risk factors*

Range of comprehensive risk factor	Classification
CRI < 60	Low
60 ≤ CRI < 120	Moderate
120 ≤ CRI < 240	High
CRI ≥ 240	Very High

3.2.7 Human Health risk assessment (HM exposure through water)

3.2.7.1Exposure assessment

The health risks of heavy metals in water by oral consumption and dermal absorption were calculated using the United States Environmental Protection Agency's (USEPA) risk assessment guideline (2004).To estimate non-cancer and cancer risks in people (children and adults), the chronic daily intake (CDI) of HMs, which represents the lifetime average daily dose (LADD) of exposure to a pollutant, was utilized (USEPA, 2004; Bamuwuwamye *et al*., 2017). The CDI of the HMs in water from oral consumption and cutaneous absorption was calculated using the following equation (Govind *et al*., 20222; Ugwu *et al*., 2022): Estimations were conducted for two groups; children (as a sensitive group) and adults (as the general population), separately.

$$CDI_{ingestion} = {}^{(C \times IR \times EF \times ED)}\big/_{(BW \times AT)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.9)$$

$$CDI_{dermal} = {}^{(C \times EF \times ED \times ET \times SA \times KP \times CF)}\big/_{(BW \times AT)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.10)$$

Where: CDI is the chronic daily intake (mg/kg/day) or also known as ADD which is the average daily dose of toxic metals through direct ingestion or dermal absorption pathways(USEPA, 2004; USEPA, 2005); C is mean concentration of heavy metal in the water (mg/L); IR is the ingestion rate per day (1 L/day for a child and 2.2 L/day for adult) (Bamuwuwamye *et al.*, 2017; Ugwu *et al.*, 2022); ED is the exposure duration (6 years for a child and 30 years for an adult) (WHO, 2015; Ahmad *et al.*, 2023); EF is the exposure frequency (365 days/year); ET is exposure time (0.58 h/day for adults; 1 h/day for children (USEPA, 2004); BW is average body weight (15 kg for a child and 60 kg for adult) (WHO, 2012) over the exposure period; AT is the average time representing the period over which exposure is averaged [(for carcinogens, AT=60×365=21900 days for both children and adults in Ethiopia; for non-carcinogens, AT=ED×365 which equals 2190 days and 10950 days for children and adults, respectively) (USEPA, 1989; USEPA, 2004)]; SA is exposed skin area available for contact (18000 cm2 for adults; 6600 cm2 for children) (USEPA, 2004); KP is dermal permeability coefficient of heavy metal in water (cm/h)[Pb (0.004), Ni (0.001), Co (0.001), Cu (0.001), Zn (0.006), Mn (0.001), Fe (0.001), and Cr (0.001)] (UNEPA, 2004); CF is unit conversion factor (0.001L/cm3) (UNEPA, 2004; Bamuwuwamye *et al.*, 2017; Govind *et al.*, 20222).

3.2.7.2 Noncarcinogenic risk assessment (HQ and HI)

The noncancer risks of HMs in water were calculated using the hazard quotient (HQ) and hazard index (HI). The hazard index (HI) is the overall potential for noncarcinogenic damage caused by various contaminants through ingestion or dermal.

HQ Ingestion = $^{CDIingestion}/_{RfDingestion}$……………………….. (3.11)

HQ dermal = $^{CDIdermal}/_{RfDdermal}$……………………………… (3.12)

HI = $\sum$HQ ………………………………………………………………..(3.13)

Where HI represents the overall potential for noncarcinogenic effects posed by more than one pollutant via ingestion or dermal pathway; HQ is the noncancer hazard quotient; CDI is the chronic daily intake (mg metal/kg/day); and RfD represents the chronic oral reference dose, which is unlikely to cause significant harm throughout life (Bamuwamye *et al*., 2015).

The oral reference doses ($RfD_{ingestion}$) of Pb, Ni, Co, Cu, Zn, Mn, Fe, and Cr are 0.0035, 0.02,0.03, 0.04, 0.3 , 0.014 , 0.7, and 0.003 mg/kg/day (USEPA, 2004; USEPA, 2005; USEPA, 2016).The dermal reference doses (RfD_{dermal}) of Pb, Ni, Cu, Zn, Co, Mn, Fe, and Cr are 0.000525, 0.0054, 0.012, 0.06, 0.016, 0.00005, 0.14 and 0.000075 (USEPA, 2002; USEPA, 2005; USEPA, 1995; Akaninyen *et al*., 2022) mg/kg/day, respectively.The potential risk to human health posed by exposure to multiple HMs was measured by the hazard index (HI), which is the sum of all HQs calculated for each heavy metal. A value of HQ or HI < 1 indicates no significant no cancer risk; a value > 1 indicates significant no cancer risk, which increases with increasing HQ or HI (Govind *et al*., 20222; Ugwu *et al*., 2022).

3.2.7.3 Carcinogenic risk assessment (CR)

The cancer risk was determined by dividing the CDI (mg/Kg/day) by the cancer slope factor (CSF) (measured in mg/kg/day)-1. The current study investigated the CR for elements that are deemed harmful to humans, such as Cr, Pb, and Ni. The carcinogenic risk (*CR*) associated with the ingestion pathway can be estimated using the following formula:

$\text{CR}_{\text{ingestion}} = \text{CDI}_{\text{ingestion}} \times \text{CSF}_{\text{ingestion}}$ ……………………….(3.14)

$\text{CR}_{\text{dermal}} = \text{CDI}_{\text{dermal}} \times \text{CSF}_{\text{derma}}$ ……………………………………..(3.15)

where $\text{CR}_{\text{ingestion}}$ = carcinogenic risk (CR) associated with ingestion; CDI = chronic intake (mg/kg/BW/day); and $CSF_{ingestion}$ = the oral carcinogenic slope factor (mg/kg/day), which is 0.0085 for Pb, 0.5 for Cr and 1.7 for Ni.CSF stands for the cancer slope factor, representing the risk associated with an average concentration of one mg/kg/day of a carcinogenic chemical over a lifetime. This factor is pollutant-specific. The acceptable threshold for a carcinogenic element, whether standalone or in a multi-element context, is taken into consideration.The total cancer risk as a result of exposure to multiple contaminants due to consumption of a particular type of water was assumed to be the sum of each metal cancer risk ($\sum$CR). The United States Environmental Protection Agency (USEPA) suggested that a$CR < 10^{-6}$ indicates no carcinogenic risk to human health; a $CR > 1 \times 10^{-4}$ indicates a high risk of developing cancer; and a risk ranging from 1×10^{-6} to 1×10^{-4} represents an acceptable risk to human health(USEPA, 1989).

3.2.8 Data analysis

Analyses of the data were carried out using IBM SPSS Statistics 21 software at a confidence level of 95%, and differences were considered to be statistically significant at $p < 0.05$.The heavy metal concentrations at each point are presented as the mean ± standard deviation of the samples analysed. Variations in the concentrations of metals between the main sites (lotic and lentic) were evaluated using a t test. The overall differences in the mean concentrations of metals between sampling points were analysed using ANOVA, whereas the differences among specific points were analysed by the Tukey method of multiple comparisons (Tukey post hoc test).

3.3 Results and Discussion

3.3.1 Heavy metal concentrations in Lower Omo River

The mean concentrations of heavy metals in the river water samples are presented in Table 3.3. The mean concentrations of the heavy metals in the river water samples followed the order Fe (8.926 mg/L) > Mn (0.439 mg/L**) >**Cr **(**0.393 mg/L)>Pb **(**0.318 mg/L**) >**Cu **(**0.168 mg/L) > Zn (0.1 mg/L) > Co (0.06 mg/L) > Ni (0.007 mg/L). Cadmiumwas not detected in any of the water samples which might be due to lack of significant level of Cadmium containing pollution sources in the nearby catchment draining into the river water. The maximum concentration of heavy metals detected in the river water was Fe (12.85mg/L) with mean level (8.926mg/L), and the minimum mean concentration was Ni (0.007 mg/L). The mean concentration of Fe in the River water of the present study was larger than that in the study by Gabriela *et al*. (2019)From Atoyac River (0.209mg/L) in Mexico and Rofhiwa *et al*.(2021)fromMutangwi River (0.24mg/L) in south Africa. The Fe levels in the River water was above the WHO (2011) and USEPA (2011) permissible limits for drinking. This could be due to the urban wastes and use of steel pipes for irrigation in the River system. The runoff from agricultural soil could also contribute to the high level of Fe in the water.

The concentration of manganese (Mn) ranged from 0.41 to 0.51 mg/L with mean level of 0.439mg/L. The Mn level of the waterinthe present study was larger than that in the study by Emily *et al*., (2023) in Kenya from Sosian River. However, lower mean level of Mn was recorded in this study than in the study by Tengku *et al*. (2020) from Malaysia (0.497mg/L) and Yasemin and Fusun (2021) from Akcay River of Turkey(6.48mg/L). The mean concentration of Mn in the present study was above the WHO (2011) and USEPA (2011) permissible limits for drinking.

The zinc level ranged from 0.04 to 0.17 mg/L with mean value of 0.1 mg/L. The mean Zn level in the present study was greater than that in the study by Azlini *et al*.(2018) from Highland River (0.033mg/L) in Malaysia However, the Zn level of the River water in this study was lower than that in earlier study by Flipos *et al*.(2021)from Megech River **(**0.13mg/L) in Ethiopia and Mariusz and Joanna (2023) from Muchawka River (176mg/L) in Poland. Its mean concentration in the present study was below the WHO (2011) permissible limits for drinking and the FAO (1985) for livestock.

The copper level of the water ranged from 0.1 to 0.27 mg kg^{-1} with themean level of 0.168 mg kg^{-1} .The mean Cu level in this study was greater than that in earlier study by Qiang *et al*., (2021) from Buerhatong River (0.01344mg/L) in China and Adem *et al*. (2023) from Borkena River (0.03 mg/L) in Ethiopia. On the other hand, the mean Cu level of the water in the present study was lower than that in previous studies by Emily *et al*., (2023) from Sosian River (0.291 mg/L) in Kenya. Its mean concentration in the present study was below the WHO (2011) permissible limits for drinking and the FAO (1985) for livestock. The high level of Cu in this study could be attributed to agrochemical use, Corrosion of household plumbing systems and erosion of natural deposit (Jaishankar *et al*., 2014).

The chromium level of the water ranged from 0.34to 0.46 mg/L with themean level of 0.393 mg/L.The concentration of Cr in this study was greater than that in previous studies by (Ibukun *et al*., 2018) from Southwest Nigeria (0.059mg/L),(Qiang *et al*., 2021) from Buerhatong River (0.00456mg/L) in China and (Tengku *et al*., 2020) from Tropical River (0.005mg/L),in Malaysia. However, the Cr level in the present study was lower than that in the study by (Yasemin and Fusun, 2021) from Ackay River (8.296mg/L)in Turkey. The mean concentrations of Cr in the present study was above the permissible limits for drinking water quality (USEPA, 2011; WHO, 2011) but below the FAO permissible limits for livestock (FAO, 1985).The high levels of in this finding Cr could be attributed to municipal wastes and upstream factories which might contain Cr in its wastewater discharge and also be from erosion of natural deposits from upstream (Gautam *et al*., 2014).

The lead level ranged from 0.25 to 0.38 mg kg^{-1} withthe mean level of0.318 mg/L. The mean concentration of Pb in the present study was greater than that in previous studies by (Emily *et al*., 2023) which was 0.105 mg/L from Kenya, (Ibukun *et al*., 2018) 0.019 mg/L from Nigeria, (Alma *et al*., 2022) 0.0021mg/L from Albania and (Flipos *et al*., 2021) 0.04 mg/L from Ethiopia. The finding of the present study was lower than in previous studies by Mariusz and Joanna (2023) which was 9.3mg/L. The mean concentrations of Pb in the present study was above the permissible limits for drinking water quality (USEPA, 2011; WHO, 2011) and FAO for livestock (FAO, 1985).The Possible sources of Pb in the present study may be due the fact that the source of pollution could be from commercial, vehicle traffic, agricultural runoff, Car washing, gas/fuel station and solid wastes which are near the River water from the Omorate town. The lead in the water could also be a result of corrosion of older fittings, combustion of leaded gasoline, corrosion of lead containing materials, irrigation system pipes, burning of building and electronic wastes with residue washed into rivers pipe. Corrosion of household plumbing systems; erosion of natural deposit in the catchment could also be the source of pollution (Abarikwu, 2013).

The variations in heavy metal concentrations from water at different sampling points are presented in Table 3.4 Mean Concentration of all HMs at all sample points in River are significantly different at 5% level of significance. To see in which sample point the mean concentration is significantly different; the Tukey test of multiple comparison was used shown in the Table 3.5.The mean concentration of Mn at site one was significantly different from the mean concentration at sites five, ten and twelve. The mean concentration of Zn at site one was significantly different from the mean concentrations at sites four to fourteen. Similarly, the mean concentration of Pb at site one was significantly different from the mean concentrations at all sites except for sites seven and fifteen. This difference might be due to the difference in the pollution sources of the heavy metals and the difference in physicochemical properties of water at different sampling points

Table 3.3 Mean concentration of heavy metals (HMs) from the River water

Heavy metals	N	Concentration		Anova	Drinking Water		Livestock FAO-1985 (mg/L)	Irrigation water (FAO, 2003))
					WHO,2017	USEPA, 2018		
		Mean	St. dev	P value				
Mn	45	0.439	0.034	0.00	0.4	1.6	NA	0.2
Zn	45	0.1	0.046	0.00	NA	5	24	2
Cu	45	0.168	0.074	0.00	2	1.3	0.5	0.2
Cr	45	0.393	0.032	0.00	0.05	0.1	1	0.1
Cd	45	ND	ND	ND	0.003	0.005	0.005	0.01
Pb	45	0.318	0.032	0.00	0.01	0.015	0.1	5
Ni	45	0.007	0.005	0.00	0.07	0.1	NA	0.2
Fe	45	8.926	2.287	0.00	0.3	0.3	NA	5
Co	45	0.06	0.014	0.00	0.01	NA	1	0.05

NB:ND= not detected; NA = not available;

Table 3.4Concentrations of heavy metals from River water at different sampling sites (multiple comparisons)

Site	Mn		Zn		Cu		Cr		Pb		Ni		Fe		Co	
	Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD	
1	0.41	0.00^{a}	0.08	0.01^{b}	0.27	0.02^{d}	0.43	0.01^{d}	0.38	0.02^{ef}	0.00	0.00^{a}	6.49	0.02^{a}	0.06	0.00^{c}
2	0.45	0.01^{a}	0.07	0.01^{b}	0.13	0.01^{b}	0.37	0.01^{c}	0.31	0.01^{bcd}	0.00	0.00^{a}	7.25	0.21^{a}	0.08	0.00^{d}
3	0.43	0.00^{a}	0.08	0.02^{b}	0.15	0.01^{b}	0.36	0.00^{b}	0.29	0.03^{abc}	0.00	0.00^{a}	7.37	0.21^{a}	0.07	0.01^{d}
4	0.42	0.00^{a}	0.15	0.00^{d}	0.24	0.01^{c}	0.38	0.00^{c}	0.32	0.01^{cdef}	0.01	0.00^{c}	8.71	1.48^{b}	0.06	0.01^{c}
5	0.48	0.05^{b}	0.17	0.00^{d}	0.23	0.01^{c}	0.39	0.00^{c}	0.28	0.02^{ab}	0.01	0.00^{c}	12.82	0.07^{c}	0.04	0.01^{ab}
6	0.44	0.01^{a}	0.06	0.01^{ab}	0.10	0.00^{a}	0.42	0.00^{d}	0.33	0.02^{def}	0.00	0.00^{a}	9.32	0.04^{b}	0.05	0.00^{ab}
7	0.41	0.00^{a}	0.04	0.07^{a}	0.11	0.01^{a}	0.44	0.01^{d}	0.35	0.01^{ef}	0.00	0.00^{a}	6.36	0.02^{a}	0.07	0.00^{c}
8	0.40	0.00^{a}	0.16	0.00^{d}	0.10	0.00^{a}	0.34	0.01^{b}	0.33	0.02^{def}	0.01	0.00^{c}	8.83	1.39^{b}	0.06	0.00^{c}
9	0.43	0.00^{a}	0.07	0.01^{ab}	0.12	0.05^{b}	0.27	0.07^{bc}	0.30	0.02^{abc}	0.00	0.00^{a}	7.34	0.21^{a}	0.09	0.00^{d}
10	0.51	0.00^{b}	0.15	0.01^{d}	0.26	0.01^{d}	0.46	0.01^{d}	0.27	0.01^{a}	0.01	0.00^{d}	12.79	0.06^{c}	0.04	0.00^{ab}
11	0.42	0.00^{a}	0.06	0.00^{ab}	0.10	0.00^{a}	0.45	0.01^{d}	0.34	0.02^{def}	0.01	0.00^{e}	9.32	0.04^{b}	0.05	0.00^{ab}
12	0.50	0.00^{b}	0.14	0.00^{d}	0.24	0.00^{c}	0.39	0.01^{c}	0.25	0.02^{a}	0.01	0.00^{c}	12.85	0.07^{c}	0.09	0.00^{d}
13	0.42	0.00^{a}	0.05	0.00^{ab}	0.14	0.00^{a}	0.36	0.01^{b}	0.34	0.01^{def}	0.01	0.00^{c}	9.37	0.04^{b}	0.05	0.00^{ab}
14	0.43	0.01^{a}	0.14	0.00^{d}	0.10	0.01^{a}	0.35	0.00^{b}	0.33	0.01^{def}	0.01	0.00^{c}	8.76	1.48^{b}	0.06	0.00^{c}
15	0.44	0.05^{a}	0.09	0.02^{b}	0.25	0.01^{d}	0.44	0.01^{d}	0.37	0.01^{ef}	0.00	0.00^{a}	6.50	0.02^{a}	0.07	0.00^{c}

The data are the average of triplicate data that the numbers followed by the same superscript letter in the same column are not significantly different according to Duncan’s multiple range tests at ($p < 0.05$).

3.3.2 Water quality for Lower Omo River due to heavy metal levels

3.3.2.1 Heavy metal pollution index of River water

The water quality pollution indices were assessedafter the concentrations of the heavy metals were determined. The heavy metal pollution index (HPI), heavy metal evaluation index (HEI), and metal index (MI)were evaluated to evaluate the quality of the River water regarding the heavy metal levels for each sampling location and are presented in table below.The heavy metal pollution index (HPI) indicates the overall quality of the water in terms of heavy metal pollution. The HPI of the River water regarding the heavy metal levels for each sampling location and are presented in Table 3.6. The HPI of the Lower Omo River ranges from 656.8 to 999.5 with a mean of 720 for drinking water while the values for irrigation usage ranges from 164.8 to 211.6 with a mean value of

182.01.The HPI value revealed that all sample sites were heavily polluted as the concentration of all exceeded the threshold value of the pollution index which is 100. This indicates that the water is unsafe for drinking and irrigation usage. The mean value of the present study (720) is lower than those reported by Josephine *et al.* (2021) in the Mgoua river (1990.64) of South-western Cameroon while it is greater than those reported by Mansour *et al*.(2018) in drinking water(HPI =48.5) from Khorramabad city in Iran

The values of HEI for drinking water ranged from 18.1 to 40.8 with a mean value of 24.01, while the values for irrigation water varied from 0.66 to 10.4 with a mean value of 4.7. The HEI values for both drinking and irrigation are greater than one which was unfit for domestic usage. According to the classification proposed by Edet and Offiong (2002), 11 samples were categorized as 'high pollution' and the rest 4 samples were found under moderate pollution category for drinking. According to MI, the maximum value of metals in the River was 40.8 for drinking water. The minimum amount for drinking water was 15.4 and that of irrigation was 0.612.The mean index for drinking and irrigation was 24.01 and 4.7 respectively.

Table 3.5 Drinking and irrigation water quality indices of River water

Stations		Drinking Water			Irrigation water		
	∑Wi	∑WiQi	HPI	HEI/MI	∑Wi	∑WiQi	HPI
1	0.151319	103.3085	682.7201	18.14433	0.0459	8.609802	187.5774
2	0.151319	122.7068	810.9143	19.13567	0.0459	8.985411	195.7606
3	0.151319	112.4682	743.2519	18.70767	0.0459	8.413108	183.2921
4	0.151319	107.7656	712.1748	24.49619	0.0459	8.129201	177.1068
5	0.151319	101.4648	670.5357	35.74019	0.0459	7.647943	166.6219
6	0.151319	101.825	672.9157	22.57867	0.0459	8.269616	180.1659
7	0.151319	112.9583	746.4908	15.043	0.0459	9.155585	199.4681
8	0.151319	106.6763	704.9763	22.00819	0.0459	7.701463	167.7879
9	0.151319	128.8824	851.7261	20.07567	0.0459	8.321857	181.3041
10	0.151319	104.0723	687.7676	36.24119	0.0459	8.440445	183.8877
11	0.151319	102.8361	679.5976	22.77152	0.0459	8.475212	184.6451
12	0.151319	151.2451	999.5112	40.79419	0.0459	9.713337	211.6195
13	0.151319	99.39883	656.8825	23.77619	0.0459	7.564809	164.8106
14	0.151319	106.8646	706.2206	21.84586	0.0459	7.902171	172.1606
15	0.151319	113.6541	751.0892	18.73467	0.0459	9.21486	200.7595
Mean	0.151319	109.0904	720.9296	24.01	0.0459	8.35	181.9

3.3.3 Ecological risks (RI) from the River water

The potential ecological risk of the River water was estimated using Risk index factor (RI) and the Comprehensive risk index (CRI) as presented in Table 3.7. The Risk index factor (RI) for the heavy metals in the River water was in the order Fe > Pb > Co > Cr > Mn > Ni > Cu > Zn. The Ri for each heavy metals in the River water show that, Zn (Ri = 0.02), Cu (Ri = 0.42, and Ni (Ri = 0.5) had no potential environmental danger, Mn (RI = 1.1), Cr (Ri= 15.72) and Co (Ri = 30) have low possible environmental risk, Pb (Ri = 159) had Considerable possible environmental risk and, Fe (RI = 297.5) had sever potential environmental risk (Table3.7). The major contribution to the risk factor (RI) was made by Iron and lead which could pose major pollution risk in the River water. According to the classification of environmental risk using Comprehensive risk factor (CRI) (Table 3.8) the lower Omo River water could be classified as very high environmental risk (CRI = 504). Thus, the results showed that the RI values of Zn, Cu, and Ni in all the sample sites were all < 1, indicating a minimal risk to organisms. However, Pb and Fe posed high risk.The RI value for Cr in the present study (15.72) was lower than those reported by Li *et al.* (2022) in surface water of the northeastern Qinghai-Tibet Plateau while it was greater than those reported by Fadlillah *et al*. (2023) in drinking water.The RI value for Fe in the present study (297.53) was lower than those reported by Fadlillah *et al*(2023) in the surface water which was 163.27.The Comprehensive risk index (CRI) value of this study (504) was higher than those study reported by Fadlillah *et al*(2023) which was 171.1.

Table 3.6 Environmental risk of the heavy metals in the River water using the risk index factor

HMs	OC	Ti	NOE	OC/NOE	RI	CRI
Mn	0.439	1	0.4	1.0975	1.0975	504.291
Zn	0.1	1	5	0.02	0.02	
Cu	0.168	5	2	0.084	0.42	
Cr	0.393	2	0.05	7.86	15.72	
Pb	0.318	5	0.01	31.8	159	
Ni	0.007	5	0.07	0.1	0.5	
Fe	8.926	10	0.3	29.75	297.53	
Co	0.06	5	0.01	6	30	

3.3.4. Human health risk assessment of HMs from the River water

A. Noncarcinogenic health risks (HQ and HI) from River Water

The CDI and HQ of the heavy metals Pb, Mn, Fe, Cu, Co, Ni and Zn for children and adults through oral and dermal routes of drinking water from Lower Omo River are presented in Table 3.7. The HQs through oral intake (ingestion) for both children and adults were in the order of Cr >Pb> Mn > Fe >Cu > Co > Ni > Zn. Similarly, the HQ via the dermal route follows the order Mn > Cr >. In the present study, the HQ greater than 1 was observed for Cr, Pb, and Mn both in children and adults through ingestion and dermal ingestion. As shown in Table 6, the hazard quotient (HQ) values for Cr (8.73**),** Pb (6.057) and Mn(2.09) in children via ingestion was intolerable risk seeing that HQ>1.Similarly, The HQs values in adults for Cr (4.67) and Pb (3.030 were greater than 1 and also unacceptable risk. Regarding the dermal route, the HQs values for Cr (2.306**)** and Pb (1.066)in children via dermal route was intolerable risk (HQ>1).The HIs of the heavy metals for children and adults via ingestion route were 18.1 and 9.1 respectively. Likewise, the HI of the heavy metals via dermal route of exposure in children was 3.6 and the value in adult was 1.41 indicating intolerable noncarcinogenic health risk effect. Chromium and lead followed by manageress contributed more to the noncancer risks both via ingestion and dermal route of exposure in children and adults. The HIs value of the present study in children were higher than those for adults indicating that children would experience more noncancer risks and absorb more chemicals than adults (Bamuwamye *et al*., 2015;Ugwu *et al*., 2022)).

The HQ value in children via ingestion for Cr, Pb, and Mn in the present study was greater than that in the study by Ibukun *et al* (2018) which was 0.48 for (Cr) , 0.33 (Pb), and 0.21 (Mn) from Dandaru River in south west Nigeria. The HQ value in children via ingestion for Cr in the present study was also greater than that in the study by Bamuwamye *et al*. (2017) from drinking Water (0.002) in Uganda for children .However, the HQ value via ingestion for Pb in children and adult of the present study was lower than that in the study by Bamuwamye *et al*. (2017) for Pb in children (46.481) and adult (19.921).Ugwu *et al*., (2022) also reported greater HQ for Pb in children (48.89) and in adult (10.48) than the present study

Table 3.7Noncancer hazard quotients for children and adults through oral and dermal routes

HMs	Concentration	CDI ingestion		CDI dermal		HQ ingestion		HQ dermal	
		Children	Adult	Child	Adult	Children	Adult	Children	Adult
Mn	0.439	0.0293	0.0161	0.000193	7.64E-05	2.09	1.04	0.201	0.0795
Zn	0.1	0.00667	0.00367	0.000264	0.000104	0.0222	0.0111	0.0044	0.00174
Cu	0.168	0.0112	0.00616	7.39E-05	2.92E-05	0.28	0.14	0.00616	0.00244
Cr	0.393	0.0262	0.0144	0.000173	6.84E-05	8.73	4.367	2.306	0.912
Cd	ND	0	0	0	0	0	0	0	0
Pb	0.318	0.0212	0.0117	0.00056	0.000221	6.057	3.029	1.066	0.422
Ni	0.007	0.000467	0.000257	3.08E-06	1.22E-06	0.0233	0.0117	0.00057	0.000226
Fe	8.926	0.595	0.3273	0.00393	0.00156	0.851	0.425	0.0281	0.0111
Co	0.06	0.004	0.00477	2.64E-05	2.26E-05	0.133	0.145	0.00165	0.00141
HI						17.31	8.737	3.6	1.41

B. Carcinogenic health risks (CR) from River water

Cancer risks were expressed in terms of incremental lifetime cancer risk (ILCR), which is the possibility that an individual may develop cancer over a 60 year lifetime due to a 24 hour exposure to a potential carcinogen (Bamuwamye *et al*., 2017).In this study, cancer risk (CR) assessed for Pb, Cr, and Ni are considered to be carcinogenic for humans. The results are presented in Table 3.9. The CRs for both children and adults followed the order Cr > Pb. The CRs of Pb, Cr, and Ni in children were 0.0001802, 0.0131, and 0.0007939 respectively. Similarly, the CRs in adults were 9.911×10^{-5} and $0.007.205\times^{-3}$, respectively. Chromium exhibited the higher probability of cancer risks (mean CR= 1.31×10^{-2}) followed by lead (mean CR= 1.8×10^{-4}) for children. The cumulative effect of the heavy metals for carcinogenic ∑CR) both in children and adults of the present study was above acceptable values (10^{-6} to 10^{-4}) which is intolerable cancer risks due to heavy metals in drinking water over a lifetime.

Table 3.8 Incremental lifetime cancer risks for the children and adult through ingestion of River water

HMs	Concentration	CDI ingestion		CR ingestion	
		Children	Adult	Children	Adult
Pb	0.318	0.0212	0.01166	0.0001802	0.00009911
Cr	0.393	0.0262	0.01441	0.0131	0.007205
Ni	0.007	0.00047	0.00026	0.0007939	0.0004369
∑CR				0.0141	0.007741

3.3.5 Concentrations of heavy metals from Omo Delta water

Table 3.9 shows the mean concentrations of heavy metals in the Delta water samples. The mean concentrations of heavy metals in LakeWater samples followed the order. Fe (8.684 mg/L) is followed by Mn (0.43 mg/L), Cr (0.382 mg/L), Pb (0.338 mg/L), Cu (0.166 mg/L), Zn (0.118 mg/L), Co (0.064 mg/L), Ni (0.008 mg/L), and Cd (ND).Cadmium was not detected in any of the Lake water samples, which could be attributed to the absence of large levels of Cadmium-containing pollution sources in the local catchment draining into the Lake water.

The mean concentration of Mn in the Lake water of the present study waslowerthan that in the study by Adimasu *et al*. (2015) from Lake Hawassa (0.489 mg/L) in Ethiopia. However, its mean concentration in the present study was higher than the study by Amare*etal* (2014) which was (0.166) and Riple *et al* (2015) which was (0.359 mg/L) from Lake Hawassa in Ethiopia. The different agricultural activities and pollution from cities and villages in the basin may have contributed the rise of Mn level in the Lake water. The zinc level ranged from 0.01 to 0.15 mg/L with mean value of 0.118 mg/L. The mean Zn level in the present study was lower than that in the study by Ermias *et al*.(2014) which was (0.253 mg/L) and Xu *et al*. (2013) which was (0.123 mg/L). However, the Zn level of the Lake water in this study was higher than that in earlier study by Ripple *et al*.(2015) which was (0.028 mg/L) and by Zhao *et al*. (2018) which was (0.0168mg/L). Its mean concentration in the present study was below the WHO (2011) permissible limits for drinking and the FAO (1985) for livestock. TheFe levels in the Lake water was above the WHO (2011) and USEPA (2011) permissible limits for drinking. This could be due to the urban wastes and use of steel pipes for irrigation in its upstream side which could enhance the drainage in to the Lake system.

The copper level of the Lake water ranged from 0.11to 0.23mg kg^{-1} with themean level of 0.166 mg kg^{-1} .The mean Cu level in this study was lower than that in earlier study by Ermias *et al*., (2014) from Lake Hawassa (0.226mg/L) and Wang *et al*. (2011) which was (0.0084 mg/L). However, the mean Cu level of the water in the present study was higher than that in the previous studies by Sorsa *et al*., (2016) which was (0.041mg/L) and Wang *et al*. (2011) which was (0.0084 mg/L). Its mean concentration in the present study was below the WHO (2011) permissible limits for drinking and the FAO (1985) for livestock.

The chromium level of the Lake water ranged from 0.34to 0.43mg/L with themean level of 0.382 mg/L.The concentration of Cr in this study was higher than that in previous studies by Li *et al*. (2010) which was (0.00814 mg/L); Sorsa *et al*.(2016) which was (0.11mg/L) and Dsikowitzky *et al*.(2013) which was (0.00185 mg/L). However, the Cr level in the present study was lower than that in the study by (Yasemin and Fusun, 2021) which was (8.296mg/L)in Turkey. The mean concentrations of Cr in the present study was above the permissible limits for drinking water quality (USEPA, 2011; WHO, 2011) but below the FAO permissible limits for livestock (FAO ,1985).The high levels of Cr could be attributed to municipal wastes and upstream factories which might contain Cr in its wastewater discharge.

The lead level ranged from 0.3to 0.39mg/Lwiththe mean level of0.338 mg/L.The mean Pb concentration in this study was more than the Pb concentrations in earlier investigations by

Dsikowitzky *et al*. (2013), Wu *et al*. (2014), and Zenebe (2011), which were 0.003 mg/L, 0.0013 mg/L, and 0.0013 mg/L, respectively. The finding of the present study for Pb was lower than in previous studies by Mariusz and Joanna (2023) which was 9.3mg/L. The mean concentrations of Pb in the present study was above the permissible limits for drinking water quality (USEPA, 2011; WHO, 2011) and FAO for livestock (FAO, 1985).The possible sources of Pb in the current study could include commercial, vehicle traffic, agricultural runoff, car washing, gas/fuel stations, and solid wastes in the vicinity of the Lower Omo freshwater. Lead in the Lake water could also be caused by corrosion of older fittings, the combustion of leaded gasoline, the corrosion of lead-containing products, irrigation system pipes, and electronic wastes, which are then carried into the Lake system.

The concentration of Co ranged from 0.03 to 0.08 mg/L with mean level of 0.064 mg/L.The study conducted by Ripple *et al*. (2015) found that the mean Co level of the lake water was 0.036 mg/L, however the mean level observed in our study was greater. This study's mean level of Co was, however, lower than that of studies conducted in Malaysia by Tengku *et al*. (2020) at 0.497 mg/L and in Turkey by Yasemin and Fusun (2021) at 6.48 mg/L.The mean concentration of Co in the present study was above the WHO (2011) and USEPA (2011) permissible limits for drinking. As presented on Table 3.10.The current study's mean concentration of Ni (0.008 mg/L) was less than that of earlier investigations by Xu *et al*. (2017), Sorsa *et al*. (2016), and Ripple *et al*. (2015), which had concentrations of 0.0085 mg/L, 0.153 mg/L, and 0.014 mg/L, respectively. Nonetheless, the mean concentration observed in this investigation was more than the value reported in Li *et al*. (2010)'s study (0.00171 mg/L).

The variations inmean heavy metal concentrations from water at different sampling points are presented in Table 3.10. Mean Concentrations of all HMs at all sample points in River are significantly different at 5% level of significance (Table 3.10). To see in which sample point the mean concentration is significantly different; the Tukey test of multiple comparison was used shown in the Table 3.11.The data are the average of triplicate data that the numbers followed by the same superscript letter in the same column are not significantly different according to Duncan’s multiple range tests at ($p < 0.05$). The mean concentration of Mn at site one was significantly different from its mean concentration at sites 4-12. The mean concentration of Zn at site one was significantly different at all points except for its mean concentrations at sites 4-6 and 7-9. Similarly, the mean concentration of Pb at site one was significantly different from its mean concentrations at all sites except for sites 7 and 10. This difference might be due to the difference in the pollution sources of the heavy metals and the difference in physicochemical properties of the Lake water at different sampling points.

Table 3.9 Mean concentration of heavy metals (HMs) from the Delta Water

Heavy metals	N	Concentration		Anova		Drinking Water		Livestock	Irrigation water (FAO, 2003))
				F	P	WHO,2017	USEPA, 2018	FAO-1985 (mg/L)	
		Mean	St. dev						
Mn	45	0.43	0.013	136	0	0.4	1.6	-	0.2
Zn	45	0.118	0.11	1996	0	-	5	24	2
Cu	45	0.166	0.044	135	0	2	1.3	0.5	0.2
Cr	45	0.382	0.025	19.3	0	0.05	0.1	1	0.1
Cd	45	ND	-	0.9	0	0.003	0.005	0.005	0.01
Pb	45	0.338	0.029	5.8	0	0.01	0.015	0.1	5
Ni	45	0.008	0.005	86.8	0	0.07	0.1	--	0.2
Fe	45	8.684	2.085	31	0	0.3	0.3	-	5
Co	45	0.064	0.013	31.5	0	0.01		1	0.05

Note: Mean Concentration of all HMs at all sample points in the Lake except are significantly different at 5% level of significance. To see in which sample point the mean concentration is significantly different; the Tukeys test of multiple comparison was considered as given in Table 3.11

Table 3.10 Heavy metal analysis of Delta water at different sample sites using Tukeys test of multiple comparison for Lake water

Site	Mn		Zn		Cu		Cr		Pb		Ni		Fe		Co	
	Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD	
1	0.42	0.00^{b}	0.05	0.00^{b}	0.15	0.00^{b}	0.38	0.01^{bcd}	0.33	0.01^{ab}	0.01	0.00^{c}	7.11	0.11^{a}	0.06	0.00^{b}
2	0.45	0.00^{b}	0.03	0.00^{b}	0.12	0.01^{a}	0.36	0.01^{abc}	0.31	0.02^{a}	0.00	0.00^{a}	9.85	0.27^{b}	0.07	0.01^{b}
3	0.43	0.00^{b}	0.06	0.00^{b}	0.21	0.01^{c}	0.43	0.02^{f}	0.34	0.01^{abc}	0.01	0.00^{ef}	5.59	1.18^{a}	0.05	0.01^{b}
4	0.39	0.00^{a}	0.02	0.00^{a}	0.2	0.01^{c}	0.42	0.01^{f}	0.32	0.02^{abc}	0.01	0.00^{def}	5.62	1.19^{a}	0.06	0.01^{b}
5	0.41	0.00^{a}	0.01	0.00^{a}	0.23	0.01^{d}	0.39	0.00^{cd}	0.39	0.02^{bc}	0.01	0.00^{f}	10.8	0.27^{b}	0.04	0.01^{a}
6	0.41	0.00^{a}	0.04	0.00^{a}	0.16	0.01^{b}	0.38	0.01^{bcd}	0.34	0.02^{abc}	0.01	0.00^{cd}	7.12	0.11^{a}	0.07	0.00^{b}
7	0.43	0.00^{c}	0.05	0.00^{b}	0.14	0.00^{ab}	0.35	0.00^{abc}	0.35	0.01^{ab}	0.00	0.00^{a}	9.82	0.28^{b}	0.06	0.00^{b}
8	0.47	0.00^{c}	0.06	0.00^{b}	0.13	0.00^{ab}	0.36	0.01^{ab}	0.28	0.01^{a}	0.01	0.00^{cde}	10.01	0.69^{b}	0.09	0.00^{c}
9	0.45	0.00^{c}	0.08	0.00^{b}	0.11	0.01^{ab}	0.37	0.01^{abcd}	0.30	0.02^{a}	0.01	0.00^{cde}	9.96	0.72^{b}	0.08	0.00^{c}
10	0.44	0.00^{c}	0.32	0.01^{d}	0.15	0.00^{b}	0.40	0.02^{d}	0.32	0.02^{ab}	0.00	0.00^{a}	10.83	0.11^{a}	0.06	0.00^{b}
11	0.48	0.00^{c}	0.29	0.00^{d}	0.12	0.01^{a}	0.36	0.01^{abc}	0.34	0.01^{abc}	0.00	0.00^{a}	9.86	0.27^{b}	0.07	0.01^{b}
12	0.40	0.00^{c}	0.35	0.01^{d}	0.11	0.00^{ab}	0.34	0.00^{a}	0.31	0.04^{a}	0.01	0.00^{cde}	9.92	0.72^{b}	0.08	0.00^{c}
13	0.42	0.00^{b}	0.15	0.00^{c}	0.25	0.01^{cd}	0.41	0.01^{d}	0.38	0.02^{bc}	0.01	0.00^{b}	10.5	0.27^{b}	0.05	0.01^{a}
14	0.43	0.00^{b}	0.12	0.00^{c}	0.22	0.01^{d}	0.39	0.00^{de}	0.39	0.02^{c}	0.00	0.00^{b}	7.14	0.24^{b}	0.03	0.00^{a}
15	0.42	0.00^{b}	0.15	0.00^{c}	0.23	0.01^{d}	0.37	0.00^{cd}	0.37	0.02^{bc}	0.01	0.00^{f}	11.1	0.25^{b}	0.04	0.01^{a}

Data are average of triplicates; numbers followed by the same letter superscripts in the same column do not vary significantly by Duncan's multiple range tests at $p < 0.05$; SD: standard deviation

3.3.6. Water quality for Omo Delta due to heavy metal levels

3.3.6.1 Heavy metal pollution index of Delta Lake

The water quality pollution indices were assessedafter the concentrations of the heavy metals were determined. The HPI, HEI, and MI weredetermined to evaluate the quality of the Lake water regarding the heavy metal levels for each sampling location and are presented in table 3.11. The heavy metal pollution index (HPI) indicates the overall quality of the water in terms of heavy metals. The HPI of the Omo Delta ranges from 5.92.1 to931.1 with a mean of 725.53 for drinking water while the values for irrigation usage ranges from 154.5 to 203.4 with a mean value of 183.The HPI value revealed that the sample sites were heavily polluted as the concentration of all exceeded the threshold value of the pollution index which is 100. This indicates that the water is unsafe for drinking and irrigation usage. The mean value of the present study (725.53) is lower than those reported by Josephine *et al.* (2021) in the Mgoua river (1990.64) of South-western Cameroon while it is greater than those reported by Mansour *et al*.(2018) in drinking water(HPI =48.5) from Khorramabad city in Iran.

The values of HEI/MI for drinking water ranged from 12.6 to 30.7 with a mean value of 24.4.The HEI values for drinkingwas greater than one which was unfit for domestic usage. According to MI, the maximum value of metals in the Lake water was 30.7. The minimum amount for drinking water was 12.6..The high pollution of the Lake water at majorities of the sites might be due the pollution load of these sites could linked with high pollution sources,the physico chemical properties of the Lake , and nature of the pollutants.

Table 3.11 Drinking and irrigation water quality indices of Delta Lake

Stations		Drinking Water			Irrigation water		
	∑Wi	∑WiQi	HPI	HEI	∑Wi	∑WiQi	HPI
1	0.151319	102.5534	677.7295	17.35286	0.0459	8.152574	177.616
2	0.151319	120.9748	799.4687	26.58433	0.0459	8.501022	185.2074
3	0.151319	89.59888	592.119	12.67319	0.0459	8.262448	180.0098
4	0.151319	99.04948	654.5738	13.25519	0.0459	8.433937	183.7459
5	0.151319	95.90531	633.7954	29.89986	0.0459	7.414634	161.5389
6	0.151319	112.6898	744.7165	18.66919	0.0459	8.517045	185.5565
7	0.151319	110.9028	732.9071	26.25833	0.0459	7.927835	172.7197
8	0.151319	140.9021	931.1591	29.22652	0.0459	9.336179	203.4026
9	0.151319	131.3452	868.0017	27.79386	0.0459	8.97394	195.5107
10	0.151319	115.9396	766.1929	29.614	0.0459	8.448979	184.0736
11	0.151319	121.3603	802.0163	27.04467	0.0459	8.588184	187.1064
12	0.151319	130.0845	859.6707	27.68952	0.0459	8.493647	185.0468
13	0.151319	105.5979	697.8497	30.27286	0.0459	8.034122	175.0353
14	0.151319	74.00521	489.0674	16.419	0.0459	7.091106	154.4903
15	0.151319	95.88883	633.6865	30.75286	0.0459	7.242137	157.7808
Mean	0.151319	109.79	725.53	24.4	0.0459	8.41	183

3.3.7 Ecological risks from the Delta Lake

The potential ecological risk of the Lake water was estimated using Risk index factor (RI) and the Comprehensive risk index (CRI) as presented in Table 3.12. The Risk index factor (RI) for the heavy metals in the Lake water was in the order Fe > Pb > Co > Cr > Mn > Ni > Cu > Zn. The RI for each heavy metals in the Lake water show that, Zn (RI = 0.0236), Cu (RI = 0.415), and Ni (RI = 0.572) had no potential environmental danger, Mn (RI = 1.075), Cr (RI= 15.28) and Co (RI = 32) have low possible environmental danger, Pb (Ri =169) had Considerable possible environmental risk and, Fe (RI = 289.467) had sever potential environmental risk (Table3.7). The major contribution to the risk factor (RI) was made byiron and lead which could posemajorpollution risk in the Lake water. According to the classification of environmental risk using Comprehensive risk factor (CRI) (Table 3.13) the Omo Delta water could be classified as very high environmental risk (CRI = 507.8).

Table 3.12Environmental risk of the heavy metals in Delta Lake water using the risk index factor

HMs	OC	Ti	NOE	OC/NOE	RI	CRI
Mn	0.43	1	0.4	1.075	1.075	507.832
Zn	0.118	1	5	0.0236	0.0236	
Cu	0.166	5	2	0.083	0.415	
Cr	0.382	2	0.05	7.64	15.28	
Pb	0.338	5	0.01	33.8	169	
Ni	0.008	5	0.07	0.11429	0.57143	
Fe	8.684	10	0.3	28.9467	289.467	
Co	0.064	5	0.01	6.4	32	

3.3.8 Human health risk assessment of HMs from Delta

A. Noncarcinogenic health risks (HQ and HI) from Delta

Table 3.13 shows the CDI and HQ of the heavy metals Pb, Mn, Cr, Fe, Cu, Co, Ni, and Zn for both adults and children when consuming drinking water from Omo Delta orally and through the skin. The HQs through oral intake (ingestion) for both children and adults were in the order of Cr >Pb> Mn > Fe >Cu > Co > Ni > Zn. In the current investigation, oral consumption and dermal contact with Cr, Pb, and Mn in both children and adults resulted in HQ values greater than 1. Table 3.13 illustrates that the hazard quotient (HQ) values for ingestion of Cr (8.5), Pb (6.5), and Mn (2.1) in children were greater than 1, indicating an intolerable risk. In a similar way, the adult HQs values for Mn (1.02), Pb (3.22), and Cr (4.24) were all higher than 1 and represent an unacceptable risk.In relation to the dermal route, children who used it showed unacceptable risk levels for Pb (1.13) and Cr (2.24) (HQ>1).By ingestion route, the HIs of the heavy metals were 18.27 and 9.22 for adults and children, respectively. Similarly, children's dermal exposure to heavy metals had an HI of 3.63, whereas adults' values were 1.44, indicating an intolerable noncarcinogenic health risk effect. Chromium and lead followed by manganese contributed more to the noncancer risks both via ingestion and dermal route of exposure in children and adults. Children will face greater noncancer risks and absorb more chemicals than adults, according to the current study's HIs values, which were higher in children than in adults (Ugwu *et al.*, 2022).

The HQ value in children via ingestion for Cr, Pb, and Mn in the present study was greater than that in the study by Ibukun *et al* (2018) which was 0.48 for (Cr) , 0.33 (Pb), and 0.21 (Mn) from in south west Nigeria. The HQ value in children via ingestion for Cr in the present study was also greater than that in the study by Bamuwamye *et al*. (2017) from drinking Water (0.002) in Uganda for children .However, the HQ value via ingestion for Pb in children and adult of the present study was lower than that in the study by Bamuwamye *et al*. (2017) for Pb in children (46.481) and adult (19.921).Ugwu *et al*., (2022) also reported greater HQ for Pb in children (48.89) and in adult (10.48) than the present study.

Table 3.13 Noncancer hazard quotients for children and adults through oral and dermal routes from Delta Lake

HMs	Concentration	CDI ingestion		CDI dermal		HQ ingestion		HQ dermal	
		Children	Adult	Child	Adult	Children	Adult	Children	Adult
Mn	0.43	0.028667	0.014333	0.000189	7.64E-05	2.047619	1.02381	0.197083	0.079569
Zn	0.118	0.007867	0.003933	0.000312	0.000104	0.026222	0.013111	0.005192	0.00174
Cu	0.166	0.011067	0.005533	7.3E-05	2.92E-05	0.276667	0.138333	0.006087	0.002436
Cr	0.382	0.025467	0.012733	0.000168	6.84E-05	8.488889	4.244444	2.241067	0.91176
Pb	0.338	0.022533	0.011267	0.000595	0.000221	6.438095	3.219048	1.133105	0.421577
Ni	0.008	0.000533	0.000267	3.52E-06	1.22E-06	0.026667	0.013333	0.000652	0.000226
Fe	8.684	0.578933	0.289467	0.003821	0.001553	0.827048	0.413524	0.027293	0.011094
Co	0.064	0.004267	0.004622	2.82E-05	2.26E-05	0.142222	0.154074	0.00176	0.001414
	HI					18.27	9.219677	3.63	1.439

3.3.8. 2 Carcinogenic health risks (CR) from Delta

The likelihood that a person may acquire cancer over the course of their lifetime as a result of a 24-hour exposure to a potential carcinogen is known as incremental lifetime cancer risk, or ILCR (Bamuwamye *et al*., 2017). According to this study, Pb, and Cr, and wereconsidered to be carcinogenic for humans.The results are presented in Table 3.14. The CRs for both children and adults followed the order Cr > Pb. The CRs of Pband Cr in children were 0.000192 and 0.0128, respectively. Similarly, the CRs in adults were 9.58×10^{-5} and 0.0064, respectively. Chromium exhibited the higher probability of cancer risks followed by lead for children. The cumulative effect of the heavy metals for carcinogenic $\sum$CR) both in children (0.006916) and adults(0.006916) of the present study were above acceptable values (10^{-6} to 10^{-4}) which is intolerable cancer risks due to heavy metals in drinking water over a lifetime.

Table 3.14 Incremental lifetime cancer risks for the children and adult through ingestion of Delta Lake water

HMs	Concentration	CDI ingestion		CR ingestion	
		Children	Adult	Children	Adult
Pb	0.393	0.0212	0.011267	0.00019153	9.577E-05
Cr	0.318	0.0262	0.012733	0.0127335	0.0063665
Ni	0.008	0.000533	0.000267	0.0009061	**0.0004539**
∑CR				0.0138	6.92E-03

3.4. Conclusions and recommendation

The present study addressed the level of heavy metals and associated ecological and human health implications from the Lower Omo River as a first hand report. Thus, this study has provided baseline information on the pollution level of heavy metals and associated health risk from Lower Omo River. The heavy metal pollution index (HPI) value indicates that the River water was polluted by heavy metals. The HQ value greater than 1 was examined for Cr, Pb, and Mn both in children and adults through ingestion and dermal route from the River and Delta Lake water. According to CRI value, the freshwater could be classified as highenvironmental risk. The mean levels of lead (Pb), manganese (Mn), and chromium (Cr) were above the acceptable limits for water set by WHO guideline values thus posing a human health concern. Therefore, regular monitoring of the River water quality with regard to heavy metal level is vital for environmental and human health concern with a particular concern on Cr, Pb, and Mn.

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CHAPTER FOUR

Levels of heavy metal in fish of Omo River and Omo Delta in Southern Ethiopia and the associated human health risks

Abstract

This study is the first to determine the levels of heavy metals in commercially important fish species, namely *Lates niloticus* and *Oreochromis niloticus* and the potential human health risks associated with their consumption from Lower Omo River and Omo Delta in Southern Ethiopia.. A total of one hundred and twenty fish samples were collected from the lower Omo River and Omo Delta, with 60 samples from each water source. The fish tissue samples (liver and muscle)were analyzed using a flame atomic absorption spectrometer to detectnine heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn).The mean levels of heavy metals detected in the liver and muscle of L.*niloticus* from the lower Omo River generally occurred in the order of Fe > Zn >Pb> Cu >Mn> Cr > Co > Ni and Pb> Cu >Mn> Co > Ni respectively.Mean while, the mean levels of metals in the muscle and liver tissues of *O. niloticus* were in the order of Fe > Pb > Zn >Mn> Cu > Cr > Co > Ni and Pb > Zn >Mn> Fe > Cu.> Co > Ni respectively. Similarly, the mean levels of heavy metals detected in the liver and muscle of *L. niloticus* from Omo delta occurred in the order of Fe > Zn >Pb> Cu >Mn> Cr > Co > Ni and Fe >Pb> Zn >Mn> Cu > Co > Cr >Ni respectively.While the mean levels in the muscle and liver tissues of *O. Niloticus* from the Omo delta were in the order of Fe > Pb > Zn >Mn> Cu > Cr > Co > Ni and Pb > Fe > Zn >Mn> Co > Cu > Ni respectively. The study revealed that the THQ values were below 1, indicating that *L. niloticus* and *O. niloticus* do not pose potential non carcinogenic health risk. Although the TCR values for Pb in this study were within the tolerable range, it’s mean concentration in the muscle and liver tissues of both fish species from the two water bodies exceeded the permissible limit established by FAO/WHO. This is a warning sign for early intervention, and it emphasizes the need for regular monitoring of freshwater fish. Therefore, it was imperative to investigate the pollution levels and human health risks of heavy metals in fish tissues from lower Omo River and Omo delta for environmental and public health concerns.

Keywords: Heavy metals, Human health risk, Omo Delta, Omo Rive

4.1. Introduction

Aquatic products including fish are becoming increasingly popular as a source of protein, omega-3 fatty acids, vitamins, selenium, and calcium for human consumption (Kalantzi *et al*., 2016). The American Heart Association recommends consuming two servings of fish per week as part of a balanced diet(Neff *et al*., 2014). However, it worth noting that aquatic products may also contain contaminants due to their high fat and protein contain, which can have negative effects on human health (Usydus *et al*., 2009).

Various natural and human caused factors, such as sewage discharge from homes or industrial, storm runoff, leaching from landfills/dumpsites, and atmospheric deposits, can cause heavy metals to accumulate in aquatic environments (Rahman *et al*., 2016). Heavy metals are significant pollutants in freshwater ecosystems and food supplies (Manal *et al*., 2014) and can pose sever risks to both humans and aquatic life (Solomon *et al*., 2016).The risk of consuming heavy metals from contaminated food is increasing in developing countries like Ethiopia (Berehanu *et al*., 2016, Samuel *et al*., 2020). fish muscles that have accumulated heavy metals can be consumed by humans (Lubna *et al*., 2015, Gure *et al*., 2019), which can pose health risks to various vital organs such as the kidney (Manal *et al*., 2014), liver , and brain (Safiur *et al*., 2012),lung , and heart (Mir *et al*., 2021),and reproductive system at the cellular, tissue, and organ levels (Javed and Usmani,2011).Excessive heavy metals in fish tissues can negatively impact early development, growth, behavior, and reproduction, and damage the neurological systems of fish species (Taslima *et al*., 2021).Thus, the accumulation of heavy metals in human diets, including fish, is an urgent global treat that requires attention, especially in developing countries like Ethiopia.

In recent years, human activities such as agriculture, industrial, and economic development have affected the lower Omo River(Lotic) and the Omo delta (Lentic) (USEPA, 2010, Wakjira and Getahun, 2017).These activities have threatened the quality of the water bodies (Ojwang *et al*., 2010, Avery, 2012),have been linked to the presence of heavy metals in fish tissues**.** Studies have also shown that fish tissues from Lake Turkana, which is located close to the Omo delta, contain higher levels of heavy metals (Magu *et al*., 2016, Christof *et al*., 2017).

To the best of our knowledge, no study has been reported on the level of heavy metals in fish tissues and associated human health risks in the lower Omo River (Lotic) and the Omo delta (Lentic). However, some studies have been performed on the concentrations of heavy metals in fish tissue from Lake Turkana on the Kenyan side (Magu *et al*., 2016, Christof *et al*., 2017), which is the point where the southernmost tip of the Omo River extends into it. Therefore, it is crucial to determine the concentrations of heavy metals in fish tissues from the lower Omo River (Lotic) and the Omo delta (Lentic) for environmental and public health issues). The sample were tested for the presence of nine heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn), and carcinogenic health risks to adults and children associated with consuming fish were calculated. Thus, the current study aimed to evaluate the human health risks associated with heavy metals present in commonly consumed fish spices (*L. niloticus* and *O. niloticus*) collected from the lower Omo River (Lotic) and the Omo delta (Lentic).

4.2 Materials and methods

4.2.1 Description of the study area

Descriptions of the study are presented in chapter one of section 1.9.1 (Table1.1, figure1.1 & figure1.2)

4.2. 2 **Fish sample collection and storage**

Thirty samples of fish from each species, namely *L. niloticus* and *O. niloticus* were collected from the Omo Delta Lake and the River water. The sampling and storage of these samples strictly followed APHA and EMERGE procedures (Rosseland *et al*., 2001, APHA, 2017). The fish samples were collected from fishermen who used plastic nets to trap fresh *L. Niloticus* and *O. niloticus from* the sampling sites as presented in section 1.81. Of Table 1.1. The fish samples were washed with deionized water just before dissecting the tissues. The fish were then dissected in the field using plastic blades to obtain liver and muscle tissue. After removal, each liver and muscle tissue samples was carefully covered with aluminum foil and sealed simultaneously in polyethylene bags. The tissues were then separately labeled based on species and tissue type. The wrap samples were cautiously placed in an icebox, and immediately transported to the Arbaminch Minch University of Chemistry Laboratory after dissection and wrapping in an icebox. The samples were then preserved in a freezer at -20 °C until analysis. The Field experiments were approved by research council of Hawassa University (Approval number bio/499/13).

4.2.3 Sample preparation and digestion

The fish tissue samples were prepared according to the guideline of the United State Environmental Protection Agency (USEPA, 2010).The muscle and liver tissues were separately oven dried at 60° until they reached constant weight. The dried tissues were then crushed in to a powdered using mortar and pestle. The powdered tissue samples weighing 0.5geach were ready for digestion. Ash digestion was carried out by taking 0.5 grams of muscle and liver tissue, which was subjected to a temperature of 550°C for 4 hours. After each sample was entirely turned in to ash, it was removed and cooled in desiccators. The ash samples were mixed with 10 ml of 20% HNO_3 in 50 ml beakers, placed on a hot plate, and heated slowly at 120 °Cfor 30 minutes. After digestion and cooling, dilution and filtration were done using distilled water and filter paper (Whatman No. 42). Digestion was performed following analytical method protocol for atomic absorption spectrometry(Perkin, 1996).

4.2.4 Sample analysis

The analysis was conducted according to APHA guidelines of 2017. Fish tissue samples were tested for heavy metal content using a flame atomic absorption spectrometer (FAAS, novAA400p). Calibration curves were prepared using analytical grade standards of each target heavy metal.

4.2.5 Human health risk assessment

A. Noncarcinogenic risks

The study aimed to determine the potential health risks posed by consuming heavy metals found in fish muscle. This was done by calculating target hazard quotient (THQ) and hazard index, which help to determine the likely hood of non-carcinogenic health hazards in humans. The THQ result assess the risk posed by a single heavy metals ,while HI results calculate the cumulative risk from all heavy metals found in fish muscle. Values of THQ and HI < 1 indicate that the risk of health effects is low, while values greater than 1.0 suggest that potential noncarcinogenic health hazards are likely to occur individuals who consumed fish muscle. The greater the THQ value is, the greater the possibility of risk to the exposed individuals(USEPA, 2011).The noncarcinogenic risk was assessed for both adults and children who ingested fish muscle from the lower Omo River andOmo

Delta ,one to seven days per week. The THQ and HI were estimated using EPA guidelines(USEPA, 2011, USEPA, 2019)using equations 1 and 2 below

$$\mathrm{THQ} = \frac{(EF\times \mathrm{ED}\times \mathrm{IR}\times \mathrm{Cm})}{(\mathrm{RfD}\times \mathrm{WAB}\times \mathrm{AT})}10^{-3} \quad \dots\dots\dots\dots \quad \mathrm{Eq}(4.1)$$

$$HI = \sum \mathrm{THQ} \dots\dots\dots\dots\dots\dots\dots\dots\dots \mathrm{Eq}(4.2)$$

Where: THQ is a non-carcinogenic health risk; the average life expectancy in Ethiopia is 65 years for adults and 6 years for children. ED is the exposure duration (USEPA, 2005, WHO, 2015);EF is the exposure frequency which is 365 days/year for people who eat fish muscle 7 times a week and 52 days/year for those who eat once a week (FAO, 2014), and IR is the average fish ingestion rate of an individual in a day (g/day/person) which is 30g for adults and 15g for children in Ethiopia (USDA, 2000, USEPA, 2005).The RfD is the oral reference dose which is the daily ingestion of a contaminant that is unlikely to cause health effects during a life time as defined by the USEPA (2003) in mg kg^{-1}/day which is 0.001for Cd, 0.003 (Cr) , and 0.03; 0.040 (Cu), 0.7, 0.020 (Ni), 0.14 (Mn), 0.0035 (Pb) and 0.30 (Zn);BW is the average body weight equivalent to 60 kg for adults and 21kg for children in Ethiopians (WHO, 2012); AT is the average exposure time for non-carcinogens which is 365 days/year x ED;Cm is the average concentration of heavy metals in fish muscles (mg/kg dry weight);WAB is the average body weight .

B. Carcinogenic risk (TCR)

The target carcinogenic risks (TCR) test estimates an individual's possibility of developing cancer over a lifetime while exposed to a potential carcinogen and the acceptable risk levels for carcinogens range from 10^{-4} to 10^{-6} '(USEPA, 1989).The TCR was estimated using equation 3 below.

$$\mathrm{TCR} = \frac{(EF\times \mathrm{ED}\times \mathrm{Cm}\times \mathrm{IR}\times \mathrm{CSFO})\times 10-3}{(\mathrm{WB}\times \mathrm{AT})} \dots\dots \mathrm{Eq} \dots\dots\dots\dots\dots\dots ..(4.3)$$

where: TCR is the target cancer risk; CPSO is an oral carcinogenic slope factor in mg/kg/day with values include1.7 mg kg^{-1}/day for Ni, and 0.5 (Cr), 0.001(Cd) and 0.0085 for Pb(USEPA, 2010). The other parameters are presented in Equations 1 and 2.

4.2.6 Data quality

Precision of the method and validation of the results were checked by the recovery test (APHA, 2017).The fish sample was spiked with known concentration of heavy metals and spiked samples were digested in triplicate using the same method used for the original samples. The percent recovery was then calculated using equation 4.4

$$\text{Recovery} = \frac{(Spiked\ result - Unspiked\ result)}{(\text{Amount added})} \times 100\% \qquad (4.4)$$

All recovery values were within the acceptable range (80%-120%) for heavy metal analysis (Harvey, 2000) and are summarized in Fig 4.1 below

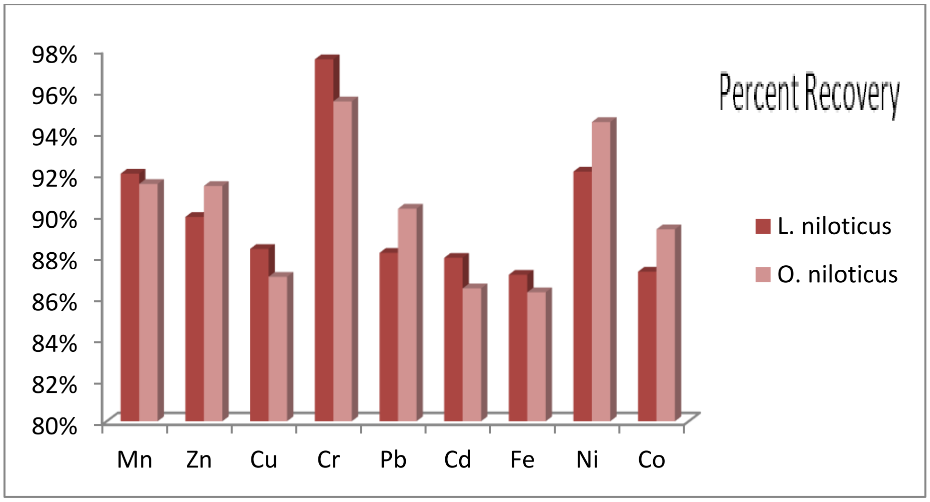


Figure 4.1 *Percentage recovery in muscle of L. niloticus* and *O.niloticus*

4.2.7 Data analysis

The data were analyzed using IBM SPSS 21 statistical software. To determine a normal distribution and homogeneity of variance, Levine's test was applied. Variations in the mean levels of heavy metals between fish muscle and liver and species were evaluated using a *T*-test. A Pearson correlation coefficient matrix was used to determine the correlation between metal in the fish tissues.

4.3 Results and discussion

4.3.1 Heavy Metal Concentrations in fish from Lower Omo River and its associated human health risks

4.3.1.1 Heavy metal concentrations in fish from Lower Omo River

The mean concentration of detected metals in liver and muscle *tissues of L. niloticus* and *O. niloticus* are presented inTable 4.1. The tissue levels of heavy metals in the present findings and the previous reports of the same species are also compared in table 4.2. Generally, the mean heavy metal levels ranged from 0.019 to 2.918 mg kg^{-1} .The maximum mean level of heavy metals detected in muscle of *L. niloticus* was Fe (2.918 ± 1.47 mg kg^{-1})) and the minimum mean level was Ni (0.019 ± 0.006).Likewise, the maximum mean level in muscle of *O. niloticus* was Pb (0.79 ± 0.173 mg/kg and the minimum muscle level was for Ni (0.01± 0.002 mg /kg).Mean levels of the metals in liver and muscle of *L. niloticus* generally occurred in an order of Fe > Zn > Pb > Cu > Mn > Cr > Co > Ni and Pb > Cu > Mn > Cr > Co >Ni respectively. Similarly, mean concentrations in the liver and muscle tissues of *O. niloticus* were in the array Fe > Pb > Zn > Mn > Cu > Cr > Co > Ni and Pb > Zn > Mn > Fe > Cu.> Co > Ni respectively. Except for Cd, all investigated heavy metals were detected in the liver tissues of both species. Neither Cd nor Cr was detected in the muscle of *L. niloticus* and *O. niloticus*. Higher levels of the metals were generally observed in the liver tissues. Pb level of muscle and liver tissues in both fish species was above FAO/WHO (1998) permissible limit.

Manganese (Mn) had a mean concentration that varied from 0.391 mg kg^{-1} to 0.356 mg/kg^{-1}.The maximum and minimum mean concentrations were observed in liver of *L. niloticus and O. niloticus* respectively following in an order *L. niloticus (*liver*)> L. niloticus (*muscle*) >O. niloticus (*muscle*)> O. niloticus* (liver).The detected concentration is below the FAO/WHO (1989) permissible human diet ingestion and are comparable to those reported in muscle of *O. niloticus* species from Lake Hawassa by Abayneh *et al*. *(*2003).The Mn content of muscle tissues (O. *niloticus)* in the current finding was lower than the previous report in Ethiopia from Lake Hawassa by Ermias *et al*.. (2015) and from the Volta River Basin of Ghana by Emmanuel *et al*. *(*2021).

Mean Zinc (Zn) level ranged from 1.01 mg/kg to 0.424 mg/kg.The maximum mean level was detected in the liver of *L. niloticus*, whereas the minimum was observed in the muscle of *O. niloticus* following the order *L. niloticus (*liver*)> L. niloticus (*muscle*) >O. niloticus (*liver*)> O. niloticus (muscle).*The Zn content in muscle tissues of the present findings were comparable with the reports in the earlier studies by Zenebe (2011) in Ethiopia and Magu *et al*. (2014) from Kenyan freshwater fish. But, the content in the muscle of *the same species* was lower than the earlier studies from Ethiopia's freshwater fish by (Abayneh *et al*., 2003; Ermias *et al*., 2015; Samuel *et al*., 2020) and from Langat River of Malaysia by Lubna *et al*. (2015). Similarly, Zn level of liver tissues in *O. niloticus* of the current investigation was higher than the study report of the same species by Dugasa and Endale (2018).

Copper (Cu) level of the tissues ranged from 0.481 mg kg^{-1} to0.129 mg kg^{-1}. The maximum and minimum mean Cu level was detected in the liver of *L. niloticus and in* muscle tissue of *O. niloticus*, respectively. Order of Cu concentrations were *L. niloticus (*liver*)>O. niloticus (*liver*)>L.*

*niloticus (*muscle*) >O. niloticus* (muscle).The levels are below the FAO/WHO (1989) maximum permissible limit in the human diet. The mean Cu content of muscle tissues in *O. niloticus and L. niloticus* of this study was higher than the earlier reports by Zenebe (2011) and Magu *et al*. (2014) respectively. However, the content of muscle tissues in *O. niloticus* was lower than the studies by (Magu *et al*., 2014; Ermias *et al*., 2015; Gure *et al*., 2019). Likewise, concentration of Cu in the liver tissues of *O. niloticus* in the present finding was higher than the finding report by Dugasa and Endale (2018).The mean muscle content of Cu *in L. niloticus* of the current study was lower than the previous study report viaFelly *et al*. (2020).

Higher level of Cr was observed in L. niloticus which was detected only in the liver tissues of both fish species. It was not detected from the muscle tissues of O. niloticus and L. niloticus of the present finding, which was similarly reported in the earlier study by Ermias *et al*. (2015). However, the content of Cr in the liver tissue of both fish species was higher than the study reported by Dugasa and Endale (2018) and lower than the finding report of Gure *et al*. (2019) from Gibe River in Ethiopia. Cadmium was not observed in liver and muscle of both species. This was similarly reported by (Zenebe, 2011; Ermias *et al*., 2015).

The Lead (Pb)level of tissues ranged from 0.79 to 1.009 mg kg^{-1}.The maximum mean concentration of Pb was recorded in the liver tissue of *L. niloticus,* whereas the minimum muscle level of Pb was observed in *O. niloticus following the order L. niloticus (*liver*)>O. niloticus (*liver*)>L. niloticus (*muscle*) >O. niloticus (*muscle).The mean Pb levels in the muscle of both species were above the FAO/WHO recommended limits in the human diet (FAO/WHO, 1998). The Pb content of muscle tissues in both species of this finding was higher than earlier report by (Magu *et al*., 2014; Samuel *et al*., 2020). However, the Pb content of liver tissue of *O. niloticus of the current finding was* lower than reported by Dugasa and Endale (2018).

Mean concentration of Iron (Fe) ranged from 2.918 mg kg^{-1} to 0.268 mg kg^{-1}.The maximum mean Fe level was detected in the liver of *L. niloticus,* whereas the minimum was detected from muscle of *O. niloticus* and followed an order *L. niloticus*(liver)>*O. niloticus (*liver*)>L. niloticus (*muscle*) >O. niloticus (*muscle).The tissue levels of Fe are below the FAO/ WHO (2011)allowable limit and are below those records in muscle of *O. niloticus* by (Abayneh *et al*., 2003; Samuel *et al*., 2020).The current findings show that O. niloticus and L. niloticus have lower Fe contents in their muscle tissues than those found in research by (Abayneh *et al*., 2003; Dugasa and Endale, 2018; Emmanuel *et al*., 2021).In contrast, the Fe content of liver in *O. niloticus* of the current finding was higher than the previous report by Dugasa and Endale (2018).

Mean concentrations of Nickel (Ni) in the fish ranged from 0.01 to 0.019 mg kg^{-1}.Maximum mean concentration was detected in liver tissue of *L. niloticus,* while the minimum level was detected in muscle of *O. niloticus* and followed the order *L. niloticus (*liver*)> L. niloticus (*muscle*) >O. niloticus (*liver*)> O. niloticus (muscle).*These concentrations are within the FAO/WHO (1998) recommended permissible human diet intake levels which could not impose an immediate adverse health effects. The Ni contents of muscle tissues in *O. niloticus and L. niloticus* of the present finding were comparable with the reports by (Zenebe, 2011; Samuel *et al*., 2020) and lower than the studies recorded by (Magu *et al*., 2014; Emmanuel *et al.,* 2021).

Cobalt (Co) content in live and muscle tissues ranged from 0.054 to 0.097 mg kg^{-1}.Maximum mean content of Co was detected in liver of *L. niloticus,* while the minimum was detected in the muscle of *O. niloticus* and followed the order *L. niloticus (*liver*)> L. niloticus (*muscle*) >O. niloticus (*liver*)> O. niloticus (muscle).*The mean muscle level Co in *O. niloticus was comparable* with the previous report by Samuel *et al*. (2020) .However; the mean Co level of the current finding was lower than the study recorded in the muscle and liver tissue of *O. niloticus by* Gure *et al*. (2019).

The t-test (*P<0.05*) revealed that there were significant differences in the mean level of all heavy metals except for Co in muscle and liver tissues of *Nile perch*. Similar differences were found in the mean levels of heavy metals in O. niloticus muscle and liver tissue, with the exception of Mn, Zn, and Cu. There were also species-dependent statistically significant differences in mean content of Fe, Pb, Ni, and Co in liver tissues of *Nile perch* and *Nile tilapia*. Likewise, the average contents of heavy metals except for Pb, Zn, and Cu in tissues of both fish species were significantly different (*P<0.05*).It was addressed by many researchers that fish species-dependent differences in metal accumulation might be associated with feeding habits such as being carnivores, herbivores, or omnivores and habitat of fish species (Yılmaz *et al*., 2005; Kamal *et al*., 2023).Variations in the mean concentrations of heavy metals between L. *niloticus* and O. *niloticus* in the current study may be attributed to Variations in feeding habits and habitat use (Elias *et al*., 2014; Samuel *et al*., 2020). Biological factors including age and growing rates of fish species could also attribute to differences in heavy metal concentrations between *L. niloticus* and *O. niloticus (*Yılmaz *et al*., 2005; Ahmed *et al*., 2015) in the present study.

L. niloticus showed higher burden of heavy metals than *O. niloticus.* This could be due to differences of the two species in their behavior and feeding habits. Thus, the relative high level of metals in *L. niloticus* tissues of the present study could be accredited to their feeding habits as they are bottom-dwelling carnivores which feed on zooplankton, shrimp, clams, snails, insects and other fish species as compared to *O. niloticus* which feeds on algae and other vegetables (Magu *et al*., 2016; Elias *et al*., 2005**)**. Carnivores are likely to accumulate high metal content of heavy metals than other fish (Ahmed *et al*., 2015).

Differences in mean level of heavy metals between the fish tissues (liver and muscle) in this finding could be due to the ability of various metals to induce binding with carboxylate oxygen, the amino functional group, and nitrogen in the metal-binding proteins (Uysal *et al*., 2009; Gure *et al*., 2019; Pramita *et al*., 2021).The variations between tissue contents of metals could also be ascribed due to differences in the physiological role of each tissue in which muscle generally accumulates lower levels of heavy metals *(*Ahmad *et al*., 2015;Olawusi *et al*., 2019).Many studies also confirmed that there was variation in heavy metal levels among fish tissues and species (Samuel *et al*., 2020; Gure *et al*., 2019), which was also observed in the current finding.

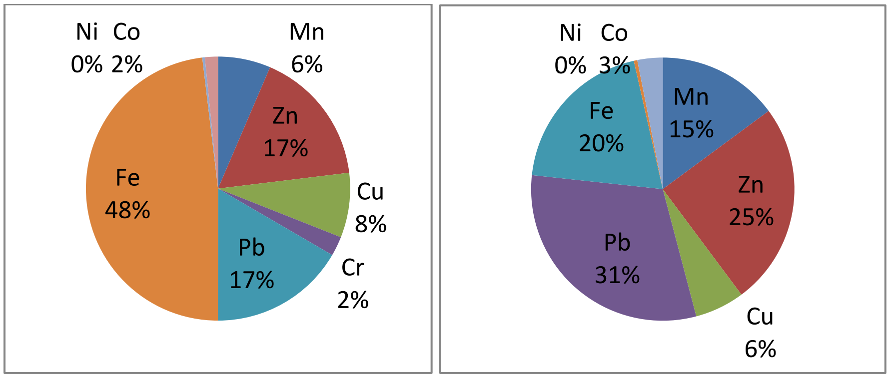
The Cu content in fish tissues may occur from agrochemicals through use of fungicides, algaecides, and insecticides in the agricultural land, which could be drained by runoff to freshwater fish (Pramita *et al*., 2021**).**Thus, the occurrence of Cu in fish tissues of this study could be from agrochemicals that may arise from irrigation land along the Omo River. Pb concentration in the freshwater fish may rise from different anthropogenic sources of agricultural discharges, factories, solid waste and wastewater that may get in the freshwater (Manal *et al*., 2014). Consequently, the occurrence of Pb in the fish tissues of the current study could be attributed to agrochemicals from intensive irrigation farm land to the river, urban discharges and solid wastes from Omorate town which is adjacent to the river, wastewater from upstream factories and other anthropogenic activities. The presence of Ni in the fish tissues of this finding could be due to location of the river in the rift valley and it is naturally abundant in the earth's crust **(**Magu *et al*., 2016).The occurrence of Zn in fish tissues of the current finding could be due to urban runoff, waste water and agrochemical use observed in the catchments of present study **(**Olawusi *et al*., 2019)**.**

Table 4.1Mean Concentrations of heavy metals (mg/kg) in *Lates niloticus* and *Oreochromis niloticus* from lower Omo River

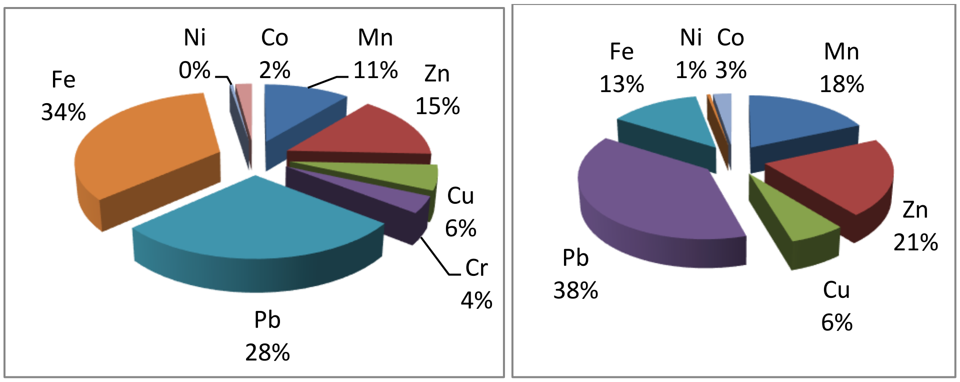
Heavy Metals	Mean ± Sd of heavy metal concentrations (mg/kg dry weight) in tissues of the two fish species				MPL (mg/kg)	Reference
	Lates niloticus		*Oreochromis niloticus*			
	Liver	Muscle	Liver	Muscle		
Mn	0.391 ±0.003	0.383 ±0.003	0.356 ±0.005	0.379 ±0.003	1.0	FAO/WHO, 1989
Zn	1.01 ±0.482	0.642 ±0.474	0.477 ±0.424	0.424 ±1.017	40	FAO/WHO, 1989
Cu	0.481 ±0.459	0.157 ±0.273	0.189 ±0.283	0.129 ±0.236	3.0	FAO/WHO, 1989
Cr	0.145 ±0.021	ND	0.126 ±0.075	ND	0.15	FAO/WHO, 1989
Cd	ND	ND	ND	ND	0.2	FAO/WHO, 1989
Pb	1.009±0.215	0.793 ±0.173	0.908 ±0.210	0.79 ±0.173	0.5	FAO/WHO, 1998
Fe	2.918 ±1.476	0.509 ±0.273	1.100 ±0.354	0.268 ±0.059	100	FAO/WHO, 2011
Ni	0.019 ±0.006	0.011 ±0.003	0.014 ±0.002	0.010 ±0.002	0.15	FAO/WHO, 1989
Co	0.097 ±0.023	0.080 ±0.028	0.068 ±0.020	0.054 ±0.017	-	-

ND: not detected; MPL: maximum permissible limit in human diet

Percentage contributions of each heavy metal in liver and muscle tissues of both fish species are presented in fig 4.3 below. Fe and Pb had the highest contribution to heavy metal exposure in the liver and muscle of both fish species, respectively. Ni had the lowest contribution to heavy metal exposure in liver and muscle tissues of *L. niloticus* and *O. niloticus*.



(a) (b)



(c) (d)

Figure 4.2 Percentage contribution of each heavy metal in L. niloticus the liver (a), muscle (b), and in O. niloticus liver (c), and muscle (d).

Missing heavy metals in each tissue of the two fish species in the figure are those which were not detected. Burdens of each metal in tissues of L. niloticus and *O. niloticus* are summarized in Fig 4.3 below. The burden of heavy metals in L. niloticus was higher compared to O. niloticus, which could be attributed to the fact that *L. niloticus* is at higher trophic level which may accumulate higher heavy metals. Feeding habits and habitats of fish species may also contribute to the accumulation. Similarly, burden of heavy metals in liver tissue was higher than the muscle tissue, which could be due to fish muscle is less active in accumulating heavy metals in contrast to liver tissues (Kamal *et al*., 2023).

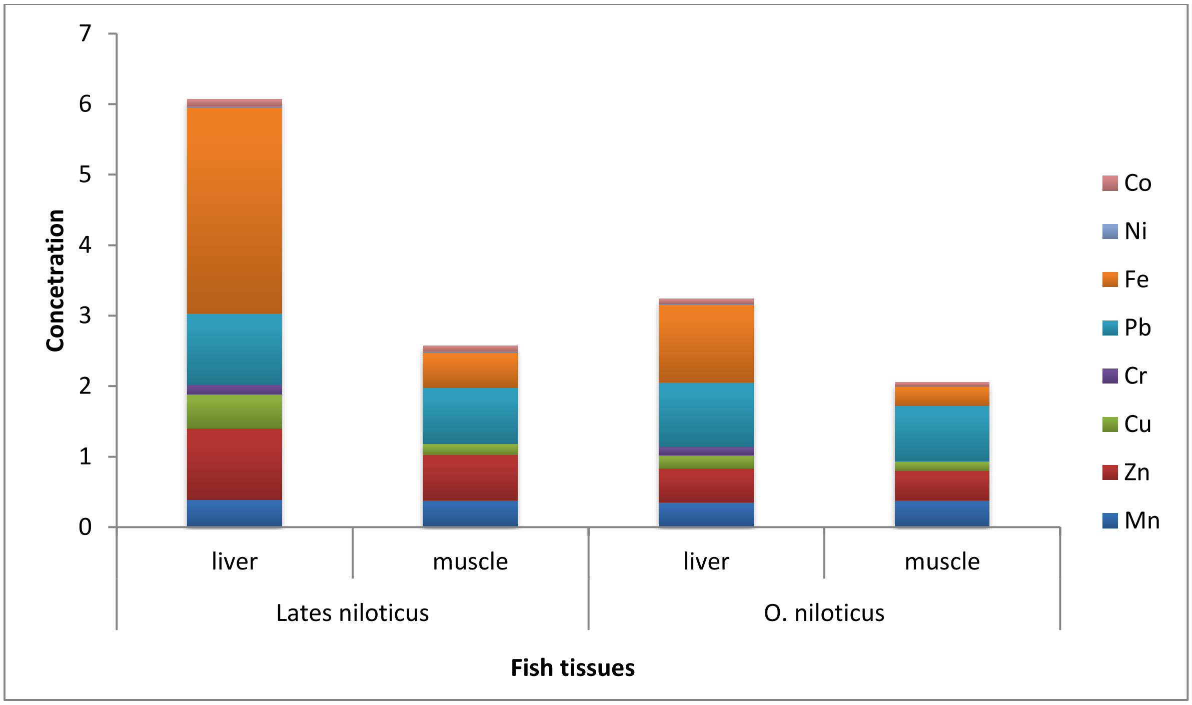


Figure 4.2 Burden of heavy metals in muscle and liver issues of L. niloticus and O.niloticus)

The findings obtained from muscle and liver tissues of the present study were compared with the literatures values of the previous study report from freshwater fish of the same species as presented in table 4.2. The current finding was contrasted with the FAO/WHO (1989) permitted limit. Except for Pb, the amounts of heavy metals were below the FAO/WHO (1989) maximum dietary values for fish.The results of the current study may be comparable to and concur with previous literature reports on freshwater fish (*L. niloticus and O. niloticus*).

Table 4.2 Comparison of muscle and liver level of heavy metals of the present study (Lower Omo River) with other reported literature values.

Fish species	Tissues	Heavy metal concentrations(mg/kg)									Source
		Mn	Zn	Cu	Cr	Cd	Pb	Fe	Ni	Co	
Oreochromis niloticus	Muscle	0.55	4.76	0.31	-	-	-	5.49	-	-	Abayneh *et al*.(2003)
	Liver	-	0.074	0.029	0.038	0.027	1.630	0.809	-	-	Dugasa and Endale(2018)
	Muscle	-	0.3	0.03	-	-	ND	-	0.04	-	Zenebe(2011)
	Muscle	0.77	0.97	-	0.10	-	-	11.09	0.65	-	Emmanuel *et al.(*2021)
	Liver	-	-	8.28	18.31	0.36	6.02	-	-	6.11	Gure *et al*.(2019)
	Muscle	-	-	4.64	10.31	ND	8.39	-	-	3.10	Gure *et al*.(2019)
	Muscle	-	16.5	0.92	0.14	-	0.014	9.45	0.09	0.01	Samuel *et al*.(2020)
	Muscle	-	0.647	0.419	-	0.0193	0.238	-	0.380	-	Magu *et al*.(2014)
	Muscle	-	19.36	1.33	0.19	-	0.015	11.34	0.05	0.02	Samuel *et al*.(2020)
	Muscle	-	-	2.26	-	0.67	9.99	-	-	-	Felly *et al*.(2020)
	Muscle	1.972	21.110	13.833	ND	ND	ND	-	ND	ND	Ermias *et al*.(2015)
	Muscle	-	0.26	0.04	-	-	ND	-	0.05	-	Zenebe(2011)
	Muscle	-	-	-	-	0.1	5.8	-	-	-	Fredrick *et al*., 2021)
	Muscle	-	8.25	1.37	1.48	0.01	0.05	0.75	-	-	Lubna *et al*.(2015)
	Liver	0.356	0.477	0.189	0.126	ND	0.908	1.100	0.014	0.068	Present study
	Muscle	0.379	0.424	0.129	ND	ND	0.79	0.268	0.010	0.054	Present study
	Muscle	-	-	0.024	-	-	0.327	-	0.444	-	(Magu *et al*., 2014)
Lates niloticus	Muscle	-	-	0.65	-	0.15	7.23	-	-	-	(Felly *et al*., 2020)
	Muscle	-	-	-	-	2.5	3.5	-		-	Fredrick *et al*.(2021)
	Muscle	-	0.01	0.97	-	0.04	0.08	-	-	-	Jhon (2007)
	Liver	0.391	1.01	0.481	0.145	ND	1.009	2.918	0.019	0.097	Present study
	Muscle	0.383	0.642	0.157	ND	ND	0.793	0.509	0.011	0.08	Present study
	Muscle	1.0	40	3	0.15	0.2	0.5	100	0.15	-	FAO/WHO (1989/2011)

Lake Turkana (Keneya)	Muscle	-	26.9	0.808	0.232	<0.005	<0.007	-	-	-	Plessl *et al.* (2017),
	Liver		75.5	96.8	0.107	0.255	<0.007	-	-	-	Plessl *et al.* (2017),
	Muscle		426	0.63	ND	0.56	0.012	-	-	-	Plessl *et al.* (2017)
	Liver		89.2	17.2	ND	11.5	0.015				Otachi *et al.* (2015)

MPL= Permissible limit in human diet; ND= Not detected; - = Not investigated

4.3.Human health risk associated with HMs in fish from Lower Omo River

The non-carcinogenic health risks associated with the nine heavy metals in children and adults who consumed muscle of *L. niloticus and O. niloticus from* the Lower Omo River were assessed using THQ and HI indices. The index results (THQ and HI) through eating muscle of fish within one to seven times a week are presented in Table 4.3.The THQ values in the muscle of *L. niloticus* and O. *niloticus* were in the order of Pb > Cu > Mn > Co > Zn > Fe > Ni and Pb > Cu > Mn > Co > Ni >Zn > Fe respectively. The index (HI) values due to consumption of *L. niloticus* muscle were 0.15 (for adults) and 0.21(for children). Similarly, the HI values in O. *niloticus* were 0.10 (for adults) and 0.18 (for children). Maximum THQ and HI values were observed for Pb where as the minimum was observed in Ni.

In all the evaluated samples, the THQ for heavy metals in fish muscle ingested by adults and children were less than one, which indicates that individuals are unlikely to experience considerable health risks due to ingestion of a single heavy metal through intake of the fish muscles. Similarly, the Hazard Index (HI) of the detected heavy metals was less than one indicating that there was no substantial adverse health effect due to intake of *L. niloticus and O. niloticus* muscle tissues from Lower Omo River source at the present time of study. The mean contribution of THQ value to HI showed that Pb, Cu, and Mn contributed about 97 % to HI through muscle of fish tissues. Pb while single handedly, contributed about 90% to HI via the muscle tissues of both fish species. As a result, more emphasis should be given to Pb level in the muscle of both fish species regarding the non carcinogenic risks. Emmanuel *et al*. (2021) from their study in Volta Basin River, Ghana, recorded higher THQ value for Mn (0.00325) than the present findings for Mn (0.0021). However, they reported lower THQ values for Ni (0.000108), Zn (9.2×10^{-5}), and Fe ($2.14\times10^{-8)}$ than the present study via intake of *O. niloticus* muscle *by children*. Similarly, Samuel *et al* (2020) from their study in Ethiopia from Boicha stream (Hawassa) reported higher THQ values for Fe (0.01), Co (0.001), Ni (0.002), Cu (0.02), and Zn (0.039) than the present findings. However, they reported lower THQ value for Pb (0.026) than the present finding (0.11) in muscle O. *niloticus* by an adult while consuming one to seven days a week.

Table 4.3 Estimated target hazard quotient (THQ) and hazard index (HI) in adults (a) and children (c) due to heavy metal exposure in muscle of *L. niloticus and O. niloticus from Lower Omo River*

Fish Species	Level of exposure (d/w)	Target hazard quotient (THQ) adult(a) and children (c)							Hazard Index (HI)
L. niloticus		Mn	Zn	Cu	Pb	Fe	Ni	Co	
	1	0.0002a	0.00015a	0.0002a	0.016a	0.00005a	0.00004a	0.00019a	0.0168a
		0.0003c	0.00023c	0.00043c	0.02c	0.0002c	0.00006c	0.0003c	0.0215c
	2	0.00039a	0.00031a	0.00056a	0.032a	0.0001a	0.00008a	0.00038a	0.0338a
		0.0006c	0.0005c	0.0009c	0.05c	0.00034c	0.00012c	0.0006c	0.0531c
	3	0.00058a	0.00046a	0.00084a	0.048a	0.00015a	0.00012a	0.00057a	0.0507a
		0.0009c	0.0007c	0.0013c	0.07c	0.0005c	0.0002c	0.0009c	0.0737c
	4	0.00078a	0.00061a	0.0011a	0.065a	0.00021a	0.00016a	0.00076a	0.0686a
		0.0012c	0.00093c	0.002c	0.10c	0.0007c	0.00024c	0.0012c	0.1063c
	5	0.00097a	0.00076a	0.0014a	0.081a	0.00026a	0.0002a	0.00095a	0.0855a
		0.0015c	0.0012c	0.0022c	0.12c	0.0009c	0.0003c	0.0015c	0.1384c
	6	0.0012a	0.00092a	0.0017a	0.097a	0.00031a	0.00024a	0.0011a	0.1025a
		0.0018c	0.0014c	0.0026c	0.15c	0.001c	0.0004c	0.0017c	0.1715c
	7	0.0014a	0.0011a	0.0018a	0.11a	0.00036a	0.00028a	0.0013a	0.1162a
		0.0021c	0.002c	0.003c	0.2c	0.0012c	0.00042c	0.002c	0.2107c
O. niloticus	1	0.00019a	0.00010a	0.00023a	0.016a	0.000027a	0.00004a	0.00013a	0.0167a
		0.0003c	0.00015c	0.0004c	0.025c	0.00004C	0.00005c	0.00019c	0.0261c
	2	0.00038a	0.0002a	0.00046a	0.032a	0.000055a	0.00007a	0.00026a	0.0334a
		0.0006c	0.0003c	0.0007c	0.05c	0.000083c	0.00012c	0.0005c	0.0523c
	3	0.00057a	0.00030a	0.00069a	0.032a	0.000082a	0.00011a	0.00038a	0.0341a
		0.0009c	0.0005c	0.0011c	0.07c	0.00013c	0.00016c	0.0006c	0.0734c
	4	0.00077a	0.0004a	0.00092a	0.064a	0.00011a	0.00014a	0.0005a	0.0668a
		0.0012c	0.00062c	0.0014c	0.1c	0.00017c	0.0002c	0.0008c	0.1044c
	5	0.00096a	0.0005a	0.0012a	0.080a	0.00014a	0.00018a	0.00064a	0.0836a
		0.0015c	0.0008c	0.005c	0.12c	0.0002c	0.00027c	0.001c	0.1187c

6	0.0011a 0.0018c	0.0006a 0.0008c	0.0014a 0.002c	0.096a 0.15c	0.00016a 0.00025c	0.0002a 0.00033c	0.0008a 0.0012c	0.1003a 0.1564c
7	0.0013a 0.0021c	0.00071a 0.0011	0.0016a 0.003c	0.11a 0.2c	0.00019a 0.0003c	0.00077a 0.0004c	0.0009a 0.0014c	0.1155a 0.2083c

Cd and Cr were not detected in the muscle of both fish species.

The likely target cancer risk due to ingestion of Pb and Ni through muscle of *L. niloticus* and *O. niloticus* for 1 to 7 days a week are presented in Table 4.4. The target cancer risk (TCR) values in the muscle of both *L. niloticus* and *O. niloticus* were in an order of Ni > Pb. The TCR values for Pb and Ni in this study were within the tolerable range of (10^{-6} to 10^{-4}) (USEPA, 2012) for all levels of exposure. The highest TCR value observed due to consumption of *L. niloticus* and *O. niloticus* muscle by children for Ni was $1.4 \times 10^{-5}$and 1.3×10^{-5} respectively. Similarly, the highest TCR value due to *L. niloticus* and *O. niloticus* by adults for Ni was 9.4×10^{-6} and 8.5×10^{-6} respectively. This demonstrated that, for all exposure levels, there was no risk to the health of *L. niloticus* and *O. niloticus* from ingesting Pb and Ni through muscle. It was also observed that children had a higher probability of developing risk when exposed to heavy metal pollution. Emmanuel *et al*.(2021) from their study in Volta Basin River, Ghana, reported lower target Cancer Risk (TCR) for Ni in children (5.5×10^{-8})than the present study (1.1×10^{-5}).Similarly Samuel *et al* (2020) from their study in Ethiopia from Boicha stream (Hawassa) reported higher target Cancer Risk (TCR) for Ni in adult (5.51×10^{-5}) than the present study (8.5×10^{-6}). However, they reported lower TCR for Pb (7.65×10^{-8}) than the present study (3.3×10^{-6}) via intake of *O. niloticus* muscle by adults.

Table 4.4Target cancer risk (TCR) in adults and children due to heavy metal exposure in muscle of *L. niloticus and O. niloticus from Lower Omo River*

Fish Species	Level of exposure (d/w)	Carcinogenic Risk (CR) in Adults		Carcinogenic Risk (CR) Children	
		Pb	Ni	Pb	Ni
L. niloticus	1	4.8E-07	1.3E-06	5.6E-07	2.1E-06
	2	9.6E-07	2.7E0-6	1.5E-06	4.1E0-6
	3	1.5E-06	3.4E-06	2.2E-06	6.1E-06
	4	1.9E-06	5.3E-06	2.9E-06	8.1E-06
	5	2.4E-06	6.7E-06	3.7E-06	1.0E-05
	6	2.9E-06	8.0E-06	4.4E-06	1.2E-05
	7	3.4E-06	9.4E-06	5.1E-06	1.4E-05
O. niloticus	1	4.8E-07	1.2E-06	7.3E-07	1.9E-06
	2	9.6E-07	2.4E-06	1.5E-06	3.7E-06
	3	1.4E-06	3.6E-06	2.2E-06	5.5E-06
	4	1.9E-06	4.8E-06	2.9E-06	7.4E-06
	5	2.3E-06	6.0E-06	4.2E-06	9.2E-06
	6	2.8E-06	7.3E-06	4.4E-06	1.1E-05
	7	3.3E-06	8.5E-06	5.1E-06	1.3E-05

Cd and Cr were not detected in the muscle of both fish species; E= exponent (power of ten).

4.3.2 Levels of heavy metals in fish from Omo Delta and associated human health risk

4.3.2.1 Heavy metal concentrations in fish from Omo Delta

The mean levels of the detected heavy metals in the muscle and liver *tissues of* both fish species are presented in Table 4.5. The mean level of heavy metals ranged from 0.013 mg kg^{-1} to 1.81 mg kg^{-1}.The maximum mean concentration of heavy metals detected in the liver of *L. niloticus* was Fe (1.81± 0.465 mg kg^{-1}), and the minimum mean level was Ni (0.018 ± 0.01 mg kg^{-1}), which was detected in the liver of *O. niloticus*. Similarly, the maximum mean level in muscle of *O. niloticus* was 0.89 ± 0.099 mg/kg for Fe, and the minimum muscle level was for Ni (0.013 ±0.006 mg/kg. The Fe content in the muscle tissues of O. *niloticus* in *the* present study was lower than that in the study by (Samuel *et al*., 2020) in Ethiopia from Lake Hawassa. A lower mean level of Ni was recorded in the study by (Magu *et al.*, 2016; Samuel *et al.*, 2020). The mean concentrations of the metals in the liver and muscle of *L. niloticus* generally occurred in the order of Fe > Zn > Pb > Cu >Mn> Cr > Co > Ni and Fe > Pb > Zn >Mn> Cu > Co > Cr >Ni, respectively.

Table 4.5mMean concentrations of heavy metals (mg/kg, dry weight) in L. niloticus and O. niloticus from Omo Delta

MPL is Maximum permissible limit in the diet of human according to FAO/WHO 1989

Heavy Metals	Mean ± SD of heavy metal concentrations (mg/kg dry weight) in tissues of the two fish species				MPL (mg/kg)	Reference
	Lates niloticus		*Oreochromis niloticus*			
	Liver	Muscle	Liver	Muscle		
Mn	0.394 ±0.004^{a}	0.385 ±0.005^{a}	0.387 ±0.004^{a}	0.384 ±0.006^{a}	1.0	FAO/WHO, 1989
Zn	1.127 ±0.87^{a}	0.428 ±0.393^{b}	0.556 ±0.506	0.394 ±0.26	40	FAO/WHO, 1989
Cu	0.407 ±0.419	0.129 ±0.283	0.291 ±0.424	0.071 ±0.198	3.0	FAO/WHO, 1989
Cr	0.154 ±0.023	0.039±0.085	0.151 ±0.028	ND	0.15	FAO/WHO, 1989
Cd	ND	ND	ND	ND	0.2	FAO/WHO, 1989
Pb	1.124±0.151	0.89 ±0.099	0.845 ±0.269	0.597 ±0.153	0.5	FAO/WHO, 1989
Fe	1.81±0.465	0.94 ±0.395	1.741 ±0.691	0.411 ±0.131	100	FAO/WHO, 2011
Ni	0.033 ±0.011	0.019 ±0.003	0.018 ±0.01	0.013 ±0.006	0.15	FAO/WHO, 1989
Co	0.085 ±0.015	0.045 ±0.021	0.065 ±0.029	0.082 ±0.023	-	-

Similarly, the mean concentrations in the liver and muscle tissues of *O. niloticus* were as follows: Fe > Pb > Zn >Mn> Cu > Cr > Co > Ni and Pb > Fe > Zn >Mn> Co > Cu > Ni. Except for Cd, all the investigated heavy metals were detected in the liver tissues of both species. Cadmium was not detected in the muscle and liver of *L. niloticus* and *O. niloticus* which was similarly reported in the study by Gure *et al* (2019). This might be due to the pollution sources of the freshwater fish may not contain significant level of cadmium or not at all. Higher levels of heavy metals were generally observed in liver tissues. This difference may be related to the content of the metallothioneins protein in the liver tissue which is rich in thiol content that helps to bind the heavy metals. The liver acts as a detoxifying filter by storing heavy metals. High metal accumulation capabilities make the liver the most important target and storage tissue in aquatic organisms. The

Pb levels in muscle and liver tissues from both fish species were above the FAO/WHO (1989) permissible limits. This implies that lead toxicity related health complication to human health and, decreased growth and reproductive rates in fish (Magu *et al*., 2016; Samuel *et al*., 2020).The mean concentration of manganese (Mn) ranged from 0.384 mg kg^{-1} to0.394 mg kg^{-1}.The maximum and minimum mean concentrations of Mn were observed in the liver of *L. niloticus and muscle of O. niloticus,* respectively, following the order *L. niloticus (*liver*)> O. niloticus (*liver*) >L. niloticus (*muscle*)> O. niloticus* (muscle).The detected concentration is below the FAO/WHO (1989) permissible limit for human diet and is comparable to that reported for the muscle of *O. niloticus* species from Lake Hawassa (Abayneh *et al*., 2003).The Mn content of muscle tissues (O. *niloticus)* in the present study was lower than that in previous reports in Ethiopia from Lake Hawassa (Abayneh *et al*., 2003; Ermias *et al*., 2015) and from the Volta Basin of Ghana (Emmanuel *et al*., 2021). A possible explanation might be due to different agricultural activities and pollution from cities and villages in the basin may have acted as additional Mn sources, and the continued release of Mn from estuarine soils led to Mn accumulation.

The mean zinc level ranged from 0.394 mg/kg to 1.127 mg/kg.The maximum mean level was detected in the liver of *L. niloticus*, whereas the minimum was observed in the muscle of *O. niloticus,* following the order *L. niloticus (*liver*)>O. niloticus (*liver)> *L. niloticus (*muscle*) >O. niloticus (*muscle*)> O. niloticus (muscle).*The Zn content in the muscle tissues of O. *niloticus* in *the* present study was greater than that in the study by Zenebe (2011) in Ethiopia. However, the Zn content in the muscle of *O. niloticus* in this study was lower than that in earlier studies of freshwater fish from Ethiopia (Samuel *et al*., 2020; Ermias *et al*., 2015) in the Volta Basin of Ghana (Emmanuel *et al*., 2021) and from freshwater fish in Kenya (Magu *et al*., 2016) Similarly, the level of Zn in the liver tissues of *O. Niloticus* in the present study was greater than that in previous studies of the same species (Dugasa and Endale, 2018). This difference might be due to differences in the pollution sources in the catchment area and the large amounts of agrochemicals containing zinc that may leach into freshwater, which could contribute to heavy metal pollution in fish tissue.

The copper level of the tissues ranged from 0.071 mg kg^{-1} to 0.407 mg kg^{-1}. The maximum and minimum mean Cu level was detected in the liver tissue of *L. niloticus and* inthe muscle tissue of *O. niloticus,* respectively. The order of Cu concentrations was, *L. niloticus (*liver*) >O. niloticus (*liver*) >L. niloticus (*muscle*) >O. niloticus* (muscle).The levels in all tissues are below the FAO/WHO (1989) maximum permissible limit in the human diet. The mean Cu content in muscle tissues of *O. Niloticus* in this study was greater than that in earlier reports (Zenebe, 2011). However, the Cu content in muscle tissues of *O. Niloticus* in the present study was lower than that in previous studies (Ermias *et al*., 2015; Magu *et al*., 2016; Gure *et al*., 2019). Similarly, the concentration of Cu in the liver tissues of *O. niloticus* in the present study was greater than that in the previous study (Dugasa and Endale, 2003) but lower than that reported previously (Magu *et al*., 2016). The mean muscle content of Cu in *L. niloticus* in the present study was lower than that in previous studies Felly *et al* (2020) but lower than that in studies by Magu *et al*.(2016). The concentrations of the investigated heavy metals in fishes are presented in Table 4.6 as follow.

Table 4.6Pearson correlation coefficient matrix for metal concentrations in the fish muscle

	Mn	Zn	Cu	Cr	Pb	Fe	Ni	Co
Mn	1.0							
Zn	-0.3	1.0						
Cu	.535**	-0.2	1.0					
Cr	0.2	-0.2	.388*	1.0				
Pb	0.3	-0.1	.450**	.533**	1.0			
Fe	0.3	-0.1	.442**	.705**	.489**	1.0		
Ni	0.2	-0.2	0.2	.638**	0.3	.571**	1.0	
Co	0.0	0.0	-.381*	-0.3	-0.2	-0.2	0.1	1.0

*Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level.

The chromium level ranged from being below the detection limit to0.154 mg kg^{-1}. A greater level of Cr was observed in the liver tissues of *L. niloticus*. Chromium was not detected in the muscle tissues of *O. niloticus* in the present study, which was similar to the findings of earlier study (Ermias *et al*., 2021). This difference may be due to the high binding capacity of the liver for metals in which the liver acts as a filter detoxifying by storing heavy metals.

The muscle content of Cr in *L. niloticus* in this study was lower than that in previous studies (Samuel *et al*., 2020; Emmanuel *et al*., 2021).However, the Cr content in the liver tissue of both fish species in the present study was greater than that in the study by (Dugasa and Endale, 2003) and lower than that in the study by Gure *et al*. (2019) from Ethiopia. Cadmium was not detected in the liver and muscle of both species. This might be because the pollution source of freshwater might not contain cadmium. This was similarly reported by (Ermias *et al*., 2021).

The lead level ranged from 0.597 mg kg^{-1} to 1.24 mgkg^{-1}.The maximum mean concentration of Pb was recorded in the liver tissue of *L. niloticus,* whereas the minimum level of Pb was observed in the muscle tissue of *O. niloticus,* following the order *L. niloticus (*liver*)>L. niloticus (*muscle*)>O. niloticus (*liver*) >O. niloticus (*muscle).The mean Pb levels in the muscle of both species were above the FAO/WHO recommended limits in the human diet (FAO/WHO, 1989).This finding implies that the consumption of these two fish muscles results in health complications from the toxicity of lead. The Pb content in muscle tissues of both fish species in this study was greater than that in earlier reports (Lubna *et al*., 2015; Magu *et al*., 2016)] but lower than that in previous reports (Fely *et al*., 2020). However, the Pb content in the liver tissue of O. niloticus in the present study was lower than that in previous studies (Gure *et al*., 2019; Dugasa and Endale, 2003). On the other hand, the Pb content in the muscle of *L. niloticus* in the present study was greater than that in previous reports (Magu *et al*., 2016) but lower than that in reports (Felly *et al*., 2020).This difference might be due to the difference in pollution sources in the study area.

The mean concentration of Fe ranged from 0.411 mg kg^{-1} to 1.81 mg kg^{-1}.The maximum mean Fe concentration was detected in the liver of *L. niloticus,* whereas the minimum was detected in the muscle of *O. niloticus,* followed by *L. niloticus* (liver) >*O. niloticus (*liver*)>L. niloticus (*muscle*)* >*O. niloticus (*muscle).The tissue levels of Fe in this study are below the (FAO/WHO, 2011) allowable limits and were below those recorded for the muscle of *O. niloticus* (Lubna *et al*., 2015). The present findings also indicated that O. niloticus had lower Fe contents in muscle tissues than the study reported by (Dugasa and Endale, 2003).In contrast, the Fe content in the liver of *O. Niloticus* in the present study was greater than that in a previous study (Dugasa and Endale, 2003).

The mean nickel concentration ranged from 0.013 mg kg^{-1} to 0.033 kg^{-1}. The maximum mean concentration was detected in the liver tissue of *L. niloticus,* while the minimum level was detected in the muscle tissue of *O. niloticus*, in the order *L. niloticus (*liver*)> L. niloticus (*muscle*) >O. niloticus (*liver*)> O. niloticus (muscle).*These concentrations are within the FAO/WHO (1989) recommended permissible human diet intake levels. The Ni contents of muscle tissues from *O. niloticus and L. niloticus* in the present study were comparable to those in previous reports (Zenebe, 2011; Magu *et al*., 2016; Samuel *et al*., 2020)) and lower than those in study by .(Emmanuel *et al*., 2021).

The cobalt content in the liver and muscle tissues ranged from 0.045 mg kg^{-1} to 0.085 mg kg^{-1}.The maximum mean content of Co was detected in the liver of *L. niloticus,* while the minimum was detected in the muscle of *L. niloticus,* followed by *L. niloticus (*liver*)> O. niloticus (*muscle*) >O. niloticus (*liver*)> L. niloticus (muscle).*The mean muscle level of cobalt in *O. niloticus* was greater than that in a previous report (Samuel *et al*., 2020). However, the mean Co level in the present study was lower than that in the study of the muscle and liver tissue of *O. niloticus* (Gure *et al.*, 2019).

The Cu in fish tissues may be from the agrochemicals through the use of fungicides, algaecides, and insecticides on agricultural land, which can be drained by runoff to the freshwater fish (Pramita *et al.*, 2021).Thus, the occurrence of Cu in the fish tissues in this study could be from agrochemicals that may have arisen from irrigation land along the Omo River, which may drain into the River delta. The Pb concentration in freshwater fish may increase from different anthropogenic sources, such as agricultural discharge, factories, solid waste and wastewater, that may reach the River delta and subsequently fish tissues (Manal *et al.*, 2014).Consequently, the occurrence of Pb in the fish tissues in the present study could be attributed to agrochemical activity from intensive irrigation farmland to the delta, urban discharge and solid waste from Omorate town, which is adjacent to the delta, wastewater from upstream factories and other anthropogenic activities. The presence of Ni in the fish tissues in this study could be due to the location of the river in the rift valley, where it is naturally abundant in the Earth's crust (Magu *et al.*, 2016).The occurrence of Zn in fish tissues in the present study could be due to the urban runoff, wastewater and agrochemical use observed in the catchments (Olawusi *et al.*, 2019). The occurrence of the detected heavy metals in the present study could also be attributed to Lake Turkan, which is adjacent to the present study area (Omo delta), as reported by different researchers, who revealed the presence of Cr, Cu, Mn, Ni, Pb, and Zn (Elick *et al.*, 2015; Magu *et al.*, 2016; Christof *et al.*, 2017).

The statistically significant differences in the mean contents of the detected heavy metals between the fish tissues of both fish species are presented in Table 4.7**.**A T-test ($P<0.05$) revealed that there were significant differences in the mean levels of all heavy metals except for Mn, Cu, and Ni in the muscle and liver tissues of *L. niloticus*. Similarly, significant differences in the mean levels of heavy metals were detected between the muscle and liver tissues of O. niloticus, with the exception of Zn and Co. There were also species-dependent significant differences in the mean contents of Pb, Ni, and Co in the liver tissues of *L. niloticus* and O. niloticus. Similarly, the mean contents of Pb, Fe, and Ni in the muscle tissues of both species were significantly different ($P<0.05$). Many researchers have shown that fish species-dependent differences in heavy metal accumulation might be associated with feeding habits, such as carnivores, herbivores, or omnivores, and the habitats of fish species (Yilmaz *et al*., 2005; . Kamal *et al*., 2023).Differences in habitat utilization and feeding practices may be the cause of the variations in the mean heavy metal concentrations observed in the present study between *L. niloticus* and *O. niloticus*(Elias *et al*., 2005). The differences in heavy metal concentrations between *L. niloticus* and O. niloticus (Yilmaz *et al*., 2005; Ahmed *et al.,* 2015) in the present study could be attributed to the biological factors, such as age and the growth rate of the fish species .

Table 4.7The mean difference of heavy metals among the fish's tissues

tissues o fish species	Sig. (2-tailed)							
	Mn	Zn	Cu	Cr	Pb	Fe	Ni	Co
liver and muscle of L. niloticus	0.4	0.02*	0.23	0.00**	0.00**	0.00**	0.83	0.00**
liver and muscle of O. niloticus	0.05*	0.24	0.00**	0.00**	0.00**	0.00**	0.00**	0.11
liver of *O. niloticus* and *L. niloticus*	0.806	0.775	0.464	0.769	0.001**	0.762	0.001**	0.041**
Muscle of *O. niloticus* and *L. niloticus*	0.402	0.023	0.482	0.003	0.00**	0.00**	0.00**	0.11

Note: -* is significant at the 0.05 level (2-tailed).** is significant at the 0.01 level

The differences in the mean levels of heavy metals between the fish tissues (liver and muscle) in these studies could be due to the ability of various metals to bind with carboxylate oxygen, amino functional groups, and nitrogen in metal-binding proteins(Uysal *et al*., 2009; Gure *et al*., 2019; Pramita *et al*., 2021).The variations in metal concentrations among tissues could also be ascribed to differences in the physiological role of each tissue in which muscle generally accumulates lower levels of heavy metals (Ahmed *et al.,* 2015; Olawusi *et al*., 2019). Many studies have confirmed that there is variation in heavy metal levels among fish tissues and species (Gure *et al*., 2019; Samuel *et al*., 2020), which was also observed in the present study.

In general, *L. niloticus* had a greater burden of heavy metals than *O.niloticus.* This could be due to differences in the behavior and feeding habits of the two species. Thus, the relatively high level of metals in the *L. Niloticus* tissues in the present study could be attributed to their feeding habits, as they are bottom-dwelling carnivores that feed on zooplankton, shrimp, clams, snails, insects and other fish species, unlike *O. niloticus,* which feeds on algae and other vegetables (Rosseland *et al*., 2001; Magu *et al*., 2016)**.** Carnivores are more likely to accumulate heavy metals than are other fish (Ahmed *et al*., 2015).

4.3.2.2 Human health risk associated with HMs in fish from Omo Delta

The noncarcinogenic health risks associated with the heavy metals detected in adults and children who consumed muscle from *L. niloticus* and *O. niloticus* from the Omo delta were assessed using THQ and HI indices. The human health risk was evaluated on a wet mass basis by using a conversion factor of 4.8.The index results (THQ and HI) obtained by eating the muscle of fish within one to seven times a week are presented in Tables 4.8 and 4.9 for adults and children, respectively. The THQs in the muscle of *L. niloticus* and *O. niloticus* for all the ingestion levels (1, 3 5 and 7) decreased in the order Pb > Cr > Cu >Mn> Co > Zn > Fe and Pb >Mn> Co > Cu > Zn > Fe, respectively.

Table 4.8Estimated THQ and HI in adults due to heavy metal exposure in muscle of *L. niloticus and O. niloticus*

Fish Species	Level of exposure(d/w)	Target hazard quotient (THQ)								Hazard Index (HI)
L. niloticus		Mn	Zn	Cu	Cr	Pb	Fe	Ni	Co	
	1	0.000941	0.00049	0.001104	0.004445	0.086947	4.59E-04	3.25E-04	0.000514	9.55E-02
	3	0.002822	0.001464	0.003307	0.013334	0.260837	1.38E-03	9.74E-04	0.001541	2.86E-01
	5	0.004699	0.002438	0.005515	0.022224	0.434726	2.29E-03	1.62E-03	0.002563	4.76E-01
	7	0.0066	0.003422	0.007742	0.0312	0.610286	3.22E-03	2.28E-03	0.0036	6.68E-01
O. niloticus	1	0.000936	0.000449	0.000605	ND	0.05832	2.01E-04	2.26E-04	0.000936	6.17E-02
	3	0.002813	0.001349	0.001819	ND	0.174965	6.00E-04	6.67E-04	0.002803	1.85E-01
	5	0.00469	0.002246	0.003034	ND	0.291605	1.00E-03	1.11E-03	0.004675	3.08E-01
	7	0.006581	0.003154	0.004262	ND	0.409373	1.41E-03	1.56E-03	0.006562	4.33E-01

d/w =Days per week

Table 4.9Estimated THQ and HI in children due to heavy metal exposure in muscle of *L. niloticus and O. niloticus*

Fish Species	Level of exposure(d/w)	Target hazard quotient (THQ)								Hazard Index (HI)
L. niloticus		Mn	Zn	Cu	Cr	Pb	Fe	Ni	Co	
	1	0.001344	0.000696	0.001574	0.00635	0.124205	0.000658	4.64E-04	0.000734	1.36E-01
	3	0.004032	0.002093	0.004728	0.019051	0.372619	0.001968	1.39E-03	0.002198	4.08E-01
	5	0.006715	0.003485	0.007877	0.031747	0.621034	0.003278	2.32E-03	0.003662	6.80E-01
	7	0.009427	0.004891	0.011059	0.044573	0.871838	0.004603	3.26E-03	0.005141	9.42E-01
O. niloticus	1	0.001339	0.000643	0.000869	ND	0.083318	0.000287	3.17E-04	0.001334	8.81E-02
	3	0.004018	0.001925	0.002602	ND	0.24995	0.000859	9.50E-04	0.004003	2.64E-01
	5	0.006701	0.003206	0.004334	ND	0.416582	0.001435	1.59E-03	0.006677	4.41E-01
	7	0.043886	0.004502	0.006086	ND	0.584818	0.002011	2.23E-03	0.00937	6.53E-01

ND= not detected; Cd was not detected in the muscle and liver of both fish species,d/w =days per week

The HI values due to consumption of L. niloticus muscle7 times a week were 0.668 (for adults) and 0.942 (for children). Similarly, the HI values for O. niloticus were 0.433 (for adults) and 0.653 (for children). The maximum THQs were observed for Pb in both *L. niloticus* (0.872) and *O.niloticus* (0.585), whereas the minimum THQs were observed for Fe in the muscles of *O.niloticus* and *L. niloticus*. In all the evaluated samples, the THQs for heavy metals in fish muscle ingested by adults and children were less than one, which indicates that individuals are unlikely to experience considerable health risks due to ingestion of individual heavy metals through intake of the fish muscles. Similarly, the HIs of the combined heavy metals were less than one, indicating that there was no substantial adverse health effect due to the intake of *L. niloticus* and *O. niloticus* muscle tissues from the Lower Omo River source at the present time of study. As seen from the risk assessment data, more emphasis should be given to the noncarcinogenic risk of Pb in the muscle of both fish species. A previous study in the Volta Basin River, Ghana, recorded a lower THQ value for Mn (0.00325) than for Mn (0.04389) from *O. niloticus* (Emmanuel *et al.*, 2021). They also reported lower THQs for Zn (9.2×10^{-5}) and Fe (2.14×10^{-8}) than did the present study via the intake of *O. niloticus* muscle by adults and children. On the other hand, (Samuel *et al.*, 2020) from their study in Ethiopia from Lake Hawassa, reported higher THQ values for Fe (0.01), Cu (0.02), and Zn (0.039) than did the present findings. However, (Samuel *et al.*, 2020) reported lower THQs for Co (0.001) and Pb (0.026) than for Co (0.00937) and Pb (0.872), respectively.

The probable cancer risk due to the ingestion of Cr, Pb, and Ni through the muscle of *L. niloticus* and *O. niloticus* at 1, 3, 5, and 7 days a week is presented in Table 4.10 The target cancer risk (TCR) values in the muscles of both *L. niloticus* and *O. niloticus* were in the order of Cr> Pb. All levels of exposure to Pb in this investigation had TCR values within the acceptable range (10^{-6} to 10^{-4}) (USEPA, 2012).Taken together, these findings demonstrated that eating Cr and Pb through the muscle of *L. niloticus* and *O. niloticus* at any exposure level was not a carcinogenic health concern. It was also observed that children had a greater probability of developing risk when exposed to heavy metal pollution. The results of this study showed that people who consumed *O. niloticus* muscle had a TCR for Pb of 1.22×10^{-5}, which was greater than that found in a previous study that evaluated the TCR for Pb (7.65×10^{-8}) (Emmanuel *et al.*, 2021).

Table 4.10 TCR in adults and children due to heavy metal exposure in muscle of *L. niloticus and O. niloticus*

Fish Species	Level of exposure(d/w)	Carcinogenic Risk (CR) Adults		Carcinogenic Risk (CR) Children	
		Cr	Pb	Cr	Pb
L. niloticus	1	6.67E-06	2.59E-06	9.53E-06	3.70E-06
	3	2.00E-05	7.76E-06	2.86E-05	1.11E-05
	5	3.33E-05	1.29E-05	4.76E-05	1.85E-05
	7	4.68E-05	1.82E-05	6.69E-05	2.59E-05
O. niloticus	1	ND	1.74E-06	ND	2.48E-06
	3	ND	5.21E-06	ND	7.44E-06
	5	ND	8.67E-06	ND	1.24E-05
	7	ND	1.22E-05	ND	1.74E-05

d/w= days/week, E= exponent, ND= not detected. E= exponent (power of ten). Cd was not detected in the muscle of both fish species.

The TCRs for Pb and Cr in this study were within the tolerable range of 10^{-6} to 10^{-4}(USEPA, 2012) for all levels of exposure. Taken together, these findings revealed that there was no carcinogenic health risk from the ingestion of Cr and Pb through the muscle of L. niloticus and O. niloticus at all levels of exposure in adults. It was also observed that children had a greater probability of developing risk when exposed to heavy metal pollution. A study in Ethiopia from Lake Hawassa reported a lower TCR for Pb (7.65 ×10-8) than that in the present study ($1.22 \times 10^{-5)}$ via the intake of *O. niloticus* muscle by adults (Samuel *et al.*, 2020).

4.3.3 Comparative pollution levels of heavy metals in freshwater fish from Lower Omo River and Omo Delta

4.3.3.1 Levels of heavy metals in the O. niloticus in Omo River and Omo Delta

Table 4.11 shows the average levels of different metals found in the muscle and liver tissues of O. niloticus from the Omo River and Omo delta. O. niloticus muscle and liver samples from the Omo River and the Omo delta both contained no detected amount of cadmium. Additionally the order of the detected elements in the liver of O. niloticus inhabiting both water bodies followed a similar pattern. The study found that the mean zinc concentration in the muscle tissue of O. niloticus was 0.424 and 0.394 mg kg^{-1} in Omo river and Omo delta, respectively (Table 4.11). The level of Zinc in the liver tissue of O. niloticus was 0.556 mg kg^{-1} in the Omo delta and 0.477 mg kg^{-1} in the Omo river. The mean concentration of Copper (Cu) in the liver tissues of O. niloticus were 0.189 and 0.291 mg kg^{-1} in the Omo river and Omo delta respectively.

The average Cr content in O.niloticus tissue is displayed in Table 4.11. The average Cr concentration in O. niloticus livers from the Omo River was 0.145 mg kg^{-1}, which was less than the average Cr concentration in the Omo delta, which was 0.154 mg kg^{-1}. Cr was not detected in the muscle tissues of O.niloticus in the Omo River and Omo delta. O. niloticus muscle and liver samples from the Omo River and the Omo delta both contained no detected amount of cadmium. The level of lead (Pb) in the muscle tissues ranged from 0.790 to 0.597 mg kg^{-1}. The sample from Omo river had a greater value, but the mean concentration in the muscle tissue was not significantly different (p.value > 0.05).

The analysis revealed that with the exception of iron and cobalt, the mean levels of all detected heavy metals were not significantly different (p.value > 0.05) in the muscle tissue of O. niloticus between the Omo river and Omo delta (Table 4.11).

Table 4.11Mean concentration of each HMS in liver and muscle of O. niloticus in Omo river and Omo delta.

	Omo river				**Omo Delta**				**MPL**
	Liver		Muscle		Liver		Muscle		
	Mean	Std. dev	Mean	Std. dev	Mean	Std. dev	Mean	Std. dev	
Mn	0.356	0.005	0.379^{a}	0.003	0.387	0.004	0.384^{a}	0.006	1.0
Zn	0.477	0.424	0.424^{a}	1.017	0.556	0.506	0.394^{a}	0.26	40
Cu	0.189	0.283	0.129^{a}	0.236	0.291	0.424	0.071^{a}	0.198	3.0
Cr	0.126	0.075	ND		0.151	0.028	ND		0.15
Cd	ND		ND		ND		ND		0.2
Pb	0.908	0.210	0.790^{a}	0.173	**0.845**	0.269	**0.597**^{a}	0.153	0.5
Fe	1.100	0.354	0.268^{a}	0.059	1.741	0.691	0.411^{b}	0.131	100
Ni	0.014	0.002	0.010^{a}	0.002	0.033	0.010	0.013^{a}	0.006	0.15
Co	0.068	0.020	0.054^{a}	0.017	0.065	0.029	0.080^{b}	0.023	-

Remark:mean concentration of each heavy metals for having different letter in rows are not statistically different .ND: not detected; MPL: maximum permissible limit in human diet according to FAO/WHO 1989

The study found that the mean iron concentration in the muscle tissues of O. niloticus was 0.268 mg kg−1 in the Omo River and 0.411 mg kg−1 in the Omo delta. The findings of the present study showed that the Fe concentration in the liver of O. niloticus was 1.100 mg kg−1 in the Omo River and 1.74 mg kg−1 in the Omo delta. The results of the study also showed a significant difference (p value < 0.01) in the average iron concentration between Omo River and Omo delta samples. The concentration of Cobalt and nickel in the muscle and liver tissue of O. niloticus varied in the Omo River and Omo delta. The mean nickel concentrations of O. niloticus in the muscle tissues were 0.010 and 0.013 mg kg−1 in the Omo river and Omo delta, respectively as shown in Table 4.1 1. On the other hand, the mean Ni concentrations in the liver tissue of O. niloticus in the Omo River and Omo delta were 0.014 and 0.018 mg kg−1, respectively. These findings indicate that the concentration of Ni in the liver tissue ofO. niloticus was higher than that in the muscle tissue. The result also showed that Cobaltconcentrations in the muscle tissue of O. niloticus ranged from 0.054 to 0.080 mg kg−1 inthe Omo River and Omo delta respectively. There was statistically significant variation inthe mean Co concentration in the muscle tissues of O. niloticus between the two sites (OmoRiver and Omo delta) with a p value < 0.01.

4.3.3.2 Levels of heavy metals in *L. niloticus* in the Omo River and Omo Delta

As shown in Table 4.12, the highest concentration of heavy metals detected in the liver ofL. niloticus was Fe (2.918 ± 1.47 mg kg−1) and the lowest mean concentration was Ni (0.011± 0.003 mg kg−1). *L. niloticus* muscle and liver samples from the Omo river and the Omodelta both contained no detected amount of cadmium.The concentrations of zinc in the muscle tissue of L. niloticus were 0.642 and 0.428 mgkg−1 in Omo River and Omo delta respectively. The copper (Cu) concentration inL. niloticus muscle tissues from the Omo river and Omo delta varied between 0.157 and0.13 mg kg−1, respectively. The copper concentration in L. niloticus muscle tissues from the Omo River and Omo delta varied between 0.157 and 0.13 mg kg−1, respectively. However,the mean copper concentration in liver tissues of L. niloticus ranged from 0.481 to 0.407mg kg−1 in the Omo River and Omo delta, respectively. The levels of manganese in themuscle tissue of L. niloticus were 0.383 and 0.385 mg kg−1 in the Omo River and Omo Delta,respectively.

Table 4.12The mean difference of heavy metals between Omo River and Omo Delta in *L.niloticus*

	Omo River				Omo Delta				MPL
	Liver		Muscle		Liver		Muscle		
	Mean	Std. dev	Mean	Std. dev	Mean	Std. dev	Mean	Std. dev	
Mn	0.391	0.003	0.383^{a}	0.003	0.394	0.004	0.385^{a}	0.005	1.0
Zn	1.01	0.482	0.642^{a}	0.474	1.127	0.870	0.428^{a}	0.393	40
Cu	0.481	0.459	0.157^{a}	0.273	0.407	0.419	0.13^{a}	0.283	3.0
Cr	0.145	0.021	ND		0.154	0.023	0.039	0.085	0.15
Cd	ND		ND		ND		ND		0.2
Pd	1.009	0.215	0.793^{a}	0.173	**1.124**	0.151	**0.89^{b}**	0.099	0.5
Fe	2.918	1.476	0.509^{a}	0.273	1.810	0.465	0.940^{b}	0.395	100
Ni	0.019	0.006	0.011^{a}	0.003	0.018	0.011	0.019^{b}	0.003	0.15
Co	0.097	0.023	0.080^{a}	0.028	0.085	0.015	0.045^{b}	0.021	-

Remark:mean concentration of each heavy metals for having different letter in rows are statistically different .MPL: maximum permissible limit in human diet according to FAO/WHO 1989

The concentration of chromium (Cr) was found to be below the detection limitup to 0.154 mg kg−1. The liver tissues of L. niloticus showed a higher level ofchromium, exhibited significant site dependent variation in the mean Cr concentration(p value < 0.02). The lead (Pb) level in L. niloticus muscle tissues varied between 0.793and 0.890 mg kg−1 in the Omo River and Omo delta respectively. As presented in Table 4.12,the mean Pb concentration in L. niloticus muscle tissue significantly differed by site(p value < 0.01) (Omo river and Omo delta).

The mean concentrations of Fe in the muscle tissue of L. niloticus were 0.509 and 0.94 mg kg−1 in the Omo river and Omo delta, respectively. In the Omo river and Omo delta, the mean Fe levels in L. niloticus muscle tissue differed significantly (p value < 0.01) (Table 4.12). The mean nickel (Ni) concentration ranged from 0.011 to 0.019 kg−1 in the Omo River and Omo delta,respectively. Similarly, the mean nickel concentration in L. niloticusmuscle tissue significantly differed (p value < 0.01) depending on location (Omo River andOmo Delta).

Table 4.13presents the difference in the mean level of heavy metals found in fish tissuesand species from Omo delta. The mean level of heavy metals in the liver and muscle of L.niloticus from Omo delta were significantly different for Zn, Cr, Pb, Fe, and Co. A similardifference was observed in O.niloticus for all detected heavy metals except for Zn and Co.There was a difference in the heavy metal levels based on fish species observed between theliver of O.niloticus and L.niloticus for Pb, Ni, and Co. Furthermore, a significant difference was observed between the mean heavy metal levels in the muscle of O.niloticus andL. niloticus for Pb, Fe, and Ni. The differences in the mean level of heavy metals among thefish's tissues and species from lower Omo River are also presented in (Table 4.13).

Table 4.13The mean difference of Heavy metals among the Fishes tissues in OmoDelta andOmo River

	Tissues o fish species	Sig. (2-tailed)							
		Mn	Zn	Cu	Cr	Pb	Fe	Ni	Co
Omo Delta	liver and muscle of *L. niloticus*	0.4	0.02*	0.23	0.00**	0.00**	0.00**	0.83	0.00**
	liver and muscle of *O. niloticus*	0.05*	0.24	0.00**	0.00**	0.00**	0.00**	0.00**	0.11
	liver of *O. niloticus* and *L. niloticus*	0.806	0.775	0.464	0.769	0.001**	0.762	0.001**	0.041**
Omo River	liver and muscle of *L. niloticus*	0.00**	0.02**	0.01**	0.00**	0.00**	0.00**	0.00**	0.88
	liver and muscle of *O. niloticus*	0.934	0.242	0.496	0.000**	0.075**	0.000**	0.00**	0.030**
	liver of of*O. niloticus* and *L. niloticus*	0.504	0.251	0.0227**	0.241	0.135	0.000**	0.0023**	0.0551*
	Muscle of *O. niloticus* and *L. niloticus*	0.002**	0.394	0.998	0.074*	0.969	0.001**	0.296	0.002**

Note: -* is significant at the 0.05 level (2-tailed).** is significant at the 0.01 level

4.4 Conclusions

This study had the objective of measuring the levels of heavy metals present in the liver and muscle tissues of two commercially important fish species namely *L. niloticus* and *O. niloticus* found in the Omo River Basin and Omo Delta located in southern Ethiopia. The findings of the study provided the first baseline information on the level of nine heavy metals in these fish species from Ethiopian low land freshwater. The levels of all heavy metals evaluated, except for Pb, were within the permissible limits established by the FAO/WHO (1989) for the Omo River. Similarly the levels of all heavy metals under investigation, except Pb and Cr, were within the permissible limits established by (FAO/WHO, 1989) in the Omo delta. The liver and muscle tissues of *L. niloticus* were found to have higher accumulations of heavy metals for those of *O. niloticus,* with the liver accumulating more heavy metals than muscle tissues.

The level of heavy metal pollution in fish tissue is a cause for concern. While the health risk assessments did not indicate any immediate danger to human health, , the mean levels of Pb detected in the both liver and muscle tissue of two fish from the Omo River and Omo Delta exceeded the allowed level set by FAO/WHO(1989). The elevated level of heavy metals in the liver tissues of both species is a threat for fish health due to the fact that the high level of metals in the liver might be stored in the fish body. Consequently, the elevated level in the liver tissues may adversely affect early development, growth retardation, behavioral changes and damage in the nervous system of both fish species. These suggested that regular monitoring of freshwater fish in this area is necessary. Furthermore, the TCR resulting from Ni exposure through the consumption of *L. niloticus* and *O. niloticus* muscle is alarming, as it may increase the risk of cancer in young people who engage in vigorous and prolonged developmental activities. Therefore, it is imperative to monitor heavy metal levels in the tissues of *L. niloticus* and *O. niloticus*, policy makers are advised to take appropriate action at this alarming level to safeguard freshwater fish and people from the threat of heavy metal pollution from the lower reaches of the river and Omo Delta.

4.5 Reference

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CHAPTER FIVE

Heavy metals concentrations in surface sediments of Lower Omo River and Omo Delta in Southern Ethiopia and associated ecological risk assessment

Abstract

This study presents a study conducted on the levels of heavy metals and associated ecological risks from the sediments of Lower Omo River and Delta Lake in Southern Ethiopia. A total of 30 composite samples were collected from sediments of the two water bodies (River and Delta) and analysed for nine heavy metals using a Flame Atomic Absorption Spectrometer. The study evaluated the ecological risk using risk index factor (RI), comprehensive risk index (CRI), contamination factor (CF), contamination degree (CD) and pollution load index (PLI).The mean concentrations of the detected heavy metals in mg/kg in the sediments of River and Delta Lake were 2.947 and 2.904 for (Mn), 0.801 and 0.809 for (Zn), 0.278 and 0.278 for (Cu), 0.437 and 0.434 for (Cr), 0.054 and 0.058 for (Pb), 0.009 and 0.008 for (Ni), 19.553 and 19.515 for (Fe), and0.236 and 0.223 (Co), respectively. The order for the mean concentrations of the heavy metals in the sediment of River were Fe >Mn > Zn > Cr > Cu > Co > Pb > Ni where as the order in the Delta Lake were Fe >Mn > Zn > Co > Cu >Pb > Cr > Ni. The EI results for the detected heavy metals in the sediments of River took place in the Order: Fe > Cr > Cu > Pb > Mn > Co > Zn > Ni. The results of CF indicate a low degree of contamination with CF values below 1. The mean PLI values of heavy metals in sediment revealed low metal contamination of the sediment (PLI < 1.0). Thus, the study highlighted the importance of monitoring heavy metal levels in sediments to ensure the safety freshwater ecosystem.

Keywords: Ecological risk, heavy metals, Omo River, sediment

5.1 Introduction

Contamination of aquatic systems with excess quantities of heavy metals has attracted increased attention and has become a serious ecological and public health hazard around the world (Flipos *et al*., 2022). Rapid urbanization, industrialization, and land modification have all contributed to the accumulation of pollutants in the freshwater ecosystem (Tian *et al*. 2020). Heavy metal pollution in freshwater ecosystems is a global environmental and public health problem that could originate from natural or manmade sources (Astatkie *et al*., 2021).Because of anthropogenic loadings in the freshwater ecosystem, there is a significant concentration of heavy metals in freshwater sediments. Since they are both transmitters and sinks of pollutants, sediments are sensitive markers for tracking pollution. The amounts of heavy metals in Ethiopian water bodies might vary depending on a number of circumstances which comprise a range of human-caused activities, including improper waste management in industrial settings, urbanization, land usage, and human habitation (Flipos *et al*., 2022).

5.2. Materials and methods

5.2.1 Descriptions of the study area

The descriptions of the study area are presented in section 1.9.1

5.2.2. Sediment sampling and sample collection

The sediment samples were collected from the same sites where the River and Lake Water samples were taken. A total of ninety (90) sediment samples were collected from the two water bodies (45 from each) which were then composited to thirty for analysis (15 from each water body). They were collected from the surface by using plastic sampler and transferred in polyethylene bags immediately. The collected samples were transferred to an ice box with the plastic bags and then right away to the soil laboratory of Arbaminch University.

5.2.3 Sample preparation and digestion

The sediment samples were air dried in the laboratory at room temperature for five days. The air dried samples were then grounded using mortar and pestle after being sieved with a 2 mm sieve. The samples were then made ready for digestion (Acharjee *et al.*, 2022). 0.5 gram of finely powdered sediment samples were put in digestion vials to witch 65% HNO_3 (3ml) and 70% $HClO_4$ (2ml) was added and heated over a steam bath to form a clear solution. The mixture was filtered with whatman filter paper and stored in the freezer at 4 °C.

5.2.4 Sample analysis

The absorbance of heavy metals was analysed using a flame atomic absorption spectrometer (GFAAS- novAA400p; Germany), and the concentrations of the heavy metals in the sediment samples were determined from a standard calibration curve.Analysis of each heavy metal was carried out in triplicate and the analysis was carried out according to APHA protocol (APHA, 2017).

5.2.5 Sediment contamination and ecological risk assessmentindices from River

5.2.5.1 Sediment quality guidelines (SQGs)

An important environmental problem is figuring out whether the concentrations of HMs in the sediments pose an ecological risk to aquatic life. Accordingly, the concentrations of HMs in the sediments were compared to SQGs to estimate the risk of HMs in the sediments (Costa-Boeddeker *et al.*, 2018, Fakhradini *et al.*, 2019); the indices used for this comparison were the threshold effect level (TEL) and likely effect level (PEL).

Table 5.1Sediment quality guidelines (TEL and PEL) and Background values (mg/kg**)**

HMs	Mn	Zn	Cu	Cr	Pb	Ni	Fe	Co
TEL	-	124	18.7	37.3	30.2	15.9	-	-
PEL	-	271	108	90	91.3	36	-	-
BV	-	55.3	17.54	60	11.29	36.1	-	-

TEL: threshold effect level; PEL: probable effect level, and BV : Background concentration (Burton, 2001; Solaiman *et al*., 2021).

5.2.5.2 Basic contamination index (contamination factor and contamination degree)

The contamination factor (C^i_f) and the degree of contamination (Cd) are used to determine the contamination status of sediment (Hakanson,1980).The contamination factor (Cf), which is the ratio of each metal's content to its background value, is used to display the level of contamination with a specific metal. The total of all contamination factors (Cf) is known as the contamination degree (Cd) (Liao *et al*., 2021).The degree of contamination (CD) and the contamination factor (CF) are frequently used to classify the contamination status of sediments. The key indicators of the metal pollution state of the sediment under investigation are the Contamination Factor (CF) and Contamination Degree (CD). The total of all CF values is the contamination degree (Acharjee *et al*., 2022).The CF and CD are estimated accordingly to (Hakanson, 1980) as presented in equations (5.1) and (5.2).

$$CF = \frac{\text{Cm (sample)}}{\text{Cm (background)}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5.1)$$

$$CD = \sum CF \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.2)$$

Where, the C_{sample} and $C_{background}$ are the measured and background concentration respectively. The element's baseline value is equal to the average value of the world's surface rock. Cr (100), Ni (40), Cu (45), Zn (70), Fe (47200), Mn(30), and Pb (20) mg/Kg. According to Håkanson (1980), the CF is categorized as: CF< 1, low contamination factor; 1 <CF< 3, moderate contamination factor;

3<CF< 6, considerable contamination factor; and CF> 6, very high contamination factor (Turekian and Wedepohl,1961, Samuel *et al*., 2020).The Contamination factors are graded into four classes as: as presented in Table 5.2.

Table 5.2*Description of contamination factor (CF) and contamination degree (CD)*

Contamination Factor Ranges	Description	Contamination Degree	Description
CF< 1	low contamination	CD<8	Low degree of Contamination
1 <CF< 3	moderate contamination	8< CD<16	Moderate degree of Contamination
3<CF< 6	considerable contamination	16 < CD <32	Considerable degree of contamination
CF> 6	very high contamination	CD>32	Very high degree of Contamination

5.2.5.3 Advanced indices for determination of sediment contamination

A. Modified contamination (mC_d)

$mC_d = \sum_{i=1}^{n} CF/n$ ……………………………………………(5.3)

The modified contamination degree (mCd) is classified as nil or very low mCd < 1.5, low 1.5 ≤ mCd < 2, moderate 2 ≤ mCd < 4, high 4 ≤ mCd < 8, very high 8 ≤ mCd < 16, extremely high 16 ≤ mCd < 32, and ultra-high mCd ≥ 32 (Abrahim and Parker, 2008; Hossain *et al.*, 2021a, 2021b; (Acharjee *et al.*, 2022).

B. Pollution load index (PLI)

According to Tomlinson *et al.* (1980), PLI is the nth root of the product of the metal concentrations. They classified the pollution level based on PLI values in which ≤0, 0 to ≤1, ≥1 respectively indicates pristine, baseline, and progressive deterioration. It is a recognized method for evaluating mutual contamination effects (Tian *et al.*, 2017).The PLI was used for evaluating mutual contamination effects of the eight heavy metals in the sediments of the present study (Equation 5.4).

$PLI = [CF_{Mn} \times CF_{Zn} \times CF_{Cr} \times CF_{Ni} \times CF_{Pb} \times CF_{Fe} \times CF_{Co} \times CF_{Cu}]^{1/n}$…………… (5.4)

Where CF is the contamination factor which was calculated in the Eq. (1).

Where CF denotes the contamination factor and n is the considered number of heavy metals.

5.2.5.4 Potential ecological risk index of HMs in sediment (RI)

This was formulated by Hakanson (1980) to quantify the level of ecological risk of heavy metals in sediment. The RI assesses the combined ecological and environmental toxicity to provide an overall evaluation of the potential risk of heavy metal pollution which is calculated as follow:

$EI = T_i \times CF$ (5.5)

$RI = \sum E_i$ (5.6)

Where, EI is the individual potential risk, and Ti is the toxicity effect coefficient, with Values for Mn, Zn, Cu, Cr, Pb, Ni, Fe , and Co are 1, 1, 5, 2, 5, 5,1,and 5 (Tegn *et al*., 2014). According to Hakanson (1980), and CF is the contamination factor of each metal. The potential ecological risks were classified on the basis of the values of the risk factor as presented in Table 5.3

Table 5.3Various pollution risk index and their status (Hakanson, 1980; Solaiman *et al.,* 2021)

Pollution index (PI)	Pollution status	Pollution load index (PLI)	Pollution status	EI	Risk level	RI	Potential ecologica hazard
PI＜0.7	Clean	＜1	Unpolluted	EI＜40	Weak	RI＜150	Low
0.7≤PI＜1	Basic cleaning	1≤PLI＜2	Moderately polluted	40≤EI＜80	Medium	150≤RI＜300	Modetate
1≤PI＜2	Mildly polluted	2≤PLI＜3	Strongly polluted	80≤EI＜160	Strong	300≤RI＜600	High
2≤PI＜3	Moderately polluted	PLI≥3	Very strongly polluted	160≤EI＜320	High strong	RI≥600	Significantly high
PI≥3	Strongly polluted	-	-	EI≥320	Extremely strong	-	-

5.2.6 Data analysis.

The data were analyzed using IBM SPSS 21 statistical software. The heavy metal concentrations at each point are presented as the mean ± standard deviation of the samples analysed.The overall differences in the mean concentrations of metals between sampling points were analysed using ANOVA.To see in which sample point the mean concentration was significantly different; the Tukey test of multiple comparison was used.

5. 3 Result and discussion

5.3.1 Heavy metals concentration in the sediment of River water

The mean concentrations of heavy metals in the sediment samples are presented in Table 5.4. The mean concentrations of the heavy metals in the sediment samples of the River followed the order Fe (19.55mg kg^{-1}) > Mn (0.947 mg kg^{-1})> Zn (0.801 mg kg^{-1}) > Cr (0.437 mg kg^{-1}) > Cu (0.278 mg kg^{-1}) > Co (0.236 mg/L) > Pb (0.054 mg kg^{-1}) > Ni (0.009 mg kg^{-1})> Cd (ND). The maximum mean concentration of heavy metals detected in the sediment was Fe (19.55 mg kg^{-1}) and the minimum mean concentration was for Ni (0.009 mg kg^{-1}). The mean concentration of Fe in River sedimentof the present study was lower than that in the study by Acharjee *et al*. (2022) from Surma River(291.1 mg kg^{-1}) in Bangladesh and also from the study report by Yasemin and Fusun (2021) which was (138.9 mg/kg). However, the mean level of Fe in this study of the River sediment was higher than in the study report by Azlini *et al.* (2018) from sediment of Highland River in Malaysia (0.442 mg/kg).A higher concentration of Ni was also reported in the previous study by Kwacha *et al*. (2023) from Mae Chaem River (24.0 mgkg^{-1}) in Thailand; Lan *et al*. (2014) from sediment of Centeral Bohai Sea which was 26.7 mgkg^{-1}and Acharjee *et al*. (2022) in Bangladesh (92.34 mg kg^{-1})that in the present study.The zinc level of this study at different sampling points ranged from 0.075 to 1.46 mg kg^{-1} with the mean level of0.801 mg kg^{-1}).The mean Zn level in the River sediment of the present study was lower than that in the study report by Zhou *et al*. (2015) which was (87.22 mg/kg)and Li *et al*. (2018) fromLuanhekou Estuary (31.8mg kg^{-1}).The mean Cu level in the River sediment of the present study was lower than that in the study byZhang *et al*.(2015) which was (10.99 mg/kg) and Hu *et al*. (2013b) which was (22.7 mg/kg).

The level of Cr in the present study was higher thanin the study by Tengku *et al*.(2020) from sediment of Malaysia freshwater (0.005 mg/kg) and sediment of River in Bangladesh (0.01 mg/kg

) by Simul *et al*.(2019). However, lower level of Cr was also recorded in the present study than the previous study by Feng *et al*. (2011) which was (53.1 mg/kg) and Wu *et al*. (2014) which was (102).The finding of the present study had a lower mean level of Pb than the previous studies byLin *et al*. (2013)which was 19.85 mg/kg Zhuang *et al*. (2015)which 24 2 mg/kg).

The variations in heavy metal concentrations from sediment at different sampling points are presented in Table 5.4. Mean Concentration of all HMs except for Ni, Fe, and Co at all the sample points in the sediment are significantly different at 5% level of significance. To see in which sample point the mean concentration is significantly different, the Turkeys' test of multiple comparison was consider as shown in the Table 5.4.The mean concentration of Mn at site one wasSignificantly different from the mean concentration at sites five, ten and twelve. The mean concentration of Zn at site one was significantly different from the mean concentrations at sites four to fourteen. Similarly, the mean concentration of Pb at site one was significantly different from the mean concentrations at all sites except for sites seven and fifteen. This difference might be due to the difference in the pollution sources of the heavy metals and the difference in physicochemical properties of water at different sampling points.

Table 5.4 Summary of the mean concentration of heavy metals from River sediment

HMS	**River sediment**		**Anova**		**MPL (mg/kg)**		**SQGs**	
	Mean	Std. Dev	F	p	WHO,2004	USEPA, 1999	TEL	PEL
Mn	0.947	2.787	76.9	0	NA	30	-	
Zn	0.801	0.653	415.6	0	123	110	124	271
Cu	0.278	0.088	7.3	0	31.6	16	18.7	108
Cr	0.437	0.014	157.4	0	NA	0.6	52.3	160
Cd	ND	ND	ND	ND	6			
Pb	0.054	0.007	88	0	NA	40	30.2	112
Ni	0.009	0.005	2.2	0.13	20	16	15.9	42.8
Fe	19.553	4.74	2.5	0.12	NA	30		
Co	0.236	0.128	1.6	0.13	-			

Remark: Cd not detected (ND), Fe, Ni and Co are not significant at 5% significance level.

5.3.2Assessment of sediment contamination and ecological risk of HMs from the River

Table 5.5 presents the values of the contamination factor (CF), contamination degree (CD), pollution load index (PLI), and ecological risk index (RI) from the River sediment. The CF values of the present study were arranged in the order as follows: Mn >Zn > Co > Cu >Cr > Pb Fe > Ni.The EI values for the detected heavy metals in the River sediment were also occurred in the Order: Mn > Co > Cu > Pb > Zn> Co > Zn > Ni> Fe. The results of CF indicate a low degree of pollution with CF values below 1.The mean PLI values of the heavy metals in the sediment of Lower Omo river was 0.0063 indicating low metal contamination in the sediment (PLI < 1.0). Similar finding was reported by Kwacha *et al*. (2023) from Mae Chaem River in Thailand. The mean RI value of the present study was 0.137 that indicate the low potential ecological risk of the sediment by heavy metal (Table 5.4). Compared with the SQGs, the mean concentrations of all heavy metals in the River sediments were below the TEL values suggesting that the heavy metals in the sediment were not toxic and do not tend to exhibit adverse biological effects.

Table 5.5Sediment contamination and ecological risk index of River sediments

HMs	CF	CD	mCd	Ti	EI	RI	PLI
Mn	0.03157	0.0648	0.0081	1	0.032	0.137	0.0063
Zn	0.011443			1	0.011443		
Cu	0.006178			5	0.030889		
Cr	0.00437			2	0.00874		
Pb	0.0027			5	0.0135		
Ni	0.000225			5	0.001125		
Fe	0.000414			1	0.000414		
Co	0.007867			5	0.039333		

5.3.2 Heavy metals concentration in the sediment of Delta

The mean concentrations of heavy metals in the sediment samples are presented in Table 5.6, The mean concentrations of the heavy metals in the sediment samples followed the order Fe (19.515mg kg^{-1}) > Mn (0.904mg kg^{-1})> Zn (0.809mg kg^{-1}) > Cr (0.434 mg kg^{-1}) > Cu (0.288 mg kg^{-1}) > Co (0.223 mg/L) > Pb (0.058mg kg^{-1}) > Ni (0.008 mg kg^{-1})> Cd (ND). The maximum mean concentration of heavy metals detected in the sediment was Fe (19.515mg kg^{-1}) and the minimum mean concentration was for Ni (0.008mg kg^{-1}). The mean concentration of Fe in sedimentof the present study was lower than that in the study by Acharjee *et al*. (2022) from Surma River(291.1 mg kg^{-1}) in Bangladesh but higher than the freshwater sediment concentration in Malaysia which was 1.667mg/ kg (Tengku *et al*., 2020). A higher concentration of Ni was also reported in the previous study by Kwacha *et al*. (2023**)** from Mae Chaem (24.0mg kg^{-1}) in Thailand,by Wang *et al*. (2015) which was 31.9 mg/kg andSong *et al*. (2017) which was (23.5 mg/kg) than in the present study. On the other hand, a lower concentration of Ni was recorded in sediment of Atoyac of in Mexico (0.001mg/kg) than the present study.The Mn level in the present study was lower than that in the study by Acharjee *et al*. (2022).The mean Mn level in the present study was higher than the study reported by Ibukun *et al*. (2018) in the freshwater sediment of Nigeria (0.211 mg/kg).The mean zinc level of this studywas lower than the study report by Hyun *et al*. 2007 which was 206.3 mg/kg .The mean chromium level in the present study was lower than in the study by Song *et al*. (2017) which was 55.5 mg/kg and Kassim *et al*.(2019) from Gibe Reservoir sediment (23.24 mg kg^{-1}) in Ethiopia. However, its mean level in the present study was higher than in the study by Qiang *et al*.(2021) from Buerhatong sediment in china (0.00456 mg/kg).The mean lead (Pb) level in the present study was lower than in the study byMariusz and Joanna (2023) from Muchawka sediment in Poland (9.3 mg/kg) where as its level in the present study was higher than those studies by Gabriela *et al*.(2019) in Atoyac Mexico(0.008 mg/kg) and Tengku *et al*.(2020) in Malaysia (0.01 mg/kg). The mean Cu level in the present study was lower than in the study by Yasemin and Fusun (2021) in Turkey (1.128 mg/kg) where as higher Cu level was recorded in the present study than the studies by Qiang *et al*.,(20210 which was (0.01344 mg/kg) and Adem *et al*.(2023) which was (0.03 mg/kg). The mean concentration of Co in this study was reported unvaryingly in the study by Simul *et al*.,(2019)from Brahmaputra sediment in Bangladesh (0.2 mg/kg).

The variations in heavy metal concentrations from sediment at different sampling points are presented in Table 5.4. The Mean Concentration of all HMs except for Pb in the sediment is significantly different at 5% level of significance. To see in which sample point the mean concentration is significantly different, the Turkeys' test of multiple comparison was consider as shown in the Table 5.8.The mean concentration of Mn at site one was significantly different from the mean concentration at sites seven, eight, nine, ten, and twelve.The mean concentration of Zn at site one was significantly different at all points except from the mean concentrations at sites 3,4,6, 10,11, and 14.This difference might be due to the difference in the pollution sources of the heavy metals and the difference in physicochemical properties of the freshwater at different sampling points. Similarly the mean difference of each heavy metal at all points is presented in Table 5.6 below.

Table 5.6 Summary of the mean concentration of heavy metals fromDelta Sediment

HMS	Lake sediment		Anova		MPL (mg/kg)		SQGs	
	Mean	Std. Dev	F	p	WHO,2004	USEPA, 1999	TEL	PEL
Mn	0.904	2.736	20.1	0.00	NA	30		
Zn	0.809	0.654	8.9	0.00	123	110	124	271
Cu	0.288	0.084	136.4	0.00	31.6	16	18.7	108
Cr	0.434	0.011	185.9	0.00	NA	0.6	52.3	160
Cd	ND	ND	ND	ND	6			
Pb	0.058	0.012	1.3	0.26	NA	40	30.2	112
Ni	0.008	0.007	84.7	0.00	20	16	15.9	42.8
Fe	19.515	4.802	72.0	0.00	NA	30		
Co	0.223	0.117	103.8	0.00	NA			

NB:NA= not available; ND= not detected

Table 5.7Heavy metal analysis in sediment of Lake at different sample sites (Multiple comparisons to see in which sample points the mean concentration is significantly different**)**

SN	**Mn**	**Zn**	**Cu**	**Cr**	**NI**	**Fe**	**Co**
	Mean ±SD	**Mean ±SD**	**Mean ±SD**	**Mean ±SD**	**Mean ±SD**	**Mean ±SD**	**Mean ±SD**
1	0.40 ± 0.02^{a}	0.21 ± 0.00^{ab}	0.20 ± 0.00^{bc}	0.43 ± 0.01^{c}	0.004 ± 0.001^{ab}	15.23 ± 0.16^{ab}	0.12 ± 0.01^{a}
2	0.46 ± 0.16^{a}	0.42 ± 0.00^{c}	0.22 ± 0.01^{bc}	0.41 ± 0.01^{ab}	0.039 ± 0.001^{d}	16.87 ± 0.04^{c}	0.08 ± 0.02^{a}
3	0.41 ± 0.02^{a}	0.19 ± 0.02^{ab}	0.21 ± 0.01^{bc}	0.43 ± 0.01^{bc}	0.004 ± 0.001^{ab}	15.27 ± 0.16^{ab}	0.15 ± 0.01^{a}
4	0.39 ± 0.21^{a}	0.19 ± 0.03^{ab}	0.07 ± 0.00^{a}	0.58 ± 0.01^{f}	0.019 ± 0.001^{c}	13.88 ± 0.36^{a}	0.11 ± 0.02^{a}
5	0.41 ± 0.08^{a}	0.41 ± 0.00^{c}	0.22 ± 0.01^{bc}	0.41 ± 0.01^{a}	0.041 ± 0.001^{d}	16.68 ± 0.36^{bc}	0.06 ± 0.01^{a}
6	0.40 ± 0.19^{a}	0.28 ± 0.13^{abc}	0.09 ± 0.00^{a}	0.55 ± 0.01^{f}	0.020 ± 0.001^{c}	13.84 ± 0.36^{a}	0.07 ± 0.01^{a}
7	2.43 ± 0.57^{c}	0.42 ± 0.01^{c}	0.24 ± 0.02^{c}	0.52 ± 0.01^{e}	0.010 ± 0.003^{b}	21.38 ± 0.90^{e}	0.55 ± 0.07^{c}
8	1.96 ± 0.41^{bc}	0.43 ± 0.00^{c}	0.21 ± 0.01^{bc}	0.51 ± 0.00^{e}	0.008 ± 0.005^{ab}	21.56 ± 0.97^{e}	0.50 ± 0.06^{bc}
9	2.26 ± 0.67^{c}	0.53 ± 0.21^{c}	0.19 ± 0.00^{b}	0.54 ± 0.01^{e}	0.005 ± 0.004^{ab}	21.37 ± 0.89^{e}	0.41 ± 0.03^{b}
10	1.43 ± 0.26^{b}	0.35 ± 0.00^{abc}	0.20 ± 0.01^{bc}	0.48 ± 0.01^{d}	0.019 ± 0.002^{c}	18.58 ± 0.78^{d}	0.05 ± 0.02^{a}
11	1.42 ± 0.25^{b}	0.33 ± 0.00^{abc}	0.21 ± 0.01^{bc}	0.47 ± 0.01^{d}	0.018 ± 0.004^{c}	18.07 ± 0.43^{cd}	0.10 ± 0.02^{a}
12	1.41 ± 0.25^{b}	0.34 ± 0.05^{bc}	0.20 ± 0.00^{bc}	0.50 ± 0.01^{d}	0.017 ± 0.004^{c}	18.59 ± 0.80^{d}	0.07 ± 0.01^{a}
13	0.43 ± 0.12^{a}	0.42 ± 0.01^{c}	0.23 ± 0.01^{c}	0.41 ± 0.00^{ab}	0.039 ± 0.001^{d}	16.65 ± 0.36^{bc}	0.05 ± 0.02^{a}
14	0.41 ± 0.01^{a}	0.21 ± 0.00^{ab}	0.20 ± 0.01^{bc}	0.44 ± 0.02^{c}	0.002 ± 0.001^{a}	15.14 ± 0.00^{a}	0.14 ± 0.01^{a}
15	0.39 ± 0.21^{a}	0.17 ± 0.01^{a}	0.08 ± 0.00^{a}	0.58 ± 0.00^{f}	0.020 ± 0.001^{c}	13.72 ± 0.41^{a}	0.12 ± 0.01^{a}

Cd: not detected, Pb is not significant

5.3.3 Sediment contamination and ecological risk index of Delta sediments

Table 5.8 presents the values of the contamination factor (CF), contamination degree (CD), pollution load index (PLI), and ecological risk index (RI) from the Lake sediment. The CF values of the present study were arranged in the order as follows: Mn >Zn > Co > Cu >Cr > Pb Fe > Ni.The EI values for the detected heavy metals in the Lake sediment were occurred in the Order: Mn > Co > Cu > Pb > Zn> Co > Zn > Ni> Fe. The contamination factor (CF) value for all the studied heavy metals were <1, indicating low contamination level. In terms of degree of contamination, all the values remained under the standard limit of Cd < 8, indicating a low degree of contamination. The calculated value of mCd and PLI did not exceed the baseline level of pollution (<1) indicating low contamination of the Lake sediment. In terms of ecological risk, in which Mn, Zn, Cu, Co, Cu, Cr, Pb, Ni, Fe, and Co were considered, all the ecological risk factor and risk indices were below risk level (EI < 40 and RI <150).Similar findings were presented in the study by Hossain *et al*.(2021) from freshwater sediments of Bangladesh. The low contamination level of the sediment could be due to the psychochemical nature of the sediment, and/or water and the chemical properties of the metals underinvestigation. Compared with the SQGs, the mean concentrations of all heavy metals in the Lake sediments were below the TEL values suggesting that the heavy metals in the sediment were not toxic consequently does not tend to exhibit adverse biological effects.

Table 5.8Sediment contamination and ecological risk index of Lake Sediments

HMs	CF	CD	mCd	Ti	EI	RI	PLI
Mn	0.030133	0.063377	0.007922	1	0.030133	0.135451	0.00545
Zn	0.011557			1	0.011557		
Cu	0.0064			5	0.032		
Cr	0.00434			2	0.00868		
Pb	0.0029			5	0.0145		
Ni	0.0002			5	0.001		
Fe	0.000413			1	0.000413		
Co	0.007433			5	0.037167		

The independent samples test (t-test for Equality of Means) is presented in Table 5.9. The test revealed that there was a significant statically difference in mean concentration of some heavy metals between the water bodies (River and Delta Lake). Accordingly, there was a statically significant difference in mean concentrations of all the heavy metals except for Pb. This difference in their mean concentration could be due to the difference in the physicochemical properties of the water bodies which would directly or indirectly affect the availability of the metals in the freshwater ecosystem of the water bodies. Moreover, the chemical nature of the heavy metals and difference in the source of pollution could also contribute to their mean difference in two water bodies. Difference in the physical and chemical properties of the sediment could also contribute to the difference in mean the mean concentrations of the heavy metals. The mean concentration of Pb was not significantly different which might due to the physical and chemical nature of Pb in the two water bodies.

Table 5.9 Independent samples test (t-test for Equality of Means) in sediment of Omo river and Delta

HMs	t	df	Sig	mean diff	SED	95% CI	
				Mean Difference	Std. Error Difference	Lower	Upper
Mn	16.542	88	0.000	3.385	0.205	2.978	3.792
Zn	22.277	88	0.000	0.832	0.037	0.757	0.906
Cu	15.781	88	0.000	0.185	0.012	0.162	0.208
Cr	2.877	88	0.005	0.036	0.013	0.011	0.062
Cd	3.566	88	0.001	0.004	0.001	0.002	0.006
Pb	-0.517	88	0.607	-0.009	0.018	-0.045	0.026
Ni	2.057	88	0.043	0.007	0.004	0.000	0.014
Fe	15.662	88	0.000	6.465	0.413	5.645	7.286
Co	6.411	88	0.000	0.167	0.026	0.116	0.219

5.4 Conclusions

The present study investigated the pollution level and potential ecological risks of heavy metals in the sedimentsof Lower Omo River and Omo Delta.The concentration of the detected heavy metals in the sediment samples at all sampling points were below the sediment quality guidelines (SQGs).The degree of contamination, contamination factor, modified degree of contamination and pollution load index were used to assess sediment pollution. The evaluation of the indices from the sediment concentration of heavy metals indicted a low contamination degree of the sediment from both water bodies.. In terms of ecological risk, , all the ecological risk factor and risk indices were below risk level (EI < 40 and RI <150) indicating that the concentrations of the heavy metals in the sediment could not cause potential ecological risks.

5.5 Reference

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CHAPTER SIX

Assessment of heavy metal levels of irrigated soil in the vicinity lower Omo River and ecological risk

Abstract

This study was conducted on the levels of heavy metals and associated ecological risks of the soil irrigated using Lower Omo River. A total of 15 composite samples were collected along the Omo River which was used for irrigation. The soil was analysed for nine heavy metals using a Flame Atomic Absorption Spectrometer. The study evaluated the ecological risk using risk index factor (RI), comprehensive risk index (CRI), contamination factor (CF), contamination degree (CD) and pollution load index (PLI).The mean concentrations of the detected heavy metals in mg/kg in the soil which was being irrigated by lower Omo River of River were respectively 4.4for (Mn), 1.142 for (Zn), 0.2 for (Cu), 0.43 for (Cr), 0.424 for (Pb), 0.004 for (Ni), 23.5 for (Fe), and0.588 for (Co). The order for the mean concentrations of the heavy metals in the soil were Fe >Mn > Zn > Co > Cr > Cu > NiThe EI results for the detected heavy metals in the soil irrigated from Lower Omo River were in the Order of Fe > Cu > Mn> Pb > Co > Zn > Cr> Ni. The results of CF indicated a low degree of contamination with CF values below 1. The mean PLI values of heavy metals in the soil revealedthat the soil was at a low pollution level (PLI <1.0).

. Keywords: Ecological risk, heavy metals, Omo River, Soil, heavy metals

6.1 Introduction

Soil pollution by heavy metals has become a significant global concern, principally for African countries like Ethiopia where waste management is a big issue (Samuel *et al.,* 2020).Even while heavy metals are naturally present in soil, human activities greatly increase the concentration of heavy metals in the environment. The fast pace of industrialization, urbanization, and excessive use of agrochemicals has led to the accumulation of pollutants in the soil. For the reason of unwise applicationof agrochemicals, Ethiopia's pollution levels have risen to risk levels, with rising metal levels and declining agricultural soil quality (Benti *et al*., 2016).Agrochemical use and irrigation with rivers of industrial effluents and urbanization are the main sources of heavy metal pollution in Ethiopian agricultural soils (Gebeyehu and Bayissa, 2020; Samuel *et al*., 2020).

Recently, the Omo River has seen significant developmental activity and intense agriculture along the river and its catchments, notably on the upstream side of the Omo Delta (Wakjira and Getahun, 2017). Large-scale irrigation development, industry and land use changes in the upper and middle Omo Basin in recent years have already resulted in changes in the environment of the lower Omo River basin (Ojwang *et al*., 2010). It has been inevitably altered by the rapid development of industry and agriculture in its catchment (Ojwang *et al*., 2010).The developments of irrigation and agriculture in general in the Omo River basin have led to increased use of fertilizers and pesticides. Over 30% of the Upper Omo upstream inflow will be abstracted for irrigation (Avery, 2012).

According to the results gained from other irrigation projects, large-scale irrigation development in the Lower Omo could have a significant effect on aquatic resources and water chemistry due to agrochemicals and increased nutrient levels, leading to the destruction of aquatic biota (Avery, 2012). Experience with similar projects has also indicated that proper amounts of fertilizers and pesticides are not being used, and as a result, excessive chemical runoff can occur (Gure *et al*., 2019). This improper use of agrochemicals may cause potential adverse impacts, including depreciation of downstream water quality, increased vulnerability of the ecosystem and harm to humans and livestock (Ojwang *et al.*, 2010). Chemical contamination of the lower Omo could arise from human activities. These include chemicals from large-scale irrigation projects, from construction projects (hydroelectric dams), waste discharges from factories and urban wastes (Avery, 2012; Gure *et al.*, 2019).

Thus, the present study aims to determine the pollution level of heavy metals and the associated risks from the irrigated soil in the vicinity of Lower Omo River.To the best of our knowledge, no study has been reported in the levels of HMs and their associated ecological risks of the soil from the irrigation use of Lower Omo Rive, in spite of the serious environmental concerns in the catchment.Therefore, the objective of this study was to determine the concentration of heavy metals in soil of Lower Omo Rive that was used for irrigating the soil and assess pollution status of the soil using different environmental indices such as contamination factor (CF), degree of contamination (Cd), modified degree of contamination (mCd), Pollution load index (Er), and risk index (RI).

6.2 Materials and methods

6.2.1 Descriptions of the study area

The descriptions of the study area are presented in section 1.9.1

6.2.2. Soil sampling and sample collection

The soil samples were collected from the sites where the River water was being used for irrigation purpose. A total of 45 sediment samples were collected which were then composited to 15 for analysis. They were collected by using plastic trowelandtransferred in polyethylene bags immediately. The collected samples were transferred to an ice box with the plastic bags and then right away to the soil laboratory of Arbaminch University.

6.2.3 Sample preparation and digestion

The soil samples were air dried in the laboratory at room temperature for a week. The air dried samples were then grounded using mortar and pestle after being sieved with a 2 mm sieve. The samples were then made ready for digestion (Samuel *et al*., 2020; Acharjee *et al*., 2022). 0.5 gram of finely powdered soil samples were put in digestion vials to witch 65% HNO_3 (3ml) and 70% $HClO_4$ (2ml) was added and heated over a steam bath to form a clear solution. The mixture was filtered with whatman filter paper and stored in the freezer at 4 °C.

6.2.4 Sample analysis

The samples were analyzed for heavy metal content using flame atomic absorption spectrometer (GFAAS- novAA400p; Germany), and the concentrations of the heavy metals in the samples were determined from a standard calibration curve.Analytical grade standards of each target heavy metal were used to construct calibration curves. Analysis of each heavy metal was carried out in triplicate.

6.2.5 Soil contamination and ecological risk assessment indices from River

6.2.5.1 Basic contamination index (contamination factor and contamination degree)

The degree of contamination with a particular metal is shown by the contamination factor (Cf), which is the ratio of each metal's content to its background value. The contamination degree (Cd) is defined as the sum of all contamination factors (Cf) (Liao *et al*., 2021).The contamination status of the soils is often classified using the degree of contamination (CD) and the contamination factor (CF). The Contamination Factor (CF) and Contamination Degree (CD) are the primary markers of the soil's metal contamination status that are being examined. Equations 6.1 and 6.2 present the estimated values of the CF and CD in accordance with Hakanson's (1980) methodology.

$$CF = \frac{\text{Cm (sample)}}{\text{Cm (background)}} \quad (6.1)$$

$$CD = \sum CF \quad (6.2)$$

Where, the C_{sample} and $C_{background}$ are the measured and background concentration in the soil respectively.The element's baseline value is equal to the average value of the world's surface rock. Cr (100), Ni (40), Cu (45),Co(30), Zn (70), Fe (47200), Mn (30), and Pb (20) mg/Kg. According to Håkanson (1980), the CF is categorized as: $CF < 1$, low contamination factor; $1 < CF < 3$, moderate contamination factor; $3 < CF < 6$, considerable contamination factor; and $CF > 6$, very high contamination factor (Turekian and Wedepohl,1961, Samuel *et al*., 2020).The Contamination factors are graded into four classes as: as presented in Table 6.2.

Table 6.1 *Description of Contamination Factor (CF) and Contamination Degree (CD)*

Contamination Factor Ranges	Description	Contamination Degree	Description
1 <CF< 3	moderate contamination	8< CD<16	Moderate degree of Contamination
3<CF< 6	considerable contamination	16 < CD <32	Considerable degree of contamination
CF> 6	very high contamination	CD>32	Very high degree of Contamination

6.2.5.2 Advanced indices for determination of soil contamination

A. Modified contamination (mC_d)

$$mC_d = \sum_{i=1}^{n} CF/n \quad (6.3)$$

Where mC_d is modified contamination degree (*mC_d*), $mCd < 1.5$ signifies very low and $mCd > 32$ indicate ultra-high degree of contamination respectively, (Hossain *et al.*, 2021a, 2021b).

B. Pollution load index (PLI)

Pollution load index (*PLI*) is an empirical index which provides a simple and comparative means for assessing metal pollution levels and is a geometric evaluation of the individual $C_{f.}$

To understand the heavy metals accumulation in the surface sediments of the study areas, the studied metals were evaluated with the PLI. The PLI is a recognized method for evaluating mutual contamination effects (Tian *et al.*, 2017). The PLI was used for evaluating mutual contamination effects of the eight heavy metals in the sediments of the present study and calculated in equation 5.4.The PLI was used for evaluating mutual contamination effects of the eight heavy metals in the sediments of the present study.

$PLI = [CF_{Mn} \times CF_{Zn} \times CF_{Cr} \times CF_{Ni} \times CF_{Pb} \times CF_{Fe} \times CF_{Co} \times CF_{Cu}]^{1/n}$ (6.4)

Where CF is the contamination factor which was calculated in the Eq. (1). Where CF denotes the contamination factor, and n is the considered number of heavy metals. There are three discrete categories for pollution measurement with this index. According to Tomlinson *et al.* (1980), PLI< 1 means there is no indication of pollution; if it is greater than 1, there is metal pollution (Samuel *et al.*, 2020; Acharjee *et al.*, 2022).

6.2.5.3 Potential ecological risk index of HMs in soil (RI)

This was formulated by Hakanson (1980) to quantify the level of ecological risk of heavy metals in sediment. The RI assesses the combined ecological and environmental toxicity to provide an overall evaluation of the potential risk of heavy metal pollution which is calculated as follow:

$EI = T_i \times CF$ (6.5)

$$RI = \sum E_i \quad (6.6)$$

Where, EI is the individual potential risk, and Ti is the toxicity effect coefficient, with Values for Mn, Zn, Cu, Cr, Pb, Ni, Fe , and Co are 1, 1, 5, 2, 5, 5,1,and 5 (Tegn *et al*., 2014).According to Hakanson (1980), and CF is the contamination factor of each metal. The potential ecological risks were classified on the basis of the values of the risk factor as presented in Table 6.2

Table 6.2 Various pollution risk index and their status (Hakanson, 1980; Solaiman *et al*., 2021)

Pollution index (PI)	Pollution status	Pollution load index (PLI)	Pollution status	EI	Risk level	RI	Potential ecologica hazard
PI＜0.7	Clean	＜1	Unpolluted	EI＜40	Weak	RI＜150	Low
0.7≤PI＜1	Basic cleaning	1≤PLI＜2	Moderately polluted	40≤EI＜80	Medium	150≤RI＜300	Modetate
1≤PI＜2	Mildly polluted	2≤PLI＜3	Strongly polluted	80≤EI＜160	Strong	300≤RI＜600	High
2≤PI＜3	Moderately polluted	PLI≥3	Very strongly polluted	160≤EI＜320	High strong	RI≥600	Significantly high
PI≥3	Strongly polluted	-	-	EI≥320	Extremely strong	-	-

6.2.6 Data analysis

Analyses of the data were carried out using IBM SPSS Statistics 21 software at a confidence level of 95%, and differences were considered to be statistically significant at $p < 0.05$.The heavy metal concentrations at each point are presented as the mean ± standard deviation of the samples analysed.The overall differences in the mean concentrations of metals between sampling points were analysed using ANOVA.To see in which sample point the mean concentration was significantly different; the Tukey test of multiple comparison was used.

6. 3 Result and discussion

6.3.1 Concentration of heavy metals in soil

In the present finding, the overall mean manganese (Mn) level in irrigated soil from Omo Rivers was 4.41mg/kg.The finding of the present study was higher than Mn concentrations in soil ranged from 0.450 to 0.904 mg/kg in area irrigated with canal and sewage water in Pakistan, (Khan *et al*., 2019). However, in the Alamosa River basin in Colorado, soil samples showed increased soluble manganese concentrations exceeding water quality standards (Munir *et al*., 2021). Additionally, a study in southeast Turkey found that manganese concentrations in soil were generally lower than the Earth's crustal average; with variations among different plant species (Green *et al*., 200).These findings highlight the influence of irrigation sources and soil characteristics on manganese levels in irrigated soil from rivers.The mean Zinc level in irrigated soil from Omo Riverwas 1.142 mg/kg. This findingis in line with the previous study done in the Yellow River irrigation areas(Zhang *et al*., 2011). However, our finding was lower than the mean Zinc content which was found to be 107 mg/kg in the Hetao oasis(Zhu *et al*., 2016). Furthermore, Zinc concentrations differed significantly in soils irrigated with underground water, sewage water, or a mix of the two, with the highest levels seen in soils irrigated with sewage water (Mahar *et al*., 2007).

The mean levelsof copper in irrigated soil from Omo Riverwas 0.2mg/kg ranging from 0.13 to 0.26 mg/kg which was lower than the permissible limitin soil (36 mg/ kg) .This finding contrast to the previous study conducted in Nigeria, the copper levels in the soil exceeded permissible limits, with concentrations reaching as high as 4.51 mg/kg in the Asa River downstream areas (Omar *et al*., 2016). Similarly, in the study from Iran, the wastewater-irrigated soils contained significantly higher amounts of copper compared to control soils, with concentrations being 3.0 to 4.9 times higher in different landscape positions (Ma etal., 2019). Additionally, the study from Kazakhstan highlighted the spatial and vertical variation of copper levels in irrigated soils, showing significant differences in copper contents in different soil layers across sampling regions (Rezapour *et al.*,2011).

The mean level of chromium in irrigated soil from theOmo Riverwas 0.43mg/kg. In Modjo city, Ethiopia, the chromium concentration in soil samples near tanneries ranged from 2.78 ± 0.37 to 4.57 mg $kg^{-1,}$ exceeding guideline values (.Gezahegn *et al.*, 2021) which was higher than the present study. Similarly, in the South Kaliapani chromite mine region of India, surface soils showed a mean chromium content of 11,170 mg kg−1, which decreased significantly after crop harvest (Ilker, *et al.*, 2021). Additionally, at the peripheral of Abbay River, soil samples near wastewater discharge points from industries contained an average of 232.465 ± 56.219 mg/kg of total chromium (Alemu *et al.*, 2017)which significantly higher than the present study These findings highlight the significant variability in chromium levels in irrigated soil from rivers, emphasizing the importance of monitoring and managing chromium contamination in agricultural areas.

The Omo Rivers' irrigated soil had amean lead (Pb) level of 0.424 mg/kg. The current investigation found greater lead concentration in irrigated soil than a meta-analysis in Ethiopia, which was 0.04 mg/kg (Ali *et al.*, 2022). In the Mantaro Valley, Peru, soil irrigated with contaminated water had a mean lead concentration of 57.17 mg.kg-1 for Lolium hybridum Hausskn and 57.19 mg.kg-1 for Medicago sativa (Orellana *et al.*, 2019) which were both higher than the present finding. In contrast, a meta-analysis of lead contents in irrigated Iranian soil found 441 mg/kg (Ali *et al.*, 2022).

The overall mean nickel content in Omo Rivers' irrigated soil ranged from undetectable to 0.009mg per kg. Nickel concentrations in soil varied between 0.085 and 1.611 mg/kg in the Tyume River basin (Awofolu *et al*., 2005) which was higher than the present study finding . Similarly, nickel pollution was found in soil in the Bindal river basin, with values ranging from 10 to 1000 ppm (Chakresh *et al*., 2010) which was lower than the present finding .These findings underscore the role of irrigation in raising nickel levels in soil, which may have implications for ecosystem stability. Thus, it is vital to monitor and manage nickel pollution in irrigated soils to avoid negative impacts on agricultural productivity and environmental quality.

The overall mean level of cobalt in irrigated soil from rivers range 0.52 to 0.67 mg/kg.The present finding is comparable with a study conducted in Punjab, Pakistan, cobalt concentrations in wheat plants irrigated with wastewater ranged from 0.15 to 1.20 mg/kg, within permissible limits(Khan, *et al*., 2020).In Sargodha, cobalt content significantly increased in soil and plants when irrigated with sewage water, with values up to 1.560 mg/kg in plant roots which was comparable with the present finding. Along the Kubanni stream channels in Zaria, cobalt levels in soil ranged from 0.63 to 4.07 mg/kg, exceeding permissible limits (Khan *et al*., 2020). And higher than the current study result.Lastly, in Egypt, highly polluted soils showed cobalt levels ranging from 36 to 64.69 ppm which was lower than our finding(Zohny *et al*., 2002).

Table 6.3 Heavy metal concentration of soil

SN	Mn	Zn	Cu	Cr	Pb	Ni	Fe	Co
	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD
1	4.22 ± 0.05^{d}	1.19 ± 0.01^{c}	0.16 ± 0.00^{a}	0.44 ± 0.01^{c}	0.54 ± 0.01^{d}	0.003 ± 0.00^{b}	23.56 ± 0.16^{b}	0.59 ± 0.01^{cd}
2	4.35 ± 0.01^{d}	1.20 ± 0.00^{c}	0.20 ± 0.02^{b}	0.45 ± 0.01^{c}	0.33 ± 0.02^{abc}	0.008 ± 0.00^{cd}	23.42 ± 0.05^{b}	0.61 ± 0.01^{d}
3	4.20 ± 0.02^{cd}	1.22 ± 0.02^{c}	0.13 ± 0.00^{a}	0.43 ± 0.00^{c}	0.56 ± 0.03^{d}	0.005 ± 0.00^{b}	23.56 ± 0.17^{b}	0.56 ± 0.01^{b}
4	5.19 ± 0.01^{e}	1.05 ± 0.01^{b}	0.24 ± 0.00^{b}	0.41 ± 0.01^{c}	0.55 ± 0.02^{d}	0.007 ± 0.00^{c}	24.11 ± 0.04^{c}	0.52 ± 0.01^{a}
5	5.20 ± 0.02^{e}	1.06 ± 0.01^{b}	0.21 ± 0.00^{b}	0.47 ± 0.01^{c}	0.51 ± 0.01^{d}	0.006 ± 0.00^{cd}	22.71 ± 0.05^{a}	0.54 ± 0.01^{a}
6	5.83 ± 0.73^{e}	1.09 ± 0.01^{b}	0.26 ± 0.00^{b}	0.45 ± 0.01^{c}	0.59 ± 0.01^{d}	0.004 ± 0.00^{cd}	23.41 ± 0.05^{b}	0.52 ± 0.01^{a}
7	4.43 ± 0.06^{d}	1.34 ± 0.06^{d}	0.21 ± 0.01^{b}	0.39 ± 0.01^{b}	0.39 ± 0.02^{c}	0.002 ± 0.00^{a}	23.60 ± 0.04^{c}	0.64 ± 0.01^{e}
8	4.46 ± 0.23^{d}	1.35 ± 0.07^{d}	0.23 ± 0.01^{b}	0.40 ± 0.01^{b}	0.37 ± 0.03^{bc}	0.001 ± 0.00^{a}	24.20 ± 0.04^{c}	0.67 ± 0.01^{e}
9	3.51 ± 0.00^{ab}	0.84 ± 0.04^{a}	0.14 ± 0.01^{a}	0.37 ± 0.01^{ab}	0.31 ± 0.01^{a}	0.001 ± 0.00^{a}	23.00 ± 0.06^{a}	0.58 ± 0.00^{bcd}
10	4.56 ± 0.38^{d}	1.25 ± 0.01^{c}	0.20 ± 0.01^{b}	0.48 ± 0.00^{c}	0.36 ± 0.02^{bc}	0.008 ± 0.00^{cd}	22.92 ± 0.05^{b}	0.60 ± 0.01^{d}
11	4.34 ± 0.01^{d}	1.21 ± 0.01^{c}	0.19 ± 0.01^{b}	0.45 ± 0.00^{c}	0.34 ± 0.01^{abc}	0.009 ± 0.00^{d}	23.42 ± 0.06^{b}	0.63 ± 0.01^{d}
12	4.20 ± 0.01^{bcd}	1.23 ± 0.02^{c}	0.15 ± 0.00^{a}	0.42 ± 0.01^{c}	0.54 ± 0.02^{d}	0.003 ± 0.00^{b}	23.56 ± 0.16^{b}	0.59 ± 0.01^{cd}
13	$3.57.00^{ab}$	0.83 ± 0.04^{a}	0.12 ± 0.00^{a}	0.37 ± 0.02^{a}	0.31 ± 0.03^{a}	0.000 ± 0.00^{a}	22.97 ± 0.02^{a}	0.55 ± 0.01^{bc}
14	3.52 ± 0.05^{a}	0.89 ± 0.04^{a}	0.14 ± 0.00^{a}	0.38 ± 0.01^{ab}	0.32 ± 0.01^{ab}	0.002 ± 0.00^{a}	23.00 ± 0.06^{a}	0.57 ± 0.01^{b}
15	4.43 ± 0.06^{d}	1.38 ± 0.04^{d}	0.22 ± 0.00^{b}	0.40 ± 0.01^{b}	0.34 ± 0.01^{abc}	0.001 ± 0.00^{a}	24.4 ± 0.03^{c}	0.65 ± 0.01^{e}

6.3.2 Soil contamination and ecological risk index of soil

Table 6.4 presents the values of the contamination factor (CF), contamination degree (CD), pollution load index (PLI), and ecological risk index (RI) from the Lake sediment. The mean Contamination Factors (CF) were 0.147 for Mn, 0.0163(Zn), 0.0044 (Cu), 0.0042 (Cr), 0.0212 (Pb), 0.0001 (Ni), 1.47 (Fe),and 0.0186(Co) as presented in (Table 6.4). The CF values of the present study were arranged in the order as follows: Mn >Pb >Co > Zn > Cu > Cr >Fe > Ni and the CFvalue for all the detected heavy metals were <1, indicating low contamination level.The EI values for the detected heavy metals in the soil occurred in the Order: Mn > Pb > Co > Cu > Cr>Ni > Fe. In terms of degree of contamination, all the values remained under the standard limit of Cd < 8, indicating a low degree of contamination. The calculated value of mCd and PLI did not exceed the baseline level of pollution (<1) indicating low contamination of the soil. In terms of ecological risk, all the ecological risk factor and risk indices were below risk level (EI < 40 and RI <150).

Table 6.4Soil contamination and ecological risk index

HMs	CF	CD	mCd	Ti	EI	RI	PLI	
Mn	0.147	0.214	0.027	1	0.147	0.402		0.0069
Zn	0.016			1	0.016			
Cu	0.0044			5	0.022			
Cr	0.0043			2	0.0086			
Pb	0.0212			5	0.106			
Ni	0.00023			5	0.00113			
Fe	0.00049			1	0.00049			
Co	0.02			5	0.1			

6.4 Conclusion

This study has provided baseline information for the pollution level of heavy metal as a first-hand report from irrigated soil of Lower Omo River. The heavy metals in the soil could contribute to the heavy metals pollution level in the freshwater ecosystem due to their release from the soil through leaching and flood. The mCd and PLI value did not exceed the baseline level of pollution (<1) indicating low contamination of the soil. In terms of ecological risk, all the ecological risk factor and risk indices were below risk level (EI < 40 and RI <150). Thus close monitoring of the heavy metals level of the soil and the water quality which is beingused for irrigation should be monitored. The evaluation of the ecological indexes indicates that the pollution status of the soil in the soilirrigated from the lower Omo River was low.

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CHAPTER SEVEN

Evaluating water quality of Lower Omo River and Omo Delta using water quality index (WQI), Southern Ethiopia

Abstract

This surface water study was conducted on the Lower Omo River and and Omo Delta in Ethiopia, are the most significant supplies of water for human activities, but they are also stressed by environmental factors and are in risk due to human activity. Hence, it is very essential to evaluate the water quality which is being used for domestic, agricultural and industrial purpose. The physicochemical parameters were determined using standard analytical procedures in the Laboratory. The mean BOD_5 values obtained in this study were 16.268± 1.47 mg/l and 16.28 ±1.133 mg/l in the upstream and in the downstream respectively. Chemical oxygen demand (COD) was higher in upstream water (mean 376.06000 ±130.45mg/L) than in downstream (mean 136.00± 41.52 mg/L) which could be due to nondegradable pollutants. The mean concentration of fluoride ion in the upstream area were 0.89 ±0.0135 while that of the downstream area was 2.026±0.064mg/l. The mean concentration of total nitrogen were 8.938±1.327mg/L) and 17.84 ± 4.0083mg/L) in upstream and downstream, respectively .The value for PO_4^{-3} was 1.866 ±0.625mg/L in upstream (LOR) while in downstream (ELT) , the concentration was 5.108±0.975mg/L .Mean concentrations for NH_3 were 0.54 ±.36118 and 1.354 ±0.655 in the river and lake respectively. The finding of Water quality index (WQI) revealed that the water quality status was very poor and unsuitable for drinking in the lower Omo River and Omo Delta. Hence evaluation and monitoring of the water quality status from Lower Omo River basin (Omo River and Delta) is vital to protect the freshwater from further pollution.

Keywords: Omo River; Physicochemical parameters; Surface water; Water quality index

7.1 Introduction

Fresh water is a major issue for humanity because it is directly tied to human interests. Surface water bodies are the primary sources of water for human activities, but miserably, they are suffering from antrophogenic activities. In Ethiopia, river monitoring is not sufficiently extensive to give the data required for managing the quality of the water and sediment (Zinabu *et al*., 2019). The Omo-Turkana Basin extends over a sizable area in southwestern Ethiopia and Northern Kenya (Feibel, 2011; Velpuri *et al*., 2012). A portion of its bottom half can also be found in the eastern arm of the East African Great Rift Valley, where it is predominantly found in Ethiopia's southwest highlands (Wakjira, 2016). The Omo-Gibe River, the basin's main stream, rises to a height of roughly 2,200 meters above sea level in the southwest Ethiopian highlands. The 760 km long river flows south before reaching Lake Turkana in the lowlands at an altitude of 365 m (CSA, 2017, Wakjira, 2016). It typically receives up to 2,000 mm of precipitation per year (UNEP, 2010).An area of the lake's northern part is located in Ethiopia and the lake's Ethiopian portion is around 98 km^2, which is almost the same size as Lake Hawassa in Ethiopia (FAO, 2003; Wakjira, 2016).

Recently, the lower Omo basin has experienced a rapid industrialization, urbanization, and intensive agricultural activitiese (use of agrochemicals) in its upper stream part which drains in to the delta (UNEP, 2010; Wakjira and Getahun, 2017) have already resulted in changes to the environment of the River delta and the freshwater water chemistry (Ojwang *et al*., 2010; Avery, 2012**).** This could attribute to the pollution of fresh water ecosystem. However, river monitoring in Ethiopia is not far-reaching to endow with information for freshwater quality management (Zinabu *et al*., 2019). Hence, the objective of this paper is to evaluate the water quality of the lower Omo River and the Ethiopian part of Lake Turkana, Southern Ethiopia.

7.2 Materials and methods

7.2.1 Description of the study area

The study area is presented in section 1.9.1

7.2.2 Water sample collection

Water samples were collected following the standard protocol by APHA (2017). Water samples were collected from the Delta and the lower Omo River (LOR).The Omo River was the upstream stream, and the Ethiopian portion of Lake Turkana (Delta) was the downstream stream. Five sub sampling sites with three sampling points on each water body were taken having a total of 30 sampling points from upstream and downstream and composited to ten. Thirty water samples were collected from the LOR and ELT and composited to a total of 10 composites samples for this study representing five per water body (River and Lake). Five composite samples (homogenized from a total of 15 sub-samples; three per point) were gathered at a specific water body. A 2 L plastic container was used to collect each sample and it was filled to the brim 30 cm below the water's surface. The vessels were brought to the lab and wrapped firmly for examination (Beniah, 2020).

7.2.3 Water sample analysis

Water samples were collected and analyzed for fifteen (15) physico- chemical parameters following the standard methods APHA (2017). Measurements of pH, DO, EC, TDS, Temperature and Salinity were taken in situ from the selected sampling sites of lower Omo River and Ethiopian part of Lake Turkana using a multiprobe water quality meter; multi HQ40d. Total Alkalinity was determined by titration of water samples. The following standard methods were used to determine the parameters: hardness was determined by EDTA method; BOD_5 (mg/L) by Dometric method; COD (mg/L) by Open reflex method ; Cl^- (mg/L) by Argentometric method; F^- (mg/l) by SPANDS method; NO_3^{-2} (mg/L) by Phenol Disulphonic acid method (Uv-vis spectrophotometer; Nitrite using Colorimetric method by spectrophotometer; Ammonia by Nessler method and stannous chloride method were used to determine phosphate ($PO4^{-3}$) contents of the water samples from lower Omo River and Ethiopian part of Lake Turkana (Omo Delta) as presented in Table 3.1.

Table 7.1 Summary for method of analysis of physicochemical water quality parameters (APHA, 2017).

Laboratory Measured Water quality parameters	Instruments used with its code (Analytical methods)	Reagent used	Titrants used
Turbidity (NTU)	Turbidimeter,Turbidimetric method	Distilled water	----------
T. Hardness (as $CaCO_3$), (mg/l)	EDTA Titrimetric method	Edta, Ammoniabuffer, Eriochrom black indicator	EDTA (0.01M)
Calcium Hardness (as $CaCO_3$), (mg/l)	EDTA titrimetric method	EDTA,NaOH, Murexide	EDTA(0.01M)
Magnesium Hardness (as $CaCO_3$), (mg/l)			
T. Alkalinity (as $CaCO_3$), (mg/l)	Titrimetic method	H_2SO_4, methylorange indicator, phenolphthalein indicator	H_2SO_4(0.02N)
T. Solid (mg/l)	Dry oven, Evaporating dish, dessicator, Gravimetric method	---------------	-----------------
TSS (mg/l)	Filter paper, measuring cylinder, dry oven	---------------	---------------
BOD_5 (mg/l)	BOD incubator, BOD bottle, Dometric method	Manganous sulphate, Alkali iodide azide, H_2SO_4, starch indicator,	Sodium thiosulphate
COD (mg/l)	COD digester, Open reflex method	H_2SO_4,Mercuric sulphate,silversulphate, $K_2Cr_2O_7$	Ferrous Ammonium sulphate (FAS)
Cl^{-1} (mg/l)	Argentometric method(Titrimetric method	Potassium chromate,	Silver nitrate
F^{-1} (mg/l)	SPANDS METHOD	SPANDS reagent	
Na^{+1} (mg/l)	Flame photometer	Distilled water	
K^{+1} (mg/l)	Flame photometer	Distilled water	
SO_4^{-2}(mg/l)	Turbidimetric method by Uv-vis spectrophotometer	Standard sulfate,conditioning reagent,barium chloride,	
NO_3^{-2} (mg/l)	Phenol Disulphonic acid method (Uv-vis spectrophotometer)	Phenol disulfonic acid,Aluminium hydroxide,Standard nitrate solution,Ammonium hydroxide,	
TC (mg/l)	Membrane filteration method		
FC (mg/l)	Membrane filtration method		

Phosphate	Ascorbic acid method	Antimony potassium tartrate, Ammonium molybdate, Ascorbic	
Fe^{+3} (mg/l)	Uvvis spectrophotometer	Ammonium thiocyanate,Hydrochloric acid,Potassium permanganate, Standard ferric solution	
Mg^{+2} (mg/l)	Uv-vis spectrophotometer	Special reagent, Hydrogen peroxide (H_2O_2), 30%, Standard manganese solution, ammonium persulfate, Distilled water	
Salinity	Multimeter		

7.2.4 Evaluation of water quality status

Several important parameters were taken into account when calculating the water quality index (WQI). The Water Quality Index (WQI) was determined using the World Health Organization's (WHO, 2017) recommendations for safe drinking water. The weighted arithmetic water quality index approach classified the water quality according to the degree of purity using the most frequently measured water quality variables. The obtained physicochemical parameters were used to calculate the river water's rating. The weighted arithmetic water quality index developed by Brown *et al*. (1972) was used to calculate the WQI using the following equations.

$$\mathrm{WQI} = \sum \frac{QnWn}{\sum Wn} \quad \text{……………………………Eq(7.1)}$$

Where n is the number of variables or parameters,

Qn = Quality Rating;

$$\mathrm{Wn} = \frac{\mathrm{K}}{Sn} \text{…………………………………………………Eq(7.2)}$$

$$\mathrm{Qn} = \frac{100(Vn-Vio)}{Sn-Vio} \quad \text{………………………………………Eq(7.3)}$$

Where: Vn – is the observed value for n^{th} water quality parameters of collected samples;

Sn = Standard permissible value of the n^{th} water quality parameters;

Vio: The n^{th} water quality parameter’s ideal value in pure water (all other parameters have ideal values of zero except for pH and DO, which have values of 7 and 14.6, respectively). The recommended p_H level for natural/pure water is 7.0, whereas the acceptable level for tainted water is 8.5. The optimal concentration of dissolved oxygen is 14.6 mg/L. According to (Otene and Alfred, 2019; Okey *et al*. 2021), the unit weight (Wn) was obtained by calculating a value inversely proportional to the recommended standard value (Sn) of the corresponding parameter. Wn = K/Sn: Wn = the nth parameter’s unit weight. Sn = nth parameter standard value and K is the proportionality constant, and the following equation can be used to determine it: Standard value for nth parameters is K = 1/(1/Sn), Sn = Standard value for nth parameters.

7.2. 5 Data analysis

All data analysis was conducted using the IBM SPSS Statistics Version 21. An independent t- test was used to test the mean difference. A correlation analysis was also used to test the relation among the water quality parameters.

7.3 Results and discussion

7.3.1 Investigation of physicochemical water quality parameters of Lower Omo River Basin and evaluation of the water quality using WQI

The physical and chemical characteristics of water from lake and river locations are shown in Table 1 below. Mean temperatures measured in the sampling sites were within the range of 27.428 ± 0.987 and 28.9 ± 0.845 in the river and Lake respectively. pH values in the River ranged from 7.3 to 7.9 while those of the lake ranged from 8.7 to 8.9. Mean pH values were 7.62 ± 0.259 and 8.78± 0.08 in the upstream and downstream respectively. The results indicated that the lake water was relatively basic and it was above the permissible limit of Ethiopian standard agency (ESA,

2013) and WHO (2017) for drinking water. The present finding was similar with the study report of Okey *et al*. (2021).

Conductivity is generally a very good predictor of both total cations and salinity in Ethiopian water bodies (Zinabu *et al*., 2002).The values of EC ranged from 533 µS/cm to 549 µS/cm in the upstream area (River water) and from 9580 µS/cm to 1019 µS/cm in the downstream (Lake water) with mean value of 541.4 ±6.19 and 9842.00 ±313.8 respectively. The EC value of this finding in the River water (533 µS/cm) was comparable with the previous study report (575 µS/cm) by Maryam and Seyed (2022) from Zarrineh River in Iran. The mean EC value of the current finding both in River and Lake Water was higher than the study recorded in (Dirisu and Ezenwa, 2018). However, the previous study finding by Okey *et al*.(2021) reported higher mean value of EC(756.98 µS/cm) than the present finding in the River water (541.4 µS/cm). The present study finding was above the WHO (2017) standard in the downstream (lake).The higher EC value particularly in the Ethiopian part of lake (Omo Delta) may be due to higher salinity and TDS, High content of Mg &Ca in the Lake. Industrial waste, agricultural runoff and domestic discharges could also contribute to the rise of electrical conductivity in the freshwater (Okey *et al*., 2021). In all samples had turbidity levels were higher than maximum permissible limit set by WHO (2017). The study's upstream and downstream average turbidity levels were 115.2 and 161.2 NTU, respectively.

Dissolved Oxygen (DO) in upstream and downstream was determined to be from 6.08 mg/L to 6.34 mg/L and from 5.22 mg/L to 5.93 mg/L respectively. Mean dissolved oxygen in the upstream area was 6.182 ± 0. 1031mg/L while that of the downstream area was 5.468±0. 2803mg/L.The DO value in this study of both River and Lake Water was comparable with the previous study report by Dirisu and Ezenwa (2018) from surface water. The DO value of current study both in the River and Lake Water was lower than the previous report (9.19 ±0.99) by Divya *et al*. (2016) from Tamiraparani River but higher than the WHO (2017) permissible limit.

The BOD_5 values obtained in this study ranged from 15.2 to 18.8 (mean, 16.268 ± 1.47) mg/L (in the upstream area and from 14.78 to 17.9 mg/L (mean, 16.28 ±1.133 mg/L) in the downstream area. The mean BOD5values of the current finding both in River and Lake Water were higher than the study recorded (3.91mg/L) by Dirisu and Ezenwa (2018) from surface water and (2.43mg/L) by Divya *et al*. (2016) from River water. The BOD_5 values recorded in this study both in the upstream and downstream were above the WHO (2017) permissible limits. The larger value of BOD_5 could attribute to higher degree of organic content in both water bodies (River and Lake).Values for Chemical oxygen demand (COD) were higher in upstream area water (mean 376.06 ±130.45mg/L) than in downstream area (mean 136.0 ± 41.52 mg/L).COD indicates the toxic condition, the presence of biologically resistant organic substances and large amount of oxygen demanding chemicals (Okey *et al*., 2021).

Total dissolved solids (TDS) are the density of the water which affect freshwater organisms and lessens the solubility of gases like oxygen (Ogundele and Mekuleyi, 2018).The concentration of TDS in this study ranged from 250 to 256mg/L in the upstream area (mean, 252.40 mg/L± 2.302mg/L) and from 504mg/L to 541 (mean, 519.60 ± 19.552mg/L) in downstream area (Table 7.2). The mean TDS content of the River and Lake Water of this study was higher than the earlier reports (371.4 mg/L) by Okey *et al*. (2021) from Ogbor River in Aba, Nigeria and 83.45 mg/L by Dirisu and Ezenwa (2018) from surface water. The TDS values obtained in the downstream water of this study (lake) was above WHO (2017) standard limits (500 mg/L) for drinking water. This might be complied with higher salinity content in the downstream water. High TDS values in the water body could be attributed to Surface runoffs, weathering of rocks, discharge of domestic waste and incursion of dissolved solutes from agricultural fields (Srivastava *et al*., 2007).Total alkalinity in the upstream area were from 80 to 105 mg CaCO3 /L (mean 92.0±9.083 mg CaCO3 /L) and from 724 to 960 mg CaCO3/L (mean 904.8 ±10.564mg/ mgCaCO3 /L) in the downstream area as indicated in Table 7.2.

Table 7.2 Physicochemical parameter of River andLake Water

Parameters	River water		Lake water		WHO,2017	ESA,2013
	Mean	SD	Mean	SD		
Temperature in ^{O}c	28.9	0.86	27.43	0.99	≤15	≤15
PH	7.62	0.26	8.78	0.08	6.5-8.5	6.5-8.5
EC(µS/cm)	541.4	6.19	9842.0	313.88	1000	1500
TDS (mg/l)	252.4	2.30	519.60	19.55	500	1000
DO) (mg/L)	6.18	0.10	5.47	0.28	5	5
BOD_5) (mg/L)	16.27	1.47	16.28	1.13	5	5
Salinity in percen	0.026	0.001	0.54	0.02	-	-
Total alkalinity(TA) in mg/l	92.0	9.08	904.8	101.56	120	200
Mg^{+2} (mg/l) in mg/	8.64	1.73	10.73	2.01	30	50
Ca^{+2} ion in mg/	10.20	2.04	11.44	2.32	75	75
Total hardness in mg/l	59.0	7.42	65	14.58	300	300
Cl^- (mg/l)	3.06	1.08	220.12	5.11	150	250
Fluoride ion in mg/L	0.88	0.14	2.03	0.064	1.5	3
Turbidity(NTU)	94.4	5.01	162.4	0.037	5	7
NO_3^- (mg/l)	8.94	1.33	17.84	4.01	50	50
PO_4^{-3} (mg/l)	1.87	0.63	5.11	0.98	5.5	0.02
NH_3 (mg/l)	0.54	0.361	1.35	0.66	1.0	-
NO_2^- (mg/l	1.69	0.97	0.54	0.56	0.1	0.02

Total suspended solid in mg//L were generally lower in upstream area (mean, 502.40 mg/L) than in the downstream area (mean 1088.8mg/L). The finding of this study indicated that that the water in the downstream region was more turbid than the water in the upstream area is supported by the higher total suspended solids (TSS) values obtained from upstream area water (mean, 681.4 mg/L) compared to downstream area water (mean, 1509.2 mg/L).The high values of turbidity could be mainly attributed to surface runoff from the catchment area and inflowing perennial river loaded.

Chloride: In the present study, ranged between 2.5 to 4.99 (mean, 3.058±) in the LOR) while that of the downstream area (ELT) was from 212.13 to 224.61 mg /L (mean, 220.2± 5.11mg/L). In comparison to the other anions looked in this study, chloride levels were higher in the downstream. The mean Cl^- content of the River water of this study was lower than the earlier report (5.84 mg/L) by Okey *et al*. (2021). However, the mean Cl^- content of the Lake water (220.2± 5.11mg/L) was higher than the preceding reports (23.19 mg/L) by Dirisu and Ezenwa (2018). The result found was below the WHO recommended safe limits (250 mg/L).

Flouride:The concentration of fluoride ion in the upstream area varied between 0.623 to1.552 mg/L (mean, 0.89 ± 0.0135) in the upstream area while that of the downstream area was from 1.916 to 2.071mg/L (mean, 2.026±0.064mg/l).Its presence at concentrations below 0.5 mg/l has been associated with dental caries in children, whereas concentrations above 1.5 mg/l have been connected to non-fluorosis disorders such non-dental fluorosis and skeletal fluorosis (Rofhiwa *et al*., 2011).In contrast to the upstream water (river), where low levels of mean fluoride concentration of 0.89 mg/L were found, the downstream water (lake) in this study had mean fluoride concentrations that were over the allowed range (2.026 mg/l). Fluorinated minerals are easily dissolved in an alkaline environment which may account for the lake's high fluoride levels (Feifei *et al*., 2021). This is a typical issue, particularly in the rift valley lakes of East African countries due to geological indicators (Adimasu, 2014; WHO, 2014). This finding was consistent with those study reports by Awomeso *et al*. (2019) in the Nairobi River, where the levels ranged from 2.0 to 3.34 mg/L, and Feifei *et al*. (2021) in China, where the levels were on average 0.6 mg/L. The sources of fluoride in this study could be a natural weathering of mineral bed rocks and it is also a common problem mainly in the rift valley lake of East African countries due to geological indicator (Adimasu, 2014; WHO, 2014). According to the study in Kenya by Avery

(2010) on Lake Turkana which is beneath the present study, fluoride concentration was reported as 10 to 11mg/L .

Nitrate (NO_3): The concentration of total nitrogen varied between 7.88 and 11.19 mg/L in the upstream area (mean, 8.938±1.327mg/L) and from 11.20 to 21.28mg/l (mean, 17.84 ± 4.0083mg/L) in downstream area. The finding of the present study was lower than the study report (36.32 ± 21.03) by Oluyemi *et al*. (2010). However, nitrate concentration of our finding was higher than the previous study report (0.63±1.37) by Dirisu and Ezenwa (2017). The range of NO_2^- readings in the River water was between 0.30 and 2.54 mg/l (mean, 1.69 0.9672) and the range for the Lake water was between 0.17 and 1.48 mg/L (mean, 0.54 mg/l).

Phosphate ($PO4^{-3}$): The values for PO_4 were in the limit of 1.31 to 2.84 in upstream area water (LOR) (mean 1.866 ± 0.625 mg/L) while in downstream (ELT) area, the concentrations were in the range of 4.09 to 6.22 (mean 5.108 ± 0.975mg/L). This observation is in conformity with the observations by Awomeso *et al*.(2019) in Nairobi River which ranged from 2.0 to 3.34 mg/L. Phosphate concentrations in surface water are allowed not to exceed 5.5 mg/L. Thus, values for PO_4^{-3} in the downstream (ELT) of this study were slightly above WHO limit for drinking water. The phosphate value found in this study is consistent with the findings of Okey *et al* (2021). Agricultural wastes may drain into rivers, increasing phosphate level, or phosphate additions used in detergent may have leached into water bodies through home, industrial, or municipal waste waters (Olajire and Imeokparia, 2001).The intensive agriculture practiced along the river stream may be related to the quantities of nitrates and phosphates found in this study. Higher concentrations of the distinct anions were found at the lake sampling locations than in the upstream river, which may have been caused by an increase in anthropogenic activity and other industries along the river’s route that eventually moved downstream. Water phosphate is not thought to be immediately hazardous to people or animals. However, its presence at high concentrations can cause hypoxic seas with little biotic diversity and toxic algal blooms (Wei *et al*., 2019). The nitrate concentration obtained for both water bodies did not exceed the WHO limit (50mg/l). Pollution of the River by the nutrient may be due to the application of fertilizers, domestic effluents, industrial discharge, and leachate from refuse dumps and run-off from these sources. Total nitrogen load in the lake may be resulted from the buildup of organic material from different sources**.**

TDS and EC have a good association (r = 0.995), as would be expected given that they are both directly proportional to one another, according to a correlation analysis. The value of the electric conductivity increases with the amount of solids dissolved in the water. Ions can come from a variety of sources, including the natural world (geology), human activity (such as home and industrial waste), and agricultural activity. There was also a strong correlation among: EC and Mg ion (r = 0.75) ; EC and MgH (magnesium hardness) (r = 0.826); pH and MH(r= 0.952); pH and TDS (r= 0.81);EC and salinity(r= 0.997). The values for Correlation analysis was represented in the Table 7.3

Table 7.3 .Statistical analysis on correlation result of River

Parameters	**Temperature**	**pH**	**EC**	**TDS**	**TSS**	**DO**	**BOD**	**COD**	**Salinit**	**TA**	**Mg**	**Ca**	**Ca.Har**	**Mg.Har**
Temp	1													
PH	0.48	1												
EC in mili/cm	-0.148	-.0896*	1											
TDS in mg/l	-0.090	-0.814	0.951*	1										
TSS in mg//l	-0.177	-0.584	0.404	0.512	1									
DO in mg/l	0.491	0.589	-0.688	-0.700	0.032	1								
BOD in mg/l	-0.112	0.666	-0.840	-0.667	-0.004	0.451	1							
COD in mg/l	-0.498	-0.219	-0.088	-0.360	-0.148	0.170	-0.159	1						
Salinity in %	0.042	-0.410	0.400	0.614	0.890*	-0.103	0.058	-0.579	1					
TA in mg/l	-0.439	0.510	-0.818	-0.825	-0.229	0.395	0.805	0.430	-0.389	1				
Mg in mg/l	-0.093	-0.788	0.751	0.827	0.898*	-0.274	-0.395	-0.244	0.860	-0.605	1			
Ca in mg/l	0.710	0.193	0.000	0.217	0.468	0.364	0.153	-0.767	0.707	-0.413	0.432	1		
Ca.Hardness	0.710	0.193	0.000	0.217	0.468	0.364	0.153	-0.767	0.707	-0.413	0.432	1.000**	1	
Mg.Hardness	-0.486	-0.952*	0.826	0.833	0.764	-0.549	-0.458	0.028	0.645	-0.452	0.895*	0.000	0.000	1

Independent t-test showed that there's was significant difference in temperature, COD, NO_2, NH_3 , ($P<0.05$); pH, EC,TDS,TSS, DO, NO_3, PO_4, salinity, alkalinity, Chloride ion, contents between both river and lake at ($P<0.001$). However, no significant difference exists ($P<0.05$) for BOD, Mg ion, Ca ion, Calcium hardness, Magnesium hardness, total hardness and Fluoride ion when values from both areas of upstream and downstream are compared (Table 7.4)

Table 7.4 Independent T-test

Parameters	Water body	Mean	Std. Deviation	t	Significance
Dissolved oxygen in mg/l	River	6.182	0.103	5.346	0.001
	Lake	5.468	0.280		
Biological oxygen demand in mg/L	River	16.268	1.471	.014	0.989
	Lake	16.28	1.133		
Chemical oxygen demand in mg/L	River	376.06	130.456	3.921	0.004
	Lake	136.0	41.526		
Total alkalinity in mg/L	River	92.00	9.083	-17.824	0.001
	Lake	904.80	101.564		
Total hardeness in mg/L	River	59.0	7.416	-0.820	0.436
	Lake	65.0	14.57		
Chloride ion in mg/L	River	3.058	1.084	-92.821	0.001
	Lake	220.118	5.11		
Fluoride ion in mg/L	River	125.358	278.190	0.991	0.378
	Lake	2.026	0.063		
TNO_3mg/L	River	8.93	1.32	-4.716	0.002
	Lake	17.84	4.00836		
TPO_4 mg/L	River	1.86	0.625	-6.255	0.001
	Lake	5.108	0.975		
NH_3 mg/L	River	0.540	0.361	-2.432	0.041
	Lake	1.3540	0.65		
NO_2 mg/L	River	1.690	0.967	2.303	0.050
	Lake	0.540	0.55		

On the basis of WQI scores, five categories have been introduced; WQI = 0-25 “Excellent water quality”; WQI = 26-50 “good water quality”; WQI = 51-75“, Poor water quality”; WQI =76-100 “, Very Poor water quality” and WQI > 100 “Unsuitable for drinking. The results revealed that the river water fell into the category of Very Poor water quality. Based on the results of the water quality index calculation, , it was determined that the lower Omo River area around Omorate Town’s WQI value was 76.677, which is very poor as it fell within the range of 76 to 100**(Table7.5).** The Ethiopian portion of Lake Turkana’s WQI value was found to be 142.47, which is much beyond the 100-point threshold for very poor water quality and Unsuitable for drinking (**Table7.6**).

Table 7.5Weighted Arithmetic Water Quality Index for River

Parameter Rillver	Experimental Value Cm	Standard values (sn) (WHO,2017)	Unit weights (wn)	Quality rating (Qn)	QnWn
pH	7.62	8.5	0.0672	41.4	2.783
Electrical conductivity(µs)	541.40	1000	0.00057	54.14	0.0031
Total Dissolved Solids (mg/l)	252.40	500	0.0012	50.48	0.0606
Total alkalinity mg/l	92.00	120	0.0048	76.7	0.3682
Total hardness	59.00	200	0.0029	29.5	0.0856
Total suspended solids	502.40	500	0.00115	10.48	0.1264
Calcium mg/l	10.20	200	0.02472	5.1	0.1261
Magnesiummg/l	8.641	200	0.0029	4.32	0.01253
Chlorides mg/l	3.058	250	0.00229	1.23	0.002817
Nitrate mg/l	8.938	50	0.01142	17.876	0.20415
Phosphate(mg/l)	1.866	5.5	0.104	33.93	3.529
Dissolved oxygen (mg/l	6.182	5	0.1142	87.69	10.015
BOD	16.268	5	0.1142	325.36	37.156
Fluoride mg/l	0.8834	1.5	0.381	58.89	22.4371
Ammonia mg/l	0.54	1.0	0.571	54	30.834
Summation (∑)			∑ Wn= 1.40355	Σqn= 2739.096	∑QnWn =107.62
				WQI = 76.7	

Table 7.6 Weighted Arithmetic Water Quality Index for Omo delta (lentic)

Parameter	Experiment al Value	Standard values (sn) (WHO,2017)	Unit weights (wn)	Quality rating (Qn)	QnWn
pH	8.78	8.5	0.0672	118.67	7.975
EC(µs)	9842	1000	0.00057	984.2	0.561
TDS (mg/l)	519.6	500	0.0012	103.92	0.125
TA mg/l	904.8	120	0.0048	754	3.619
Total hardness	65	200	0.0029	32.5	0.09425
TSS	1088.8	500	0.00115	217.76	0.25
Ca $^{2+}$mg/l	11.44	200	0.02472	5.72	0.1414
Mg^{2+}mg/l	10.725	200	0.0029	5.36	0.0155
Cl -1 mg/l	220.118	250	0.00229	88.05	0.202
Nitrate mg/l	17.844	50	0.01142	35.68	0.407
Phosphate(mg/l)	5.108	5.5	0.104	92.87	9.658
DO(mg/l	5.468	5	0.1142	95.125	10.86
BOD	16.28	5	0.1142	325.6	37.184
Fluoride mg/l	2.03	1.5	0.381	135.3	51.5419
Ammonia mg/l	1.354	1	0.571	135.4	77.313
Summation (∑)			∑ Wn= 1.4		ΣQnWn=199.95

$$\text{WQI} = \sum \frac{QnWn}{\sum Wn} = 142.5$$

Table 7.7Some physicochemical water quality factors of Lake Turkana from Keneya (Munene *et al*., 2023)

Parameters	Measured mean values
Temp (°C)	28.24
pH	9.34
Conductivity (Ωcm-1)	286.36
DO (mg/L)	7.04
Salinity (ppt)	1.68
TDS (mg/L)	2116.22
Nitrates (mg/L	7.65
Phosphates (mg/L)	0.47

7.4. Conclusions

This research has provided baseline information on the physicochemical parameters of freshwater and the water quality status of lower Omo River basin. The downstream of the freshwater (ELT) was more polluted as compared to the upstream (LOR) with regard to water quality parameters using WQI. The mean contents of DO, BOD, Turbidity, Phosphate, and Nitrite were above the maximum permissible limit set by WHO both in River and Lake water. The WQI showed that the quality of the lower Omo River could be regarded as very poor while the Ethiopian part of Lake Turkana was Unsuitable for drinking and need treatment before use.

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CHAPTER EIGHT

General Conclusions and Recommendations

The present study was the first to adress the environmental toxicological concerns associated about heavy metals and other water quality factors in one of Ethiopia's freshwater ecosystems. As a first-hand report, the current study examined the heavy metal pollution levels of the freshwater ecosystem of the Lower Omo River and Delta including the associated human health and ecological risks in southern Ethiopia.The study also addressed the water quality status of the lower Omo River basin for drinking. The freshwater ecosystem being studied for heavy metals detection included surface water, two fish species (L. niloticus and O. niloticus), surface sediment, and irrigated soil from the River water. Surface water, fish, and sediment samples were collected from both water bodies (Lower Omo River and Delta Lake), while soil samples were gathered near the riverside, which is frequently utilized for irrigation.

The pollution levels of Pb, Cr, Mn and Co in the River and Lake Water were above the WHO permissible limit for drinking. The water quality indices indicate that both water bodies were unsuitable for drinking in terms of heavy metals pollution with the Lake water being highly polluted than the river water. The mean values the water quality indices also indicated that the Delta water was more polluted than the River water in terms of HMs pollution and the physicochemical water quality measurements. This could be due to pollution sources from the Omo River inflow as well as pollution sources from Kenya part would accumula in the Delta. The high flood level in the Delta and sedimentation could also contribute to higher load of pollution in the Delta. Regarding the health risk, Pb, Cr, and Mn had the possible human health risk through ingestion of both the River and Lake Water.Chromium and lead followed by manageress contributed more to the noncancer risks both via ingestion and dermal route of exposure in children and adults. The health risk hazard value of the present study in children was higher than those for adults indicating that children would experience more noncancer risks and absorb more chemicals than adults. In this study, cancer risk (CR) assessed for Pb, Cr, and Ni are considered to be out of the range for carcinogenic for humans. Chromium exhibited the higher probability of cancer risks (mean CR= 1.31×10^{-2}) followed by lead (mean CR= 1.8×10^{-4}) for children. The cumulative effect of the heavy metals for carcinogenic ∑CR) both in children and adults of the present study was above acceptable values (10^{-6} to 10^{-4}) s which is intolerable cancer risks due to heavy metals in drinking water over a lifetime.Thus close monitoring of the pollution levels of these heavy metals in the freshwater ecosystem of the two water bodies are imprtant and more attention should be given to Co, Cr, Mn, and Pb in the study area for environmental and human health concern.

The levels of all heavy metals tested in freshwater fish, with the exception of Pb, were within the FAO/WHO (1989) acceptable limits for the Omo River. The liver and muscle tissues of *L. niloticus* were shown to accumulate more heavy metals than those of O. niloticus, with the liver accumulating more than muscle tissues. The mean levels of Pb detected in the liver and muscle tissue of the two fish species from the Omo River and Omo delta surpassed the FAO/WHO (1989) limitwhich was cause for alarm. These findings indicate that regular monitoring of freshwater fish in this area is required, with particular attention to Pb. Furthermore, the TCR produced by Ni exposure from the ingestion of L. niloticus and O. niloticus muscle is concerning, since it may raise the risk of cancer in young people who engage in strenuous and protracted developing activities. Therefore, it is necessary to monitor heavy metal levels in the tissues of L.

The contamination factor (CF) value for all the studied heavy metals in the sediment of both water bodies were <1, indicating low contamination level.In terms of degree of contamination, all the values remained under the standard limit of Cd < 8, indicating a low degree of contamination.The calculated value of mCd and PLI did not exceed the baseline level of pollution (<1) indicating low contamination of the Lake sediment.In terms of ecological risk, in which Mn, Zn, Cu, Cr, Pb, Ni, Fe, and Co were considered, all the ecological risk factor and risk indices were below risk level (EI < 40 and RI <150).The current study looked into the pollution levels and potential ecological consequences of heavy metals in the irrigated soil from lower Omo River. The ecological indices showed that soil pollution level was low. The evaluation of ecological risk indices indicated that the levels of heavy metals detected in the soil could pose no ecological risk.

The mean contents of DO, BOD, Turbidity, Phosphate, and Nitrite were above the maximum permissible limit set by WHO both in River and Lake water. The WQI showed that the quality of the lower Omo River could be regarded as very poor while the Delta water was Unsuitable for drinking and need treatment before use. Therefore, continuous monitoring of the psychochemical water quality is necessary before use for various domestic purposes. Thus, the pollution level of the freshwater ecosystem needs to be monitored to protect the fresh water at its early-stage pollution.

In a nutshell, the present study has come with the main findings that the mean level of Mn, Cr, Pb and Co in the River and Delta Water were above the permissible limit set by WHO which was an alarming result for early intervention. Similarly, the Pb level o the fish tissues (liver and muscle) of *L. niloticus* and *O. niloticus* was above the permissible level by FAO with higher values in the tissues of *L. niloticus*. It was also found in this study that many of the physicochemical water quality factors were above WHO permissible level which resulted in low water quality, particularly in the Lake water. All the heavy metals under investigation except for Cd were detected in water, fish, sediment, and soil samples. In this regard, many studies have been conducted to the Kenyan side on the Lake Turkana, but in Ethiopian side further study should be done and the present study was a first-hand report. Therefore, further studies and continuous monitoring of the freshwater ecosystem by the concerned bodies such as the Ethiopian’s Environmental Protection Agency (EEPA), Ministry of Health (MOH), Ministry of Water, Mines and Energy (MWME), Ministry of Agriculture (MOA) are crucial for early intervention of the freshwater ecosystem.

Annex

Health Risk Assessment of Lower Omo River Water

I.Non- Carcinogenic (River)

1. Health risk due to Ingestion(Oral uptake) for children [CDI, HQ, and HI]

	CDI ing									
							CDI ing	RfD ing		
HMs	C	IR	EF	ED	BW	AT	Child	RfD ing	HQ ing	HI
Mn	0.439	1	365	6	15	2190	0.029267	0.014	2.090476	18.18994
Zn	0.1	1	365	6	15	2190	0.006667	0.3	0.022222	
Cu	0.168	1	365	6	15	2190	0.0112	0.04	0.28	
Cr	0.393	1	365	6	15	2190	0.0262	0.003	8.733333	
Cd	0	1	365	6	15	2190	0	0.001	0	
Pb	0.318	1	365	6	15	2190	0.0212	0.0035	6.057143	
Ni	0.007	1	365	6	15	2190	0.000467	0.02	0.023333	
Fe	8.926	1	365	6	15	2190	0.595067	0.7	0.850095	
Co	0.06	1	365	6	15	2190	0.004	0.03	0.133333	

2. Health risk due to Ingestion (oral uptake) fore Adult [CDI,HQ,and HI]

			ADULT	Ingestion			CDI ing			
HMs	C	IR	EF	ED	BW	AT	Adult	RfD	HQ ing	HI
Mn	0.439	2.2	365	30	60	10950	0.016097	0.014	1.1498	10.09
Zn	0.1	2.2	365	30	60	10950	0.0036	0.3	0.012	
Cu	0.168	2.2	365	30	60	10950	0.006	0.04	0.154	
Cr	0.393	2.2	365	30	60	10950	0.014	0.003	4.803	
Cd	0	2.2	365	30	60	10950	0	0.001	0	
Pb	0.318	2.2	365	30	60	10950	0.012	0.0035	3.33	
Ni	0.007	2.2	365	30	60	10950	0.000257	0.02	0.0128	
Fe	8.926	2.2	365	30	60	10950	0.327287	0.7	0.468	
Co	0.06	2.2	365	65	60	10950	0.004767	0.03	0.1589	

3.Health risk due to Dermal uptake for children [CDI, HQ, and HI]

	Dermal	Childreen								Child	$RfD\ dermal$		
HMs	C	EF	ED	ET	SA	KP	CF	BW	AT	CDI der		HQ dermal HI	
Mn	0.439	365	6	1	6600	0.001	0.001	15	2190	0.000193	0.00005	3.8632	7.27569
Zn	0.1	365	6	1	6600	0.006	0.001	15	2190	0.000264	0.06	0.0044	
Cu	0.168	365	6	1	6600	0.001	0.001	15	2190	7.39E-05	0.012	0.00616	
Cr	0.393	365	6	1	6600	0.001	0.001	15	2190	0.000173	0.000075	2.3056	
Cd	0	365	6	1	6600	0.001	0.001	15	2190	0	0.001	0	
Pb	0.318	365	6	1	6600	0.004	0.001	15	2190	0.00056	0.000525	1.066057	
Ni	0.007	365	6	1	6600	0.001	0.001	15	2190	3.08E-06	0.0054	0.00057	
Fe	8.926	365	6	1	6600	0.001	0.001	15	2190	0.003927	0.14	0.028053	
Co	0.06	365	6	1	6600	0.001	0.001	15	2190	2.64E-05	0.016	0.00165	

4. Health risk due to dermal uptake for adult [CDI, HQ, and HI]

HMs	C	EF	ED	ET	SA	KP	CF	BW	AT	CDI der	$RfD\ dermal$	HQdermal	HI
Mn	0.439	365	30	0.58	18000	0.001	0.001	60	10950	7.64E-05	0.00005	1.52772	0.23505
Zn	0.1	365	30	0.58	18000	0.006	0.001	60	10950	0.000104	0.06	0.00174	
Cu	0.168	365	30	0.58	18000	0.001	0.001	60	10950	2.92E-05	0.012	0.002436	
Cr	0.393	365	30	0.58	18000	0.001	0.001	60	10950	6.84E-05	0.000075	0.91176	
Cd	0	365	30	0.58	18000	0.001	0.001	60	10950	0	0.001	0	
Pb	0.318	365	30	0.58	18000	0.004	0.001	60	10950	0.000221	0.000525	0.421577	
Ni	0.007	365	30	0.58	18000	0.001	0.001	60	10950	1.22E-06	0.0054	0.000226	
Fe	8.926	365	30	0.58	18000	0.001	0.001	60	10950	0.001553	0.14	0.011094	
Co	0.06	365	65	0.58	18000	0.001	0.001	60	10950	2.26E-05	0.016	0.001414	

II.Carcinogenic (CRing) River Water

1. Children carcinogenic due to ingestion

HMs	C	IR	EF	ED	BW	AT	CDI ing	CSF	CR ing	∑CR
Cr	0.393	1	365	6	15	2190	0.0262	0.5	0.0524	2.546792
Pb	0.318	1	365	6	15	2190	0.0212	0.0085	2.494118	
Ni	0.007	1	365	6	15	2190	0.000467	1.7	0.000275	

2.Adult carcinogenic due to ingestion

			ADULT	Ingestion					C	
HMs	C	IR	EF	ED	BW	AT	CDI ing	CSF	CR ing	∑CR
Cr	0.393	2.2	365	30	60	10950	0.01441	0.5	0.02882	10.1
Pb	0.318	2.2	365	30	60	10950	0.01166	0.0085	1.371765	
Ni	0.007	2.2	365	30	60	10950	0.000257	1.7	0.000151	

III. Environmental risk of toxic metal in water using risk index factor

Heavy metals	Ti	OC	NOEC	Ri	CRI
Pb	5	0.318	0.01	159	175.22
Ni	5	0.007	0.07	0.5	
Cr	2	0.393	0.05	15.72	

1.Heavy metal pollution Index for River water (Drinking Water)

Manganese(Mn)

Stations	Mi (ppb)	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	410	50	400	0.0025	360	350	102.8571	0.257143
2	450	50	400	0.0025	400	350	114.2857	0.285714
3	430	50	400	0.0025	380	350	108.5714	0.271429
4	420	50	400	0.0025	370	350	105.7143	0.264286
5	480	50	400	0.0025	430	350	122.8571	0.307143
6	440	50	400	0.0025	390	350	111.4286	0.278571
7	410	50	400	0.0025	360	350	102.8571	0.257143
8	400	50	400	0.0025	350	350	100	0.25
9	430	50	400	0.0025	380	350	108.5714	0.271429
10	510	50	400	0.0025	460	350	131.4286	0.328571
11	420	50	400	0.0025	370	350	105.7143	0.264286
12	500	50	400	0.0025	450	350	128.5714	0.321429
13	420	50	400	0.0025	370	350	105.7143	0.264286
14	430	50	400	0.0025	380	350	108.5714	0.271429
15	440	50	400	0.0025	390	350	111.4286	0.278571

2.Zinck (Zn)

Stations	Mi (ppb)	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	80	3000	5000	0.0002	2920	2000	146	0.0292
2	70	3000	5000	0.0002	2930	2000	146.5	0.0293
3	80	3000	5000	0.0002	2920	2000	146	0.0292
4	150	3000	5000	0.0002	2850	2000	142.5	0.0285
5	170	3000	5000	0.0002	2830	2000	141.5	0.0283
6	60	3000	5000	0.0002	2940	2000	147	0.0294
7	40	3000	5000	0.0002	2960	2000	148	0.0296
8	160	3000	5000	0.0002	2840	2000	142	0.0284
9	70	3000	5000	0.0002	2930	2000	146.5	0.0293
10	150	3000	5000	0.0002	2850	2000	142.5	0.0285
11	60	3000	5000	0.0002	2940	2000	147	0.0294
12	140	3000	5000	0.0002	2860	2000	143	0.0286
13	50	3000	5000	0.0002	2950	2000	147.5	0.0295
14	140	3000	5000	0.0002	2860	2000	143	0.0286
15	90	3000	5000	0.0002	2910	2000	145.5	0.0291

3.Copper (Cu)

Stations	Mi (ppb)	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	270	2000	1000	0.001	1730	1000	173	0.173
2	130	2000	1000	0.001	1870	1000	187	0.187
3	150	2000	1000	0.001	1850	1000	185	0.185
4	240	2000	1000	0.001	1760	1000	176	0.176
5	230	2000	1000	0.001	1770	1000	177	0.177
6	100	2000	1000	0.001	1900	1000	190	0.19
7	110	2000	1000	0.001	1890	1000	189	0.189
8	100	2000	1000	0.001	1900	1000	190	0.19
9	120	2000	1000	0.001	1880	1000	188	0.188
10	260	2000	1000	0.001	1740	1000	174	0.174
11	100	2000	1000	0.001	1900	1000	190	0.19
12	240	2000	1000	0.001	1760	1000	176	0.176
13	140	2000	1000	0.001	1860	1000	186	0.186
14	100	2000	1000	0.001	1900	1000	190	0.19
15	250	2000	1000	0.001	1750	1000	175	0.175

4. Chromuium (Cr)

Stations	Mi (ppb)	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	430	0	50	0.02	430	50	860	17.2
2	370	0	50	0.02	370	50	740	14.8
3	360	0	50	0.02	360	50	720	14.4
4	380	0	50	0.02	380	50	760	15.2
5	390	0	50	0.02	390	50	780	15.6
6	420	0	50	0.02	420	50	840	16.8
7	440	0	50	0.02	440	50	880	17.6
8	340	0	50	0.02	340	50	680	13.6
9	270	0	50	0.02	270	50	540	10.8
10	460	0	50	0.02	460	50	920	18.4
11	450	0	50	0.02	450	50	900	18
12	390	0	50	0.02	390	50	780	15.6
13	360	0	50	0.02	360	50	720	14.4
14	350	0	50	0.02	350	50	700	14
15	440	0	50	0.02	440	50	880	17.6

5.Lead (Pb)

Stations	Mi (ppm)	Mi (ppb)	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	0.38	380	10	100	0.01	370	90	411.11	4.11
2	0.31	310	10	100	0.01	300	90	333.33	3.33
3	0.29	290	10	100	0.01	280	90	311.1	3.1
4	0.32	320	10	100	0.01	310	90	344.4	3.4
5	0.28	280	10	100	0.01	270	90	300	3
6	0.33	330	10	100	0.01	320	90	355.6	3.56
7	0.35	350	10	100	0.01	340	90	377.78	3.8
8	0.33	330	10	100	0.01	320	90	355.56	3.56
9	0.3	300	10	100	0.01	290	90	322.23	3.23
10	0.27	270	10	100	0.01	260	90	288.89	2.9
11	0.34	340	10	100	0.01	330	90	366.67	3.67
12	0.25	250	10	100	0.01	240	90	266.67	2.68
13	0.34	340	10	100	0.01	330	90	366.67	3.7
14	0.33	330	10	100	0.01	320	90	355.56	3.55
15	0.37	370	10	100	0.01	360	90	400	4

6. Nickel (Ni)

Stations	Mi (ppb)	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	0	20	70	0.014286	20	50	40	0.571429
2	0	20	70	0.014286	20	50	40	0.571429
3	0	20	70	0.014286	20	50	40	0.571429
4	10	20	70	0.014286	10	50	20	0.285714
5	10	20	70	0.014286	10	50	20	0.285714
6	0	20	70	0.014286	20	50	40	0.571429
7	0	20	70	0.014286	20	50	40	0.571429
8	10	20	70	0.014286	10	50	20	0.285714
9	0	20	70	0.014286	20	50	40	0.571429
10	10	20	70	0.014286	10	50	20	0.285714
11	10	20	70	0.014286	10	50	20	0.285714
12	10	20	70	0.014286	10	50	20	0.285714
13	10	20	70	0.014286	10	50	20	0.285714
14	10	20	70	0.014286	10	50	20	0.285714
15	0	20	70	0.014286	20	50	40	0.571429

7. Iron (Fe)

Stations	Mi (ppb)	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	6490	200	300	0.003333	6290	100	6290	20.96667
2	7250	200	300	0.003333	7050	100	7050	23.5
3	7370	200	300	0.003333	7170	100	7170	23.9
4	8710	200	300	0.003333	8510	100	8510	28.36667
5	12820	200	300	0.003333	12620	100	12620	42.06667
6	9320	200	300	0.003333	9120	100	9120	30.4
7	6360	200	300	0.003333	6160	100	6160	20.53333
8	8830	200	300	0.003333	8630	100	8630	28.76667
9	7340	200	300	0.003333	7140	100	7140	23.8
10	12790	200	300	0.003333	12590	100	12590	41.96667
11	9320	200	300	0.003333	9120	100	9120	30.4
12	12850	200	300	0.003333	12650	100	12650	42.16667
13	9370	200	300	0.003333	9170	100	9170	30.56667
14	8760	200	300	0.003333	8560	100	8560	28.53333
15	6500	200	300	0.003333	6300	100	6300	21

8. Cobalt (Co)

Stations	Mi	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	60	0	10	0.1	60	10	600	60
2	80	0	10	0.1	80	10	800	80
3	70	0	10	0.1	70	10	700	70
4	60	0	10	0.1	60	10	600	60
5	40	0	10	0.1	40	10	400	40
6	50	0	10	0.1	50	10	500	50
7	70	0	10	0.1	70	10	700	70
8	60	0	10	0.1	60	10	600	60
9	90	0	10	0.1	90	10	900	90
10	40	0	10	0.1	40	10	400	40
11	50	0	10	0.1	50	10	500	50
12	90	0	10	0.1	90	10	900	90
13	50	0	10	0.1	50	10	500	50
14	60	0	10	0.1	60	10	600	60
15	70	0	10	0.1	70	10	700	70

9. All heavy metals (8 metals) at each sampling Points (Cumulative effects (HPI)

Stations	∑Wi	∑WiQi	HPI
1	0.151319	103.3085	682.7201
2	0.151319	122.7068	810.9143
3	0.151319	112.4682	743.2519
4	0.151319	107.7656	712.1748
5	0.151319	101.4648	670.5357
6	0.151319	101.825	672.9157
7	0.151319	112.9583	746.4908
8	0.151319	106.6763	704.9763
9	0.151319	128.8824	851.7261
10	0.151319	104.0723	687.7676
11	0.151319	102.8361	679.5976
12	0.151319	151.2451	999.5112
13	0.151319	99.39883	656.8825
14	0.151319	106.8646	706.2206
15	0.151319	113.6541	751.0892

10. Summary (mean)

HMS	**Mi (ppb)**	**Si**	**Ii**	**Wi**	**Mi-Ii**	**Si-Ii**	**Qi**	**WiQi**	**∑WiQi**	**∑Wi**	**HPI**
Mn	**439**	**400**	**50**	**0.0025**	**389**	**350**	**111.1429**	**0.277857**	**109.0904**	**0.151319**	**720.9296**
Zn	**100**	**5000**	**3000**	**0.0002**	**2900**	**2000**	**145**	**0.029**			
Cu	**168**	**1000**	**2000**	**0.001**	**1832**	**1000**	**183.2**	**0.1832**			
Cr	**393**	**50**	**0**	**0.02**	**393**	**50**	**786**	**15.72**			
Pb	**318**	**100**	**10**	**0.01**	**308**	**90**	**342.2222**	**3.422222**			
Ni	**7**	**70**	**20**	**0.014286**	**13**	**50**	**26**	**0.371429**			
Fe	**8926**	**300**	**200**	**0.003333**	**8726**	**100**	**8726**	**29.08667**			
Co	**60**	**10**	**0**	**0.1**	**60**	**10**	**600**	**60**			

Heavy metal pollution Index for River water (Irrigation Water): (FAO)

Manganese (Mn)

Stations	Mi (ppb)	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	410	50	200	0.005	360	150	240	1.2
2	450	50	200	0.005	400	150	266.6667	1.333333
3	430	50	200	0.005	380	150	253.3333	1.266667
4	420	50	200	0.005	370	150	246.6667	1.233333
5	480	50	200	0.005	430	150	286.6667	1.433333
6	440	50	200	0.005	390	150	260	1.3
7	410	50	200	0.005	360	150	240	1.2
8	400	50	200	0.005	350	150	233.3333	1.166667
9	430	50	200	0.005	380	150	253.3333	1.266667
10	510	50	200	0.005	460	150	306.6667	1.533333
11	420	50	200	0.005	370	150	246.6667	1.233333
12	500	50	200	0.005	450	150	300	1.5
13	420	50	200	0.005	370	150	246.6667	1.233333
14	430	50	200	0.005	380	150	253.3333	1.266667
15	440	50	200	0.005	390	150	260	1.3

2. Zinck (Zn)

Stations	Mi (ppb)	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	80	3000	2000	0.0005	2920	1000	292	0.146
2	70	3000	2000	0.0005	2930	1000	293	0.1465
3	80	3000	2000	0.0005	2920	1000	292	0.146
4	150	3000	2000	0.0005	2850	1000	285	0.1425
5	170	3000	2000	0.0005	2830	1000	283	0.1415
6	60	3000	2000	0.0005	2940	1000	294	0.147
7	40	3000	2000	0.0005	2960	1000	296	0.148
8	160	3000	2000	0.0005	2840	1000	284	0.142
9	70	3000	2000	0.0005	2930	1000	293	0.1465
10	150	3000	2000	0.0005	2850	1000	285	0.1425
11	60	3000	2000	0.0005	2940	1000	294	0.147
12	140	3000	2000	0.0005	2860	1000	286	0.143
13	50	3000	2000	0.0005	2950	1000	295	0.1475
14	140	3000	2000	0.0005	2860	1000	286	0.143
15	90	3000	2000	0.0005	2910	1000	291	0.1455

3.Copper (Cu)

Stations	Mi	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	270	2000	200	0.005	1730	1800	96.11111	0.480556
2	130	2000	200	0.005	1870	1800	103.8889	0.519444
3	150	2000	200	0.005	1850	1800	102.7778	0.513889
4	240	2000	200	0.005	1760	1800	97.77778	0.488889
5	230	2000	200	0.005	1770	1800	98.33333	0.491667
6	100	2000	200	0.005	1900	1800	105.5556	0.527778
7	110	2000	200	0.005	1890	1800	105	0.525
8	100	2000	200	0.005	1900	1800	105.5556	0.527778
9	120	2000	200	0.005	1880	1800	104.4444	0.522222
10	260	2000	200	0.005	1740	1800	96.66667	0.483333
11	100	2000	200	0.005	1900	1800	105.5556	0.527778
12	240	2000	200	0.005	1760	1800	97.77778	0.488889
13	140	2000	200	0.005	1860	1800	103.3333	0.516667
14	100	2000	200	0.005	1900	1800	105.5556	0.527778
15	250	2000	200	0.005	1750	1800	97.22222	0.486111

4.Chromium (Cr)

Stations	Mi	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	430	0	100	0.01	430	100	430	4.3
2	370	0	100	0.01	370	100	370	3.7
3	360	0	100	0.01	360	100	360	3.6
4	380	0	100	0.01	380	100	380	3.8
5	390	0	100	0.01	390	100	390	3.9
6	420	0	100	0.01	420	100	420	4.2
7	440	0	100	0.01	440	100	440	4.4
8	340	0	100	0.01	340	100	340	3.4
9	270	0	100	0.01	270	100	270	2.7
10	460	0	100	0.01	460	100	460	4.6
11	450	0	100	0.01	450	100	450	4.5
12	390	0	100	0.01	390	100	390	3.9
13	360	0	100	0.01	360	100	360	3.6
14	350	0	100	0.01	350	100	350	3.5
15	440	0	100	0.01	440	100	440	4.4

5.Lead (Pb)

Stations	Mi (ppb)	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	380	10	5000	0.0002	370	4990	7.41483	0.001483
2	310	10	5000	0.0002	300	4990	6.012024	0.001202
3	290	10	5000	0.0002	280	4990	5.611222	0.001122
4	320	10	5000	0.0002	310	4990	6.212425	0.001242
5	280	10	5000	0.0002	270	4990	5.410822	0.001082
6	330	10	5000	0.0002	320	4990	6.412826	0.001283
7	350	10	5000	0.0002	340	4990	6.813627	0.001363
8	330	10	5000	0.0002	320	4990	6.412826	0.001283
9	300	10	5000	0.0002	290	4990	5.811623	0.001162
10	270	10	5000	0.0002	260	4990	5.210421	0.001042
11	340	10	5000	0.0002	330	4990	6.613226	0.001323
12	250	10	5000	0.0002	240	4990	4.809619	0.000962
13	340	10	5000	0.0002	330	4990	6.613226	0.001323
14	330	10	5000	0.0002	320	4990	6.412826	0.001283
15	370	10	5000	0.0002	360	4990	7.214429	0.001443

6.Nickel (Ni)

Stations	Mi (ppb)	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	0	20	200	0.005	20	180	11.11111	0.055556
2	0	20	200	0.005	20	180	11.11111	0.055556
3	0	20	200	0.005	20	180	11.11111	0.055556
4	10	20	200	0.005	10	180	5.555556	0.027778
5	10	20	200	0.005	10	180	5.555556	0.027778
6	0	20	200	0.005	20	180	11.11111	0.055556
7	0	20	200	0.005	20	180	11.11111	0.055556
8	10	20	200	0.005	10	180	5.555556	0.027778
9	0	20	200	0.005	20	180	11.11111	0.055556
10	10	20	200	0.005	10	180	5.555556	0.027778
11	10	20	200	0.005	10	180	5.555556	0.027778
12	10	20	200	0.005	10	180	5.555556	0.027778
13	10	20	200	0.005	10	180	5.555556	0.027778
14	10	20	200	0.005	10	180	5.555556	0.027778
15	0	20	200	0.005	20	180	11.11111	0.055556

7.Iron (Fe)

Stations	Mi	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	6490	200	5000	0.0002	6290	4800	131.0417	0.026208
2	7250	200	5000	0.0002	7050	4800	146.875	0.029375
3	7370	200	5000	0.0002	7170	4800	149.375	0.029875
4	8710	200	5000	0.0002	8510	4800	177.2917	0.035458
5	12820	200	5000	0.0002	12620	4800	262.9167	0.052583
6	9320	200	5000	0.0002	9120	4800	190	0.038
7	6360	200	5000	0.0002	6160	4800	128.3333	0.025667
8	8830	200	5000	0.0002	8630	4800	179.7917	0.035958
9	7340	200	5000	0.0002	7140	4800	148.75	0.02975
10	12790	200	5000	0.0002	12590	4800	262.2917	0.052458
11	9320	200	5000	0.0002	9120	4800	190	0.038
12	12850	200	5000	0.0002	12650	4800	263.5417	0.052708
13	9370	200	5000	0.0002	9170	4800	191.0417	0.038208
14	8760	200	5000	0.0002	8560	4800	178.3333	0.035667
15	6500	200	5000	0.0002	6300	4800	131.25	0.02625

8.Cobalt

Stations	Mi	i	Si	Wi	mi-li	si-Ii	Qi	WiQi
1	60	0	50	0.02	60	50	120	2.4
2	80	0	50	0.02	80	50	160	3.2
3	70	0	50	0.02	70	50	140	2.8
4	60	0	50	0.02	60	50	120	2.4
5	40	0	50	0.02	40	50	80	1.6
6	50	0	50	0.02	50	50	100	2
7	70	0	50	0.02	70	50	140	2.8
8	60	0	50	0.02	60	50	120	2.4
9	90	0	50	0.02	90	50	180	3.6
10	40	0	50	0.02	40	50	80	1.6
11	50	0	50	0.02	50	50	100	2
12	90	0	50	0.02	90	50	180	3.6
13	50	0	50	0.02	50	50	100	2
14	60	0	50	0.02	60	50	120	2.4
15	70	0	50	0.02	70	50	140	2.8

9. Cumulative effect of heavy metals at each sampling points

Stations	∑Wi	∑WiQi	HPI
1	0.0459	8.609802	187.5774
2	0.0459	8.985411	195.7606
3	0.0459	8.413108	183.2921
4	0.0459	8.129201	177.1068
5	0.0459	7.647943	166.6219
6	0.0459	8.269616	180.1659
7	0.0459	9.155585	199.4681
8	0.0459	7.701463	167.7879
9	0.0459	8.321857	181.3041
10	0.0459	8.440445	183.8877
11	0.0459	8.475212	184.6451
12	0.0459	9.713337	211.6195
13	0.0459	7.564809	164.8106
14	0.0459	7.902171	172.1606
15	0.0459	9.21486	200.7595

10.Summary (Mean): Irrigation

HMS	Mi (ppb)	Si	Ii	Wi	Mi-Ii	Si-Ii	Qi	WiQi	∑Wi	∑WiQi	HPI
Mn	439	200	50	0.005	389	150	259.3333	1.296667	0.0459	8.35	182.01
Zn	100	2000	3000	0.0005	2900	1000	290	0.145			
Cu	168	200	2000	0.005	1832	1800	101.7778	0.508889			
Cr	393	100	0	0.01	393	100	393	3.93			
Pb	318	5000	10	0.0002	308	4990	6.172345	0.001234			
Ni	7	200	20	0.005	13	180	7.222222	0.036111			
Fe	8926	5000	200	0.0002	8726	4800	181.7917	0.036358			
Co	60	50	0	0.02	60	50	120	2.4			

11.Summary of HPI for both Drinking and Irrigation

Stations	Drinking Water			Irrigation water		
	∑Wi	∑WiQi	HPI	∑Wi	∑WiQi	HPI
1	0.151319	103.3085	682.7201	0.0459	8.609802	187.5774
2	0.151319	122.7068	810.9143	0.0459	8.985411	195.7606
3	0.151319	112.4682	743.2519	0.0459	8.413108	183.2921
4	0.151319	107.7656	712.1748	0.0459	8.129201	177.1068
5	0.151319	101.4648	670.5357	0.0459	7.647943	166.6219
6	0.151319	101.825	672.9157	0.0459	8.269616	180.1659
7	0.151319	112.9583	746.4908	0.0459	9.155585	199.4681
8	0.151319	106.6763	704.9763	0.0459	7.701463	167.7879
9	0.151319	128.8824	851.7261	0.0459	8.321857	181.3041
10	0.151319	104.0723	687.7676	0.0459	8.440445	183.8877
11	0.151319	102.8361	679.5976	0.0459	8.475212	184.6451
12	0.151319	151.2451	999.5112	0.0459	9.713337	211.6195
13	0.151319	99.39883	656.8825	0.0459	7.564809	164.8106
14	0.151319	106.8646	706.2206	0.0459	7.902171	172.1606
15	0.151319	113.6541	751.0892	0.0459	9.21486	200.7595
Mean	0.151319	109.0904	720.9296	0.0459	8.354259	182.01

3. Heavy Metal Evaluation Index (HEI), Metal index and Contamination degree for River water (Drinking Water): (WHO, 2017)

1. Manganess (Mn)

Stations	HC (ppm)	Hc (PPB)	Hmac	Hc/Hmac	Cfi
1	0.41	410	400	1.025	0.025
2	0.45	450	400	1.125	0.125
3	0.43	430	400	1.075	0.075
4	0.42	420	400	1.05	0.05
5	0.48	480	400	1.2	0.2
6	0.44	440	400	1.1	0.1
7	0.41	410	400	1.025	0.025
8	0.4	400	400	1	0
9	0.43	430	400	1.075	0.075
10	0.51	510	400	1.275	0.275
11	0.42	420	400	1.05	0.05
12	0.5	500	400	1.25	0.25
13	0.42	420	400	1.05	0.05
14	0.43	430	400	1.075	0.075
15	0.44	440	400	1.1	0.1

Zinck (Zn)

Stations	Hc	Hmac	Hc/Hmac	Cfi
1	80	5000	0.016	-0.984
2	70	5000	0.014	-0.986
3	80	5000	0.016	-0.984
4	150	5000	0.03	-0.97
5	170	5000	0.034	-0.966
6	60	5000	0.012	-0.988
7	40	5000	0.008	-0.992
8	160	5000	0.032	-0.968
9	70	5000	0.014	-0.986
10	150	5000	0.03	-0.97
11	60	5000	0.012	-0.988
12	140	5000	0.028	-0.972
13	50	5000	0.01	-0.99
14	140	5000	0.028	-0.972
15	90	5000	0.018	-0.982

3.Copper (Cu)

Stations	**Hc (ppm)**	**Hc ppb**	**Hmac**	**Hc/Hmac**	**Cfi**
1	0.27	270	1000	0.27	-0.73
2	0.13	130	1000	0.13	-0.87
3	0.15	150	1000	0.15	-0.85
4	0.24	240	1000	0.24	-0.76
5	0.23	230	1000	0.23	-0.77
6	0.1	100	1000	0.1	-0.9
7	0.11	110	1000	0.11	-0.89
8	0.1	100	1000	0.1	-0.9
9	0.12	120	1000	0.12	-0.88
10	0.26	260	1000	0.26	-0.74
11	0.1	100	1000	0.1	-0.9
12	0.24	240	1000	0.24	-0.76
13	0.14	140	1000	0.14	-0.86
14	0.1	100	1000	0.1	-0.9
15	0.25	250	1000	0.25	-0.75

4.Chromium (Cr)

Stations	**Hc (ppm)**	**HC ppb**	**Hmac**	**Hc/Hmac**	**Cfi**
1	0.43	-730	50	-14.6	-15.6
2	0.37	-870	50	-17.4	-18.4
3	0.36	-850	50	-17	-18
4	0.38	-760	50	-15.2	-16.2
5	0.39	-770	50	-15.4	-16.4
6	0.42	-900	50	-18	-19
7	0.44	-890	50	-17.8	-18.8
8	0.34	-900	50	-18	-19
9	0.27	-880	50	-17.6	-18.6
10	0.46	-740	50	-14.8	-15.8
11	0.45	-900	50	-18	-19
12	0.39	-760	50	-15.2	-16.2
13	0.36	-860	50	-17.2	-18.2
14	0.35	-900	50	-18	-19
15	0.44	-750	50	-15	-16

5.Lead (Pb)

Stations	**HC (ppm)**	**Hc (ppb)**	**Hmac**	**Hc/Hmac**	**Cfi**
1	0.38	380	100	3.8	2.8
2	0.31	310	100	3.1	2.1
3	0.29	290	100	2.9	1.9
4	0.32	320	100	3.2	2.2
5	0.28	280	100	2.8	1.8
6	0.33	330	100	3.3	2.3
7	0.35	350	100	3.5	2.5
8	0.33	330	100	3.3	2.3
9	0.3	300	100	3	2
10	0.27	270	100	2.7	1.7
11	0.34	340	100	3.4	2.4
12	0.25	250	100	2.5	1.5
13	0.34	340	100	3.4	2.4
14	0.33	330	100	3.3	2.3
15	0.37	370	100	3.7	2.7

6.Nickel (Ni)

Stations	**Hc**	**Hc ppb**	**Hmac**	**Hc/Hmac**	**Cfi**
1	0	0	70	0	-1
2	0	0	70	0	-1
3	0	0	70	0	-1
4	0.01	10	70	0.142857	-0.85714
5	0.01	10	70	0.142857	-0.85714
6	0	0	70	0	-1
7	0	0	70	0	-1
8	0.01	10	70	0.142857	-0.85714
9	0	0	70	0	-1
10	0.01	10	70	0.142857	-0.85714
11	0.01	10	70	0.142857	-0.85714
12	0.01	10	70	0.142857	-0.85714
13	0.01	10	70	0.142857	-0.85714
14	0.01	10	70	0.142857	-0.85714
15	0	0	70	0	-1

7.Iron (Fe)

Stations	**Hc**	**Hc ppb**	**Hmac**	**Hc/Hmac**	**Cfi**
1	6.49	6490	300	21.63333	20.63333
2	7.25	7250	300	24.16667	23.16667
3	7.37	7370	300	24.56667	23.56667
4	8.71	8710	300	29.03333	28.03333
5	12.82	12820	300	42.73333	41.73333
6	9.32	9320	300	31.06667	30.06667
7	6.36	6360	300	21.2	20.2
8	8.83	8830	300	29.43333	28.43333
9	7.34	7340	300	24.46667	23.46667
10	12.79	12790	300	42.63333	41.63333
11	9.32	9320	300	31.06667	30.06667
12	12.85	12850	300	42.83333	41.83333
13	9.37	9370	300	31.23333	30.23333
14	8.76	8760	300	29.2	28.2
15	6.5	6500	300	21.66667	20.66667

8.Cobalt (Co)

Stations	**Hc**	**Hc ppb**	**Hmac**	**Hc/Hmac**	**Cfi**
1	0.06	60	10	6	5
2	0.08	80	10	8	7
3	0.07	70	10	7	6
4	0.06	60	10	6	5
5	0.04	40	10	4	3
6	0.05	50	10	5	4
7	0.07	70	10	7	6
8	0.06	60	10	6	5
9	0.09	90	10	9	8
10	0.04	40	10	4	3
11	0.05	50	10	5	4
12	0.09	90	10	9	8
13	0.05	50	10	5	4
14	0.06	60	10	6	5
15	0.07	70	10	7	6

9. The cumulative values of the heavy metals at each satation (8 heavy metals at each station)

Stations	**HEI**	**CD**
1	∑Hc/Hma	∑Cfi
2	18.14433	10.14433
3	19.13567	11.13567
4	18.70767	10.70767
5	24.49619	16.49619
6	35.74019	27.74019
7	22.57867	14.57867
8	15.043	7.043
9	22.00819	14.00819
10	20.07567	12.07567
11	36.24119	28.24119
12	22.77152	14.77152
13	40.79419	32.79419
14	23.77619	15.77619
15	21.84586	13.84586
1	18.73467	10.73467
Mean	24.01	16.1