RISK ASSESSMENT OF HEAVY METALS IN WATER AND SEDIMENTS IN THE MARA RIVER AND ITS TRIBUTARIES

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A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Environmental Science and Engineering of the Nelson Mandela African Institution of Science and Technology

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ABSTRACT

The present study assessed the levels of As, Cd, Cr, Hg, and Pb in water and sediments from the Mara River and its tributaries in Tanzania. The Mara River has recently been exposed to anthropogenic activities including, mining, industrial, and farming activities, which are potential sources of heavy metals pollution. These emerging anthropogenic activities with a destructive impact on the environment motivated the author to conduct a risk assessment of heavy metals in the Mara River and its tributaries. In this endeavor, the author used indices, principal component analysis (PCA), and sediment quality guidelines (SQGs) tools to study the heavy metals pollution status in the area comprehensively. The study was conducted in the dry and rainy months of May and October 2019, respectively. Geochemical indices used in the present study were geo-accumulation index (I_{geo}), enrichment factor (EF), contamination factor (CF), modified contamination degree (mCd), pollution load index (PLI), potential ecological risk factor (E_r^i), and potential ecological risk index (R_I). Moreover, the sediment quality guidelines (SQGs) were used for result comparisons. The principal component analysis (PCA) results indicated dominant loadings for As and Pb in sediments during the rainy month. Comparing sediment concentrations with sediment quality guidelines (SQGs) revealed that As and Cd may harm sediments-dwelling aquatic organisms. Correlation coefficient results indicated that As had a strong negative correlation with the other elements in sediments during the dry month. The analysis of environmental risk indices revealed significant enrichment of sediments with As and Cd. Contamination of As, Cd, and Pb along the Mara River was extremely severely enriched and linked to anthropogenic sources. Moreover, Cd and As in tributaries were elevated in the rainy month than in the dry months of 2019. As a result, enrichment factors of As, Cd, and Pb were extremely severely enriched. However, low contamination degree and very low pollution existed in water and sediments in the study area. Depending on rain and drought conditions, differentiated efforts are needed to minimize the effects of elemental loadings in the Mara basin ecosystem—with special attention for mitigation to be paid for As and Cd.

DECLARATION

I, Mihayo Sahani Nkinda, do hereby declare to the senate of Nelson Mandela African Institution of Science and Technology that this dissertation is my own original work and that it has neither been submitted nor being concurrently submitted for degree award in any other institution.

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CERTIFICATION

The undersigned certify that they have read and hereby recommend for acceptance by the NM-AIST a dissertation titled: "*Risk Assessment of Heavy Metals in Water and Sediments in the Mara River and its Tributaries*" in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy (PhD) in Environmental Science and Engineering of the Nelson Mandela African Institution of Science and Technology (NM-AIST).

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DEDICATION

To my parents, Luzaria Ng’wandu Nkinda and the late Malemba Golani Matina, my wife, Hellena Daniel and my sons, Emanuel, and Daniel Mihayo. Dedication is extended to members of the Seventh Day Adventist Church - External, Ubungo Hill, Dar es Salaam, for their prayers and blessings during my studies at NM-AIST - Arusha, Tanzania.

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LIST OF ABBREVIATIONS AND SYMBOLS

APHA	American Public Health Association
ASM	Artisanal and Small-Scale Mining
BOD	Biochemical Oxygen Demand
DO	Dissolved Oxygen
EC	Electrical Conductivity
EF	Enrichment Factor
EPA	Environmental Protection Agency
ERL	Effects Range Low
E_r^i	Ecological Risk Factor
GGM	Geita Gold Mine
GPS	Global Positioning System
HDPE	High-Density Polyethylene
HG-AAS	Hydride Generated Atomic Absorption Spectrophotometer
HMs	Heavy Metals
HNO_3	Nitric Acid
IBM	International Business Machines Corporation
*I*geo	Geo-accumulation Index
ITCZ	Inter-Tropical Convergence Zone
LEL	Lowest Effect Level
mA	milliamperes
MET	Minimal Effect Level
MPa	Megapascal Pressure Unit
MS	Microsoft
*m*Cd	Modified Contamination Degree
nm	nanometer
NMGM	North Mara Gold Mine
NTU	Nephelometric Turbidity Units
PCA	Principal Component Analysis
PC1	Principal Component One
PLI	Pollution Load Index
R_1	Ecological Risk Index
SPSS	Statistical Package for the Social Sciences
SQGs	Sediment Quality Guidelines
TCU	True Color Unit

TDS	Total Dissolved Solids
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WQGs	Water Quality Guidelines

CHAPTER ONE

INTRODUCTION

1.1 Background of the Problem

“Heavy metals” is a name assigned to metals and metalloids associated with contamination and potential toxicity (Donati, 2016; Koller & Saleh, 2018). The phrase "heavy metals" implies metallic elements with high atomic weight and whose specific gravity is five times the specific gravity of water at 4°C (Iyama & Edori, 2020). Heavy metals from aquatic systems enter the food chain through benthic species (Majnoni *et al.*, 2015). Elevated concentrations of As, Cd, Cr, Hg and Pb have been reported to cause various pathological effects on organisms, including humans (Gautam *et al.*, 2016; Lucia *et al.*, 2010). Rivers and lakes act as hydrographic units for natural materials interaction and exchange (Potasznik *et al.*, 2016). The river flow across urban and rural areas transport metals are partly dissolved and partly adsorbed on floating materials. Reports related to heavy metals in waters and sediments exceeding the recommended guideline limits in the environments are not rare (Luqueño *et al.*, 2013). For example, Cd level from waste incineration, power generation, and metal production in Europe has been estimated to range between 485 and 257 tons for the years between 1990 and 2003, respectively (WHO, 2007). In sub-Saharan Africa, especially where mining and other human activities are conducted, heavy metal contamination in water and sediments has resulted in a high risk to aquatic and terrestrial organisms (Okolo *et al.*, 2018). Moreover, Shakoor *et al.* (2013) reported that Pb pollution from battery recycling in the Dominican Republic had been a significant public health problem. According to Abah *et al.* (2016), 45% of the streams assessed in the United States were classified as polluted. In addition, 43% of monitored rivers in China were polluted and unsuitable for domestic use in 2011 (Abah *et al.*, 2016).

The Mara River is one of the seven rivers in the Lake Victoria Basin flowing into Lake Victoria. The river acts as a backbone for water supply for domestic consumption, agriculture activities, livestock keeping, and wildlife conservation. The river supports wildlife survival and biodiversity conservation. It acts as a guidepost for the annual migration of more than 1 million ungulates that crosses the river twice in the Serengeti-Mara Ecosystem (Subalusky *et al.*, 2017). The river and its catchment area indirectly serve as a foreign exchange earner for Kenya and Tanzania through tourism, fisheries, industrial and mining activities (WREM, 2008).

However, despite these advantages, the environmental status of the Mara River Basin continued to decline (WREM, 2008). Deforestation at Mau Forest for tea plantations, farming, and timber harvesting has been reported (Mwangi *et al.*, 2017). Environments and ecosystem protections are

essential for ensuring sustainable development for both nations. The assessment of heavy metal contamination in the study area is not new. An assessment of the influence of anthropogenic activities on heavy metals contamination at the Mau complex (the upper reaches of the Mara River basin) in water springs was conducted by Owuor *et al.* (2018). Their results were reported based on concentration units alone. The results indicated higher levels of heavy metals in some springs in the wet seasons while others were higher in the dry season (Owuor *et al.*, 2018). The distribution of metals along Simiyu wetland of Lake Victoria basin by Henry and Mamboya (2012) indicated higher levels of manganese and zinc in most samples evaluated based only on their content levels.

Moreover, assessments of Zn, Cu, Pb and Ni contamination in wetland soils of the Lake Victoria basin by Nabulo *et al.* (2008) were also analyzed and reported only on its content levels. The present study revealed that using powerful methods like geochemical indices, principal component analysis (PCA), and sediment quality guidelines (SQGs) to comprehensively evaluate the status of heavy metals pollution in the area has not yet been established. Previous studies conducted by Almås *et al.* (2009), and Kihampa and Wenaty (2013) could not differentiate pollution levels of heavy metals caused by natural processes and anthropogenic activities. Besides, for the Mara Basin, the present levels of heavy metal contamination compared to pre-industrial levels and the degree of sediment degradation is not yet established. Therefore, information based on heavy metal contents analysis alone does not provide complete insight into the risk of heavy metals in aquatic systems (Kowalska *et al.*, 2018).

The present study has introduced the concept of applying geochemical indices, PCA, and SQGs to quantitatively assess the heavy metal contamination in the area. El-Hamid and Hegazy (2017) reported that the use of geochemical indices, principal component analysis (PCA), and sediment quality guidelines (SQGs) is a powerful method for assessing heavy metals contamination in a broad range of ecosystems (Oumenskou *et al.*, 2018). The current study has applied seven geochemical indices: Contamination factor (*CF*), contamination degree (*m*Cd), pollution load index (*PLI*), enrichment factor (*EF*), geo-accumulation index (I_{geo}), potential ecological risk factor (E_r^i), and potential ecological risk index (R_I) to assess the environmental health risk of heavy metals in sediments in the Mara River and its tributaries. The main objective of this study was to assess the risk of heavy metals in water and sediments in the Mara River and its tributaries.

1.2 Statement of the Problem

Environments and ecosystem protections are essential for ensuring sustainable development for both nations. Unfortunately, little research has been conducted on the Mara River system (Nzeyimana, 2003; Rwetabula *et al.*, 2005). Information related to the risk assessment of heavy

metals in the study area is inadequate. Earlier studies conducted by Mataba (2016) and Mohamed *et al.* (2016) could not differentiate between pollution levels caused by natural processes and anthropogenic activities. Besides, for the Mara Basin, the present levels of heavy metal contamination compared to pre-industrial levels and the degree of sediment degradation are not yet established. The Mara River basin is part of a larger Lake Victoria Basin and large-scale gold mining operations have highly influenced the region. The known gold mining sites in the lake catchment area are Geita gold mine (GGM), North Mara Gold Mines (NMGM), Tulawaka, Buzwagi, Bulyanhulu, Buhemba, Kiabakari, Ikungu, Nyakafuru and Kibara (Lawley *et al.*, 2014; Merket, 2018). Uncontrolled mining activities can negatively impact the basin's ecological system through the downstream deposition of heavy metals (Fashola *et al.*, 2016). The spread of waste mining materials contaminated with heavy metals in the vicinity of large-scale mines is likely to extend its influence on river systems. According to Bitala *et al.* (2009), the lack of proper control and management of mining wastes in the Mara River catchment has been causing environmental degradation and human exposure to toxic elements. Thus, environmental degradation caused by improper handling of mining wastes demands intensive research to assess the risk of heavy metals in water and sediments in the Mara River and its tributaries.

1.3 Rationale of the Study

The level of heavy metal contamination in the Mara River and its tributaries is inadequately studied due to the lack of a national water quality monitoring program (LVEMP, 2005). The area has few published studies on heavy metal contamination from point and non-point sources, including natural, domestic, industrial, transport, agriculture, and mining (Rwiza *et al.*, 2016). The Mara River basin is part of a larger Lake Victoria basin that highly influences large-scale gold mining activities in the region. Following the presence of mining activities in the area, many pollutants may negatively impact the ecological system of the basin through the downstream deposition of heavy metals (Fashola *et al.*, 2016). The spread of heavy metals in the vicinity of large-scale mines is likely to extend its influence to river systems through soil erosion and storm runoff (Jarsjö *et al.*, 2017). Improper control of mining wastes in the Mara River and its tributaries may facilitate environmental health degradation. The present work identified heavy metals' sources, emissions, pathways, and fate in the study area. Dinis and Fiúza (2011) reported that environmental contamination of heavy metals might affect the central nervous system; impair blood composition, kidneys, lungs, liver, and other vital organs in animals. Therefore, pollution caused by heavy metals may pose adverse health effects to people and other animals throughout the food chain (Akpor *et al.*, 2014). A risk assessment study of heavy metals will help researchers and policymakers develop a risk mitigation plan for the Mara River and its tributaries.

1.4 Research Objectives

1.4.1 General Objective

The main objective of this study was to assess the risk of heavy metals in water and sediments in the Mara River and its tributaries.

1.4.2 Specific Objectives

(i) To assess the impacts of heavy metals on the quality of water and sediments of the Mara River and its tributaries using seven (7) geochemical indices and SQGs.

(ii) To compare seven (7) geochemical indices and PCA to study the distribution of heavy metals in water and sediments in the Mara River and its tributaries.

(iii) To establish baseline information on the present status of heavy metals pollution in the Mara River and its tributaries.

1.5 Research Questions

The following research questions guided the present study:

(i) What are the impacts of heavy metals on the quality of water and sediments in the Mara River and its tributaries using the selected pollution indices and SQGs?

(ii) What is the distribution of heavy metals in water and sediments in the Mara River and its tributaries when seven (7) geochemical indices and PCA are compared?

(iii) What baseline information can be drawn from the pollution status of heavy metals in the Mara River and its tributaries?

1.6 Significance of the Study

Risk assessment of heavy metals in water and sediments is essential for evaluating their impacts on aquatic environments. The present study assessed the risk of heavy metals in water and sediments using geochemical indices, principal component analysis (PCA), and sediment quality guidelines (SQGs). The application of indices, PCA, and SQGs are a more efficient method for acquiring comprehensive information about environmental conditions than measuring the concentration of heavy metals alone. The use of results from the investigation of pollution indices has been proven to prevent severe ecological problems (Akan *et al.*, 2012). Measuring heavy metal concentrations alone does not show the pollution intensity of any ecological system (Karbassi & Pazoki, 2015).

The discharge of heavy metals from anthropogenic sources into water bodies, e.g., rivers, lakes, oceans, and others, causes adverse ecological effects on aquatic and non-aquatic organisms (Karmakar & Musthafa, 2012). The information from the present study will help design and monitor conservation programs for marine ecosystems (Long & MacDonald, 1998).

The present study applied geochemical indices, sediment quality guidelines, correlation analyses, and principal component analysis to assess the risk of As, Cd, Cr, Hg and Pb in the Mara River and its tributaries. These methods have been globally used to evaluate the contamination of heavy metals in the environment. However, for most rivers in sub-Saharan Africa, information about pollution indices related to sediments is sparse. Compared to other locations, especially in the Global North, pollution indices have been scantly used in sub-Saharan Africa to study the impacts of anthropogenic activities on water and sediment quality. Sedimentological research of rivers that empty into Lake Victoria is highly patchy and wide apart. Previous studies could not differentiate pollution trends caused by natural processes from those that come by means of anthropogenic activities. Moreover, for many rivers in sub-Saharan Africa, current heavy metal loadings compared to pre-industrial levels and the degree of sediment degradation are not yet established.

Investigation of the impacts of heavy metals using only metal contents is insufficient to produce conclusive information. Hence, the application of a combination of geochemical indices, sediment quality guidelines, correlation analysis, and principal component analysis is important in addressing the existing literature gap. For that reason, the methodology used in the present study is part of the novelty and scientific contribution to the body of research related to environmental monitoring and assessment.

The study has also revealed that some sampling points were highly enriched with Cd and As with a potential of negatively impacting the aquatic and sediment-dwelling organisms. Although the identification of specific sources of these heavy metals was not the aim of this study, the information herein suggests that anthropogenic activities in the area, e.g., mining, agriculture, timber logging, and industry, could be significantly contributing to the elevated levels of elements in sediment and water samples. Thus, isotopic studies are recommended for the investigation of the input sources, especially for As, Cd, Cr, Hg, and Pb in the Mara River and its tributaries. Geochemical indices and principal component analysis are powerful tools for decision-makers to mitigate, manage, and control pollution sources. The present research, the methods used, and the recommendation proposed will significantly contribute not only to science but also to policy and decision-making.

1.7 Delineation of the Study

The present study has introduced the concept of applying geochemical indices, PCA, and SQGs to quantitatively assess the heavy metal contamination in the area. It further applied seven geochemical indices: contamination factor (*CF*), contamination degree (*m*Cd), pollution load index (*PLI*), enrichment factor (*EF*), geo-accumulation index (I_{geo}), potential ecological risk factor (E_r^i), and potential ecological risk index (R_I) to assess the environmental health risk of heavy metals in sediments in the Mara River and its tributaries.

CHAPTER TWO

LITERATURE REVIEW

2.1 Preamble to the Literature Review

The present Chapter deals with the literature review of risk assessment of heavy metals in water and sediments. The Chapter provides detailed information on the risk assessment of heavy metals based on the existing literature. The Chapter is organized into two sections: Section 2.2 describes the occurrences and the impact of heavy metals on the environment. Section 2.3 explains the risk assessments of heavy metals in the environment. It covers the meaning of risk assessment and the physical nature of chemical elements, particularly heavy metals. It also points out organisms that are likely to be affected by heavy metal pollution in water and sediments. Moreover, the section explains the previous and recently used methods for risk assessment of heavy metals in the study area.

2.2 Occurrence and Impact of Heavy Metals in the Environment

The environment can be defined as all the earth's components, including air, land, water and organic and inorganic matter in which human exists (Singh, 2006). Population growth, industrialization, and urbanization have contributed significantly to environmental degradation (Bharti, 2012). Despite the natural existence of heavy metals, human activities contribute to a high degree of heavy metal pollution in the environment. Heavy metals can be emitted into the environment by both natural and anthropogenic causes. The accumulation of heavy metals in water and sediments of rivers has been reported to cause an impact on flora and fauna. The mechanisms through which organisms are exposed to heavy metals have been extensively studied (Wendling *et al.*, 2018). Anthropogenic activities usually influence the unnatural enrichment condition of heavy metals on the soil profile, leading to surface soil pollution. Enriched soils may cause adverse health effects on people, plants, and animal tissues via dermal contact, inhalation, and ingestion pathways (Sulieman *et al.*, 2017). Cadmium, mercury, arsenic, lead, and chromium are globally reported to be the most toxic and carcinogenic heavy metals in aquatic ecosystems (Manoj & Padhy, 2014). Heavy metals enter the aquatic environments mainly from atmospheric deposition, soil erosion due to anthropogenic activities, landfill leaching, industrial discharge, municipal leachates, mining and domestic wastes (Donati, 2018).

The Mara River basin is an essential transboundary water resource for supporting the Maasai Mara National Game Reserve in Kenya and the Serengeti National Park in Tanzania. It's a world tourism destination and has recently been categorized as the New Seven Wonders of the World (Osoro *et*

al., 2018). The basin is a good wetland for communities' socioeconomic, sustaining ecosystem and social welfare of biodiversity. Recently the Mara River basin has faced severe environmental problems caused by intensive settlements, and poor cultivation activities leading to soil erosion, loss of vegetation cover, and sedimentation. Intensive farming activities cause non-point source pollution that is diffuse and has complicated spatial and temporal dimensions.

Furthermore, mining operations (more extensive scale, artisanal and small-scale mining) have dramatically increased in the area. The mining operation, which exposes heavy metals, may contribute to the ecological degradation of marine lakes and rivers like the Mara River (Heileman, 2006). Generally, the increase in human population, farming activities, deforestation, overgrazing, hunting, and tourism threaten the biodiversity in the Mara River basin (Johnson *et al.*, 2008). The WHO and USEPA have established the maximum permissible limit values for As, Cd, Cr, Hg, and Pb concentrations (mg/L) in aquatic environments (Table 1).

Table 1: Allowable limits of heavy metals in surface water

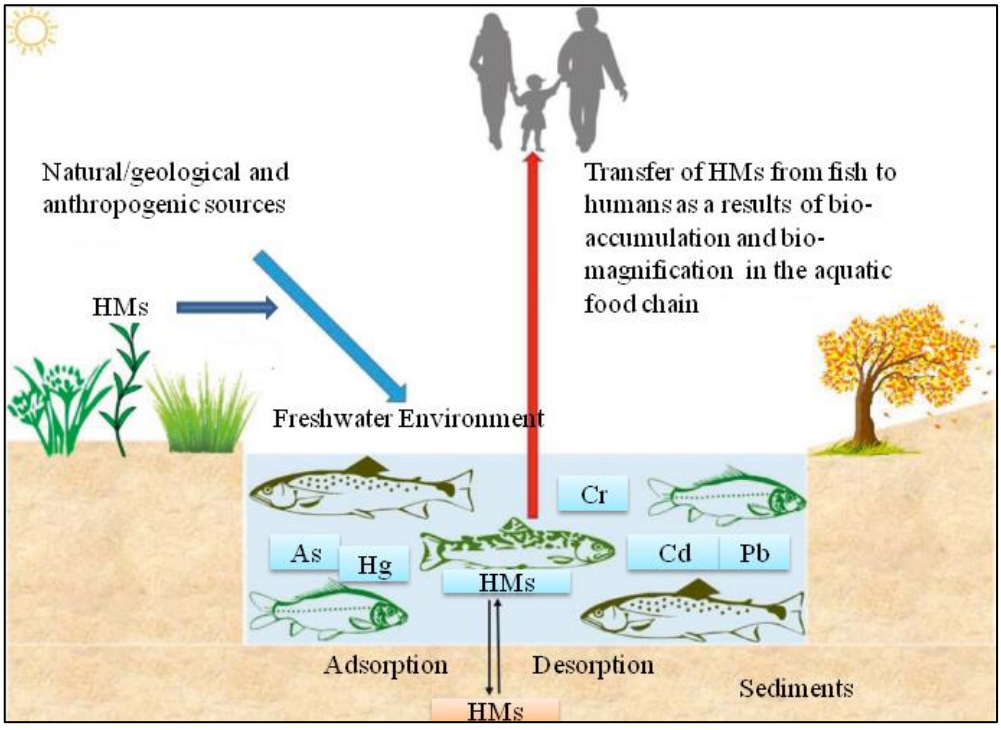
Element	WHO[(a)] Guideline (mg/L)	USEPA[(b)] Guideline (mg/L)
Lead (Pb)	0.01	0.015
Arsenic (As)	0.01	0.01
Cadmium (Cd)	0.005	0.005
Mercury (Hg)	0.001	0.002
Chromium (Cr)	0.05	0.1

[(a), (b)]*Source*: Adopted from Abdullahi *et al.* (2016), EPA (2018), Mohod and Dhote (2013)

When water and sediments are contaminated with heavy metals, they threaten aquatic organisms in the benthic environments by exposing them to toxic chemical elements (Shah & Altinda, 2003). Some marine microorganisms may cope and adapt to certain pollutants; however, severe pollution levels may change the population of flora and fauna in a particular ecosystem. Globally, elevated As, Cd, Pb and Hg levels have been reported to cause significant human health problems (Balali-Mood *et al.*, 2021). The adverse health effects of As, Cd, Pb and Hg were known as far back as the second century BC in ancient Greece (Hutton, 1987). Studies conducted by Andjelkovic *et al.* (2019) on the toxic effect of acute cadmium and lead indicated that exposure to Cd and Pb induced acute toxic effects in the blood, liver and kidneys of adult Wistar rats. One study conducted in adult Korea showed that Pb, Cd and Hg were significantly associated with liver injury (Kim *et al.*, 2021).

According to Xu *et al.* (2018), concentrations of As, Cd, Cr, and Pb in the tributaries of Dongting Lake (China) were caused by frequent mining and agricultural cultivation. Moreover, elevated concentrations of As and Cd in the Ulukisla River (Turkey) were reported by Lermi and Sunkari (2020) to be caused by mining, agrochemical application, and natural process. Studies conducted

by Yacoub *et al.* (2012) show that mining activities were probably the primary sources of heavy metals in the Jequetepeque River-Peru. Likewise, in the Mara River basin, various active mining gold, slates and sands prevail. The open-pit gold mines at Buhemba (Musoma district) and Nyamongo (Tarime district) may pose long-term environmental despoliation (Commission, 2012). Tigithe River contamination by mining wastewater was reported to cause death to eighteen villagers from the Nyamongo area (Seeteram *et al.*, 2019). The Mara River basin has received pollutants from large and small-scale gold mines, agricultural activities, industrial wastes and animal husbandry (Mayo *et al.*, 2013). Land degradation accompanied by land clearing, poor soil conservation, deforestation, and cultivation along the Mara River banks have been reported (Hagai, 2018). Heavy metal contamination may follow cyclical order, starting from industry, atmosphere, land, water, phytoplankton, zooplankton, fish and humans (Rodríguez *et al.*, 2015). Recent research on different fish species in the Mara River indicated that elevated concentrations of Cr, Ni, Cu in lungfish and Cu and Se in catfish from downstream of the river were probably caused by contamination from the mining activities of NMGM (Mohamed *et al.*, 2016). According to literature, fish's position in the trophic transfer of heavy metals through the aquatic food chain and food menu (Fig. 1) poses a higher risk to public health (Levit, 2010; Obiakor *et al.*, 2015). Regarding the previous studies and the dangers caused by As, Cd, Cr, Pb, and Hg, Nyairo *et al.* (2015) decided to assess the As, Cd, Cr, Pb and Hg levels in the Mara River and its tributaries.



HMs-Heavy Metals

Figure 1: Atrophic transfer of heavy metals through the food chain (Ali *et al.*, 2019)

2.2.1 Heavy Metals and Metalloids: The Sources

In the present study, the term "*heavy metals*" (Fig. 2), has been used to encompass the two scenarios of metals and metalloids having a specific gravity greater than five times that of water with toxic effects on plants and animals (Rajeswari & sailaja, 2014). In the present study, the context of heavy metals includes As, Cd, Cr, Hg, and Pb (Gautam *et al.*, 2014). The impact of environmental degradation in the study area has been reported (Matano *et al.*, 2015; Mati *et al.*, 2008). The contamination level of As, Cd, Cr, Hg and Pb in the study area are enumerated in the next section.

(i) Arsenic (As)

Although the risk assessment of As contamination in the study area is limited. A previous study indicated that As contamination up to 8 mg/L and other heavy metals were found in ponds and streams downstream of a leachate pond in the NMGM (Lucca, 2017). In addition, studies conducted by Kassenga *et al.* (2008) showed that 41% of the drinking water sources in the Lake Victoria Basin had arsenic levels exceeding the WHO. Moreover, arsenic contamination in gold mining areas in Tanzania (North Mara, Geita and Rukwa) was reported by Irunde *et al.* (2016) to be higher than recommended WHO guidelines and the Tanzania Bureau of Standards. Arsenic is exposed through pesticide manufacturing, rodenticides, paints, pigments and alloys (Jha *et al.*, 2002). Other significant sources of arsenic are weathering of sulphide ore, wood preservatives, mining of arsenopyrite, electrical waste, insecticides, weed controller, disposal of industrial waste, sewage materials and paint products (Golfinopoulos *et al.*, 2021; Jang *et al.*, 2016).

Arsenic is toxic to plants by inhibiting root extension and proliferation, biomass production and interfering with metabolic activities (Ackova, 2018). The inorganic form (As^{3+} or As^{5+}) of arsenic is reported by Jang *et al.* (2016) to be highly toxic and mobile in the environment than the organic form (As^{3-} or As^{5-}). Specifically, arsenite (As^{3+}) is found to be more toxic than arsenate (As^{5+}) (Jang *et al.*, 2016). According to Jang *et al.* (2016), about 42 nations, including China, Australia, Cambodia, Vietnam, Bangladesh and India, have elevated contamination of arsenic in some of their drinking water sources. Escobar *et al.* (2006) reported that the consumption of groundwater through constructed wells to replace polluted surface water supplies has resulted in widespread As poisoning in Asia (Escobar *et al.*, 2006). Likewise, Ma *et al.* (2021) reported that Pb isotope analysis results indicated that approximately 21% of As in the soils in Korea was impacted by smelters and geological processes. According to Martin *et al.* (2014), more than 50 000 registered abandoned mines in Australia and over 21.7 million hectares in Mexico are affected by mining activities.

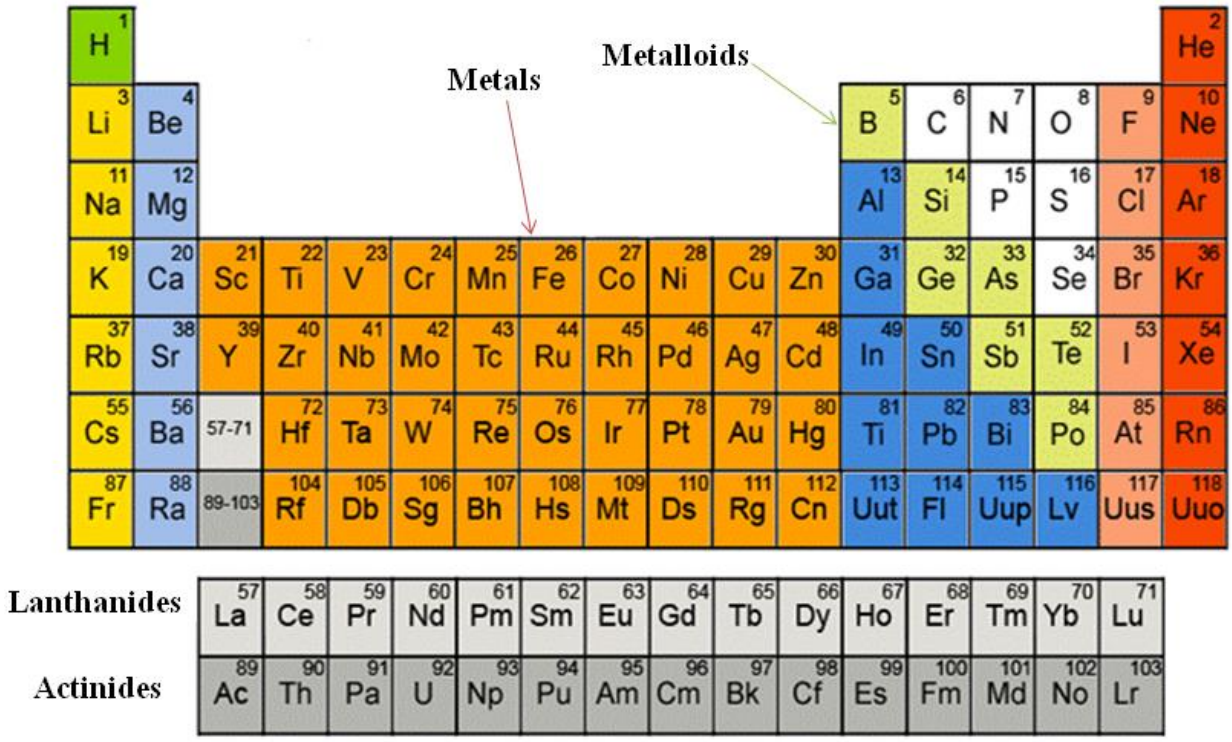


Figure 2: Position of heavy metals in the Periodic Table (Hoodaji *et al.*, 2012)

(ii) Cadmium (Cd)

Studies conducted by Nkinda *et al.* (2021) on risk assessment of heavy metals in water and sediments revealed that Cd and other heavy metals were highly enriched in sediments in the study area. Heavy metal enrichment in the area was probably caused by artisanal and small-scale mining (Laniyan & Adewumi, 2020). However, low levels of cadmium in Nile perch (*L. niloticus*) fish from samples collected from fish processing factories at the shores of Lake Victoria Mwanza were reported (Ngila *et al.*, 2009). The low cadmium level in Nile perch was probably favored by bioavailability factors (El-Sadaawy *et al.*, 2013). However, the determination of total elements does not give accurate estimates of the likely environmental impact on aquatic organisms in a particular basin (El-Sadaawy *et al.*, 2013). Moreover, research on monitoring heavy metal loading into the wetlands in the Lake Victoria basin indicated the level of cadmium to range from 0.04-0.57 mg/kg from samples analyzed from 5 wetlands in the area (Mutakyahwa *et al.*, 2009). These revealed that Cd contamination is minimal in some places.

Heavy metals bind to cell protein by displacing functional metallic elements on the cell's protein side, causing cell malfunction and toxicity. Heavy metals such as cadmium cause chlorosis in plants, reducing photosynthesis and lowering carbohydrate production (Jamal *et al.*, 2013). Cadmium is a more toxic heavy metal than others and causes detrimental effects on plants, animals, and human beings (Abiya *et al.*, 2019). Cadmium tends to compete for iron, zinc, copper and manganese absorption (Alia *et al.*, 2015). In some cases, cadmium hinders the rate of new cell

production and induces changes in plants' biochemical, physical, and genetic levels (Alia *et al.*, 2015).

(iii) Chromium (Cr)

Machiwa (2010) reported chromium contamination was higher in soil samples collected in Mwanza City (the area within the Lake Victoria Basin). Studies on metal pollutants distribution within the Lake Victoria basin by Christopher (2014) indicated high chromium contamination in sediments. The Mara River basin has widespread anthropogenic contaminants due to nutrient runoff from agricultural fields, domestic wastes, industrial, tourism establishments and mining wastes from artisanal gold mining (Dutton *et al.*, 2019). Chromium induces toxicity by inhibiting cell division and reducing plant root elongation, shortening plant roots' overall length. The condition may lead to water and other nutrients being restricted from reaching other plant parts (Emamverdian *et al.*, 2015). Unlike chromium III, which is essential for human nutrition, chromium VI compounds are environmentally toxic to microorganisms and larger animals. Therefore, chromium VI is suspected to be carcinogenic and harmful to plants. Chromium III is an essential micronutrient in humans and is generally harmless. A health risk study showed that arsenic and chromium throughout the food chain are the most contributors to human cancerous risk (Hezbullah *et al.*, 2016). Moreover, Cr's acute effects include negative impacts on fertilization, decreased blood clotting, increased spleen-to-body ratio, and decreased glycogen contents in different fish species (Aslam & Yousafzai, 2017). According to Kamunda *et al.* (2016), carcinogenic risk in Witwatersrand gold mining basin, South Africa found to be 1.7×10^{-4} showing that 1 person in every 5882 adults may be affected.

(iv) Mercury (Hg)

Mercury contamination was reported by Dutton *et al.* (2019) to be of particular concern in the lower portion of the Mara River basin. Artisanal and small-scale gold mining was commonly engaged in mercury in one of their gold processing steps in the area (Dutton *et al.*, 2019). According to Campbell *et al.* (2003), mercury contamination in the Lake Victoria basin sediments from ponds directly influenced by mining activity was elevated mercury levels. A study on water, communities, and development in the Lake Victoria Basin indicated that mercury contamination in soil was localized (Kayombo & Jorgensen, 2006; Muyodi *et al.*, 2005). The study on water quality and ecosystem management by Dhungana and Nimnee (2017) indicated that mercury contamination in the Mara River basin was higher in Maasai-Mara National Reserve and lowest in the farming area (Dhungana & Nimnee, 2017).

According to Wuana and Okieimen (2011), industrial expansion, mine tailings, animal Manure, sewage sludge, pesticides, wastewater irrigation, and coal and electronic waste may contaminate heavy metals. Mercury, especially methyl mercury, may be taken through diet when contaminated fish or fish products are consumed (Kimakova *et al.*, 2018). According to Kimakova *et al.* (2018), chronic mercury exposure may be associated with a wide range of adverse health effects on humans including the nervous system and the kidneys. Pandey *et al.* (2012) reported that in the 1950s, a severe incident caused by industrial pollution and Hg poisoning in a small seaside town in Minamata -Japan occurred. The incident was come to be known as the Minamata-Bay incident where elevated contamination of Hg levels in people of Minamata led to severe neurological damage and killed more than 900 people (Pandey *et al.*, 2012). The incidence led to approximately 2 million people from Minamata suffering from environmental health contamination. In the environment, methyl mercury accumulates through the marine food chain, which may impact brains and other human organs (Holm *et al.*, 2002). Mercury species in the form of Hg^{2+} is toxic to plants by inducing injuries and physiological disorders. The elevated level of Hg^{2+} interferes with mitochondrial activities, leading to oxidative stress by producing reactive oxygen species (ROS), which disrupt the bio-membrane lipids and plant cellular metabolism (Yadav, 2010)

(v) Lead (Pb)

The contamination of lead and other elements in the river in the study area was within the WHO guidelines (Njuguna *et al.*, 2020). However, the study conducted by Nkinda *et al.* (2020) indicated that lead contamination along the Musoma - Silari traffic highway at Kirumi Bridge was elevated. Furthermore, another study of lead and other heavy metals assessment in sediments and water samples indicated a higher level of lead contamination in sediments than in water samples (Mhina, 2016). Excessive heavy metals in water and sediments have disrupted plants, natural aquatic fauna, and soil microflora (Kunjam *et al.*, 2014). In addition, heavy metals tend to bio-accumulate and bio-magnify in living organisms, which has led to severe toxicity problems (El Khalil *et al.*, 2008).

Lead (Pb) is entirely unavailable even though many heavy metals are harmful to plants; Pb is altogether elusive. Some metals are insoluble and interact with soil particles (Janadeleh *et al.*, 2015). Lead pollution in many developed countries had significantly reduced in children by 1992 after introducing lead-free fuel (Baby *et al.*, 2010). According to Baby *et al.* (2010), lead pollution levels have been increasing in the urban areas of developing countries. More than 90% of the children in some African cities suffer from lead poisoning. Generally, natural processes such as

volcanic activities, weathering of rocks, and forest fires contribute significantly to the loadings of heavy metals in the Mara River Basin (Sankhla *et al.*, 2016).

Artisanal and small-scale mining (ASM) may lead to water pollution reported elsewhere in the literature (Plate 1). Thus, heavy metals are the primary contaminants in areas where ASM is operational in soil river systems. Such heavy metals may induce chemical reactions and processes in river channels and floodplains near mine sites (Krzemińska *et al.*, 2015). It is hereby inferred that natural runoff and soil erosion from the Mara River tributaries are likely to collect heavy metals from mining sites and convey them to the Mara River ecological system (Yager, 2009). The Mara River's contamination routes and its tributaries demand intensive study to assess the risk of heavy metals in the basin using SQGs, PCA, and geochemical indices.

Plate 1: Gold amalgamation at Buhemba gold mine – Mara – Tanzania (URT, 2017)

2.2.2 Heavy Metals in Aquatic Systems

Water contaminated with heavy metals typically relates to pollutants in the environment. Atmospheric precipitations such as rainfall, drizzles, snow and hail collect various atmospheric impurities in the air. As rain turns into water, it flows on the ground as surface runoff to small streams, forming rivers, which dissolve many pollutants from uncontrolled wastes (Salem *et al.*,

2000). Surface water bodies such as rivers, lakes, and oceans are more susceptible to contaminants, including heavy metals than groundwater. Pollution caused by heavy metals in rivers is undesirable and has health implications for aquatic life and people throughout the food chain (Zeng *et al.*, 2013).

Once metal ions enter aquatic systems, they are absorbed by particulate substances forming either free metal ions or soluble metal complexes (Živković *et al.*, 2019). Finally, they settle down and get incorporated into sediments. The study of heavy metals in sediments is one of the best techniques for quantifying water quality in the environment (Chen *et al.*, 2015). Contamination of heavy metals in aquatic environments causes devastation in the recipient ecological systems (Baby *et al.*, 2011). For instance, in a polluted marine environment, the accumulation of toxic heavy metals in fish muscles impairs their beneficial nutritional values to consumers. Heavy metals such as Cd, Pb, and Hg are included in European Union regulations for toxic metals in fish and seafood (Mehouel *et al.*, 2019).

Recently, the Tanzanian Lake Victoria Basin, where the catchment of the Mara River is located, has been experiencing significant environmental degradation (Kweka, 2009). Environmental pressure caused by human activities is one of the main factors threatening the area's ecological system (Ogello *et al.*, 2013). The area is reported in many publications as a leading gold production zone (Veiga, 2004). It accounts for 80% of the large-scale mining activities and approximately 95% as a national gold producer in Tanzania (Makene *et al.*, 2012). It consists of many goldfields, collectively known as Lake Victoria goldfields (Mshiu *et al.*, 2015). The Victoria goldfield makes Tanzania a third gold producer in Africa, after South Africa and Ghana. The gold mining sites within Victoria goldfields in Tanzania are Geita gold mining (GGM), north Mara gold mine (NMGM), Tulawaka, Buzwagi, Bulyanhulu, Buhemba, Kiabakari, Ikungu, Nyakafuru, and Kibara. Besides, diamond is mined in Mwadui – Shinyanga (Taylor, 2009).

The Mara River basin is inhabited by more than 27 million people, with a population growth rate of 6% per annum (WWF, 2010). The population within the basin has led to increased anthropogenic activities, leading to an increase in toxic heavy metals (Sida, 2018). Rivers and streams, which collect water from mining areas and land farms in the basin, convey toxic heavy metals into Lake Victoria. The human and environmental toxicity of heavy metals has received the attention of scientists due to their persistence and detrimental effects (Izah *et al.*, 2017). Heavy metal toxicity is usually induced by forming complexes with sulfur, oxygen, and nitrogenous compounds, causing cellular dysfunction (Singh *et al.*, 2017). Different methods are used to assess the risk of heavy metals in the environment. In the present study, the risk assessment of five heavy metals, namely mercury, cadmium, chromium, lead, and arsenic, in water and sediments was assessed. The study

focused on evaluating the concentration of heavy metals using pollution indices and sediment quality guidelines (SQGs). Pollution indices that were used included contamination factor (*CF*), contamination degree (C_d), pollution load index (*PLI*), enrichment factor (*EF*), geo-accumulation index (I_{geo}), potential ecological risk factor (E_r^i), and potential ecological risk index (R_I).

2.2.3 Heavy Metals in Sediments

Sediments are good indicators of heavy metal pollution in natural environments (Kruopiene, 2007). Sediments carry and sink most pollutants in aquatic environments and are a good source of nutrients for marine organisms. Usually, the attachment of heavy metals to sediments causes the metals to be inert and highly conservative. However, natural disturbances such as earthquakes, volcanic eruptions, or severe storms may alter the metal-sediment equilibrium posing environmental and human health risks (Mortuza & Al-Misned, 2017). Chemical speciation and chemical forms of heavy metals in sediments determine their transport mode and fate in aquatic ecosystems (Ferraro, 2015). The natural characteristics of sediments in terms of organic matter content, redox status, and pH influence the distribution of metal ions and bioavailability in an ecosystem. In addition, other physicochemical parameters such as temperature, dissolved oxygen (DO), salinity, and sediment grain size enhance the accumulation and toxicity of heavy metals to the environment (Aldwila *et al.*, 2018).

Heavy metals exist in both free ionic states and compound forms in sediments. However, the free ionic species are almost limited; most heavy metals occur in complex structures with insoluble inorganic and organic ligands (Ho *et al.*, 2010). Generally, heavy metals in river systems exist in two phases: The residual and labile fractions. In labile phases, heavy metals are involved in solid-liquid, adsorption-desorption, co-precipitation, and surface reactions with diverse solid particles such as clay minerals, oxides, carbonates and organic matter (Mortatti & Jean-Luc, 2010). Despite all these reactions usually involved in geochemical reactions in water and sediments, heavy metals remain persistent, non-degradable, and toxic to aquatic life (Helali *et al.*, 2016). Higher heavy metals in sediments may lead to acute or chronic toxicity to benthic organisms. The effects of heavy metals pollution on sediments and water have been reported to cause the loss of many aquatic species such as shellfish, fish, mollusks and crustaceans in estuarine and coastal areas (Egbenni *et al.*, 2010).

The toxicity of heavy metals is usually evaluated by conducting chemical analyses of respective elements in water and sediments (Dapam *et al.*, 2018). Sediments in river systems facilitate heavy metals to sink and accumulate. Heavy metals accumulate during low water discharge and are later transported downstream during floods and rainy seasons (Ignatavičiusa *et al.*, 2017). Therefore,

heavy metals' contents and distribution patterns in lakes or river sediments indicate natural imports of heavy metals from river systems (Vukovic *et al.*, 2011).

The Mara River basin is estimated to occupy 13 750 km^2, supporting vital biodiversity components by providing water, food, fertile soil, plants, wildlife protection, aquatic organisms and habitat to people (WWF-ESARPO, 2010). It is a transboundary river between two countries; Tanzania, which occupies (35%), and Kenya (65%) (LVBC, 2012). The basin is an arid system with natural resources incompatible with biodiversity and human residence. The basin faces massive destruction of its natural resources through deforestation, overfishing, land degradation, environmental pollution, overgrazing, and unplanned solid waste disposal (Anyona *et al.*, 2014; WWAP, 2012). Besides, the incidence of excessive agrochemical disposal from agricultural land, untreated wastewater from industrial activities, and gold mining are some of the environmental degradation problems that have been reported in the basin (GLOWS-FIU, 2007). Moreover, the pollution impacts related to the aforementioned problems of the local biota are not yet understood.

The Mara River consists of several small tributaries, including Somoche, Tobora, Nyarusondobiro, Nyarwera, Tigithe and Gurubi on the Tanzanian side of the river (LVBC, 2011; Zermoglio *et al.*, 2019). Studies conducted by Tilumanywa (2014) called for urgent research on risk assessment of the Mara River due to land degradation and poor handling of mining waste such as that emanating from the North Mara mine operations (Plate 2). Furthermore, unsafe mining methods and uncontrolled disposal of toxic chemicals due to artisanal mining activities are still a challenge.

Plate 2: Tailing dam at North Mara gold mine (Rutenge, 2016)

The hydrological nature of particular wetlands and their sediment properties control heavy metals availability (Hu *et al.*, 2015). Rivers are naturally open and more accessible to toxic heavy metals within their catchments. Risk assessment of heavy metals in river systems gives helpful information about pollution in aquatic ecosystems (Al-Wesabi *et al.*, 2015).

2.3 Risk Assessment of Heavy Metals

The word “risk” is the combination of the probability or likelihood of an event occurring and its negative impacts on the environment including people (Rovins *et al.*, 2012). Risk assessment refers to the process of assessing the possibility or chance that adverse effects may occur to the environmental values of human activities in a particular area (MELP, 2000). This implies that risk assessment involves the process of comparing various indicators of environmental values over time (Bernard *et al.*, 2000). According to Sinha (2019), risk assessments comprise hazard identification, deciding who might be harmed, risk evaluation, recording of the findings, and finally reviewing the risk assessment. Rivers from highly anthropogenic regions are highly vulnerable to heavy metals (Barakat *et al.*, 2012). Heavy metals in the environment may exceed the thresholds leading to bioaccumulation and biomagnifications at different trophic levels (Yi *et al.*, 2011). Through the food and nutrient chain, heavy metals may be transferred into living systems, leading to interference in flora and fauna's physiological functions, including humans (Iqbal & Munir, 2014). However, not all chemical elements are toxic to organisms. Some heavy metals add nutritional value to different organisms, while others do not. Metals, which add nutritional values to humans include: Co (II, III); Cr (III), Cu (0, I, II); Fe (II, III); Mg (II), Mn (II, IV); Mo (IV, VI); Se (II, IV, VI); and Zn (II). While metals such as Cr (VI); As (III, V); Cd (II), Pb (II, IV); Hg (0, I, II); Au (0, I, III); and others are known carcinogens (EPA, 2007).

2.3.1 Anthropogenically-Caused Metals: Impacts on Human and Environmental Health

Indiscriminate discharge of mining wastes, agrochemicals, and industrial influents to marine environments affects aquatic organisms' survival, physiology, growth, metabolism and reproduction (Solomon, 2008). Heavy metals are persistent in environments and undergo bioaccumulation in living tissues and food chain magnifications. Essential elements are usually less toxic than non-essential elements. The most toxic heavy metals to organisms and environments include As, Cd, Cr, Pb, and Hg (Jakimska *et al.*, 2011). Their characteristics and mechanisms of accumulation in body tissues of living organisms are species-dependent and are usually related to detoxification mechanisms and metabolic activity. Generally, different organisms in the same place can have dissimilar metals in their tissues (Jakimska *et al.*, 2011). Accumulation of heavy metals in animal tissues depends on the metal concentration in water, exposure period and other

environmental factors such as salinity, pH, temperature, and water hardness (Yilmaz *et al.*, 2018). Heavy metal accumulation in animal tissues may cause chronic illness and potential damage to entire populations (Shah & Altinda, 2003).

Many aquatic organisms such as aquatic plants, plankton, invertebrates, and vertebrates may be negatively affected by toxic heavy metals even at low concentrations (Atici *et al.*, 2008). For instance, heavy metals can cause chronic stress in fish at low concentrations, leading to low body weight and small body size, thus reducing their capacity to compete for food and habitats (Chavan & Muley, 2014; Rostern, 2017). Furthermore, the toxic effects of heavy metals depend on pH values; at around neutral pH, heavy metals are less toxic, while at low pH, they are very toxic to aquatic organisms (Rostern, 2017). Manganese, for example, can induce an iron deficiency in blue-green algae leading to inhibition of chlorophyll syntheses (WHO, 2005). This happens due to the competition for active sites with iron required for functional integrity (WHO, 2005). A study on copper (Cu^{2+}) and zinc (Zn^{2+}) by Tang *et al.* (2013) reported the strain effects of these heavy metals on ovaries and ova of the loaches (*Misgurnus anguillicaudatus*).

The Mara River, shared by two countries, Kenya and Tanzania, has great potential for supporting communities and habitats for various aquatic organisms (Sumari, 2017). However, the environmental damage caused by human activities such as gold mining operations within the Mara River Basin has been reported (Hawkins, 2010). Furthermore, the River basin receives various pollutants due to increased agricultural activities, animal husbandry, intensive settlements, and land degradation (Hawkins, 2010). Some of the Mara River tributaries in the study area originated from ASM-dominated areas. Furthermore, a previous study carried out in Lake Victoria, where the Mara River conveys its water, indicated undesirable chemical substances in water and sediments (Njiru *et al.*, 2012). This prompts an immediate response to conduct a risk assessment of heavy metals in the Mara River and its tributaries to establish the impacts of mining and other anthropogenic activities on the benthic and aquatic ecological health of the Mara system.

Usually, people get exposed to toxic elements through direct workplace contact, inhalation and dietary intake of contaminated food and water. Released heavy metals may accumulate in the soils, water and crops, gradually affecting human health through the food chain (Yan *et al.*, 2018). Generally, heavy metals are toxic to people; even those essential nutrients may induce toxicity when they are in excess amounts. Heavy metals-based pollution is very prominent in areas with active and closed mines. They are leached out, and on steep slopes, they are washed out through water runoff to water bodies (Duruibe *et al.*, 2007). Their bioaccumulation and persistence may adversely affect plants, animals, and humans. The toxicity effects of heavy metals on humans are

mainly associated with the brain and kidneys (Hu, 2002). Most heavy metals are toxic even at low concentrations; others are non-degradable by microbial activities and are persistent in the environment (Manoj *et al.*, 2018). However, under low concentrations, some heavy metals such as Cu, Zn and Fe are essential for human and environmental health (Jamshaid *et al.*, 2018). Other metals such as Cd and As are grouped as human carcinogens; As is linked to human cancer, while As is known to cause kidney damage and various cancers. Antimony (Sb) is known to cause heart disease and blood cholesterol. Lead (Pb) has been shown to cause anemia, whereas Hg damages the liver and kidney (Qa & Khan, 2016).

Therefore, determining the levels, toxicity, and risk of heavy metals in the aquatic environment is necessary. Risk assessment of heavy metals in water and sediments in rivers is a management tool for evaluating marine systems' health quality (Mortazavia & Hatamia, 2018). Assessment methods of heavy metal contamination in the Mara River and its tributaries have previously been based on heavy metal content alone. The recently developed risk assessment methods such as geochemical indices, PCA, and sediment quality guidelines (SQGs) have not yet been applied in the Mara River and its tributaries. To fulfill the existing gap, the present study has used geochemical normalization factors, risk factors, risk index, PCA and SQGs to assess the impacts of heavy metals in the study area. The method has been used globally to determine the risk of heavy metals pollution in aquatic and terrestrial environments (Aigberua & Tarawou, 2018; Jiao *et al.*, 2018).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Mateirlas

3.1.1 Preamble

In this Chapter, the materials and methods used for risk assessment of heavy metals in water and sediments in the Mara River and its tributaries have been described. Sediments and water samples from the Mara River and its tributaries were collected in May and October 2019. The selected sampling points along the Mara River were Mara Darajani, Nyantare Area, Somoche Factory, and Kirumi Bridge. Sampling sites from the Mara River tributaries were Tobora, Somoche, Gurubi, Tigithe, Nyarwera, and Nyarusondobiro. During sampling, pH, total dissolved solids (TDS), electrical conductivity (EC), temperature (ºC), turbidity, and color were determined in situ. Water samples were collected and stored in high-density polyethylene (HDPE) bottles, washed using HNO_3, and rinsed three to four times using distilled water. During collection, water samples were preserved using two drops of HNO_3, and there were no chemical pre-treatments for sediment samples. Water samples were digested and analyzed using the nitric acid method, manual hydride generation, and cold vapor atomic absorption spectrometry, respectively. Sediment samples were digested using EPA method 3050B (SW-846), Method 245.5 and EPA method 7062. The hydride-generated atomic absorption spectrophotometer was used for As, Cd, Cr, Hg and Pb determination. Data were analyzed using Origin® Pro. 9.0, IBM® SPSS Statistics (Version 21), and MS Excel (Version 2010). Finally, the Chapter describes the risk assessment of heavy metals using pollution indices, sediment quality guidelines (SQGs), water quality guidelines (WQGs) as well as principal component analysis (PCA).

(i) Study Area

The Mara River is among many rivers that discharge water and sediments into Lake Victoria (Ahmed *et al.*, 2007). Mara River basin lies between 35.78º E and 0.43º S in Kenya's southwest and 33.78º E to 1.48º S in the northeast of Tanzania mainland (Njigua, 2006). The Mara River is shared between Kenya and Tanzania. Its basin coverage area is about 13 750 km^2, where 65% belongs to Kenya, and the remaining 35% is located in Tanzania. The river originates from Mau Forest escarpments of Kenya in the Eastern Great Rift Valley. The river meanders through large-scale agricultural lands and enters the Maasai-Mara and Serengeti National Parks in Kenya and Tanzania, respectively (UNDP, 2012). The river conveys water and sediments into Lake Victoria, covering a distance of 394 km from Mara wetlands (Fig. 3). The Mara River falls in an inter-tropical zone

where the Inter-tropical Convergence Zone (ITCZ) and the Indian Ocean sea surface temperatures influence its climate (Zermoglio *et al.*, 2019). The annual range of the river precipitation at the upper catchment area averages 1500 mm and 800 mm at the river mouth (McClain *et al.*, 2014). The flood flow at the upper catchment zone average from 8 to over 150 m^3/s with an average of 30 m^3/s, while in lower areas, the flood flow ranges from 90 to over 400 m^3/s with an average of 300 m^3/s (McClain *et al.*, 2014).

The seasonal rainfall distribution along the Mara River is highly unimodal, the wet season spanning from November to June and the dry season spanning from July to October (Bartzke *et al.*, 2018). However, due to climatic changes in the Mara-Serengeti ecosystem, severe drought with low rainfall (below 800 mm at the mouth) in the wet season followed by a long period of drought in the dry season was experienced in 2019. As a result, the dry season reversed, spanning from May to September, followed by severe floods in October 2019 (TRCS, 2019). Due to the extreme drought and seasonal rainfall variability of 2019, water flow along the Mara River declined except at the river mouth near Lake Victoria (WWF, 2019).

The Mara River basin is within the larger Lake Victoria basin, where the lake basin has recently been reported to be adversely impacted by various anthropogenic activities, including gold mines (Dybas, 2011). Uncontrolled mining activities can negatively impact the basin's ecological system resulting in a considerable loading of heavy metals. The extensive spread of heavy metals in mines' vicinity is likely to extend its roots to river systems through soil erosion, storm runoff and may accumulate in benthic zones. Furthermore, the lack of proper control and management of mining wastes in the river catchment causes environmental degradation, leading to ecological and human health risks (Lugoe, 2011). Indeed, environmental degradation caused by anthropogenic activities demands intensive research to assess the risk of heavy metals in water and sediments in the Mara River and its tributaries.

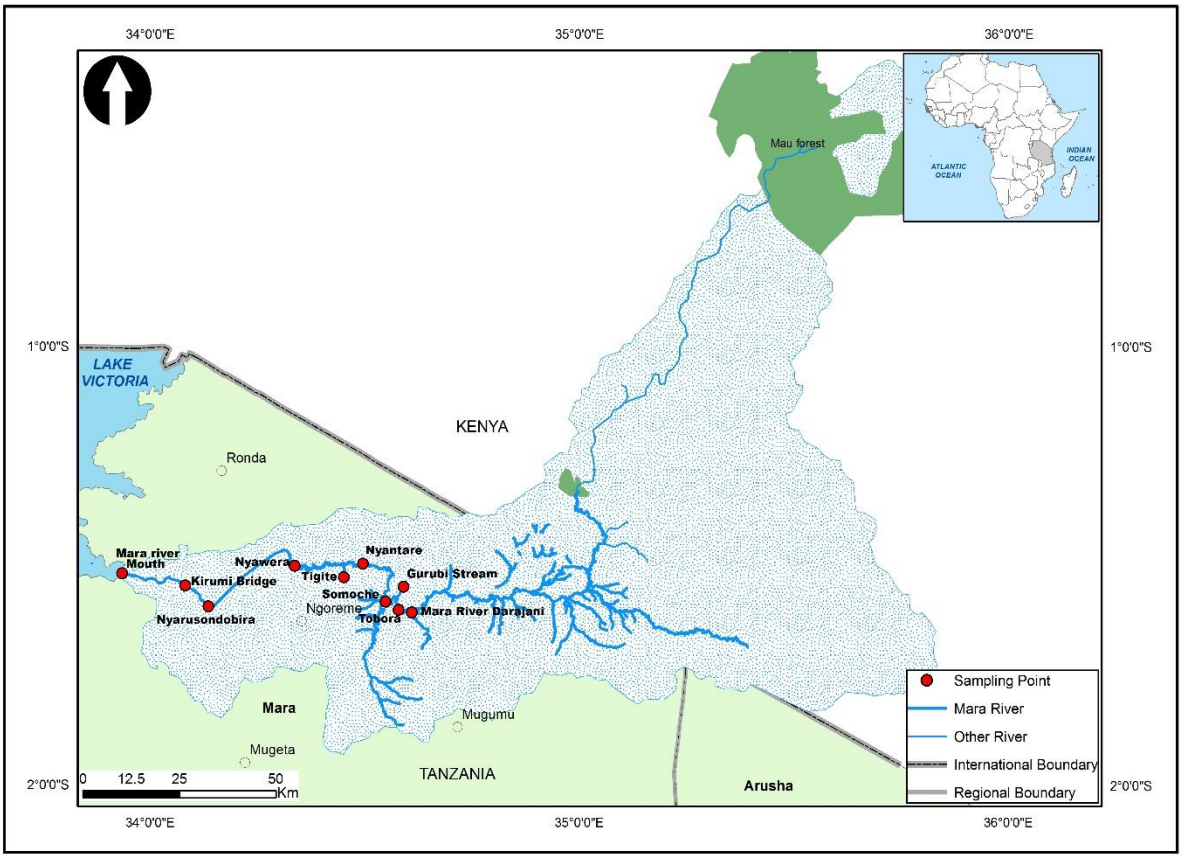


Figure 3: A map of northern Tanzania and southwest Kenya indicating the Mara River system and sampling locations

3.1.2 Reagents

The reagents used in the present research were of analytical grade, mainly: Concentrated nitric acid, HNO_3 (65%) from (Riedel-deHaën, Germany), hydrogen peroxide, $H_2O_2(30\,\%)$, from British Drug House (BDH) Chemicals Ltd, concentrated hydrochloric acid, HCL (10%), Sigma-Aldrich, Germany, and locally acquired distilled water. These reagents were used for water and sediment sample digestion. Analar was used to treat hand-operated manual augers before being wrapped in pre-cleaned aluminium foil.

3.1.3 Apparatus Sterilization and Pre-Treatment

Laboratory apparatus such as Erlenmeyer flasks, griffin beakers, volumetric flasks, watch glass, and measuring cylinders were washed with liquid detergents and rinsed three times with distilled water followed by oven drying. In addition, new sample bottles of high-density polyethylene (HDPE) were procured within-country and washed with liquid detergent, followed by rinsing with distilled water before use. Clean aluminium foil was used for wrapping on hand-operated manual augers. Moreover, during water sampling, the sampling bottles were rinsed three times again with river or stream water following approved water sampling protocols (APHA, 2017).

3.1.4 Sampling Equipment

Hand-operated manual augers and stainless scoop were used for sediment sampling. An overboard dinghy with an outboard engine was used to reach deep-water locations for water and sediment sampling. Other sampling equipment included a sediment digestion vessel, Kjeldahl (Avishkar International PVT LTD, Mumbai)**,** drying ovens, hot plates, a centrifuge, analytical balances, and HG-AAS (Hydrate generated atomic absorption spectrophotometer model WFX 210 from Ray Leigh Co. LTD). The Kjeldahl, drying ovens, hot plates, centrifuge machines, and HG-AAS were used for sediment digestion, dying samples, turbidity removal, weighing, and sample analysis.

3.2 Methods

3.2.1 Sampling Process

(i) Sampling Sites, Water, and Sediment Samples

Water and sediment samples from ten sampling sites were collected during the dry and rainy months of May and October 2019 respectively. Out of the ten sampling sites, six were obtained from Tobora, Somoche, Gurubi, Tigithe, Nyarwera, and Nyarusondobiro tributaries. The remaining four designated sampling sites of Mara Darajani, Nyantare Area, Somoche Factory and Kirumi Bridge were sampled along the Mara River. The sampling locations were referenced using a handheld GPS unit (Map 62 Garmin), and the coordinates were tabulated accordingly (Table 2).

Table 2: Description of sampling locations and sites

Locations	Coordinates	Location descriptions
Mara Darajani	S. 01.3630 E. 0343627	Farming activities and it is the border between Serengeti and Tarime district.
Tobora	S. 01.3630 E. 034.3626	Small-scale farming and human settlements. The stream originates from Marenga artisanal gold mine and then feeds into the Mara River.
Somoche Bridge	S. 01.3525 E. 034.3219	Small-scale farming feeds into the Mara River.
Somoche Factory	S. 01.3503 E. 034.3223	Mine slates and small-scale farming closer to Mara River.
Gurubi	S. 01.3209 E. 034.3520	In small-scale farming and human settlements, the stream originates from Mara artisanal gold mine and feeds into the Mara River.
Nyantare Area	S. 01.2947 E. 034.2947	Small-scale farming, and gold mine activities and located about 10 km from the NMGM tailing dam.
Tigithe	S. 01.3708 E. 034.1443	Piles of rock wastes surround human settlements. The stream originates from the Nyamongo area (NMGM), feeding the Mara River.
Nyarwera	S. 01.3708 E. 034.1443	Originates from Sirori-Simba artisanal gold mine and feeds into the Mara River.
Nyarusondobiro	S. 01.3811 E. 034.0706	Originates from the Buhemba gold mine and feeds into the Mara River.
Kirumi Bridge	S. 01.3156 E. 034.5856	The bridge is located where the Mara River meets Lake Victoria, with small-scale fishing, and horticulture activities.

Criteria for selecting particular sampling locations were based on the existing literature gap (Weinfurtner & Kördel, 2012). The random sampling method was used to collect water and sediment samples from the study area. Representative water and sediment samples from tributaries were collected when a selected tributary coincided with the main river course.

(ii) The Mara River sampling Sites

The Mara River discharges its water and sediments into Lake Victoria (Ahmed *et al.*, 2010). The river supports a wide range of socio-economic and environmental needs in both countries of

Tanzania and Kenya. The river is a socio-economic backbone that supports water supply services for domestic and industrial purposes in rural and urban areas for mining, agriculture and fisheries. The Mara River is also a focal point for wildlife and biodiversity conservation. It acts as a guidepost for the annual migration of wildebeests within the Serengeti-Mara ecosystem (Seeteram *et al.*, 2019). To cover an area of anthropogenic significance, four sampling sites of Mara Darajani, Nyantare Area, Somoche Factory and Kirumi Bridge were purposely selected (Fig. 4). Moreover, the knowledge of the bottom dynamics like soil erosion, transportation, and accumulation from previous works was used to decide the total number of sampling sites (Smodiš *et al.*, 2003).

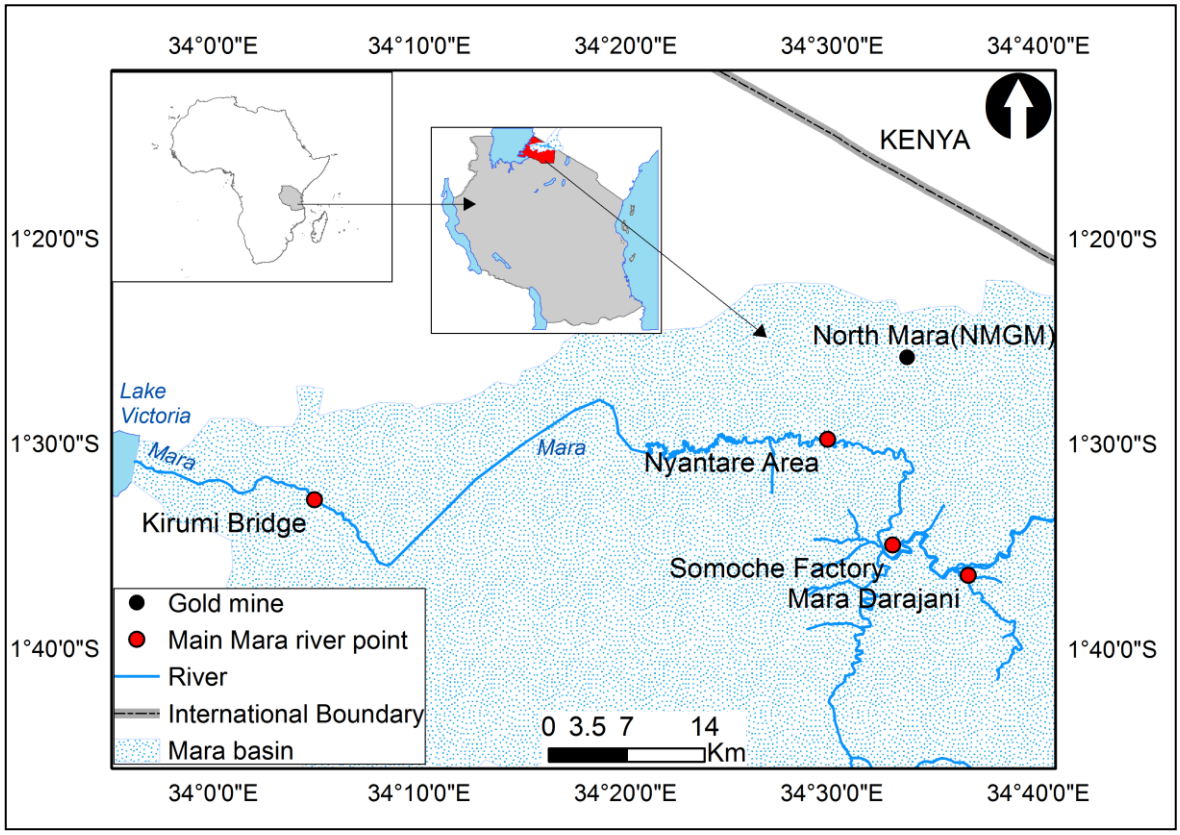


Figure 4: A map of Tanzania indicating the sampling location and sites. The water flow of the Mara River is from East to West towards the Lake Victoria

(iii) The Mara River Tributaries Sampling Sites

The Mara River tributaries lie within the Mara River basin. The Mara River basin is part of the Lake Victoria basin. It has a large catchment area of about 13 504 km^2 shared between Kenya and Tanzania (Castillo, 2009). On the Tanzanian side, the Mara River consists of several small tributaries of Somoche, Tobora, Nyarusondobiro, Nyarwera, Tigithe and Gurubi (Fig. 5) (MoWI, 2020).

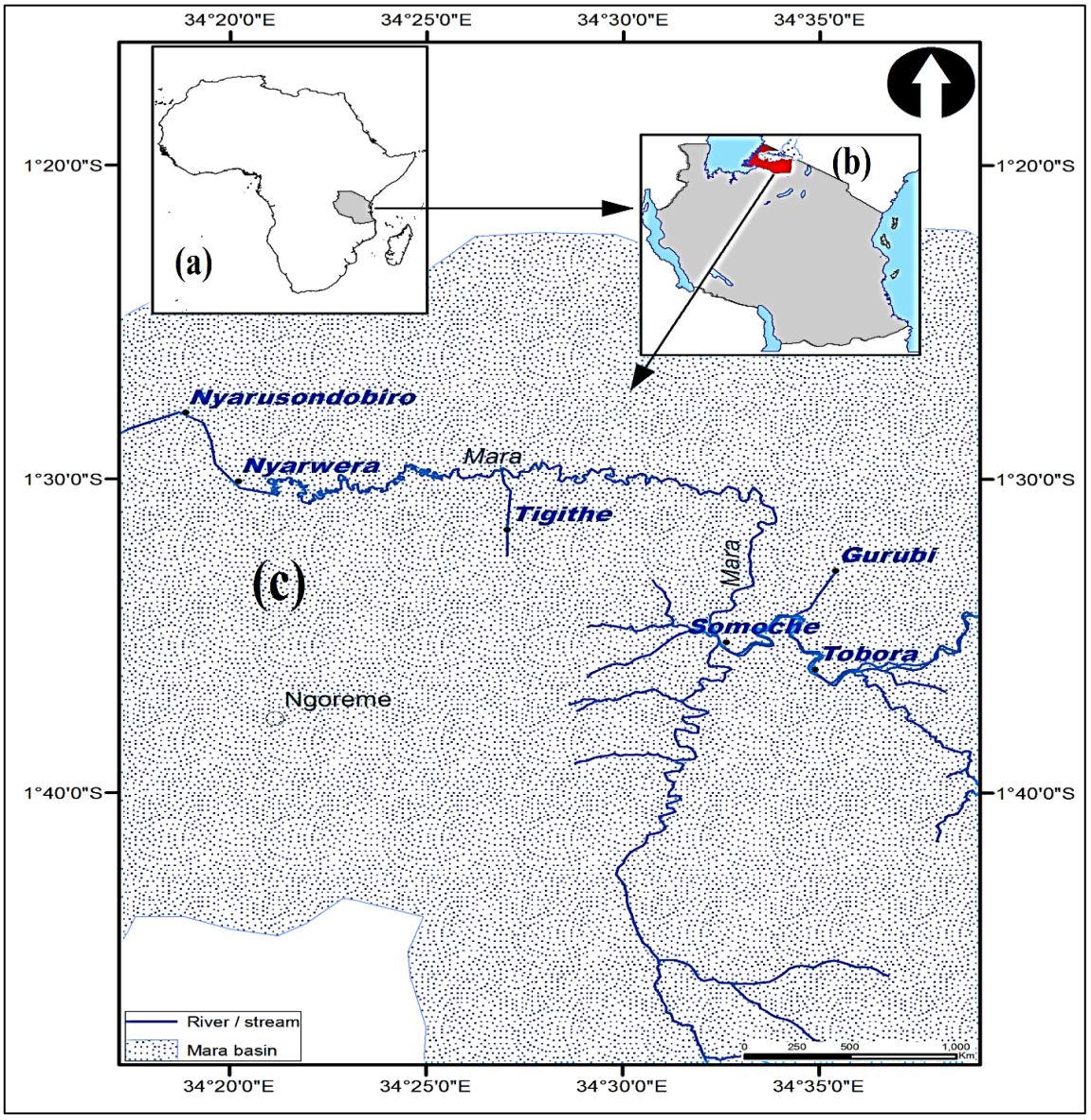


Figure 5: **A map of (a) Africa (b) Tanzania (c) The Mara River tributaries; the general flow of the Mara River is from East to West toward Lake Victoria (not shown). In inset (b), the red region denotes the Mara River basin**

Tributaries of the Mara River fall within the Mara administrative region of Tanzania. The area falls into three climatic zones: the Northern, the Central, and the Southern zone (Majule, 2010). The average rainfall within the northern zone lies between 1250 and 2000 mm per year and spans September to June. The central area receives between 900 and 1300 mm of rain per year, and the Southern zone does not fall in the Mara River Basin (Majule, 2010). The basin is home to more than 1 million people, which sustain the Maasai-Mara National Reserve in Kenya, the Serengeti National Park in Tanzania (Plate 3), and biodiversity wetlands bordering Lake Victoria (Initiative, 2020). The Mara River Basin's social-economic importance includes small scale-farming that supports livelihoods, tea and wheat production, safari tourism, fisheries, and mining activities (WWF, 2017).

Plate 3: Wildebeests at the Serengeti National Park - Arusha– Tanzania (Present study)

3.2.2 Water Sampling, Preservation, Storage, and Transportation

Storage of water samples was done using 1 L high-density polyethylene (HDPE) bottles prewashed using 10% v/v HNO_3 (Plate 4) and rinsed several times using distilled water. During sampling, each pre-washed sampling bottle was rinsed three times again with river/stream water. All members of the sampling team wore disposable hand gloves, raincoats, and other protective gear. Samples were collected at varying depths from 0 to 15 cm below the water surface by submerging uncapped sampling bottles upside down. The uncapped bottles were tipped upright to allow water into the bottles. In deep water locations, sampling was supported by a dinghy with an outboard engine (Plate 5). Samples were acidified to a pH < 2 by adding two drops of HNO_3 and screwing them tight before being kept in ice-cooled box containers (APHA, 2017).

Plate 4: **Water samples were collected using high-density polyethylene bottles (HDPE) (Present study)**

Sample bottles were labeled by writing on top using water-resistant ink. Detailed information like the name of the stream, point name, sample code, name of the acid used for preservation, and sampling dates was shown on bottle labels. Moreover, other information such as river flow, nature of the surrounding landscape, weather conditions, e.g., cloud cover, sunshine, air temperature, and water condition such as temperature, color, pH, TDS and EC were recorded. Samples were packed in an ice-cooled box container and transported to the Musoma Water Quality laboratory for temporary storage in a refrigerator maintained at 1 ℃ to 4 ℃ (APHA, 2017). After two days, the samples were transported by bus to Arusha Technical College Laboratory – Arusha, Tanzania, for further analysis.

Plate 5: A dinghy with an outboard engine was used to reach deep water sampling sites (Present study)

3.2.3 Sediment Sampling, Preservation, Storage, and Transportation

Surface sediment samples from ten selected zones were collected twice in May and October 2019. Samples were collected using a stainless scoop and hand-operated augers and stored in polyethylene bags. Before sampling, hand-operated manual augers were pre-cleaned with AnalaR and then wrapped in a cleaned aluminium foil. The augers were kept wrapped in aluminium foil until when required for use. The auger head was attached to the extension rod's required length of the "T"-handle. The auger was inserted into the sediment at a 20° angle from vertical to minimize spillage of the sample. After that, it was rotated clockwise to cut off a chunk of sediment and withdrawn slowly. Polyethylene bags were used to collect samples and kept in the ice-cooled box container without chemical pre-treatment (APHA, 2017). Likewise, in shallow sluggish water or dryer locations, the handheld stainless scoop was used for sediment sample collection (Plate 6). Sediment sampling was conducted by carefully removing the desired thickness and sediment volume from the sampling point. Samples were then transferred into polyethylene bags and were collected at a similar location and time to where water samples were taken. The samples were labeled by writing on each polyethylene bag using water-resistant ink.

Plate 6: Collection of sediment samples from a dry riverbed using a stainless-steel scoop (Present study)

Information such as the stream, point name, sample code, and sampling date was shown on each polyethylene bag. Furthermore, environmental conditions at the sampling sites such as river flow, nature of the surrounding landscape, weather conditions (cloud cover, sunshine, air temperature), and water temperature, color, pH, TDS and EC, were also recorded. Samples were packed in the ice-cooled box and transported to Musoma Water Quality Laboratory for temporary storage. After two days, the samples were transported by bus to Arusha Technical College – Arusha, Tanzania, for analysis. Sediment sampling, preservation, storage, and transportation were performed under procedures described in the standard method for examining water and wastewater (APHA, 2017).

3.2.4 Physicochemical Parameters

Physicochemical parameters measured *in situ* were pH, total dissolved solids (TDS), electrical conductivity (EC), temperature (°C), turbidity (NTU), and color (°H). Calibrated instruments were used to measure the above parameters at each sampling site. Sampling data were recorded correctly in a logbook immediately before the team left the sampling location. Samples were collected in triplicate at each sampling site. Each sampling site was referenced using a GPS unit. A portable DR/890 colorimeter (Hach 1997/2009) was used to take water turbidity and color readings.

Moreover, a calibrated portable waterproof Hanna HI98129 pH/EC/TDS/Temperature meter was used to record readings for the pH, electrical conductivity (EC), total dissolved solids (TDS), and sample temperature. Measurement of pH values was obtained by selecting the pH mode with the

Set/Hold button. The electrode was submerged in 50 mL of water in a 100 mL clear plastic beaker, left for a few minutes to stabilize, and the reading was recorded in a logbook. The pH values were automatically compensated for temperature readings. The same procedures for electrical conductivity (EC) and total dissolved solids (TDS) readings were carried out. Ultimately, the probe was rinsed thoroughly with a sample to be measured to avoid cross-contamination before taking the subsequent measurement.

Physical parameters are environmentally significant for controlling chemical, biological, and physical processes in any ecological system (Masood *et al.*, 2015). Good water quality depends on a good range of physicochemical parameters in aquatic environments (Tukura *et al.*, 2012). The abundance, distribution, composition, movement, and diversity of marine organisms depend on the interaction of water's physiochemical properties (Mbalassa *et al.*, 2014). Any physical and chemical parameters imbalance may harm flora and fauna (Nadeem & Saeed, 2018). In the present study, physicochemical parameters were measured to assess heavy metals' pollution status in water and sediments. Moreover, Papastergios *et al.* (2009) reported that positive correlations exist between physicochemical parameters and heavy metals distributions in aquatic environments (Alkam *et al.*, 2012).

3.2.5 Sample Determination and Digestion

(i) Digestion of Water Samples

Water samples were digested using three different methods: (a) nitric acid digestion, APHA Method 3030E; (b) manual hydride generation, APHA Method 3114B; and (c) cold vapor atomic absorption spectrometry, EPA Method 245.1 (APHA, 2017; Studies, 2004). The acid digestion method APHA 3030E mainly determined Pb, Cr and Cd in water samples. The manual hydride generation method APHA 3114B was used to determine As, while a cold vapor atomic absorption spectrophotometer, EPA method 245.1, was used to determine Hg in water samples. Digestion was carried out to reduce the interference of organic matter and convert metals into a free-ion state. The water digestion procedures used for the present research are well described in Appendices (1), (2), and (3).

(ii) Digestion of Sediment Samples

Sediment samples were digested using EPA Method 3050B (SW-846), Method 245.5 and EPA Method 7062. The EPA digestion method 3050 B was used for Pb, Cr and Cd determinations, while the EPA Method 245.5 and 7062 were used for As and Hg determination, respectively. The sediment digestion procedures are explained in appendices (iv) and (v).

(iii) Determination of Heavy Metals

Heavy metals were determined by a hydride generation atomic absorption spectrophotometer (HG-AAS, Model WFX 210, Beijing Rayleigh). The HG-AAS determines the ground state of the test samples' free atomic vapor. It absorbs the characteristic spectral radiations of the elements to be determined. The instrument's basic working principle is that the light source emits radiant energy of the element's characteristic wavelength to be determined. The energy is absorbed by the atoms of the elements and is transferred to an excited state (Helaluddin *et al.*, 2016). Since the light beam's wavelength is the characteristic of the element being investigated, the amount of light energy absorbed in the sample is directly proportional to the sample concentration (IAEA, 2011).

Adjustment of the instrument parameters was according to the manufacturer's instructions. For every metal determination, a relevant hollow cathode lamp, double distilled water, and analytical grade reagents were used. Laboratory blanks and field duplicates improved quality assurance during sample analyses. The slit width was 0.4 nm, and the wavelength of elements was 193.7 nm, 228.8 nm, 357.9 nm, 253.7 nm, 283.3 nm and 248.3 nm for As, Cd, Cr, Hg, Pb and Fe, respectively. In the present study, the recovery percentage varied between 90 and 103%. The warning limits for matrix spike recoveries from the standard varied from 87 to 113%, indicating a good recovery range (Sany *et al.*, 2012). The operation condition of the instrument, preparation, and storage of standard solution for every heavy metal under investigation were as follows:

Chromium

The instrument's optimum operating condition was 357.9 nm wavelengths, 3.0 mA lamp current, yellow oxidizing flame, and other settings. The standard series in 2% HCL solution prepared were 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 µg Cr in per milliliter. The linear range of the Cr standard curve was 0 – 5 µg/mL. After the instrument was arranged and calibrated, the determination of chromium in every sample commenced.

Mercury and Arsenic

The HG-AAS was calibrated using analytical grade reagents before determination. The reagent used was 0.4% NaBH, 40% HCL, and other solutions were prepared immediately before use. The concentration ranges of the standard solution were 5 mg/L to 20 mg/L for arsenic and 20 mg/L to 80 mg/L for mercury. The acetylene flow rate was set to 1600 mL/mm. Under the manufacturer's instructional manual, other standard operating procedures determined arsenic and mercury in inorganic samples.

Lead

The instrument's operating condition was 283.3 nm wavelengths, 0.4 nm spectral bandwidth, 0.3 mA lamp current, and the flame produced was oxidizing blue flame. The other operation conditions were 0.3 MPa air pressures, 0.09 MPa acetylene pressure, 7.0 L/min airflow, and different settings described in the manufacturer's instruction manual. The standard series prepared in 2% HNO_3 solution were 0.0, 2.0, 4.0, 6.0, 8.0, and 10 µg Pb per milliliter. Thus, the linear range of the Pb working curve was 0.0 – 10.0 µg/mL.

Cadmium

The instrument's optimum working condition was 3 mA lamp current, 228.8 nm wavelength, 7.0 L/Min airflow, 1.0 L/Min acetylene flow, and the flame type was oxidizing blue flame. The standard solution "A" of cadmium was prepared to contain 1 mg/mL Cd, while the "B" solution had 20 mg/mL Cd. The standard solution "B" was used to aspirate 0, 20, 40, 60, 80 and 100 µg into a 100 mL measuring flask. The HCL of 4 mL (1+1) was added and diluted to the scale mark with distilled water. Other procedures used were under the manufacturer's instruction manual provided.

Iron

The instrument's optimum operational conditions were 248.3 nm wavelength, 0.2 nm spectral bandwidth, 3.0 mA lamp current, 0.3 MPa air pressure, 0.09 MPa acetylene pressure, 7.0 L/min airflow, 1.7 L/min acetylene flow, and oxidizing blue flame. The linear working ranges in 2% HCL solution, the standard series prepared were 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 µg Fe per milliliter. The linear range of the (Fe) standard curve was 0.0 – 5 µg/mL. Other working conditions of the instrument were set according to the manufacturer's instruction manual. The iron (Fe) was selected as the immovable element for calculation and reference materials.

3.2.6 Statistical Data Analysis

Data were analyzed using Origin® Pro 9.0, the IBM® SPSS® Statistics 21 software, and Microsoft® Excel for Windows 2010. The Origin® Pro 9.0 software was used for graphical information presentations and the principal component analysis (PCA). The IBM® SPSS® statistic 21 software was used for Pearson correlation matrix presentations. Furthermore, sediment quality guidelines (SQGs) were used for result comparisons (Simpson *et al.,* 2013). Finally, Microsoft® Excel for Windows 2010 was used for pollution indices calculations and table presentations.

(i) Heavy Metals Assessment Techniques

Apart from determining metal concentration in water or sediments of a particular environment, pollution indices and SQGs can be used to accomplish the assessment (Nweke & Ukpai, 2016). Three classes of pollution indices were used in the present study to assess the contamination of heavy metals. These classes were: (a) contamination indices (*CF* & *PLI*), (b) background enrichments (I_{geo} & *EF*), and (c) ecological risk indices (E_r^i & R_I) (Praveena *et al.*, 2007). These indices are efficient and rapid tools for producing a single value emanating from different parameters. Most of these indices have been employed globally to study the contamination of toxic heavy metals in river sediments (Ali *et al.*, 2015; Liu *et al.*, 2016; Singh *et al.*, 2018). Pollution indices are powerful tools for evaluating, developing, and conveying raw environmental data into more meaningful information for politicians or decision-makers (Harikumar *et al.*, 2010). Moreover, water quality guidelines and the eco-toxicology senses of heavy metals contamination using sediment quality guidelines (SQGs) were used. Similarly, the principal component analysis (PCA) and Pearson correlation analysis were used in an attempt to associate the five heavy metals with particular input sources.

(ii) Geo-accumulation Index

The geo-accumulation index I_{geo} helps determine the contamination of heavy metals in sediments by comparing the current concentration and pre-industrial levels (Banu *et al.*, 2013). The I_{geo} values can be calculated using Equation (1) (Grba *et al.*, 2015).

$$I_{geo} = log_2 \left(\frac{C_n}{1.5B_n}\right) \quad (1)$$

where C_n is the measured concentration of metal "*n*" in sediment, and B_n is the geochemical background value for the metal "*n*" in sediments. At the same time, the 1.5 factor accounts for the possible variation in background data caused by lithology effects (Odukoya, 2015). The I_{geo} is divided into seven classes. The classes are $0 \leq I_{geo}$ unpolluted; $0 \leq I_{geo} \leq 1$ unpolluted to moderately polluted; $1 \leq I_{geo} \leq 2$ moderately polluted; $2 \leq I_{geo} \leq 3$ moderately to strongly polluted; $3 \leq I_{geo} \leq 4$ strongly polluted; $4 \leq I_{geo} \leq 5$ strongly to extremely polluted; and $I_{geo} \geq 5$ extremely polluted (Al-Hejuje *et al.*, 2018).

(iii) Enrichment Factor

The enrichment factor (*EF*) was an indicators index used to evaluate the availability and intensity of anthropogenic contamination in sediments or soil surfaces (Zhao *et al.*, 2015). In the present

study, iron (Fe) concentration was used for geochemical normalization and shale reference. Iron (Fe) has been used for material references due to its higher natural concentrations in the earth's crust than any other metal. The enrichment factor expression is shown in Equation (2):

$$EF = \frac{[Metal/Fe]_{Sample}}{[Metal/Fe]_{UCC}} \quad (2)$$

where $[Metal]_{sample}$ is the amount of metal in sediments and $[Metal]_{UCC}$ refers to the concentration of the same metal in the upper continental crust (UCC). The values used for UCC in this study were correspondingly 0.056 for Hg, 0.1 for Cd, 2 for As, 17 for Pb, 35 for Cr, and 30 890 for Fe. Using EF values, the contamination can be classified as follows: $EF \leq$ for 1 no enrichment; $1 < EF \leq 3$ for minor enrichment; $3 < EF \leq 5$ for moderate enrichment; $5 < EF \leq 10$ for moderately severe enrichment; $10 < EF \leq 25$ for severe enrichment; $25 < EF \leq 50$ for very severe enrichment; and $EF > 50$ for extremely severe enrichment. Additionally, a condition $0.5 < EF < 1.5$ may signify that the contamination originates from the natural weathering processes. However, when the values are above 1.5, it may indicate an anthropogenic contribution (Guimarães *et al.*, 2011).

(iv) Contamination Factor

The contamination factor (*CF*) was used to determine the overall contamination of heavy metals in water and sediment samples (Zemełka, 2019). The contamination factor (*CF*) was calculated by the following expression, Equation (3):

$$CF = \frac{M_c}{B_c} \quad (3)$$

where M_c and B_c are the metals' measured concentration and background values, respectively (Al Obaidy *et al.*, 2014), the contamination factor is categorized into four classes for water and sediment samples. The classifications are as follows: low contamination ($CF < 1$); moderate contamination ($1 \leq CF < 3$); considerable contamination ($3 \leq CF < 6$); and $CF \geq 6$ for very high contamination (Sany *et al.*, 2013).

(v) Contamination Degree

The contamination degree (mC_d) is used to measure the overall contamination in the sampling sites' surface layer (Rezaee *et al.*, 2010). In addition, it is used in research to indicate sediment contamination in aquatic systems (Javed *et al.*, 2017). In the present study, the calculation of the degree of contamination was based on Equation (4) (Hakanson, 1980; Ozkan, 2012):

$$mC_d = \sum_{i=1}^{n} CF_i \quad (4)$$

where mC_d is the degree of contamination, and *CF* is the contamination factor. The corresponding classifications of sediment contamination are: $mC_d < 6$ implies a low degree of contamination; $6 < mC_d < 12$ means a moderate degree of contamination; $12 < mC_d < 24$, which denotes a considerable degree of contamination; and $mC_d > 24$ a high degree of contamination (Ahdy & Khaled, 2009).

(vi) Pollution Load Index

The pollution load index (*PLI*) indicates the number of heavy metal concentrations in sediments, which exceed that of the background concentration in the study area. The concentration reflects the toxicity of heavy metals in sediment samples (Shirani *et al.*, 2020). The *PLI* is represented by the following Equation (5):

$$\mathrm{PLI_{site}} = \sqrt[n]{\mathrm{CF_1} \times \mathrm{CF_2}, \ldots, \times \mathrm{CF_n}} \quad (5)$$

where "*n*" is the number of trace metals under investigation and "*CF*" is a contamination factor (Loskaa *et al.*, 2004). When the value of *PLI* > 1, it indicates that pollution exists. When the value of *PLI* < 1 indicates that there is no pollution with heavy metals. Likewise, when the value of *PLI* = 1, it is an indication that the heavy metals concentration is closer to the background level (El-Anwar, 2019).

(vii) Potential Ecological Risk Factor and Potential Ecological Risk Index

The potential ecological risk factor ($\mathrm{E_r^i}$) was developed by Hakanson (1980) to assume that the aquatic system's sensitivity depends on its productivity. Using this assumption, the aquatic pollution assessment methodology becomes feasible (Krupadam *et al.*, 2006). In the aquatic system, the risk factor expresses the given contaminants' ecological risk (Zarezadeh *et al.*, 2017). On the other hand, the potential ecological risk index (R_I) was used to evaluate the harm of heavy metals in sediment samples. Their expressions are shown in equation (6):

$$R_I = \sum_{i=1}^{n} E_r^i; \qquad E_r^i = T_r^i \times C_f^i; \qquad C_f^i = \frac{C_s^i}{C_n^i} \quad (6)$$

where T_r^i is the toxic-response factor for a given substance "*i*". The toxicity response factors for investigated metals were as follows: Hg = 40, Cd = 30; As = 10, Cr = 5, Pb = 2. E_r^i is the potential ecological risk factor for the element ''*i*'; while C_f^i represents the contamination factor for the

element "*i*"; C_s^i is the concentration of the element ''*i*'' in a sample; and $C_n{}^i$ is the concentration for the element in the reference sediments ''*i*''. The grades used for ecological factors (E_r^i) were as follows: $E_r^i < 40$ low risk; $40 \leq E_r^i < 80$ moderate risks; $80 \leq E_r^i < 160$ considerable risk; $160 \leq E_r^i < 320$ high risks and $E_r^i \geq 320$ for very-high risk. The R_I values were calculated and categorized into four classes: $R_I < 150$ low risks, $150 \leq R_I < 300$ moderate risks, $300 \leq R_I < 600$ considerable risks and $R_I \geq 600$ for high risk (Sobhanardakani *et al.*, 2016).

(viii) Sediment Quality Guidelines

Environments with contaminated sediments are toxic to sediment-dwelling organisms. Contaminated sediments can adversely affect the survival of benthic microorganisms, fishes, birds, and even aquatic mammals (MacDonald & Zajdlik, 2009). In the present study, sediment quality guidelines (SQGs) were used to compare results to determine levels of heavy metals in sediment samples compared to the published guidelines (Burton & Allen, 2002). The aim was to investigate whether the level of heavy metals in the investigated sediments exceeded the recommended threshold.

(ix) Water Quality Guidelines

Water quality guidelines are thresholds of pollutants in water deemed sufficient to protect public health based on scientific experiments and extrapolations. In the present study, they were used for result comparisons for parameters determined in-situ and those done in the laboratory. Normally, surface water with appreciably high levels of heavy metals may affect aquatic organisms and human health. Moreover, elevated turbidity levels, color, dissolved solids, temperature, pH, and electrical conductivity may indicate abnormality and may alter marine organisms' survival (Dallas & Day, 2004). Therefore, the WHO and EPA water quality maximum limits reported in the literature for heavy metals and physical-chemical parameters were used for result comparisons.

(x) Multivariate Statistical Analysis

The principal component analysis (PCA) and Pearson correlation analysis were used to distinguish the possible sources of As, Cd, Cr, Hg and Pb in the study area. The PCA can examine the multivariate relationship and reduce data dimension, extracting highly correlated variables into independent factors (Zhiyuan *et al.*, 2011). Similarly, the Pearson correlation coefficient was used to investigate the relationship between heavy metals in water and sediments (Xie *et al.*, 2016). Correlation analysis measures the statistical relationship between two or more quantitative variables, fluctuating together (Gogtay & Thatte, 2017). Data are correlated when the change in the

magnitude of one variable results in a modification of the extent of other variables either in the same direction (positive correlation) or in the opposite direction (negative correlation) (Schober *et al.*, 2018). Correlation can have a value of "1" for a perfect positive correlation, "0" for no correlation (values are not interrelated at all), and "-1" for a perfect negative correlation. In statistics, three types of correlations are frequently used: Pearson correlation, Kendall rank correlation, and Spearman correlation. Pearson correlation coefficient was used in the present study to measure the strength of a linear association between variables (Rebekić *et al.*, 2015). The SPSS Statistic Version 21 software was used in the present study for the Pearson correlation coefficient matrix calculations and interpretation. The PCA was used in the present study to identify sources of heavy metals hypothetically in the study area (Bhardwaj *et al.*, 2019).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Overview

This Chapter describes results from the analysis of physicochemical parameters and heavy metals in samples collected from the Mara River and its tributaries. The physicochemical parameters were measured and recorded *in situ*, while heavy metals were determined in the laboratory. The determination of As, Cd, Cr, Hg and Pb in surface water and sediment samples was conducted using a hydrate-generated atomic absorption spectrophotometer (HG-AAS). The aim was to investigate the level of heavy metals in surface water and sediments. To understand heavy metals' impacts on sediments, seven pollution indices were used together with sediment quality guidelines (SQGs). Besides, the WHO and EPA water quality guidelines were used to compare the analytical results from field samples with the stipulated water safe limits for drinking water. Moreover, the Pearson correlation matrix and principal component analysis (PCA) were used to evaluate the relationship between parameters and elucidate the possible sources of heavy metals.

4.2 Physicochemical Parameters

For the present study, the determined physicochemical parameters included temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), turbidity and color. The maximum mean range of turbidity, color and pH was above the WHO guidelines in all tributaries in the dry month of May 2019 (Table 3). A higher level of turbidity and other parameters in the dry period may be attributed to land use, including sand extraction and agricultural activity in the river (Girardi *et al.*, 2016). A similar result of higher pH value in the dry period was also reported by Edokpayi *et al.* (2015). Studies conducted by Araoye (2009) reported that the photosynthesis process from aquatic plants removes carbon dioxide during daylight from the medium, causing increased pH in water. Likewise, the conversion of CO_2 to organic carbon by the processes of photosynthesis in warm waters increases the pH levels. Higher pH levels of 9 to 8.9 were recorded in both months and a drop in pH was only recorded in rainy months (Table 3). This drop-in pH from 9 to 7.6 was probably due to the stirring effect of the incoming water from the Mara basin towards tributaries resulting in the mixing of alkaline or acidic water with alkaline surface waters (Araoye, 2009). Maximum mean levels for temperature, electrical conductivity, and total dissolved solids in May 2019 were within the WHO-recommended range of 20–35 ºC, 100 – 2000 µS/cm, and 1000 mg/L, respectively (Table 3). In the rainy month of October 2019, the value of pH = 9.00, EC = 2103.0 µS/cm, TDS = 1052.0 mg/L, turbidity = 528.67 ± 0.58 NTU**,** and color = 528.67 ± 0.58 ºH were above the WHO-

recommended limits. Generally, the variations in the physicochemical parameters observed in May and October 2019 were probably attributable to rainfall influence (Ling *et al.,* 2017). Except for color, turbidity, and pH, the mean range of EC, temperature, and TDS fell within the WHO guidelines in the dry and rainy months along the Mara River and its tributaries. Similar findings were reported by Fawaz *et al.* (2013) and Muniz *et al.* (2020), who concluded that it was probably attributed to higher ion dilution in water.

The minimum and maximum mean temperature of water samples in tributaries in May 2019 were 24.70 ± 0.20 ºC and 32.50 ± 0.60ºC at Tigithe and Nyarusondobiro, respectively (Table 3 and Fig. 6a). The minimum and maximum mean water temperatures recorded along the Mara River in the same month were 25.70 ± 0.40 ºC and 28.40 ± 0.50ºC at Kirumi Bridge and Mara Darajani, respectively (Table 3 and Fig. 6b). In all sampling locations, the mean temperatures in May 2019 were within the standard acceptable range of 20 to 35ºC for aquatic environments. Water temperature in aquatic environments acts as a master of biotic systems. It influences all the life processes of aquatic poikilothermic organisms (Dallas & Ross-Gillespie, 2015). Moreover, it is a driver of aquatic organisms' existence, including feeding, growth, metabolisms, emergence, fecundity and survival (Dallas & Ross-Gillespie, 2015). According to Kale (2016), warm water does not hold enough oxygen for aquatic organisms to survive. At high temperatures, oxygen solubility in water decreases, reducing its concentration and availability to marine organisms (Kale, 2016). Moreover, the elevated water temperature facilitates heavy metals sorption by minerals (Huang *et al.*, 2017).

Table 3: Mean physicochemical parameters of water samples collected from the Mara River tributaries for two months of 2019

Site name	Temp (ºC)	pH	EC (µS/cm)	TDS (mg/L)	Turbidity (NTU)	Color (ºH)
Dry month (May 2019)						
Tobora	32.0 ± 0.52	8.90 ± 0.10	958.33 ± 0.58	478.33 ± 0.58	31.67 ± 0.58	277.00 ± 1.00
Somoche	27.80 ± 0.20	8.70 ± 0.50	186.67 ± 0.58	93.00 ± 1.00	1159.33 ± 0.58	2332.33 ± 0.58
Gurubi	28.20 ± 0.50	8.60 ± 0.10	398.00 ± 0.00	199.00 ± 0.00	1693.67 ± 0.58	10953.33 ± 0.58
Tigithe	24.70 ± 0.20	8.70 ± 0.00	576.67 ± 0.58	288.3 ± 1.50	98.00 ± 1.00	804.33 ± 0.58
Nyarwera	27.80 ± 0.60	8.60 ± 0.10	278.67 ± 0.58	138.7 ± 1.20	1170.33 ± 2.08	9384.33 ± 0.58
Nyarusondobiro	32.50 ± 0.60	8.70 ± 0.00	791.33 ± 0.58	395.67 ± 0.58	1046.67 ± 2.89	6880.0 ± 1.00
Mini.	24.70 ± 0.20	8.60 ± 0.10	186.67 ± 0.58	93.00 ± 1.00	31.67 ± 0.58	277.00 ± 1.00
Max.	32.50 ± 0.60	8.90 ± 0.10	958.33 ± 0.58	478.33 ± 0.58	1693.67 ± 0.58	10953.33 ± 0.58
Rainy month (October 2019)						
Tobora	29.40 ± 0.40	9.00 ± 0.00	684.00 ± 0.00	343.00 ± 0.00	44.00 ± 0.00	404.00 ± 0.00
Somoche	27.00 ± 0.40	7.60 ± 0.10	164.00 ± 0.00	82.00 ± 0.00	528.67 ± 0.58	4245.33 ± 1.00
Gurubi	27.50 ± 0.50	8.60 ± 0.00	594.33 ± 0.58	297.30 ± 0.58	225.33 ± 0.58	1565.33 ± 0.58
Tigithe	27.00 ± 0.00	9.00 ± 0.00	706.00 ± 0.58	352.00 ± 0.00	41.00 ± 0.00	268.00 ± 1.00
Nyarwera	27.10 ± 0.00	8.60 ± 0.00	488.00 ± 0.00	291.00 ± 0.00	512.00 ± 0.00	3944.00 ± 0.00
Nyarusondobiro	26.50 ± 0.00	8.90 ± 0.00	2103.00 ± 0.00	1052.00 ± 0.00	322.00 ± 0.00	2640.00 ± 0.00
Mini.	26.50 ± 0.00	7.60 ± 0.10	164.00 ± 0.00	82.00 ± 0.00	41.00 ±0.00	268.00 ± 1.00
Max.	29.40 ± 0.40	9.00 ± 0.00	2103.00 ± 0.00	1052.00 ± 0.00	528.67 ± 0.58	4245.33 ±1.00
[(a)]WHO	20 - 35	6.50 – 8.50	100 – 2000	1000	5.0	15.0

[(a)]WHO = World Health Organization

Heavy metals released in aquatic environments are pH - and temperature-dependent. At low pH and elevated temperatures, heavy metals are more easily released into the water (Kumar *et al.*, 2019).

4.2.1 Temperature Variations in Water Samples

Measurement of water temperature was repeated in October 2019 in the same sampling sites. The second round of sampling aimed to ascertain whether there was any variation between the two months. Dramatic changes in water temperature may result in respective fauna distributional changes in the aquatic ecosystems (Wałkuska & Wilczek, 2010). The results indicated that the minimum and maximum temperatures in October 2019 were 26.5ºC and 29.40 ± 0.40ºC at Nyarusondobiro and Tabora tributaries, respectively (Table 3 and Fig. 6a). Likewise, along the Mara River, the minimum and maximum water temperatures in October 2019 were 24.40 ± 0.70ºC and 27.50 ± 0.20ºC at Kirumi Bridge and Nyantare Area, respectively (Table 4 and Fig. 6b). The study area's water temperatures were within the acceptable WHO limits reported across the literature (Nkang, 2014). It is interesting to note that irrespective of the sites, water temperatures during the dry month were higher than temperatures during the rainy month.

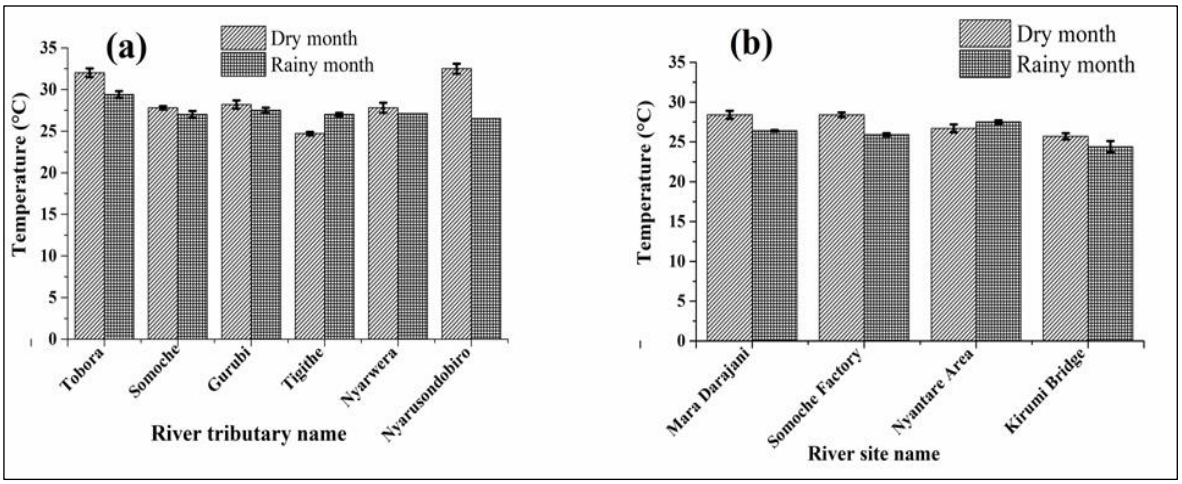


Figure 6: Mean temperatures of water samples collected from (a) river tributaries and (b) Mara River main course in the dry and rainy months

Table 4: Mean physicochemical parameters of water samples collected from the Mara River for two months of 2019

Site name	Temp (ºC)	pH	EC (µS/cm)	TDS (mg/L)	Turbidity (NTU)	Color (ºH)
Dry month (May 2019)						
Mara Darajani	*28.40 ± 0.50*	*9.10 ± 0.00*	*619.67 ± 0.58*	*309.70 ± 0.60*	*269.73 ± 0.64*	*1961.89 ± 0.84*
Somoche Factory	*28.30 ± 0.30*	*9.30 ± 0.10*	*564.33 ± 0.58*	*381.33 ± 0.58*	*506.33 ± 0.58*	*3648.33 ± 0.58*
Nyantare Area	*26.70 ± 0.50*	*8.50 ± 0.10*	*386.33 ± 0.58*	*193.33 ± 0.55*	*711.33 ± 0.58*	*3773.33 ± 0.58*
Kirumi Bridge	*25.70 ± 0.40*	*7.80 ± 0.10*	*334.33 ± 0.58*	*167.00 ± 0.00*	*16.33 ± 0.58*	*308.33 ± 0.58*
Mini	*25.70 ± 0.40*	*7.80 ± 0.10*	*334.33 ± 0.58*	*167.00 ± 0.00*	*16.33 ± 0.58*	*308.33 ± 0.58*
Max	*28.40 ± 0.50*	*9.30 ± 0.10*	*619.67 ± 0.58*	*381.33 ± 0.58*	*711.33 ± 0.58*	*3773.33 ± 0.58*
Rainy month (October 2019)						
Mara Darajani	26.40 ± 0.10	8.60 ± 0.70	99.30 ± 0.60	49.30 ± 0.60	349.67 ± 0.58	2956.67 ± 0.84
Somoche Factory	25.90 ± 0.20	7.70 ± 0.00	100.00 ± 0.00	50.00 ± 0.00	396.33 ± 0.58	2957.00 ± 0.58
Nyantare Area	27.50 ± 0.20	7.40 ± 0.10	107.67 ± 0.58	54.00 ± 0.00	521.33 ± 0.60	3614.00 ± 0.58
Kirumi Bridge	24.40 ± 0.70	7.60 ± 0.30	262.00 ± 1.00	132.00 ± 2.60	96.00 ± 1.00	1135.67 ± 0.58
Mini	24.40 ± 0.70	7.40 ± 0.10	99.30 ± 0.60	49.30 ± 0.6	96.00 ± 1.00	1135.67 ± 0.58
Max	27.50 ± 0.20	8.60 ± 0.70	262.00 ± 1.00	132.00 ± 1.00	521.33 ± 0.6	3614.00 ± 1.00
[(a)]WHO	20 - 35	6.5 – 8.5	100 - 2000	1000	5	15

[(a)]WHO = World Health Organization

4.2.2 pH variations in Water Samples

The pH scale is used to measure the intensity of acidity or alkalinity of water-based solutions (Rajendran *et al.*, 2015). The pH values in natural water are governed by carbon dioxide, bicarbonates, and carbonate ions in the equilibrium state (Bouaoun & Nabbout, 2016). The pH of water samples in May 2019 for all sampling tributaries ranged from pH 8.60 ± 0.10 to pH 8.90 ± 0.10 (Table 3 and Fig. 7a) for the minimum and maximum values, respectively. The minimum pH of 8.60 ± 0.10 was measured at Nyarwera and Nyarusondobiro tributaries, whereas the maximum pH = 8.90 ± 0.10 was measured at Tobora tributary. Likewise, along the Mara River, the minimum and maximum pH values in May were 7.80 ± 0.10 and 9.30 ± 0.10 at Kirumi Bridge and Somoche Factory, respectively (Table 4 and Fig. 7b).

Besides, during the rainy month, the minimum pH was pH = 7.60 ± 0.10 at Somoche tributary, while the maximum pH value of 9.0 was at Somoche and Tobora tributaries (Table 3 and Fig. 7a). The minimum and maximum pH along the Mara River in the same rainy month was pH = 7.40 ± 0.10 and 8.60 ± 0.70 at Nyantare Area and Mara Darajani, respectively (Table 4 and Fig. 7b).

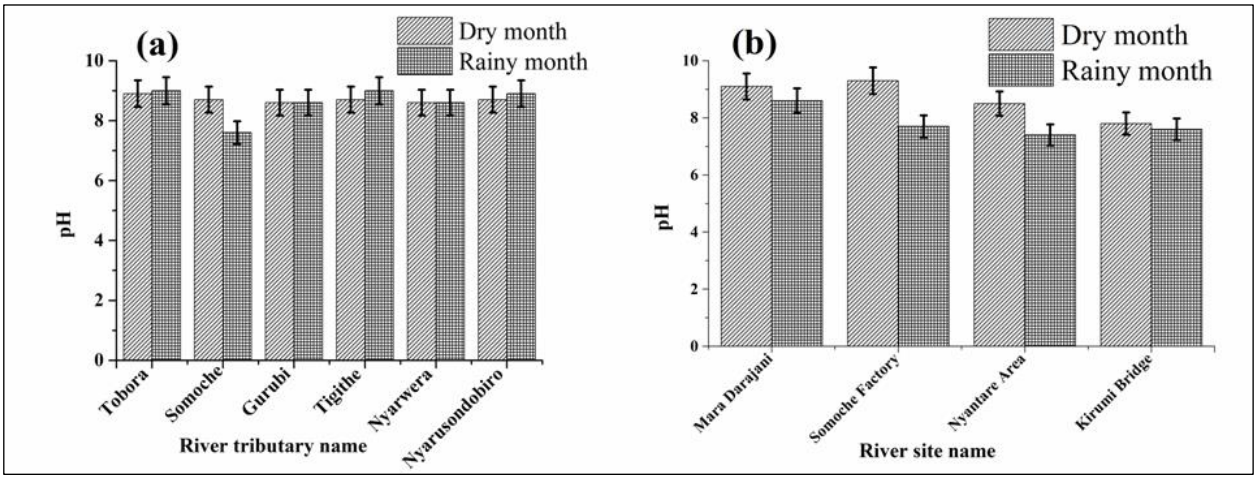


Figure 7: Mean pH values of water samples collected from (a) river tributaries and (b) Mara River main course in the dry and rainy months

The acceptable guideline values of pH by the US-EPA for aquatic environments are between pH= 6.5 and pH = 8.5 (EPA, 2006). For tributary samples, during the dry month, all pH values were slightly above the US-EPA guideline. According to Edokpayi *et al.* (2017), water with pH $<$ 4 and pH $>$ 9 tends to increase the toxicity and bioavailability of heavy metals and ammonium ions, respectively. For the tributary samples, during the dry month, none of the sites' pH values fell below pH 4, and none of the sites' pH values exceeded pH 9. It may, therefore, be concluded that the tributary surface water pH regime during the dry month did not indicate signs of heavy metals bioavailability and toxicity. During the rainy month, there were slight changes in the pH regime for

tributary water samples. Some sampling sites, e.g., Somoche, registered a pH value that is acceptable by US-EPA and WHO guidelines. However, the rest of the sampling stations' pH values exceed the US-EPA and WHO maximum values of 8.5. Again, none of the sites' pH was above 9.0 – indicating acceptability in terms of metal ion mobility, bioavailability, and toxicity to the environment (Edokpayi *et al.*, 2017).

For the main river course samples, during the dry month, Mara Darajani and Somoche factory samples indicated some concerns. The pH values for the two sites mentioned above were 9.10 and 9.30, respectively, during the dry month (Table 4, Fig. 7b). This would mean that, during the dry month, for the Mara River main course samples, at Mara Darajani and Somoche Factory, there was a possibility of metal mobilization, bioavailability, and toxicity (Edokpayi *et al.*, 2017; Jhariya *et al.*, 2016). It should be noted that the Somoche Factory site was located close to a stone-cutting facility (Plate 7) – this could have led to the pH changes observed. However, during the rainy month and for the samples collected from the main course of the Mara River, the pH regime indicated that no sample posed a threat in terms of metal mobility and toxicity.

Plate 7: Somoche Factory for cutting of natural rocks used to make house tiles (Present study)

4.2.3 Water samples' EC values

The EC is defined as the capacity of water or an aqueous solution to conduct an electric current (Shigut *et al.*, 2016). The ability to conduct electric current depends on the concentration and mobility of ions, valence electrons, and liquid temperature (Gorde & Jadhav, 2013). The minimum

and maximum EC values for tributary samples in May 2019 were 186.67 ± 0.58 µS/cm and 958.33 ± 0.58 µS/cm at Somoche and Tobora, respectively (Table 3 and Fig. 8a). The minimum and maximum EC values along the Mara River in the same month were 334.33 ± 0.58 µS/cm and EC 619.67 ± 0.58 µS/cm at Kirumi Bridge and Mara Darajani, respectively (Table 4 and Fig. 8b). For samples collected from the main river course, the EC values were in decreasing order downstream. This would mean that downstream samples were less polluted compared to upstream ones. Higher EC values at Mara Darajani (upstream) would also mean that there were probably some anthropogenic inputs due to farming, small factories, and mining activities (Table 4 and Fig. 8b). Clay soils and polluted materials may ionize into the water, raising the EC in water solutions (Bhateria & Jain, 2016).

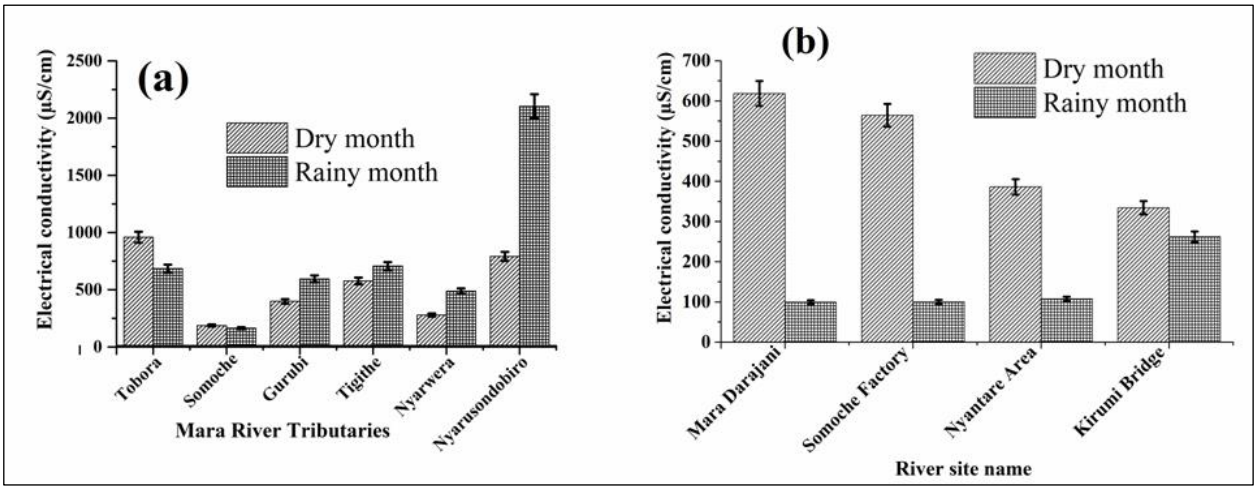


Figure 8: Mean EC values of water samples collected from (a) river tributaries and (b) Mara River main course in the dry and rainy months

During the rainy month of October 2019, the minimum and maximum EC in Mara River tributaries were EC 164.0 µS/cm and EC 2103.0 µS/cm at Somoche and Nyarusondobiro (Table and Fig. 8a). The EC along the Mara River in the same month was 99.30 ± 0.60 µS/cm and 262.00 ± 1.00 µS/cm at Mara Darajani and Kirumi Bridge, respectively **(**Table 4 and Fig. 8b). The allowable limit EC values by WHO are EC 100–2000 µS/cm (Daghara *et al.*, 2019). The EC values in aquatic environments are good indicators of water salinity (Akther *et al.*, 2018; Seng *et al.*, 2018). The EC in all sampling sites was within the WHO guideline values. However, samples collected from the Nyarusondobiro tributary (2103.0 µS/cm) EC were above the WHO guideline limit. The EC in aquatic environments is usually affected by dissolved solids like sulfate, aluminium, nitrate, iron, magnesium and others (Al-Badaii *et al.*, 2013). The EC at Nyarusondobiro was high in the rainy month (Table 3 and Fig 8a). The high EC at Nyarusondobiro may be due to the high levels of charged particles that increase the conductivities (Tutmez *et al.*, 2006).

4.2.4 Variations in water Total Dissolved Solids

Total dissolved solids (TDS) comprise organic matter measures, inorganic salts, and other dissolved substances in water (Scannell & Duffy, 2007). The most common constituent ions in water are magnesium, calcium, sodium and potassium. Other ions are carbonates, hydrogen carbonates, chlorides, sulfates, and nitrate ions (Islam *et al.*, 2017). In practice, measurements of total dissolved solids do not identify the individual ions or compounds in the solution and their sources, but it measures the total amount of dissolved solutes (Benham *et al.*, 2011). The minimum and maximum TDS in tributaries measured in the dry month were 93.00 ± 1.0 mg/L and 478.33 ± 0.58 mg/L at Somoche and Tobora, respectively (Table 3 and Fig. 9a). During the dry month, along with the Mara River sites, the minimum and maximum TDS were 167.0 mg/L and 381.33 ± 0.58 mg/L at Kirumi Bridge and Somoche Factory respectively (Table 4 and Fig. 9b). The guideline limit for TDS by WHO is around 1000 mg/L (Tadesse *et al.*, 2018). In dry months, the TDS in all sampling sites was less than 1000 mg/L, favorable for aquatic environments.

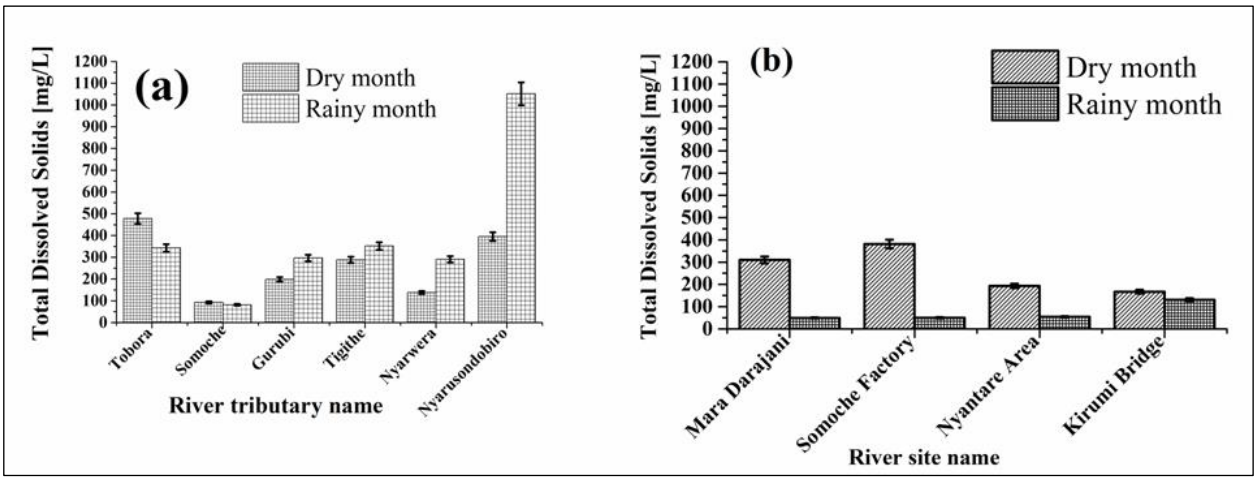


Figure 9: Mean TDS values for water samples collected from (a) river tributaries and (b) Mara River main course in the dry and rainy months

In the rainy month, the minimum and maximum TDS in tributaries were 82.0 mg/L and 1052.0 mg/L at Somoche and Nyarusondobiro, respectively (Table 3 and Fig. 9a). Along the Mara River, the minimum and maximum TDS were 49.30 ± 0.60 mg/L and 132.00 ± 1.0 mg/L at Mara Darajani and Kirumi Bridge, respectively (Table 4 and Fig. 9b). In the rainy month, all the measured TDS levels in tributaries and along the Mara River fell within the acceptable WHO guideline of less than 1000 mg/L (Rahmanian *et al.*, 2015). In addition, the levels of TDS at Mara Darajani (upstream) to downstream (Kirumi Bridge) followed a generally decreasing trend (Fig. 9b) – a probable linkage to polluting activities in the upstream areas (Wozniak, 2011).

4.2.5 Turbidity Levels in Water

Turbidity is a handy indicator for providing valuable information about pathogenic microorganisms and abnormal conditions in the water system (WHO, 2017). Turbidity is a condition caused by dissolved or suspended chemicals or biological particles in water, which cause light scattering and make the water appear cloudy (Gebreyohannes *et al.*, 2015). In the dry month, the minimum and maximum turbidity levels in tributaries were 31.67 ± 0.58 NTU and 1693.67 ± 0.58 NTU at Tobora and Gurubi, respectively (Table 3 and Fig. 10a). Likewise, the minimum and maximum turbidity levels along the Mara River during the dry month (Table 4 and Fig. 10b) were 16.33 ± 0.58 NTU and 711.33 ± 0.58 NTU Kirumi Bridge and Nyantare Area, respectively. The turbidity levels in all tributaries were very high compared to WHO guidelines for drinking water quality of 5 NTU reported by Achieng *et al.* (2019). High water turbidity was probably caused by colloidal, fine particles of clay silt (Davies-Colley & Smith, 2007). All tributaries received water from artisanal mining, farming areas, and village settlements, which could have contributed to the observed turbidity levels (Mujere & Isidro, 2016).

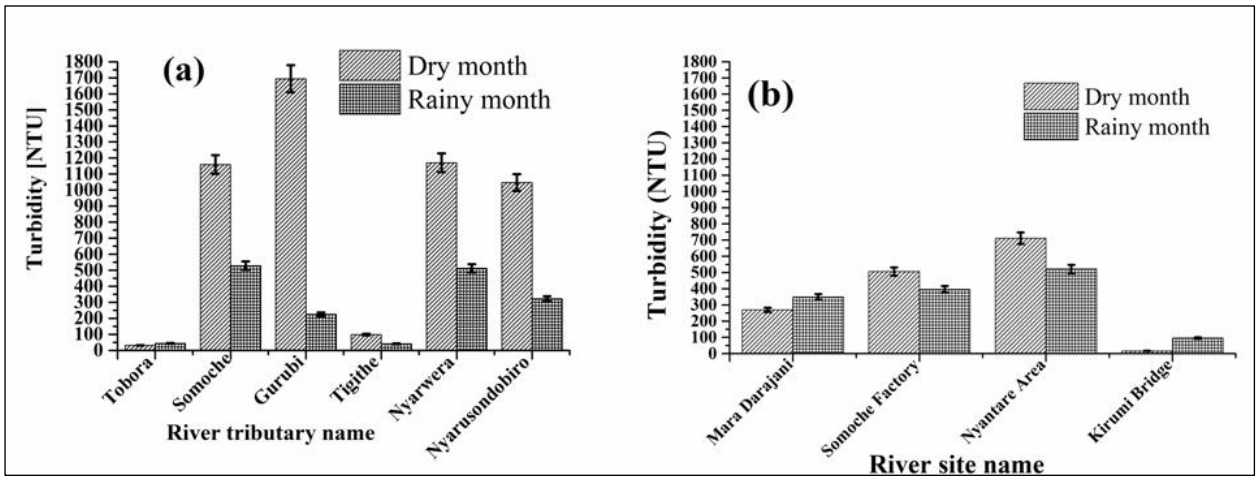


Figure 10: Mean turbidity levels for water samples collected from (a) river tributaries (b) Mara River main course in the dry and rainy months

During the rainy month, the minimum and maximum turbidity levels recorded in tributaries were 41.0 NTU and 528.67 ± 0.58 NTU at Tigithe and Somoche, respectively (Table 3 and Fig. 10a). Besides, along the Mara River, the minimum and maximum turbidity levels recorded in the rainy month were 96.00 ± 1.00 NTU and 521.33 ± 0.60 NTU at Kirumi Bridge and Nyantare Area, respectively (Table 4 and Fig. 10b). The high turbidity levels in the Mara River and its tributaries were probably attributed to human activities in their catchment areas (Søndergaard & Jeppesen, 2007).

4.2.6 Watercolor Variations

Colour in water can be caused by dissolved metals, humic, and fulvic materials (UNICEF, 2008). The minimum and maximum mean recorded color contents in tributaries in the dry month were 277.00 ± 1.00 ºH and 10953.33 ± 0.58 ºH at Tobora and Gurubi, respectively (Table 3 and Fig. 11a). Along the Mara River, the minimum and maximum mean color levels during the same month were 308.33 ± 0.58 ºH and 3773.33 ± 0.58 ºH at Kirumi Bridge and Nyantare Area, respectively (Table 4 and Fig. 11b). The WHO recommended guideline limit for watercolor (true color unit) should be TCU < 15 (Kordach *et al.*, 2018). A high level of color in water tributaries was probably associated with plankton, weed species, industrial waste, humus, peat materials, and metallic elements (Wilson, 2010). Tobora and Gurubi tributaries collect water from artisanal gold mining, responsible for water contamination with iron, manganese, and copper.

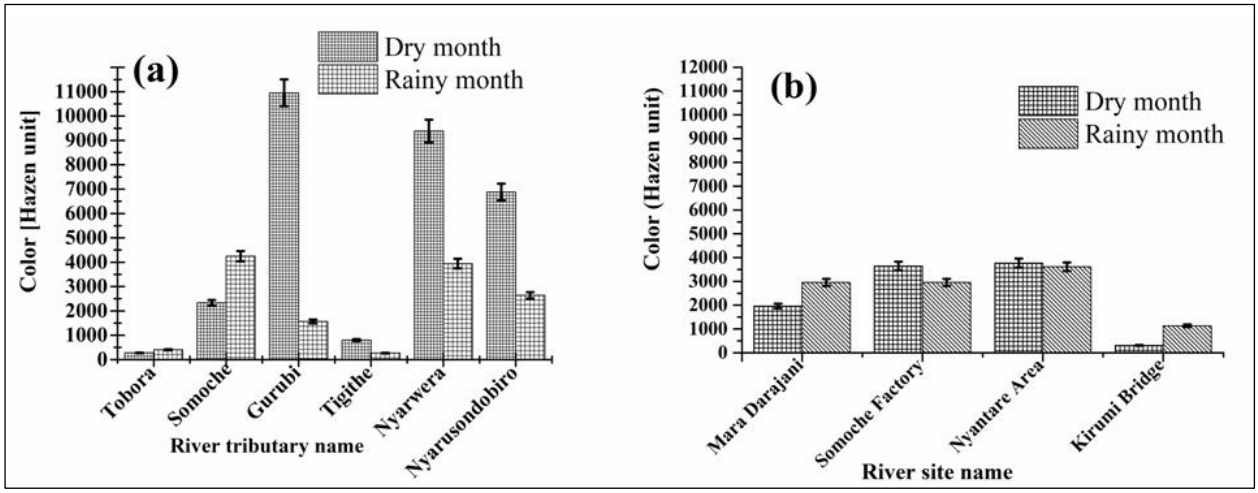


Figure 11: Color for (a) tributary water samples and (b) the main river samples in the dry and rainy months

During the rainy month, the minimum and maximum levels of color in water tributaries were 268.00 ± 1.00 ºH and 4245.33 ± 1.00 ºH at Tigithe and Somoche, respectively (Table 3 and Fig. 11a). Besides, along the Mara River, the minimum and maximum recorded watercolors were 1135.67 ± 0.58 ºH and 3614.00 ± 1.00 ºH at Kirumi Bridge and Nyantare area, respectively (Table 4 and Fig. 11b). A similar condition was reported by other researchers to be associated with the dissolution of chemical elements from artisanal mining due to natural water runoff in stream catchments (Rajaee *et al.*, 2015). Along the Mara River, the watercolor level decreased from upstream downwards. This was probably due to water dilution along the river (Khatri & Tyagi, 2014).

4.3 Heavy Metals in the Sediments from Mara River Tributaries

The mean concentrations of As, Cd, Cr, Hg and Pb in Mara River tributaries in sediments during the dry and rainy months are presented in Table 5. The mean value for As concentration was 20.78 ± 0.15 mg As/kg and ranged from 11.77 ± 0.02 mg As/kg to 30.81 ± 0.02 mg/kg. The concentration of As in sediments in the dry month was higher than Cd, Cr, Hg, and Pb, and above the consensus-based concentration (TEC) (Baeyens *et al.*, 2019). The concentrations of Cd, Cr, Hg and Pb ranged from 0.17 ± 0.02 mg/kg to 1.30 ± 0.09 mg/kg, 0.97 ± 0.49 mg/kg to 1.56 ± 0.50 mg/kg, 0 to 0.01 mg/kg, and 8.36 ± 0.51 mg/kg to 17.45 ± 1.22 mg/kg, respectively. The mean values for Cd, Cr, Hg and Pb were 0.41 ± 0.29, 1.25 ± 0.45, 0 and 13.00 ± 0.64 mg/kg, respectively.

During the rainy month, the concentration of As ranged from 24.25 ± 0.02 mg As/kg to 53.11 ± 0.02 mg As/kg with an average value of 36.45 ± 0.09 mg/kg (Table 5). The Cd concentration ranged from 0.95 ± 0.20 mg Cd/kg to 2.25 ± 0.35 mg Cd/kg with an average value of 1.46 ± 0.27 mg Cd/kg. The Cr concentration ranged from 1.21 ± 0.46 mg Cr/kg to 2.58 ± 0.57 mg Cr/kg with an average value of 1.71 ± 0.42 mg Cr/kg. The Hg and Pb concentrations ranged from 0 to 0.012 mg/kg, 2.45 ± 0.05 mg/kg to 4.37 ± 0.28 mg/kg with their mean value of 0.01 mg/kg and 2.98 ± 0.17 mg/kg, respectively. Likewise, the concentration of As in sediments during the rainy month was more elevated than that of Cd, Cr, Hg and Pb. Arsenic sources in surface and subsurface waters and sediments may be natural or anthropogenic (Ahoulé *et al.*, 2015). Studies from different literature (Perera *et al.*, 2016; Tareq *et al.*, 2011) reported that elevated levels of As during the rainy season are attributed to erosion from agricultural land, mining areas as well as weathering of As-bearing minerals. Geographically, the Mara basin is widely impacted by the spread of human activities such as the expansion of agricultural land, deforestation, excessive use of fertilizers, mining operations, and progressive urbanization (Bich *et al.*, 2017). The Mara River has been most vulnerable to flow alterations under low flow conditions (NELSAP-CU, 2020). A decrease in river flow conditions and low oxygen levels in water may lead to elevated As concentrations in water and sediments (Robinson *et al.*, 2015). According to Feng *et al.* (2013), adsorption and desorption of As in As-bearing minerals may affect the mobility, toxicity, and bioavailability of As in sediments. Mining and processing of As-bearing minerals in the study area may have contributed to the high concentrations of As in water and sediments in the rainy period (Drewniak & Sklodowska, 2013).

Results from heavy metal concentrations in sediments were compared to well-known statistical data levels in the SQGs reported in the literature (Burton & Allen, 2002). When the concentrations of As, Cd, Cr, Hg, and Pb in sediment were compared to SQGs values, they revealed that only As and

Cd were likely to impact ecological on sediment-dwelling organisms. Elevated As concentration in the environment may cause skin cancer, urethra cancer, and liver cancer in people throughout the food chain (Ackova, 2018). In addition, elevated As in sediments may inhibit root extension in aquatic plants. The sources of As in the environment could be both natural and anthropogenic. Cadmium is the most toxic heavy metal to most organisms (Mahdi *et al.*, 2021). The Cd is known to have a long biological half-life that accounts for more than 20 years (Suwazono *et al.*, 2009). Cadmium has higher mobility in soil-plant systems and may impact the ecosystem (Haider *et al.*, 2021). The level of Cd was 1.30 ± 0.09 mg Cd/kg at Somoche tributary in the dry month, which was likely to be contributed by natural and, to some extent, anthropogenic activities (Table 5 and Fig. 13).

Table 5: Heavy metals concentrations in sediments during the dry and rainy months in the Mara River tributaries

	Elemental concentrations ± SD[(a)] (mg/kg DW[(b)])				
Site name	**As**	**Cd**	**Cr**	**Hg**	**Pb**
Dry month (May 2019)					
Tobora	14.51 ± 0.18	0.18 ± 0.70	1.18 ± 0.70	0	17.45 ± 1.22
Somoche	19.63 ± 0.20	1.30 ± 0.90	0.97 ± 0.49	0	12.82 ± 0.89
Gurubi	29.99 ± 0.02	0.27 ± 0.05	1.25 ± 0.44	0	14.09 ± 0.65
Tigithe	17.97 ± 0.11	0.23 ± 0.02	1.36 ± 0.37	0	14.35 ± 0.28
Nyarwera	30.81 ± 0.02	0.32 ± 0.05	1.18 ± 0.18	0.011	8.36 ± 0.51
Nyarusondobiro	11.77 ± 0.02	0.17 ± 0.02	1.56 ± 0.50	0	10.92 ± 0.31
Mean	20.78 ± 0.15	0.41 ± 0.29	1.25 ± 0.45	0	13.00 ± 0.64
Mini	11.77 ± 0.02	0.17 ± 0.02	0.97 ± 0.49	0	8.36 ± 0.51
Max	30.81 ± 0.02	1.30 ± 0.09	1.56 ± 0.50	0.01	17.45 ± 1.22
Rainy month (October 2019)					
Tobora	27.20 ± 0.18	0.95 ± 0.20	1.54 ± 0.40	0.004	2.45 ± 0.05
Somoche	40.52 ± 0.20	1.53 ± 0.56	1.21 ± 0.55	0	4.37 ± 0.28
Gurubi	41.44 ± 0.02	1.45 ± 0.22	1.78 ± 0.20	0.004	2.64 ± 0.17
Tigithe	32.19 ± 0.11	1.34 ± 0.22	1.21 ± 0.46	0	2.65 ± 0.10
Nyarwera	53.11 ± 0.02	2.25 ± 0.35	1.94 ± 0.35	0.012	2.98 ± 0.26
Nyarusondobiro	24.25 ± 0.02	1.21 ± 0.06	2.58 ± 0.57	0.007	2.81 ± 0.13
Mean	36.45 ± 0.09	1.46 ± 0.27	1.71 ± 0.42	0.01	2.98 ± 0.17
Mini	24.25 ± 0.02	0.95 ± 0.20	1.21 ± 0.46	0	2.45 ± 0.05
Max	53.11 ± 0.02	2.25 ± 0.35	2.58 ± 0.57	0.012	4.37 ± 0.28
TEL[(c)]	5.9	0.596	37.3	0.174	35
LEL[(d)]	6	0.6	26	0.2	31
MET[(e)]	7	0.9	55	0.2	42
ERT[(f)]	33	5	80	0.15	35
Consensus Based TEC[(g)]	9.79	0.99	43.4	0.18	35.8
Bckgr.[(h)]	0.08	0.186	18.79	39.8	53.71

[(a)]SD = Standard deviation; [(b)]DW = dry weight; [(c)]TEL = Threshold effect level; [(d)]LEL = Lowest effect level; [(e)]MET = Minimal effect threshold; [(f)]ERL = Effects range low; [(g)]TEC = Threshold effect concentration; Bckgr. = Background values.

Compared to the SQGs, the measured levels of Cr, Hg, and Pb were unlikely to cause serious ecological damage to sediment species (Table 5). The levels of As in all tributaries were elevated

during the rainy month. This is not surprising because As has been reported by Renard *et al.* (2015) to be present in carbonates and iron-oxide minerals. The leaching of As in sediments is usually a season-dependent phenomenon (wet or dry); also, As mobilization depends much on available organic compounds, which vary over time (Hwang *et al.*, 2019). Intense precipitation during the rainy periods and enhanced mineral desorption from parent rocks were reported by Luo *et al.* (2021) to increase the release of As multifold.

Studies conducted by Kassenga and Mato (2008) in the Lake Victoria basin where the Mara River is found revealed that As contamination in mining areas was prevalent. Exposure of As in the environment is facilitated through oxidation of sulfide minerals as well as the dispersion from secondary processed materials, mainly As-containing oxides. So, mine wastes, especially those relating to As–bearing minerals such as arsenopyrite, marcasite, dimorphs, orpiment, and tailings, are known to be significant sources of As in the environment and have to be adequately managed (Craw & Bowell, 2014).

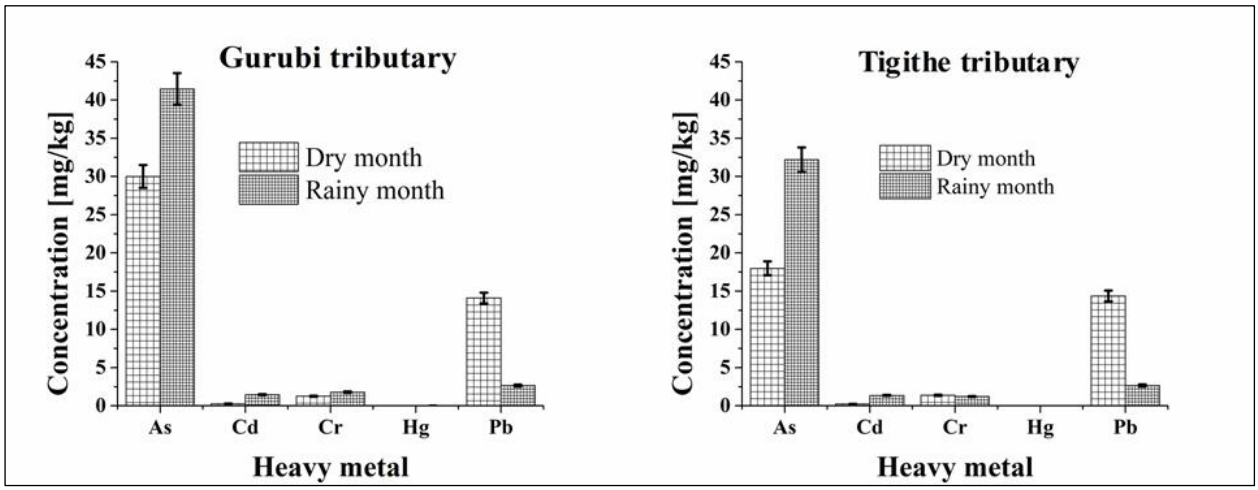


Figure 12: Levels of heavy metals in sediments at Gurubi and Tigithe tributaries in the dry and rainy months of 2019

Besides, concentrations of As, Cd, Cr, Hg and Pb in sediments were also compared to background values (Table 5) (Sany *et al.*, 2012). Results revealed that the concentration of As and Cd exceeded the background values in both months. The concentration of As and Cd in sediments was above background values, suggesting that they probably originated from anthropogenic sources (Table 5, Fig. 12, 13 and 14). Furthermore, Cr, Hg and Pb concentrations were less than the background values at all sites, implying that they probably originated from natural sources (Table 5, Fig. 12, 13 and 14). Contamination of As, Cd, Cr, Hg and Pb in dry and rainy months followed the series: As > Pb > Cr > Cd > Hg (Table 5, Fig. 12, 13 and 14). The series of five heavy metals studied when ranked shows As as the most contaminants heavy metals during the dry and rainy months. The As is mobilized and produced naturally in water and soil through weathering processes and

microbial activities. Moreover, anthropogenic activities, mainly metal mining, groundwater abstraction and application of As-based pesticides in agriculture and forest preservation, increase the contamination of As in water and sediments (Appelo *et al.*, 2008).

Lead (Pb) is the most natural abundant xenobiotic metal in the environment (Karrari *et al.*, 2012). Its application comprises more than 900 industries, including mining, smelting, refining, and battery manufacturing (Karrari *et al.*, 2012). Concentrations of Pb in the natural environment are usually relatively low. However, due to human activities, the levels of Pb in a particular area may exceed that of natural abundance (Adeyemo, 2010). Thus far, the sources of Pb in sediments and water are both natural processes and anthropogenic activities. The natural sources of Pb include volcanic activity and the weathering of rocks. Mobilization of Pb from anthropogenic sources such as fossil fuels; extracted and treated metals; mining and processing activities; incineration for municipal waste; open burning of dumpsites; mine tailings; and smelter slag may contaminate water sources (UN, 2010). Although the Pb contents in the samples were ranked at the second-highest level, their consensus-based threshold effect concentrations (TEC) were deficient and indicated no impact on aquatic-dwelling organisms (Table 5, Fig. 12, 13 and 14).

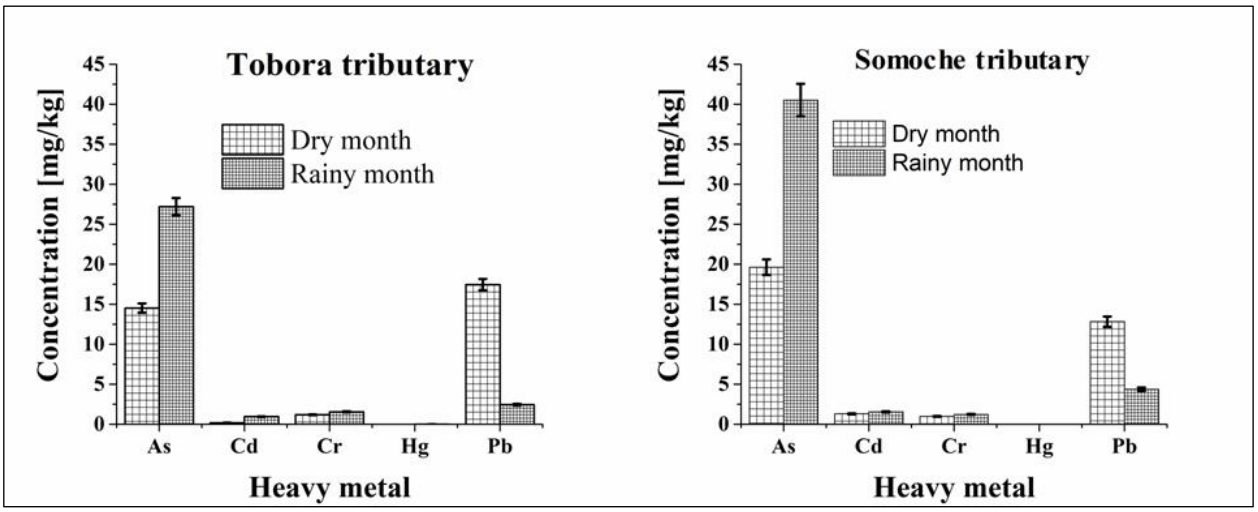


Figure 13: Level of heavy metals concentrations in sediments at Tobora and Somoche tributaries in the dry and rainy months of 2019

Cadmium (Cd) is considered a highly toxic element in the environment, and its concentration directly impacts human health (Rzętała, 2016). The Cd can be taken in the body through air and water intake and thereafter accumulates in the kidney, which may cause cancer and cardiovascular ailments. The Cd can cause adverse health effects to people even at deficient dose intakes leading to cough, headaches, nausea, and vomiting. At high intake dosages, Cd accumulates in the kidney and liver, leading to calcium displacement in bones, causing bone disorders and, at times, renal failure (Burke *et al.*, 2016). The consensus-based threshold effect concentration (TEC) for Cd in

sediments is 0.99 mg Cd/kg. The Cd is naturally found in rocks, coal, and petroleum in a very low concentration (Burke *et al.*, 2016). The level of Cd at Somoche tributary exceeded the TEC and background values in the dry month and may impact sediment-dwelling organisms (Table 5). The Cd levels were above the TEC and background values in all river tributaries except at Tobora tributary (Table 5 and Fig. 13). The elevated levels of Cd, Pb, and As in all tributaries during the rainy month were probably caused by poor management of mining wastes emanating from artisanal and small-scale mining (ASM). Similar findings were reported by Chiba *et al.* (2011) that elevated contamination of metallic elements were probably caused by poor disposal of solid waste.

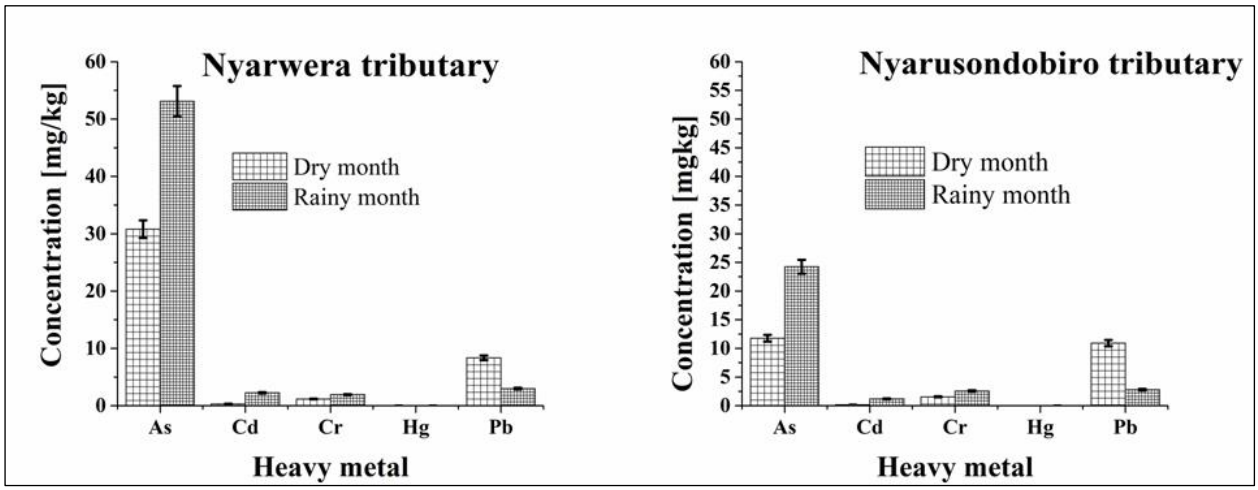


Figure 14: Level of heavy metals concentrations in sediments at Nyarwera and Nyarusondobiro tributaries in the dry and rainy months of 2019

(i) Pearson Correlation Analysis for Sediment Metals

A positive correlation between As and Hg ($r = 0.66$, $p < 0.01$) in sediments during the dry month was observed (Table 6). This positive correlation between arsenic and mercury in sediments during the dry month could indicate that these two elements in sediments probably came from a similar source of input (Pal *et al.*, 2017). Furthermore, a negative correlation between As and Cr ($r = -0.56$, $p < 0.05$), As and Pb ($r = -0.63$, $p < 0.05$), Cd and Cr ($r = -0.74$, $p < 0.05$), Hg and Pb ($r = -0.72$, $p < 0.05$ were observed in sediments in the dry month. This negative correlation could signify diversity and independence in the sources of these pairs of heavy metals in sediment contamination (Jiao *et al.*, 2018). It is also known that the correlation of heavy metals in the environment poses complicated relationships (Li *et al.*, 2012).

Table 6: Pearson correlation matrix of heavy metals in sediment tributaries in the dry and rainy months of 2019

	As	Cd	Cr	Hg	Pb
Dry month (May 2019)					
As	1.0				
Cd	0.34	1.0			
Cr	-0.54	-0.74	1.0		
Hg	0.66	-0.33	0.06	1.0	
Pb	-0.63	-0.09	-0.14	-0.72	1.0
Rainy month (October 2019)					
As	1.0				
Cd	0.92**	1.0			
Cr	-0.17	0.07	1.0		
Hg	0.39	0.60	0.65	1.0	
Pb	0.33	0.29	-0.34	-0.40	1.0

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

Likewise, in the rainy month significant positive correlation was found between As and Cd (r = 0.92, p < 0.01), and positive correlation between Cd and Hg (r = 0.60, p < 0.01), Cr and Hg (r = 0.65, p < 0.01). Heavy metals with a high correlation may indicate a similar origin and controlling factors (Pande *et al.*, 2015). Weak correlation coefficients for some of the heavy metal pairs were probably caused by dilution effects (Zhang, 2018).

(ii) PCA for Sediment Metals

The biplot of PC1 versus PC2 in Fig. 15 (a) with eigenvalues greater than 1 accounted for 87.07% of the total cumulative variance. The PC1 was loaded with As, Hg and Pb, which explains 48.17% of the total variance. Moreover, PC2 was loaded with Cr, Hg and Cd, accounting for 38.89% of the total variance.

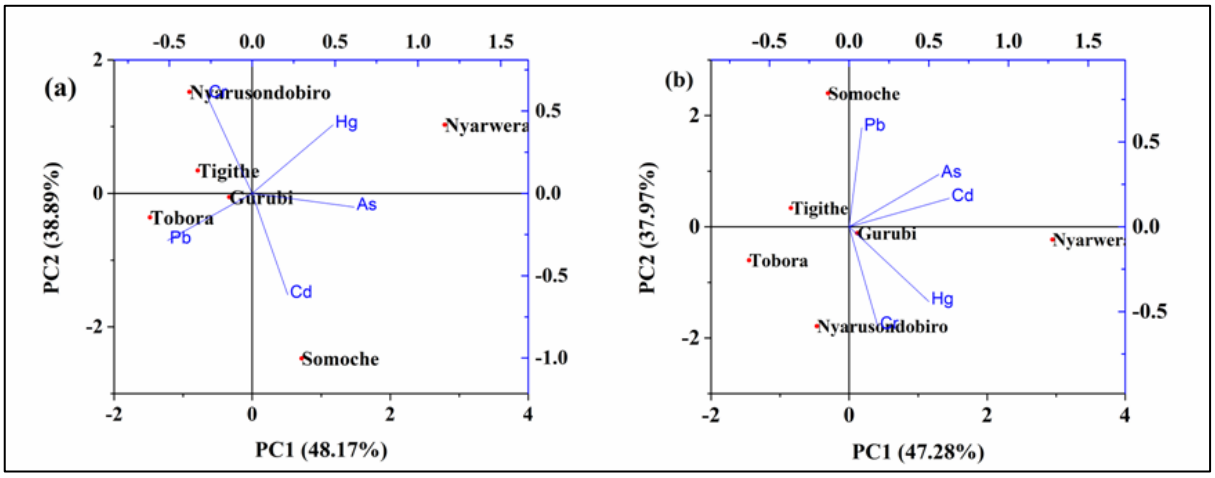


Figure 15: PCA biplots of heavy metals in sediments for Mara River tributaries in (a) dry month (b) rainy month

Sampling locations at Gurubi, Tobora, Tigithe and Nyarwera in sediment were moderately contaminated by As, Pb and Hg in PC1 (Fig. 15a). Therefore, contamination of As, Pb and Hg were probably coming from natural or anthropogenic sources. In PC2 (Fig. 15a), sediments in river tributaries of Nyarusondobiro, Gurubi, Tigithe were moderately contaminated by Cd, Cr and Hg in the same month. Therefore, Cd, Cr, and Hg could have originated from a similar geological or anthropogenic source, e.g., agriculture (pesticide and fertilizer applications (Yi *et al.*, 2020).

In the rainy month (Fig. 15b), the PC1 was loaded with As, Cd, and Hg, accounting for 47.28% of the total sources. Similarly, PC2 (Fig. 15b) in the same month accounted for 37.97% of the total variance and was loaded with Pb, Cr, and Hg. Hence, the total cumulative variance for PC1 and PC2 with Eigenvalues greater than 1 accounted for 85.25%. Moderate to elevated contamination of As, Cd, and Hg at Nyarwera, Gurubi, Tigithe and Tobora tributaries was found in PC1 (Fig. 15b). A significant correlation between As and Cd depicted in Table 15 and PC1 during the rainy month was probably due to the churning of sediments due to water increase in streams (Čmelík *et al.*, 2019). Contamination of As, Cd and Hg in tributaries may have come through varied pathways, including point and nonpoint sources. The point sources could have been related to discharges from mine wastes through pipes or drains. Nonpoint sources were probably associated with silt-laden runoff from excavated land, and leachate, which contributes to heavy metals discharge into aquatic environments (Duncan *et al.*, 2018). Similarly, in PC2, Pb, Cr, and Hg, contamination was observed at Somoche, Gurubi and Nyarusondobiro sites. Contamination of Pb in PC2 may have come from forest fires and wood burning reported in the study area (LVBC, 2011). Similarly, Cr and Hg in PC2 contamination could have originated from bedrock weathering and mine waste (Zhou *et al.*, 2020).

4.4 Heavy Metals in Tributary Waters

The concentration and distribution of As, Cd, Cr, Hg and Pb in water samples collected from river tributaries during the dry and rainy months are hereby indicated (Table 7, Fig. 16, 17 and 18). The concentration of As, Cd, Cr, Hg and Pb ranged from minimum 0.09 ± 0.03 to maximum value of 0.47 ± 0.06; 0.52 ± 0.07 to 0.74 ± 0.10; 0.46 ± 0.05 to 0.68 ± 0.09; 0.01 to 0.04 and 0.40 ± 0.05 to 0.76 ± 0.09 mg/L in the dry month, respectively. Moreover, the concentrations of As, Cd, Cr, Hg, and Pb were 0.09 ± 0.03 to 0.47 ± 0.06; 0.24 ± 0.03 to 0.48 ± 0.03; 0.20 ± 0.05 to 0.55 ± 0.03; 0 to 0.03; and 0.28 ± 0.04 to 0.56.0 in mg/L in the rainy month, respectively. Compared to the US-EPA and WHO guidelines, the concentrations of As, Cd, Cr, Hg and Pb exceeded the recommended limits in all tributaries (Table 7, Fig. 16, 17 and 18) (Dkhar *et al.*, 2014). Environmental processes, e.g., land degradation, deforestation, and poor mining waste management, may have led to the

observed distribution of As, Cd, Hg and Cr. Some human-caused with a mix of nature-cause forces, e.g., soil weathering, forest fires, and volcanic activities, may have influenced Pb levels in the studied samples (Zhang *et al.*, 2015). The pattern of heavy metals concentration in the dry and rainy months followed the order: $\mathrm{Pb} > Cd > Cr > As > Hg$ and $\mathrm{Pb} > Cr > Cd > As > Hg$, respectively (Table 7, Fig. 16, 17 and 18).

Table 7: Heavy metals concentration in surface water collected from the river tributaries in the dry and rainy months of 2019

	Elemental concentrations ± SD[(c)] (mg/L)				
Site name	**As**	**Cd**	**Cr**	**Hg**	**Pb**
	Dry month (May 2019)				
Tobora	0.47 ± 0.06	0.56 ± 0.60	0.53 ± 0.06	0.01 ± 0.00	0.59 ± 0.06
Somoche	0.37 ± 0.05	0.52 ± 0.07	0.46 ± 0.05	0.03 ± 0.01	0.42 ± 0.07
Gurubi	0.32 ± 0.05	0.74 ± 0.10	0.55 ± 0.06	0.01 ± 0.00	0.76 ± 0.09
Tigithe	0.23 ± 0.08	0.62 ± 0.06	0.47 ± 0.03	0.01 ± 0.00	0.66 ± 0.05
Nyarwera	0.09 ± 0.03	0.66 ± 0.10	0.57 ± 0.06	0.03 ± 0.01	0.40 ± 0.05
Nyarusondobiro	0.22 ± 0.00	0.63 ± 0.05	0.68 ± 0.09	0.04 ± 0.00	0.75 ± 0.06
Mean	0.28 ± 0.05	0.62 ± 0.16	0.54 ± 0.06	0.02	0.60 ± 0.06
Min	0.09 ± 0.03	0.52 ± 0.07	0.46 ± 0.05	0.01 ± 0.00	0.40 ± 0.05
Max	0.47 ± 0.06	0.74 ± 0.10	0.68 ± 0.09	0.04 ± 0.00	0.76 ± 0.09
	Rainy month (October 2019)				
Tobora	0.40 ± 0.03	0.24 ± 0.03	0.42 ± 0.03	0	0.30 ± 0.04
Somoche	0.34 ± 0.07	0.42 ± 0.00	0.35 ± 0.03	0.02	0.41 ± 0.04
Gurubi	0.29 ± 0.02	0.40 ± 0.03	0.53 ± 0.06	0	0.34 ± 0.04
Tigithe	0.20 ± 0.04	0.31 ± 0.04	0.20 ± 0.05	0	0.28 ± 0.04
Nyarwera	0.09 ± 0.03	0.48 ± 0.03	0.55 ± 0.03	0.02	0.56 ± 0.00
Nyarusondobiro	0.22 ± 0.00	0.28 ± 0.03	0.55 ± 0.03	0.03	0.39 ± 0.03
Mean	0.26 ± 0.03	0.36 ± 0.03	0.43 ± 0.04	0.01	0.38 ±0.03
Min	0.09 ± 0.03	0.24 ± 0.03	0.20 ± 0.05	0	0.28 ± 0.04
Max	0.40 ± 0.03	0.48 ± 0.03	0.55 ± 0.03	0.03	0.56
[(a)]USEPA	0.05	0.005	0.05	0.002	0.05
[(b)]WHO	0.05	0.005	0.05	0.001	0.05

[(a)]USEPA = United States Environmental Protection Agency; [(b)] WHO = World Health Organization; [(c)]SD = Standard deviation.

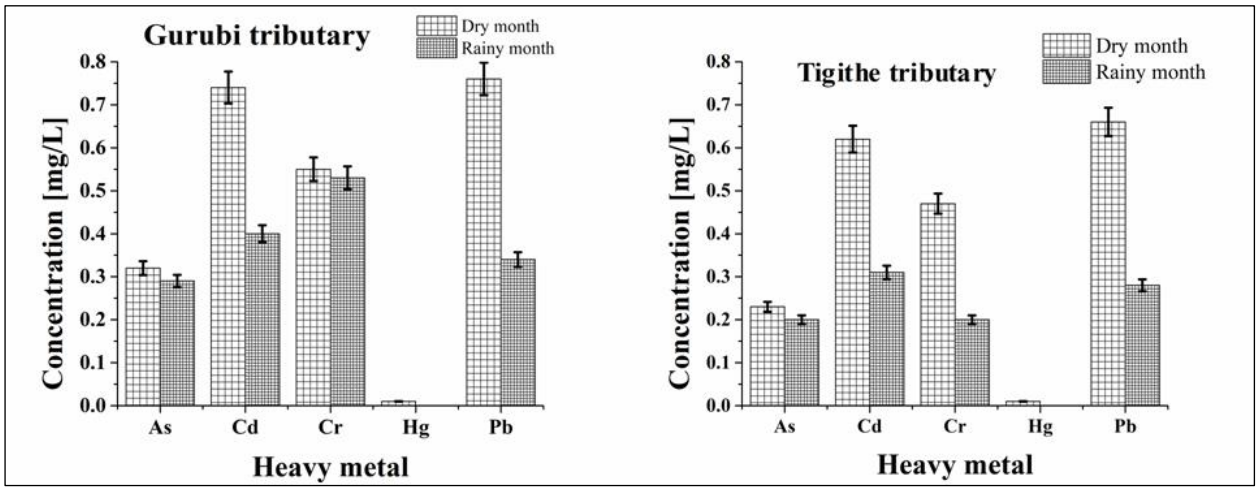


Figure 16: The concentration of heavy metals in surface water during the dry and rainy months at Gurubi and Tigithe tributaries

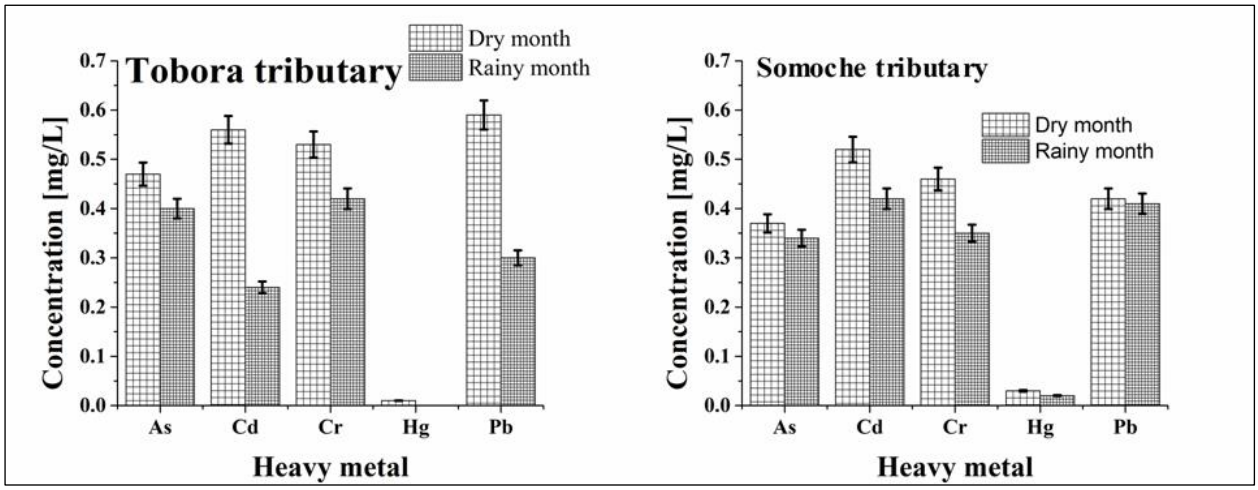


Figure 17: The concentration of heavy metals in surface water during the dry and rainy months at Tobora and Somoche tributaries

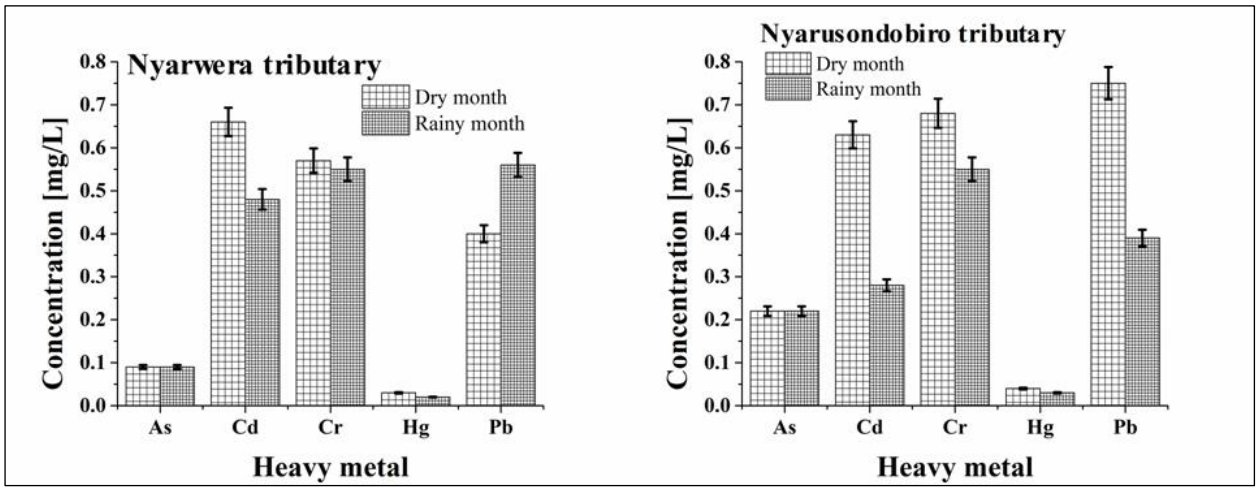


Figure 18: The concentration of heavy metals in surface water during the dry and rainy months at Nyarwera and Nyarusondobiro tributaries

(i) Metal Correlation Analysis for Tributary Waters

The correlation analysis of heavy metals in river tributaries during the dry and rainy months was carried out (Table 8). Results indicated that moderate positive correlation exhibited between Cd and Cr (r = 0.40, $p < 0.05$), Cd, and Pb (r = 52, $p < 0.05$), Cr and Hg (r = 0.56, $p < 0.05$), and Cr and Pb (r = 0.43, $p < 0.05$) in water during the dry month. However, As showed negative moderate correlation with Cd (r = -0.47, $p < 0.05$), and Hg (r = -0.46, $p < 0.05$) during the same month. The observed negative correlation of elements may indicate the inexistence of heavy mineral residues, which have other metals in their structure (Souza *et al.*, 2016).

Table 8: Pearson correlation matrix of heavy metals in water samples collected from tributaries of the Mara River in the dry and rainy months of 2019

	As	Cd	Cr	Hg	Pb
Dry month (May 2019)					
As	1.0				
Cd	-0.47	1.0			
Cr	-0.37	0.40	1.0		
Hg	-0.46	-0.19	0.56	1.0	
Pb	0.14	0.52	0.43	-0.27	1.0
Rainy month (October 2019)					
As	1.0				
Cd	-0.49	1.0			
Cr	-0.21	0.26	1.0		
Hg	-0.38	0.25	0.45	1.0	
Pb	-0.63	0.76	0.57	0.68	1.0

Similarly, in the rainy month, positive correlation between Cd and Pb ($r = 0.76$, $p < 0.05$), Cr and Hg ($r = 0.45$, $p < 0.05$), Cr and Pb ($r = 0.56$, $p < 0.05$), Hg and Pb ($r = 0.68$, $p < 0.05$) of heavy metals were observed in water samples collected from river tributaries. The positive correlation of heavy metals probably indicated that the pair of heavy metals originated from similar sources (Bhuyan *et al.*, 2019). Likewise, moderate negative correlation was found between arsenic and cadmium ($r = -0.49$, $p < 0.05$), Pb ($r = -0.63$, $p < 0.05$) in water during the rainy month (Table 7). The mixing influence of stormwater feeding into the tributaries probably resulted in the observed negative correlations (Allafta & Opp, 2020).

(ii) Principle Component Analysis for Tributary Waters

The mean concentrations of As, Cd, Cr, Hg and Pb in water collected from river tributaries were evaluated using the PCA technique for both the dry and rainy months (Fig. 19). The PCA is a linear combination of measurements and analyses of common variance and unique variance (the variance of the set of variables) (Kim, 2008). During the dry month (Fig. 19a), PC1 was loaded with As, Cd, and Cr, which accounted for 42.93% of the total variance. Similarly, Pb, Hg, and Cd accounted for 33.27% of the total sources loaded in PC2. Both PC1 and PC2 accounted for 76.26% of the cumulative total variance with Eigenvalues greater than 1. The distribution of As, Cd, and Cr in PC1 and Pb, Hg and Cd in PC2 was moderately contaminated in river tributary waters. Contamination with As, Cd, and Cr in PC1 and Pb, Hg, and Cd in PC2 in water depicted a seasonal variation (Pobi *et al.*, 2019).

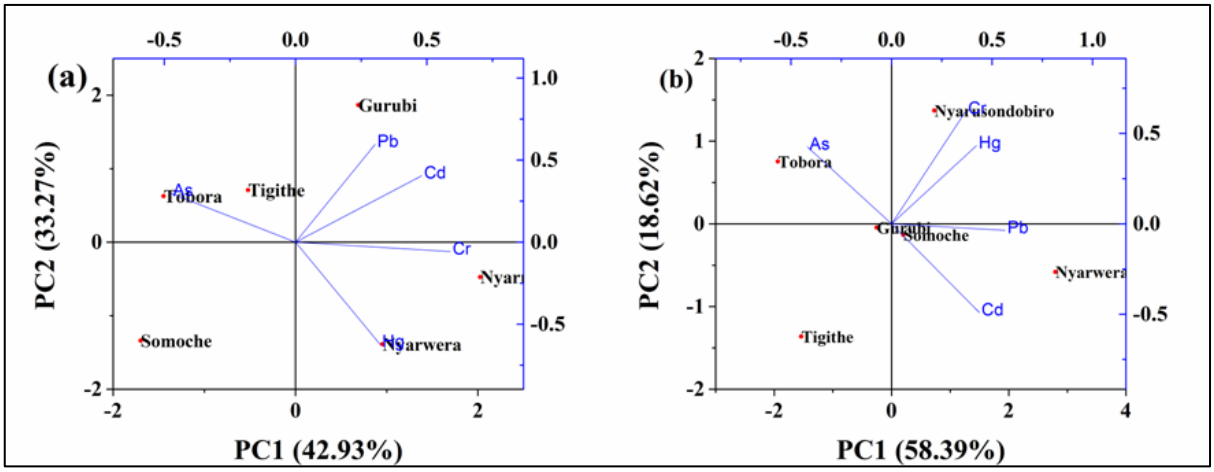


Figure 19: PCA biplots of heavy metals in water for the Mara River tributaries in (a) the dry month and (b) rainy month

The tributaries in PC1 in the dry month with higher As, Cr and Cd were Tobora and Nyarwera streams. Moreover, tributaries of Gurubi, Tigithe and Nyarwera in PC2 were contaminated with Hg, Pb and Cd (Fig. 19a). During the rainy month (Fig. 19b), the PC1 accounted for 58.39% of the total variance, positively loaded with Pb. Likewise, low to moderate loading of As, Hg, and Cd in PC1 was observed. Sources of Pb, As, Hg, and Cd in tributary waters may have come from human activities, including burning fossil fuels, mining, smelting metal ores, agriculture and industry (Wasike *et al.*, 2019). The PC2 in the same month accounted for 18.62% of the total variance. The PC2 was low-to-moderately loaded with Cd, Hg, As and Cr. The PC1 and PC2 accounted for 77.02% of the total cumulative variance, with Eigenvalues greater than 1. Generally, low to moderate concentrations of As, Cd, and Hg in the rainy month were observed in sediment samples (Fig. 19b). Allafta and Opp (2020) reported that low contamination of heavy metals during the rainy month was associated with higher river flows, producing dilution effects, and causing metal concentrations in water and sediments to decline.

4.5 Heavy Metals in Sediments from the Main River Course

The mean concentrations of heavy metals in the dry and rainy months along the Mara River are presented in Table 9. The mean concentrations of As, Cd, Cr, Hg and Pb in the dry month were 10.21 ± 0.07, 0.26 ± 0.04, 0.76 ± 0.12, 0.01 ± 0.00, 10.16 ± 0.48 in mg/kg at Mara Darajani, Somoche Factory, Nyantare Area and Kirumi Bridge, respectively. The highest As value in the same month was 11.04 ± 0.13 mg As/kg in samples collected at Mara Darajani (Table 9 and Fig. 20). Similarly, the lowest As concentration value (7.81 ± 0.04 mg As/kg) was recorded at Nyantare Area (Fig. 21). Overall, there was no significant variation in the levels of As among the sampling sites (Table 9, Fig. 20 and 21). The As migration from bedrock materials to sediment surfaces under the diagenetic process's influence may pose contamination to water wells and other aquatic

environments (Salim *et al.*, 2009). Occurrences of As in the environment are strongly associated with areas of active tectonic plates, magmatism, hydrothermal activity, and high erosion rates. Hydrothermal water, sulfide, volcanic ash, and arsenide minerals are the primary sources of As in the environment. In addition, anthropogenic activities linked to geothermal and mining activities may also increase arsenic contamination in the environment (Masuda, 2018). Therefore, both natural and anthropogenic activities probably contributed to the levels of arsenic along the Mara River. The Mara River traverses through varied landscapes of the Mara River basin, which has experienced population increase, human settlements, industrial, and tourist activities, and urban centers (Martin *et al.*, 2018). Increased human activities associated with deforestation, poor handling of mining wastes, and agricultural inputs may impact the Mara River sediment quality (Owuor *et al.*, 2018).

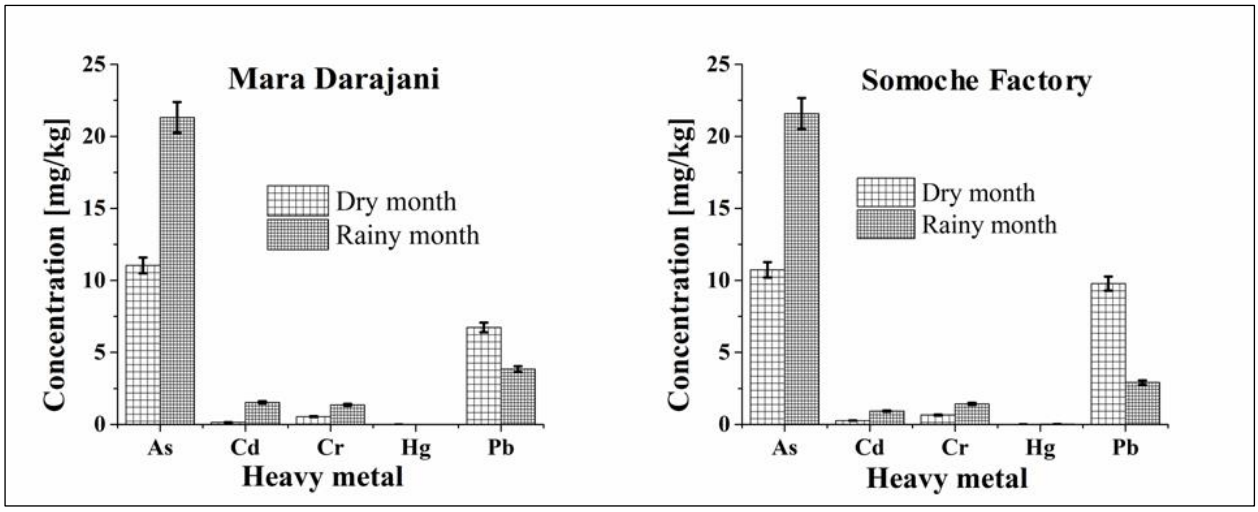


Figure 20: Heavy metals concentrations in sediments at Mara Darajani and Somoche Factory in the dry and rainy months of 2019

The dry month levels of Cd ranged from 0.14 ± 0.01 to 0.43 ± 0.05 mg Cd/kg and indicated no significant variations (Table 9, Fig. 20 and 21). A similar trend was followed for Cr with values ranging from 0.54 ± 0.14 to 1.02 ± 0.29 mg Cr/kg sediments (Table 9, Fig. 20 and 21). Levels of Hg concentration in dry month samples were negligible (Fig. 20 and 21). The level of Pb concentrations was significantly higher than those of Cd, Cr and Hg (Fig. 20 and 21). The US Environmental Protection Agency (USEPA) sets sediment quality guidelines (SQGs) above which harmful effects are likely to occur (Burton & Allen, 2002). Compared with the SQGs, the level of As in sediments during the dry month was above the consensus-based threshold effect concentration. Levels of Cd, Cr, Hg and Pb were below the threshold effect concentration in the same month (Table 9, Fig. 20 and 21). High levels of Pb at the Nyantare Area (16.36 ± 0.58 mg Pb/kg) were probably due to the location's closeness to downstream proximity of the North Mara

Gold Mines (Fig. 21). The high levels of Pb might be due to the surface and underground seepage of waste mining materials from the mine operations (Plate 8) (Mohapatra & Kirpalani, 2016).

Plate 8: Mined rock piles near Nyantare Area gold mine (NMGM) (Present study)

During the rainy month, the mean concentrations of As, Cd, Cr, Hg and Pb in sediment samples were 20.45 ± 0.07, 1.31± 0.16, 1.30 ± 0.62, 0.01 ± 0.00 and 3.10 ± 0.26 mg/kg (Table 9, Fig. 20 and 21), respectively. Levels of heavy metals samples indicated more elevated As values in sediments at Kirumi Bridge (Table 9 and Fig. 21). Kirumi Bridge is a point located downstream, closest to Lake Victoria. Other sampling sites along the Mara River with elevated levels of As were Mara Darajani and Somoche Factory, and the lowest was recorded at Nyantare Area (Fig. 21). Natural exposure of weathered rocks at Mara Darajani and the factory for cutting natural rocks at Somoche Factory were likely to have raised the levels of As in Mara River sediments (Plate 9) (Dinwiddie & Liu, 2018). Accumulation of As in sediments during the rainy month was higher in downstream samples at Kirumi Bridge compared to upstream samples (O'Sullivan *et al.*, 2016; Shanbehzadeh *et al.*, 2014).

Plate 9: Extrusive rocks at Mara Darajani, Nyansurare village, Serengeti district (Present study)

There was a slight increase in Cd concentrations, Cr and Hg in sediment samples collected during the rainy month compared to the dry month samples (Fig. 20 and 21). However, lower Pb concentrations were found in sediments collected during the rainy month than those gathered in the dry month (Fig. 20 and 21). During the rainy month, the decrease in Pb may be attributed to oxidation and the resulting precipitation processes that may have been triggered by sediment mixing during the rainy month (Akpan *et al.*, 2002).

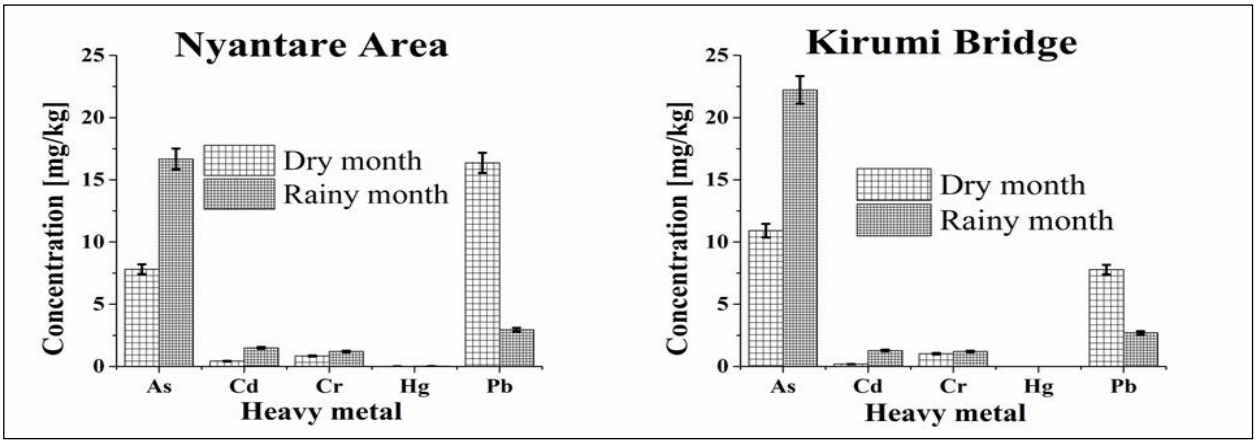


Figure 21: Heavy metals concentrations in sediments at Nyantare Area and Kirumi Bridge during the dry and rainy months

Table 9: Heavy metals concentrations in sediments during the dry and rainy months of 2019 along the Mara River

Site name	Elemental concentrations ± SD[a] (mg/kg DW[b])				
	As	Cd	Cr	Hg	Pb
Dry month (May 2019)					
Mara Darajani	11.04 ± 0.13	0.14 ± 0.01	0.54 ± 0.14	0	6.73 ± 0.27
Somoche Factory	10.73 ± 0.04	0.27 ± 0.06	0.65 ± 0.04	0.01	9.78 ± 0.66
Nyantare Area	7.81 ± 0.04	0.43 ± 0.05	0.84 ± 0.01	0.01	16.36 ± 0.58
Kirumi Bridge	10.91 ± 0.05	0.19 ± 0.04	1.02 ± 0.29	0	7.78 ± 0.40
Mean	10.21 ± 0.07	0.26 ± 0.04	0.76 ± 0.12	0.01	10.16 ± 0.48
Mini	7.81 ± 0.04	0.14 ± 0.01	0.54 ± 0.14	0	6.73 ± 0.27
Max	11.04 ± 0.13	0.43 ± 0.05	1.02 ± 0.29	0.01	16.36 ± 0.58
Rainy month (October 2019)					
Mara Darajani	21.31 ± 0.13	1.53 ± 0.15	1.36 ± 0.53	0	3.84 ± 0.34
Somoche Factory	21.58 ± 0.04	0.92 ± 0.18	1.43 ± 0.46	0.03	2.91 ± 0.32
Nyantare Area	16.67 ± 0.04	1.49 ± 0.06	1.20 ± 0.37	0.02	2.95 ± 0.23
Kirumi Bridge	22.22 ± 0.05	1.28 ± 0.25	1.20 ± 1.11	0	2.70 ± 0.16
Mean	20.45 ± 0.07	1.31 ± 0.16	1.30 ± 0.62	0.01	3.10 ± 0.26
Mini	16.67 ± 0.04	0.92 ± 0.18	1.20 ± 0.11	0	2.70 ± 0.16
Max	22.22 ± 0.05	1.53 ± 0.15	1.43 ± 0.46	0.03	3.84 ± 0.34
TEL[c]	5.90	0.59	37.30	0.17	35.0
LEL[d]	6.0	0.60	26.0	0.20	31.0
MET[e]	7.0	0.90	55.0	0.20	42.0
ERT[f]	33.0	5.0	80.0	0.15	35.0
Consensus Based TEC[g]	9.79	0.99	43.40	0.18	35.80
Bckgr.[h]	0.08	0.19	18.79	39.8	53.71

[a]SD = Standard deviation; [b]DW = dry weight; [c]TEL = Threshold effect leve; [d]LEL = Lowest effect level; [e]MET = Minimal effect threshold; [f]ERL = Effects ra`nge low; [g]TEC = Threshold effect concentration; Bckgr. = Background values.

Compared with the SQGs, the concentrations of As and Cd were above the threshold effect level concentration in the rainy month (Table 9, Fig. 20 and 21) (Luo *et al.*, 2010). Levels of As and Cd contamination may harm sediment-dwelling organisms in the Mara River during the rainy month (Luo *et al.*, 2010). When the results of As, Cd, Cr, Hg and Pb concentrations were compared to background values in the dry and rainy months, As and Cd in all sampling sites were above the background values (Table 9).

(i) Metal Correlation Analysis for River Sediments

The Pearson correlation matrix for heavy metals in sediments along the Mara River is indicated in Table 10. The results indicate a strong significant positive correlation between Cd and Pb ($r = 0.99$, $p < 0.01$). Likewise, moderate positive correlation between Cd and Hg ($r = 0.69$, $p < 0.05$), Hg and Pb ($r = 0.62$, $p < 0.05$) in the dry month were observed. The Cd, Pb, Cr and Hg were probably coming from a similar pollution source (Huang *et al.*, 2018). However, strong negative correlations of As with Cd ($r = -0.94$, $p < 0.05$) and Pb ($r = -0.98$, $p < 0.01$) were observed in the same month.

Strong negative correlations in these metal pairs were probably indicative that As, Cd, and Pb originated from different sources.

During the rainy month, a moderate positive correlation was found between As and Cr ($r = 0.45$, $p < 0.05$), Cd and Pb ($r = 0.52$, $p < 0.05$), Cr and Pb ($r = 0.42$, $p < 0.05$. The moderate positive correlation of As, Cr, Cd and Pb in river sediments may point to similar origins (Ramasamy *et al.*, 2011). Moreover, a moderate negative correlation between As and Cd ($r = -0.46$, $p < 0.05$), Cd and Hg ($r = -0.62$, $p < 0.05$) existed in the rainy month (Table 10). The moderate negative correlation between As, Cd, Cr and Hg was probably associated with the diversity and independence of sediment metal sources (Jiao *et al.*, 2018).

Table 10: Correlation matrix of heavy metals concentration in sediments along the Mara River in the dry and rainy months of 2019

	As	Cd	Cr	Hg	Pb
Dry month (May 2019)					
As	1.0				
Cd	-0.94	1.0			
Cr	-0.25	0.25	1.0		
Hg	-0.46	0.69	-0.29	1.0	
Pb	-0.98*	0.99**	0.25	0.62	1.0
Rainy month (October 2019)					
As	1.0				
Cd	-0.46	1.0			
Cr	0.45	-0.54	1.0		
Hg	-0.36	-0.63	0.39	1.0	
Pb	0.07	0.52	0.42	-0.38	1.0

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

(ii) PCA for river sediment samples

As indicated in PCA biplots (Fig. 22), there are two seasonal months—the dry and rainy months. The PCA biplots for the dry month consist of PC1 and PC2 which characterize a cumulative contribution of 99.98% of the total variance with Eigenvalues greater than 1. Since the high percentage of PC1 accounted for 92.01% of the total variance loaded with Cd, Cr and Hg, then contamination of Cd, Cr and Hg reflected some local nonpoint sources along the Mara River (Fig. 22a) (Paladino *et al.*, 2017). However, the most affected areas with nonpoint sources of pollution of Cd, Cr, and Hg were Somoche Factory, Kirumi Bridge, and Mara Darajani (Fig. 22a). The second PC2 contributed 7.97% of the total variance and was considered to describe random variations departing from the typical contamination situation (Paladino *et al.*, 2017). The Pb contamination at Nyantare Area was dominated by random variation (Fig. 22a).

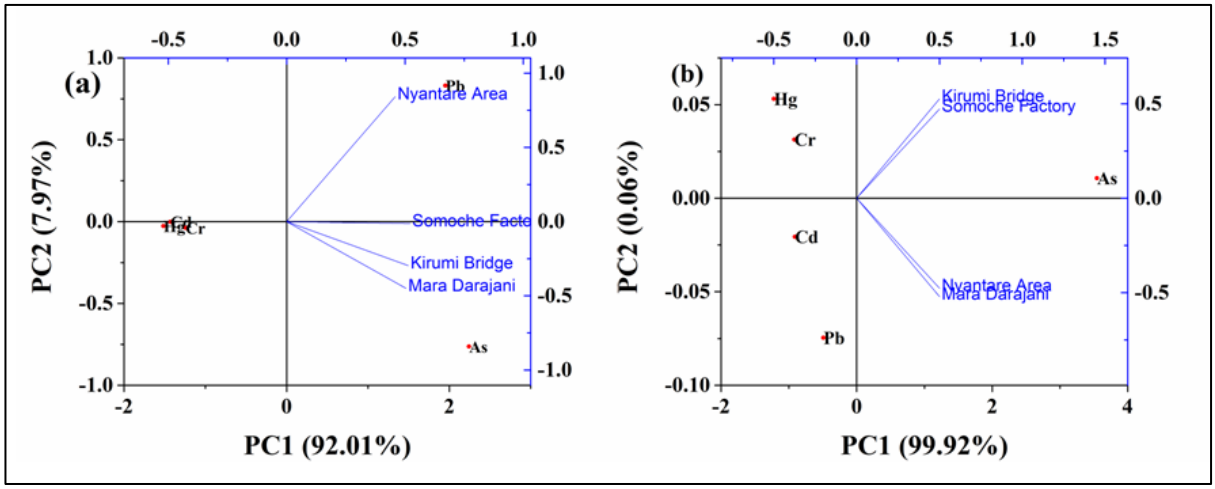


Figure 22: PCA biplots of heavy metals and metalloids in sediments of the Mara River (a) dry month (b) rainy month of 2019

Besides, the PCA for the biplot of heavy metals during the rainy month is indicated (Fig. 22b). The biplot consists of PC1 and PC2, which contribute 99.99% of the total cumulative variance in the rainy month with Eigenvalues greater than one (Fig. 22b). The PC1 accounted for 99.92% of the total variance and was moderately loaded with As, Cd, Cr Hg and Pb. The contamination of As, Cd, Cr, Hg and Pb also reflected local nonpoint sources along the Mara River (Fig. 22b). The PC2 in the same month accounted for 0.06% of the total variance and was dominated by random variation (Jolliffe, 2002).

4.6 Heavy Metals in River Waters

Concentration results for As, Cd, Cr, Hg and Pb in water collected from the Mara River during the dry and rainy months are indicated (Table 11). In the dry month, the mean concentration of As, Cd, Cr, Hg and Pb ranged from 0.14 ± 0.01 to 0.20 ± 0.11; 0.32 ± 0.06 to 0.76 ± 0.09; 0.44 ± 0.09 to 0.64 ± 0.05; 0.01 to 0.03; and 0.40 ± 0.05 to 0.63 ± 0.08 in mg/L, respectively. In the rainy month, concentration of As, Cd, Cr, Hg and Pb ranged from 0.14 ± 0.01 to 0.30 ± 0.05; 0.15 ± 0.00 to 0.30 ± 0.04; 0.23 ± 0.03 to 0.47 ± 0.04; 0 to 0.02 and 0.14 to 0.53 ± 0.04 in mg/L, respectively. The concentration of As, Cd, Cr, Hg and Pb (Table 11) along the Mara River was above the US-EPA and WHO guidelines (Abah *et al.*, 2016). Both anthropogenic and natural sources probably caused elevated As, Cd, Cr, Hg and Pb in river water. Land degradation, underground seepage from mining waste, and natural rocks may influence As, Cd, Hg and Cr contamination enrichment in surface water (Sahni, 2011).

Table 11: Heavy metals concentration in surface water collected from the Mara River in the dry and rainy months of 2019

Elemental concentrations ± SD[(c)] (mg/L)					
Site name	**As**	**Cd**	**Cr**	**Hg**	**Pb**
Dry month (May 2019)					
Mara Darajani	0.15 ± 0.00	0.76 ± 0.09	0.64 ± 0.05	0.03	0.45 ± 0.06
Somoche Factory	0.14 ± 0.01	0.63 ± 0.06	0.53 ± 0.10	0.01	0.40 ± 0.05
Nyantare Area	0.19 ± 0.01	0.46 ± 0.14	0.47 ± 0.07	0.01	0.63 ± 0.08
Kirumi Bridge	0.20 ± 0.11	0.32 ± 0.06	0.44 ± 0.09	0.01	0.56 ± 0.09
Mean	0.17 ± 0.03	0.54 ± 0.09	0.52 ± 0.08	0.02	0.51 ± 0.07
Min.	0.14 ± 0.01	0.32 ± 0.06	0.44 ± 0.09	0.01	0.40 ± 0.05
Max.	0.20 ± 0.11	0.76 ± 0.09	0.64 ± 0.05	0.03	0.63 ± 0.08
Rainy month (October 2019)					
Mara Darajani	*0.17 ± 0.02*	*0.30 ± 0.04*	*0.35 ± 0.02*	*0.02*	*0.53 ± 0.04*
Somoche Factory	*0.14 ± 0.01*	*0.21 ± 0.06*	*0.47 ± 0.04*	*0*	*0.38 ± 0.04*
Nyantare Area	*0.19 ± 0.01*	*0.16 ± 0.04*	*0.28 ± 0.05*	*0*	*0.25 ± 0.01*
Kirumi Bridge	*0.30 ± 0.05*	*0.15*	*0.23 ± 0.03*	*0*	*0.14*
Mean	*0.20 ± 0.02*	*0.21 ± 0.07*	*0.33 ± 0.04*	*0.01*	*0.33 ± 0.06*
Mini	*0.14 ± 0.01*	*0.15*	*0.23 ± 0.03*	*0*	*0.14*
Max	*0.30 ± 0.05*	*0.30 ± 0.04*	*0.47 ± 0.04*	*0.02*	*0.53 ± 0.04*
[(a)]USEPA	*0.05*	*0.005*	*0.05*	*0.002*	*0.05*
[(b)]WHO	*0.05*	*0.005*	*0.05*	*0.001*	*0.05*

[(a)]USEPA = United States Environmental Protection Agency; [(b)]WHO = World Health Organization; [(c)]SD = Standard deviation

During the dry month, the As contamination was ascending from upstream downward (Fig. 23 and 24). This increasing trend of As concentration downstream may impact the Mara River as the Lake Victoria ecosystem where the river empties its contents (Yu *et al.*, 2019). The opposite trend was observed for Cd and Cr contaminations, of which concentrations decreased from upstream downward (Fig. 23 and 24). Moreover, Hg levels remained mostly unchanged throughout (Fig. 23 and 24). The highest Pb level was recorded at Nyantare Area, a place closer to NMGM (Fig. 24). For Pb, a general decreasing-downstream trend was observed. The distribution of Pb may have been influenced by dilution effects (Zhao & Marriott, 2013). Contamination variations of heavy metals from upstream to downstream have been reported by Nambatingar *et al.* (2017) to be attributable to and exacerbated by anthropogenic sources.

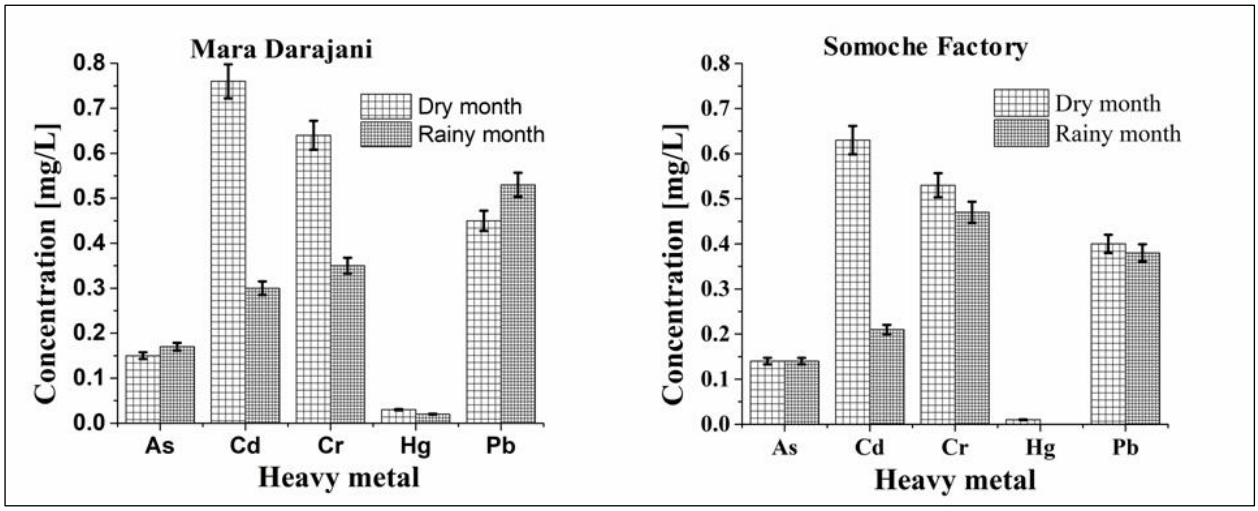


Figure 23: The concentration of heavy metals in surface water at Mara Darajani and Somoche Factory during the dry and rainy months of 2019

The small- and large-scale gold mining activities along the Mara River may influence As enrichment in the surface water (WWF, 2019). Contamination by Cd, Hg and Pb was higher at Mara Darajani, the point closest to the Marenga artisanal gold mine (Fig. 23). Moreover, the extrusive rocks at Mara Darajani may have influenced Pb contamination in water through natural seepage from rocks (Okolo *et al.*, 2018). According to Clausen *et al.* (2011), heavy metals from mining wastes may migrate to near-surface water and cause pollution. Heavy metals accumulate and undergo food chain magnification, affecting organism-level and ecosystem-based processes (Baby *et al.*, 2011).

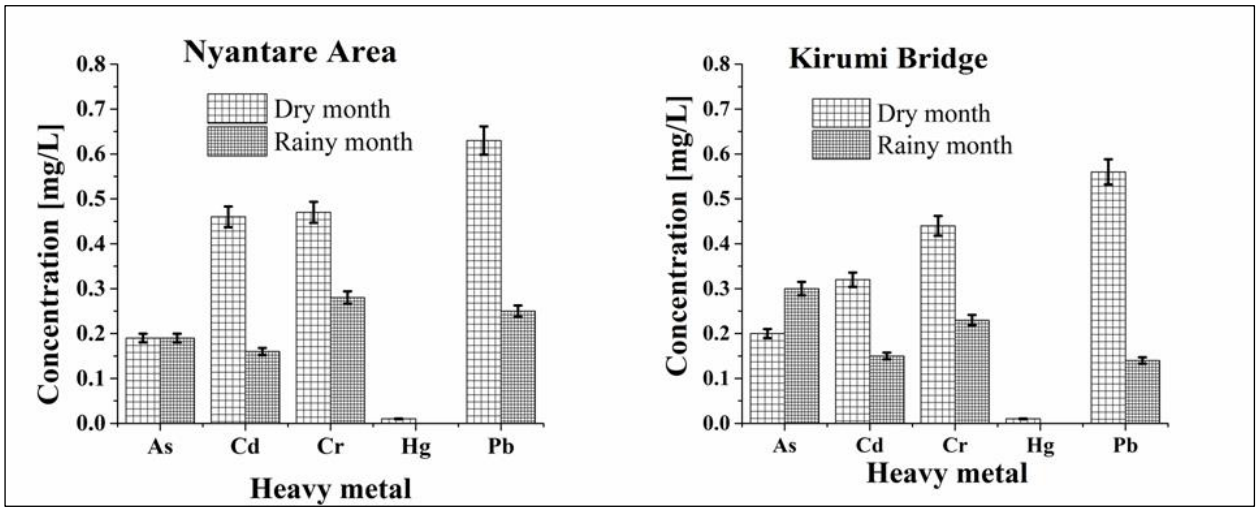


Figure 24: The concentration of heavy metals in surface water at Nyantare Area and Kirumi Bridge during the dry and rainy months of 2019

(i) Correlation Analysis for River Waters

In the present study, the Pearson correlation analysis was applied to investigate the relationships between heavy metals concentration in water, as indicated in Table 12. In the dry month, Cd versus Cr (r = 0.96, p < 0.05) was significantly correlated. Moreover, a positive correlation coefficient between As and Pb (r = 0.91, p < 0.05), Cd and Hg (r = 0.75, p < 0.05), Cr and Hg (r = 0.91, p < 0.05) was found in water, an indication of a probable common source (Ho *et al.*, 2010). However, negative correlation between As and Cd (r = -0.90, p < 0.05) and Cr (r = -0.78, p < 0.05) in water existed pointing to some distinctive sources (Akobundu, 2012).

Table 12: Correlation matrix of heavy metals concentration in surface water along the Mara River in the dry and rainy months of 2019

	As	Cd	Cr	Hg	Pb
Dry month (May 2019)					
As	1.0				
Cd	-0.90	1.0			
Cr	-0.78	0.96*	1.0		
Hg	-0.45	0.75	0.91	1.0	
Pb	0.91	-0.73	-0.66	-0.38	1.0
Rainy month (October 2019)					
As	1.0				
Cd	-0.57	1.0			
Cr	-0.85	0.48	1.0		
Hg	-0.287	0.92	0.11	1.0	
Pb	-0.77	0.96*	0.65	0.81	1.0

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

In addition, during the rainy month Cd showed a positive correlation with Cr (r = 0.48, p < 0.05), Hg (r = 0.92, p < 0.05) and Hg (r = 0.96, p < 0.05). Similarly, a positive correlation between Cr and Pb (r = 0.65, p < 0.05), Hg and Pb (r = 0.81, p < 0.05) were found for the river water samples. This positive correlation of heavy metals in river water could be a signal that these metals had similar points of origin (Howard & Olul, 2012). Furthermore, a negative correlation coefficient were existed between As and Cd (r = 0.57, p < 0.05), Cr (r = -0.85, p < 0.05), and Pb (r = -0.77, p < 0.05) in water, an indication of varying sources. Moreover, no or poor correlation among heavy metals could mean that the metals were not controlled by a single factor (Hadiyanto *et al.*, 2018).

(ii) Principle Component Analysis – Mara River waters

The relationships between As, Cd, Cr, Hg and Pb in water along the sampling sites are indicated in Fig. 25. During the dry month, the PCA biplot had Eigenvalues > 1, which explained 99.71% of the total cumulative variance (Fig. 25a). The PC1 biplot explained 88.10% of the variance and was moderately loaded with As, Hg, Cr and Cd. Likewise, PC2 was positively loaded with Pb and moderately negatively loaded with Hg, which explained 11.61% of the total variance (Fig. 25a). Thus PC1 and PC2 represented similar input sources for As, Hg, Cr and Cd in water along the Mara River and a different source of Pb (Huang *et al.*, 2018). The Pb river water was probably a source of human activities, e.g., mining, highway transport, smelting, and other small-scale but significant industrial activities in the area (Plate 10) (Makokha *et al.*, 2008). Elevated Pb levels were found at Kirumi Bridge, a site located closer to the Musoma–Sirari highway (Fig. 25a). Charkiewicz and Backstrand (2020) reported that in Poland, road transport ranked third as Pb contributor to pollution, the first and second were waste management and industrial activities, respectively.

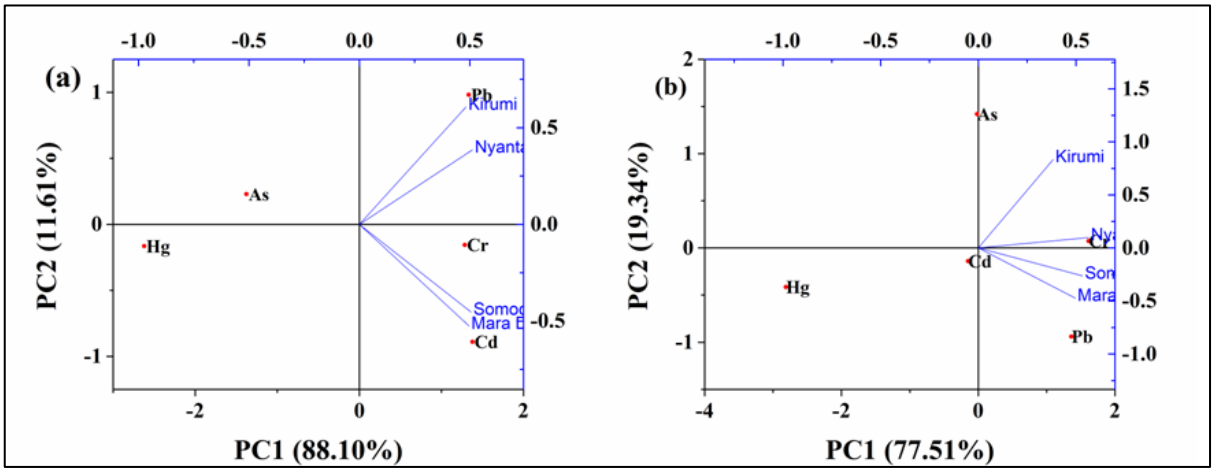


Figure 25: PCA biplots of heavy metals in surface water for the Mara River in (a) dry month and (b) rainy month

In the environment, Cd contamination is usually caused by the weathering of minerals, atmospheric deposition, smelters, coal combustion, refuse incineration, steel industries, industrial effluents, domestic effluents and spoil heaps (Fatoki *et al.*, 2004). The application of phosphate fertilizers in surrounding farms and operations of mines were probably the leading causes of Cd along the Mara River (Kubier *et al.*, 2019). Mine operations at Marenga artisanal mines may have influenced both Cd and Cr levels at Mara Darajani in PC1 (Fig. 25a) (Lu *et al.*, 2019). Similarly, gold mining at a larger scale at the NMGM closer to Nyantare Area was a more likely source of As, Pb and Hg in PC1 (Fig. 25a) (Gafur *et al.*, 2018).

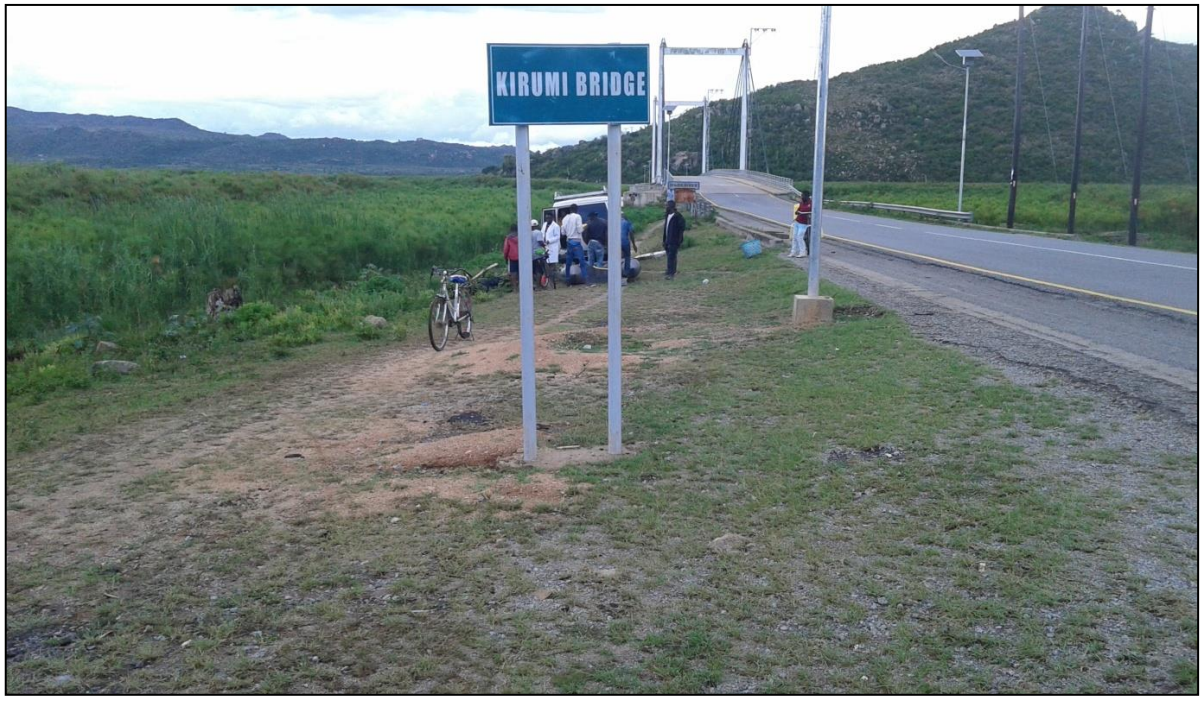


Plate 10: A picture of the Musoma-Sirari highway taken at the Kirumi Bridge sampling location during the present study

During the rainy month, PC1 and PC2 with Eigenvalues greater than 1 explained 96.85% of the total cumulative variance (Fig. 25b). The PC1 explained 77.51% of the total variance with moderately favorable loading of Cr, Cd, and Pb at Nyantare Area, Mara Darajani, and Somoche Factory (Fig. 25b). The PC2 explained 19.34% of the total variance with strong positive loading of As and moderate negative loading of Hg at Kirumi Bridge and Mara Darajani (Fig. 25b). The primary sources of Cr, Cd and Pb at Nyantare Area, Mara Darajani, and Somoche Factory were probably linked to mining operations at the NMGM, Sirori-Simba, and Somoche Factory, respectively (Fig. 25b). Mine operations at NMGM, a site close to the Nyantare Area, may have influenced Cr, Cd and Pb levels, probably through atmospheric deposition and groundwater seepage (Luo, 2019). Similarly, artisanal and small-scale mines at Marenga gold mine and mining of natural rocks for domestic tiles at Somoche Factory were likely to increase Cr, Cd and Pb levels indicated in PC1 (Fig. 25b) (Demková *et al.*, 2017). The contaminations of As at Kirumi Bridge were probably caused by downstream accumulation. Abdullah *et al.* (2007) reported contaminants transported from their sources through the river system and deposited downstream.

4.7 Pollution Indices for the Tributary Sediment Samples

The risk assessment constants that were used for pollution indices calculation are presented in Table 13. The upper continental crust (UCC) was used to calculate the enrichment factor (EF) of heavy metals as the concentration (mg/kg) factor of heavy metals relative to the reference metal. The reference elements used for calculating EF are Cr, Ca, Fe and Al. However, in the present study,

iron (Fe) was used as the normalization reference metal. The reason for using Fe as a normalization reference element for calculating EF is due to its stability in soil with no degradation and the absence of vertical mobility (Pesantes *et al.*, 2019). The toxic response factor was used to calculate the risk factor (E_r^i) for single heavy metal pollution. Finally, background values were used to calculate the geo-accumulation index (I_{geo}) of the elements in sediment samples.

Table 13: The upper continental crusts, background values, pre-industrial reference levels, and toxic response factors for studied heavy metals

Elements	Hg	Cd	As	Pb	Cr	Fe
UCC (mg/kg)	0.056	0.102	2	17	35	30890
Background values	0.08	0.186	18.79	39.8	53.71	
Pre-industrial reference level	0.25	1.0	15	70	90	
Toxic response factor	40	30	10	5	2	

Source: Adopted from Odukoya *et al.* (2016)

The background values express the natural content of a substance in the soil. It depends on the compositional and mineralogical characteristics of the parent geological material (Barbieri, 2016). The pre-industrial reference level of elements was used in the calculations to obtain the contamination factor (*CF*) of the elements.

(i) Geo-accumulation index

The geo-accumulation index (I_{geo}) with its respective scales reported by Nikolaidis *et al.* (2010) was used to compare the current concentration of heavy metals in sediments with that of the pre-industrial period. The calculated I_{geo} indices of heavy metals in the dry and rainy months are presented in Fig. 26. The I_{geo} values of Cd in the dry month ranged from moderately contaminated to uncontaminated (Fig. 26a). The Hg, Cr, and Pb with I_{geo} values below unity were uncontaminated. Results for the geo-accumulation index of heavy metals in the dry and rainy months indicated temporal variations. The Cd and As indices at Somoche, Nyarwera, and Gurubi tributaries were above the baseline contamination zone in the dry month. The I_{geo} value of Cd at Somoche indicated a strongly polluted status.

Moreover, the I_{geo} values at Nyarwera for Cd and As indicated a moderately-polluted status. The I_{geo} values for Cr, Hg and Pb in the dry month were indicative of an uncontaminated status. Furthermore, for Tobora, Tigithe, and Nyarusondobiro tributaries, As and Cd indicated an uncontaminated level.

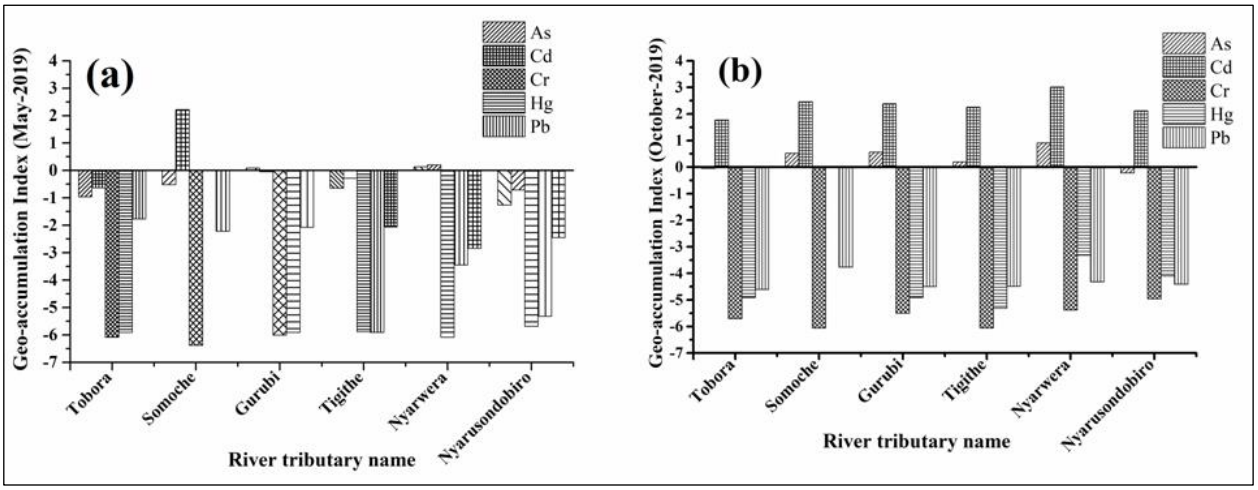


Figure 26: The geo-accumulation indices for sediments from the Mara River tributaries for (a) dry month and (b) rainy month

In the rainy month, the I_{geo} index values for Cd and As were above the baseline contamination zone (Fig. 26b). The I_{geo} values of Cd at Tobora, Somoche, Gurubi, Tigithe, Nyarwera, Nyarusondobiro were below three, indicating a strongly-polluted status. The observed Cd contamination in tributary sediments was probably due to some anthropogenic process. The I_{geo} values for As at Somoche, Gurubi, Tigithe, and Nyarwera were less than unity, implying a moderately-polluted level. However, As accumulation in sediments at Nyarusondobiro tributary indicated an uncontaminated status. I_{geo} values for Cr, Hg and Pb during the rainy month indicated an uncontaminated site.

(ii) Enrichment Factor

The mean concentration of As in sediments during the dry and rainy months showed signs of significant enrichment (Fig. 27). Their values in all sampling locations were above 50, indicating extremely severe enrichment (Fig. 27) (Silva *et al.*, 2019). The high EF values for As was probably attributed to anthropogenic sources from mining activities. At Nyarwera tributary, EF values of 1553.07 and 3667.55 for As concentration was found for the dry and rainy months, respectively. This level of As enrichment at Nyarwera tributary was probably contributed to by human activities. During the field survey, most of the Mara River tributaries ran through different artisanal gold mining operations. Similarly, the Cd EF value was above 50 in the dry and rainy months, indicating an extremely severe enrichment (Zhuang, 2014).

For Cd, the highest *EF* value of 316.29 was found at Nyarwera, indicating an extremely severely enriched status for this site. The *EF* value for Pb (49.58) in the same tributary was indicated a severely enriched status. However, *EF* values for Cr and Hg indicated that there was no enrichment risk relating to these elements in sediments. Gurubi tributary with an *EF* value for As of 819.32 received its water from streams that ran through artisanal mining areas. Furthermore, *EF* values at

Gurubi tributary indicated an enriched status with Cd (44.63) and Pb (45.29). At Somoche tributary, As with an EF value of 712.12 and Cd with an EF value of 924.71 showed an extremely severe enrichment (Fig. 27a). A highly elevated EF value for As of 670.36 in the dry month was also found at Tobora tributary. Tobora tributary collected its water from a nearby artisanal gold mine where As, Cd, and Pb were probably enriched. It was also found that *EF* values for Cd (163.06) and Pb (94.85) at Tobora indicated extremely severe enrichment. A similar status was recorded for As, Pb, and Cd at Tigithe, As and Cd at Nyarusondobiro. Generally, the mean enrichment of heavy metals in the Mara River tributaries in the dry month followed the following order: As > Cd > Pb > Hg > Cr (Fig. 27a).

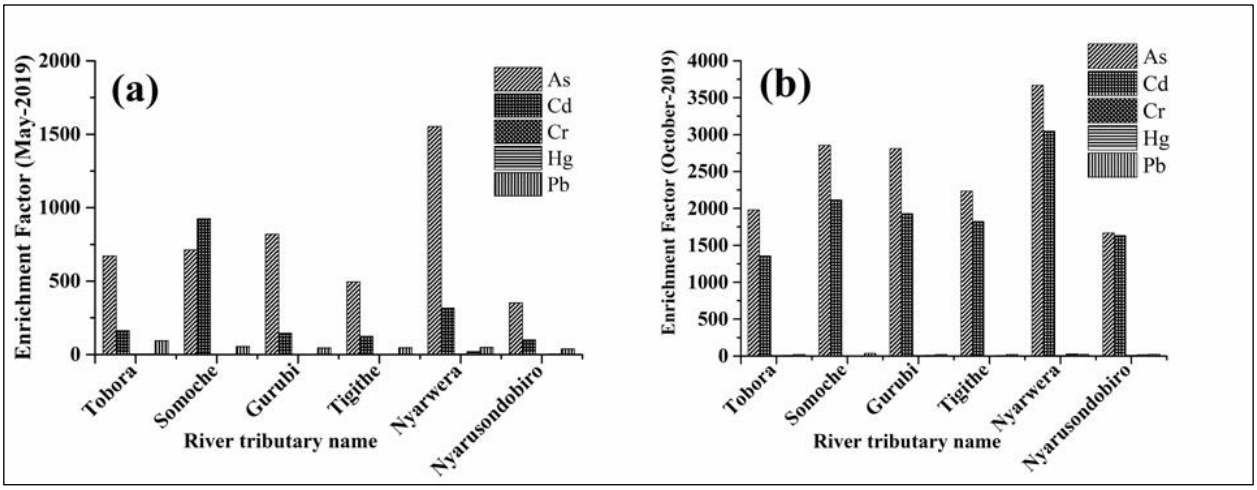


Figure 27: Enrichment factors for the Mara River tributaries in (a) dry month (b) rainy month of 2019

During the rainy month, EF values for As and Cd indicated an extremely severe enrichment (Fig. 27b). Enrichment values for Cr (6.79), Hg (12.38), and Pb (24.47) ranged from moderately severe to very severe. Bibak *et al.* (2018) revealed that heavy metals enrichment in river sediments do vary seasonally. High incidence of contamination and ecological risk of heavy metals in sediments have been reported in the rainy month than in the dry month (Ntakirutimana *et al.*, 2013). The order of enrichment in the Mara River tributaries in the rainy month followed the order of As > Cd > Pb > Hg > Cr (Fig. 27b).

(iii) Contamination Factor

The background values listed in (Table 13) were used to deduce *CF* of single parameters under investigation. During the dry and rainy months, the mean *CF* for As in tributaries were below three and were thus categorized as moderately contaminated. The highest *CF* values for As in the dry month were determined at Nyarwera with a *CF* value of 2.05 and Gurubi with a *CF* value of 2 (Fig. 28a). Nyarwera and Gurubi tributaries received water and sediments probably from catchment areas

dominated by mining activities. Mining activities are good contributors to heavy metals in streams, rivers, and other aquatic systems (Okegye & Gajere, 2015).

The CF values for Cd at Somoche (1.3) indicated a moderately contaminated status. The CF values for other tributaries were below unity and ranked as of low contamination status (Fig. 28a). Furthermore, Cr with a CF value of 0.02 and Hg with a CF of 0.04 in sediments during the dry month also indicated low contamination status. The general trends of *CF* values in the dry month followed the order of: As > Cd > Pb while Cr and Hg were similar in magnitudes.

The Cd and As contamination were evenly distributed in the rainy month in tributaries (Fig. 28b). Contaminated sediments transported from mining areas probably contributed to the observed CF values for Cd in the rainy month. On the other hand, CF values for Pb, Cr and Hg were extremely low during the rainy month. Rainfall events could have contributed to water dilution of Pb, Cr and Hg in streams causing the observed low CF values (Nehme *et al.*, 2014). Generally, the order of CF during the rainy month was as follows: As > Cd > Pb > Cr = Hg (Fig. 28b).

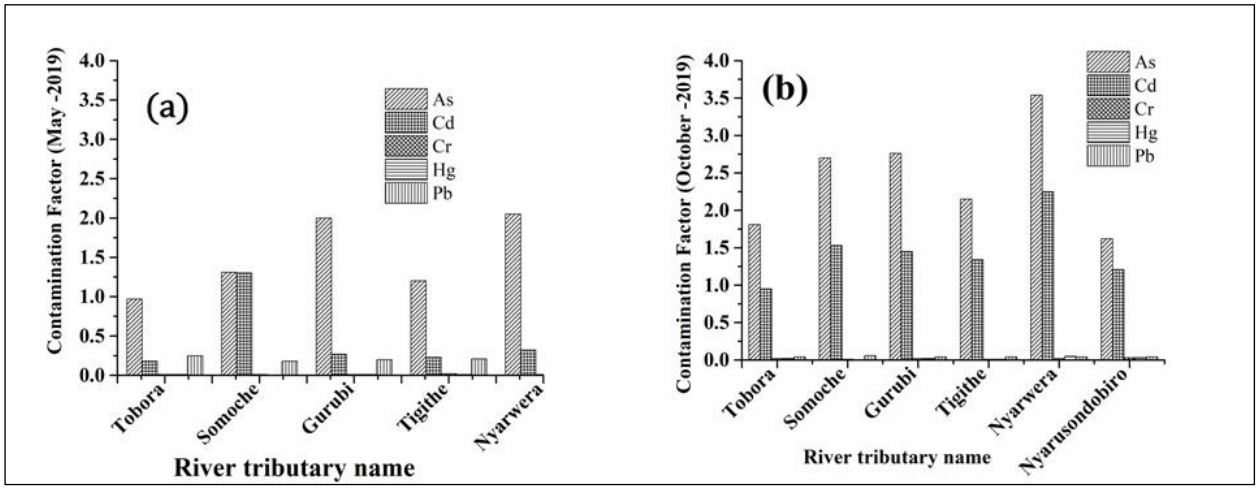


Figure 28: Contamination factor values for the Mara River tributaries in (a) dry month and (b) rainy month of 2019

(iv) Pollution Load Index

The PLI values during both the dry and rainy months were below unity (Fig. 29a). When the pollution index is less than unity, no pollution in sediments may occur (Naggar *et al.*, 2018). However, the highest PLI values were recorded at Nyarwera tributary in the dry and rainy months (Fig. 29a). The tributary originates from Sirori-Simba gold mines, where mining wastes may deteriorate surface water quality. Furthermore, the PLI values were extremely low at the Somoche tributary in the dry and rainy months (Fig. 29a). Therefore, the lack of pollution peak revealed no Hg enrichments at Somoche tributary indicative of no or low pollution at this site (Duncan *et al.*, 2018).

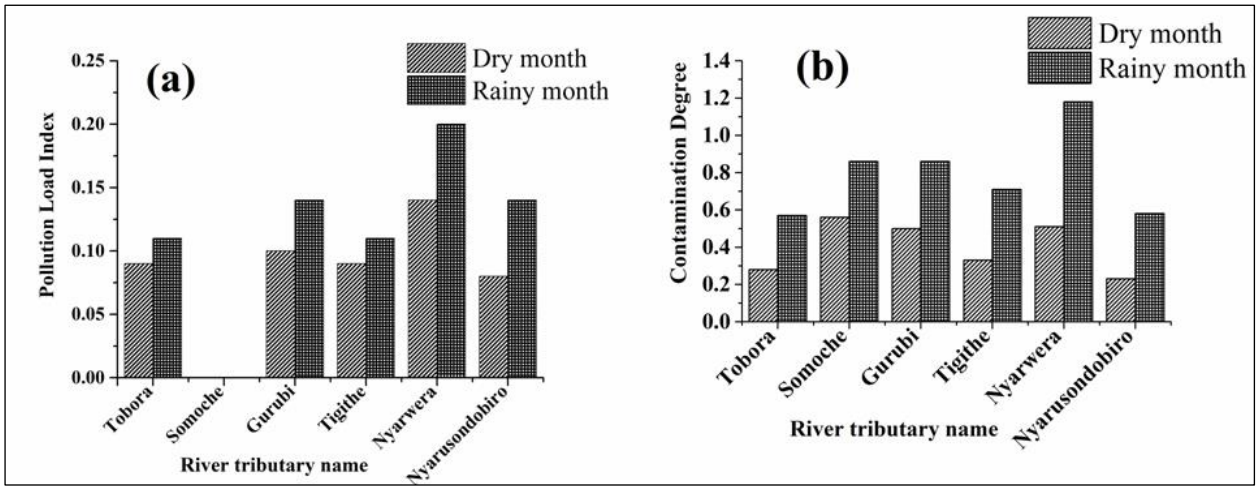


Figure 29: Pollution and contamination indices: (a) pollution load index and (b) modified contamination degree for the Mara River tributaries

(v) Contamination Degree

The *m*Cd values at Nyarwera tributary were higher than other tributaries in the rainy month (Fig. 29b). However, in the dry month, the *m*Cd values were high at Somoche tributary than in other tributaries (Fig. 29b). Generally, the *m*Cd values in tributaries in the dry and rainy months were less than unity showing a low degree of contamination (Ozkan, 2012). The *m*Cd in the dry and rainy month trended in the following order: > Nyarwera > Gurubi > Tigithe > Tobora > Nyarusondobiro and Nyarwera > Somoche = Gurubi > Tigithe > Nyarusondobiro > Tobora respectively (Fig. 29b).

(vi) Ecological Risk Assessment

The risk factor values determined in the dry month were below 40, indicating low ecological risk (Fig. 30a) (Vu *et al.*, 2017). The ecological risk factor for cadmium at Somoche tributary in the dry month was higher than at other sites. The risk factor for heavy metals in the dry month followed the order Cd > As > Hg > Pb > Cr (Fig. 30a). Furthermore, the risk index (R_I) was used to study the impacts of heavy metals in sediments. In the dry month, the maximum R_I value for heavy metals in tributaries was 53 at the Somoche tributary (Fig. 31). An R_I below 50 has a low ecological impact (Vu *et al.*, 2017). The R_I values of Mara River tributaries in the dry and rainy months followed the series Somoche > Nyarwera > Gurubi > Tigithe > Tobora > Nyarusondobiro and Nyarwera > Somoche > Gurubi > Tigithe > Nyarusondobiro > Tobora, respectively (Fig. 31).

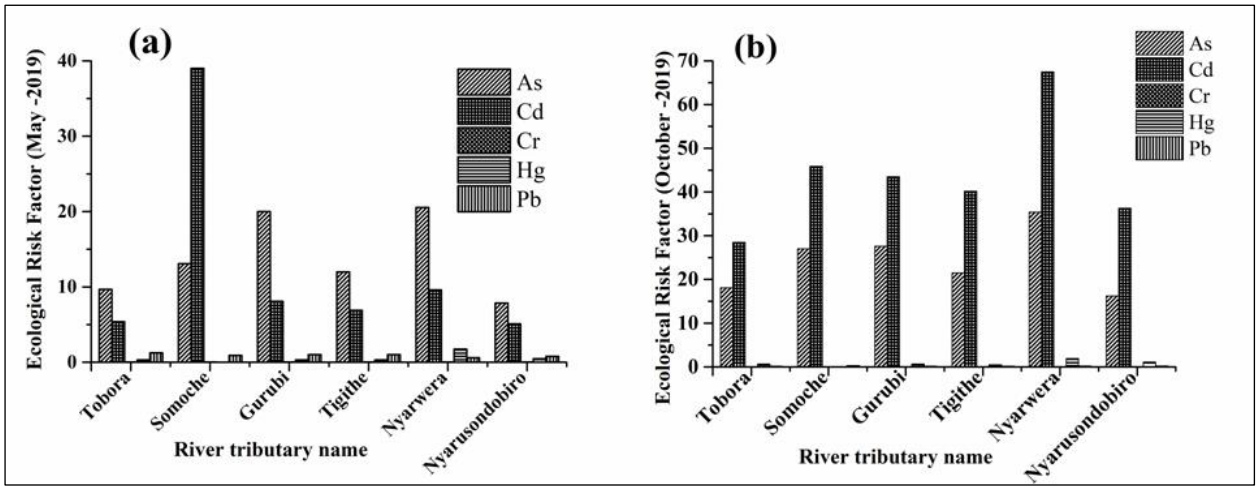


Figure 30: Ecological risk factors for the Mara River tributaries in (a) dry month and (b) rainy month of 2019

In the rainy month, the R_I values for As, Cr, Hg, and Pb were less than 40, indicating a low ecological risk (Fig. 30b). However, Cd with R_I values above 40 and below 80 values indicated a moderate ecological risk. The observed R_I values for Cd in the Mara River tributaries may cause moderate ecological damage, especially in rainy month. The R_I values in the rainy month followed the order Cd > As > Hg > Pb > Cr (Fig. 30b). In the rainy month, the value for the ecological risk index indicated R_I (105) at Nyarwera tributary showed a moderate risk (Fig. 31). Normally, pH and electrode potential (Eh) changes may influence heavy metal mobility in sediments resulting in increased R_I values (Rinklebe *et al.*, 2016).

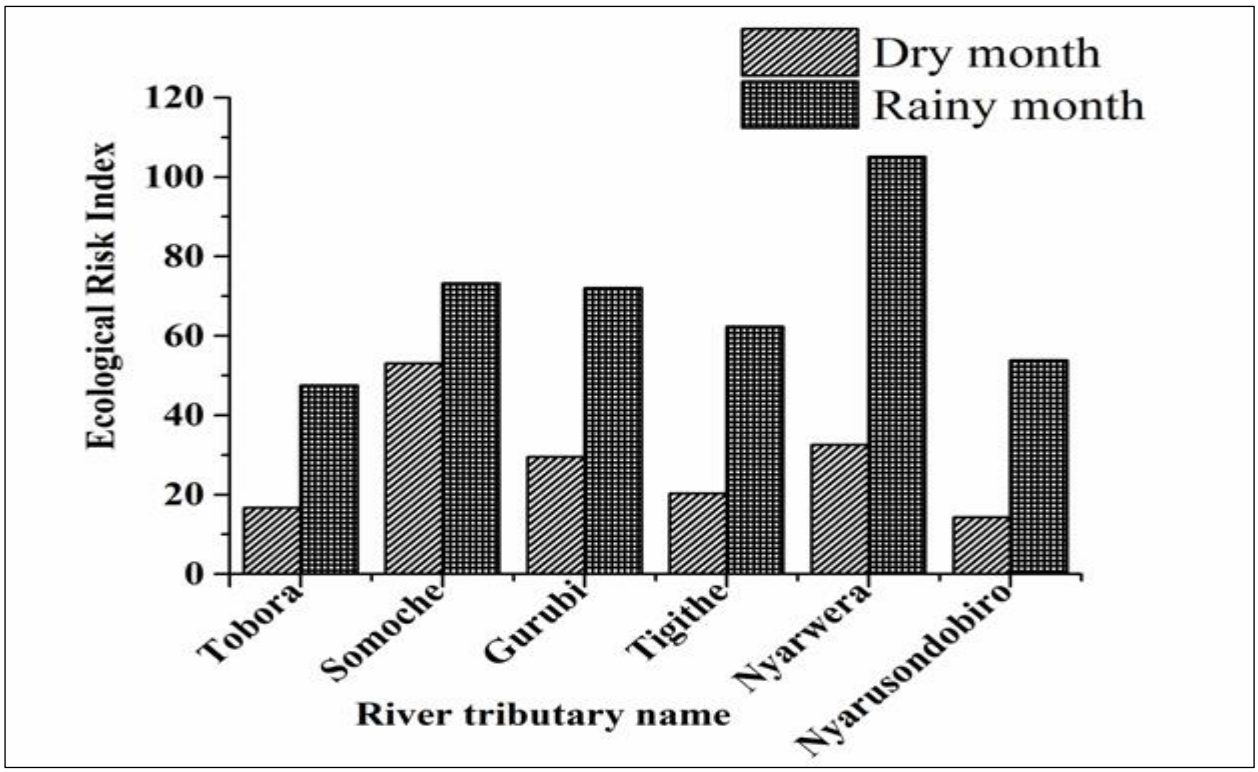


Figure 31: Ecological risk index in River tributaries

4.8 Pollution Indices for the River Sediment Samples

(i) Geo-accumulation index

When comparing results from the two months using the Igeo values, an interesting contrast emerged. In the dry month, almost all study sites and elements had values below zero (Fig. 32a). This meant that almost all studied sites were unpolluted. The only exception was for As at Nyantare Area, which indicated no-pollution to moderate-pollution levels (Zhuang & Gao, 2014). In the rainy month, all four study sites were polluted to Cd levels (Fig. 32b). Samples from the Somoche Factory site indicated a moderate level of pollution. Samples from the remaining three sites were moderate to heavily polluted. This observation of Cd pollution during the rainy month may be linked to human activities such as industry, mining and agriculture, and seasonal mobility (Charzyński *et al.*, 2017; Gómez-álvarez *et al.*, 2011). During the rainy month, the other four elements, i.e., Hg, Pb, Cr and As, indicated an unpolluted status at all four sites.

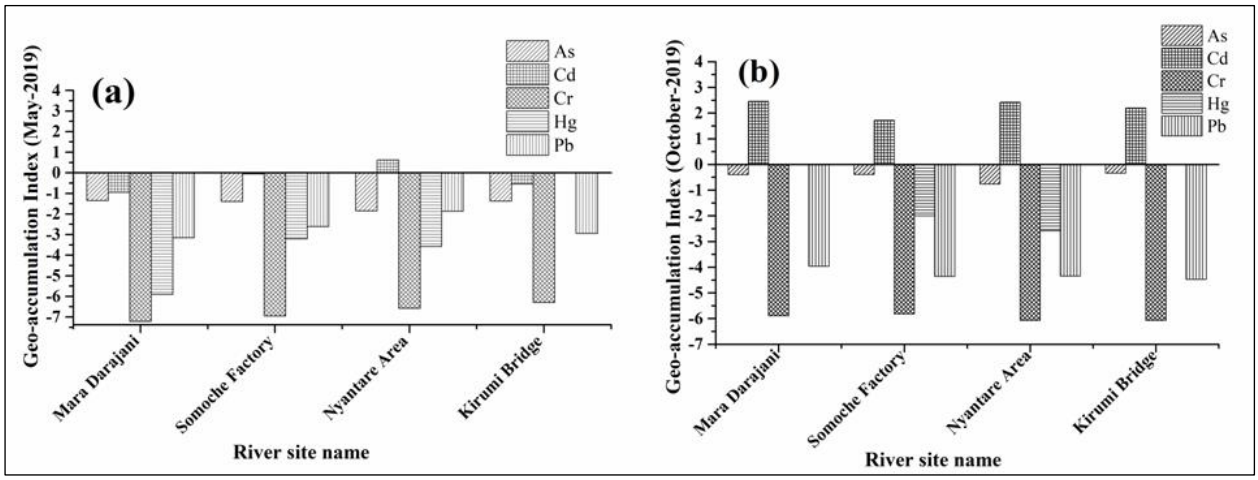


Figure 32: Geo-accumulation index values along the Mara River for (a) dry month and (b) rainy month of 2019

(ii) Enrichment Factor

In the present study, there was extremely high enrichment for the dry month samples with respect to As followed by Cd (Fig. 33a). For both As and Cd in the dry month, *EF* values were substantially above 40. For Pb, in the dry month, extremely high sediment enrichment was found at Somoche Factory and Nyantare Area with 45 and 48 *EF* values, respectively (Fig. 33a). Mara Darajani and Kirumi Bridge sediment samples had Pb *EF* values of 35 and 26, respectively, indicating a very high Pb enrichment level. For Cr and Hg, EF values were well below 2, signifying minimal enrichment of these two toxic heavy metals in the dry month (Fig. 33a).

Generally, Cd was more enriched in the rainy month than As (Fig. 33b). However, both Cd and As had *EF* values well above the 40-mark indicative of extremely high enrichment levels. Moreover, compared to the dry month, EF values in the rainy month were significantly higher (Fig. 33b). Interestingly, however, in the rainy month, *EF* values for Pb decreased significantly. In the rainy month, *EF* values for Pb ranged from 23.7 to 31.9, meaning that no site had extreme Pb enrichment. This lessening in Pb enrichment may be attributed to the dilution effect caused by rainfall (Yahaya *et al.*, 2009). For Cr, sediment *EF* values in the rainy month ranged between 4.8 and 5.6, indicating significant enrichment. For Hg, there was extremely high enrichment at Somoche Factory and Nyantare Area, with *EF* values of 74 and 50, respectively. The elevated *EF* values for Cd, As and Hg during the rainy month could be indicative of anthropogenic inputs as well as mine rock weathering (Mohiuddin *et al.*, 2011; Tchounwou *et al.*, 2012; Wei *et al.*, 2018).

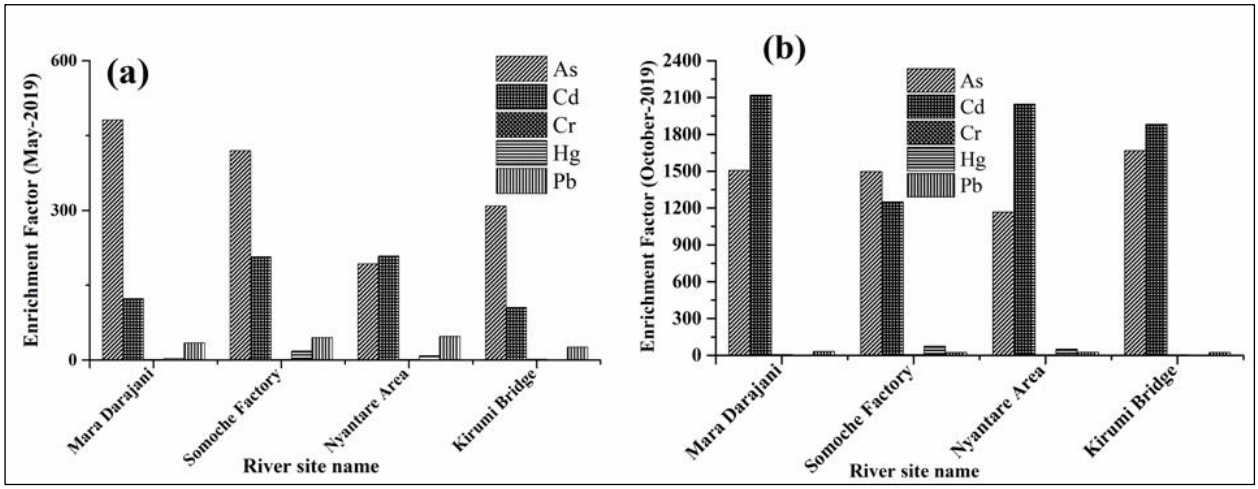


Figure 33: Enrichment factor along the Mara River for (a) dry month and (b) rainy month of 2019

(iii) Contamination Factor

In the dry month, all sediment samples attained contamination factor (*CF*) values below unity, meaning that there was a low degree of contamination in the dry month (Fig. 34a). In the rainy month, CF values for Cd and As on all sites were such that $1 \leq CF < 3$, indicating a moderate degree of contamination (Fig. 34b). For Cr, Hg, and Pb, a low degree of contamination was retained even in the rainy month (Fig. 34b). Seasonal variations in temperature and rainfall affect the levels and distribution of certain heavy metals in aquatic systems. These climatic variations are known to have specificity in affecting different heavy metals (Wijngaard *et al.*, 2017).

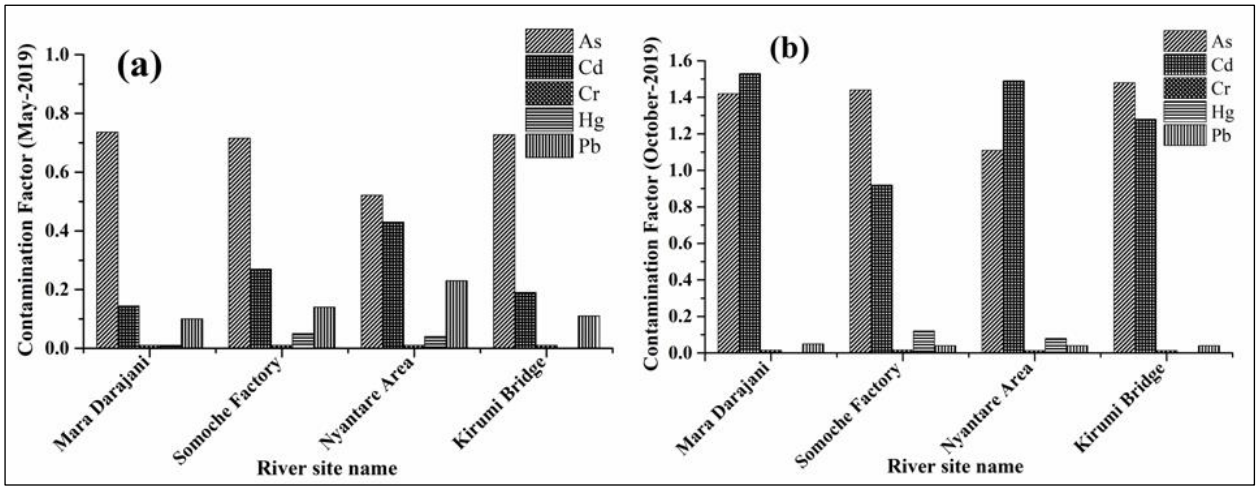


Figure 34: Contamination factor values along the Mara River for (a) dry month and (b) rainy month of 2019

(iv) Pollution Load Index

The *PLI* is both a site- and a pollutant-specific index. In the present study, four locations and five pollutants were considered in the dry and rainy months. The values of *PLI* at all sites were greater than zero but less than one, indicating minimal site deterioration (Fig. 35a) (Sulaiman *et al.*, 2016). At the Kirumi Bridge site, signs of site deterioration were detected only during the dry month and were absent during the rainy month. At Somoche Factory, site deterioration signs were present during both the dry and rainy months but more predominant in the rainy month. A similar trend to that of Somoche Factory was observed at the Nyantare site. No signs of site deterioration were observed at Kirumi Bridge in both the dry and rainy months. Both Nyantare and Somoche sites were located close to the North Mara gold mine. Mine site operations may have contributed to the observed sediment quality deterioration (Younger & Wolkersdorfer, 2004).

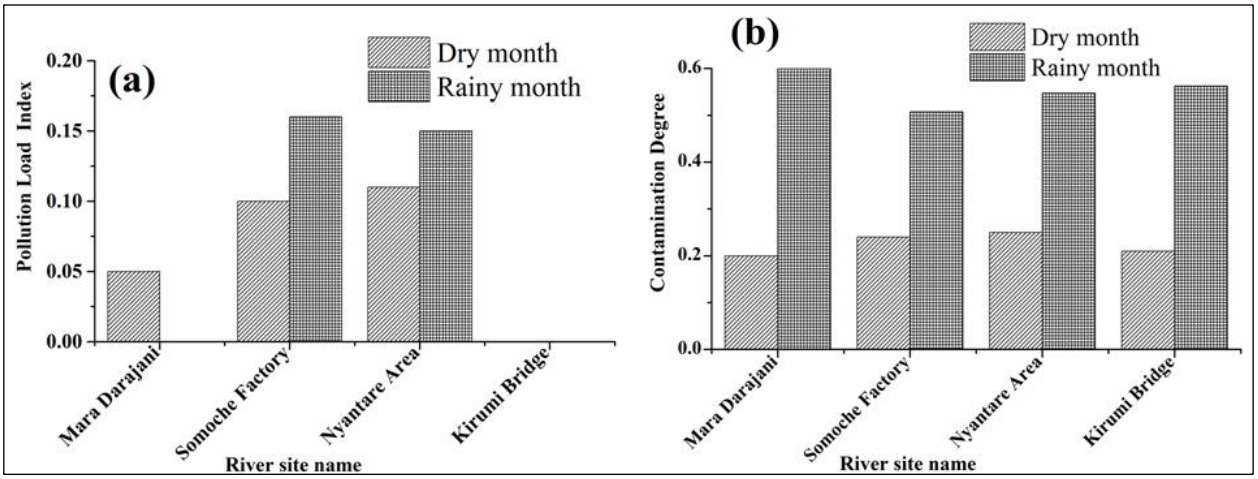


Figure 35: Pollution and contamination indices: (a) pollution load and (b) modified contamination degree along the Mara River

(v) Contamination Degree

Like the *PLI*, the modified contamination degree (*m*Cd) values were below unity at all sites but with notable temporal differences (Fig. 35b). Unlike the *PLI*, the *m*Cd indicated signs of contamination for all sites and both months. However, all the *m*Cd values were lower than 1.5, indicating a none to very low contamination regime (Kolawole *et al.*, 2018). Like all the indices discussed above, the *m*Cd also revealed that samples collected in the rainy month were more contaminated than those collected in the dry month (Fig. 35b). Contaminant mobilization and influences of anthropogenic activities close to the Mara River may have resulted in higher *m*Cd values during the rainy month.

(vi) Ecological Risk Assessment

In the present study, all the ecological risk indices fell below 40 in the dry month (Fig. 36a). It is an indication that for the studied metals, none of them posed any pollution risk in the sediments during the dry month. Figure 36a indicates that Cd posed the most significant threat at Nyantare Area in the dry month, followed by Cd at Mara Darajani. Of all the studied heavy metals, Cr posed the lowest ecological risk in the dry month. During the rainy month, Cd posed a moderate ecological threat at Mara Darajani and Nyantare Area (Fig. 36b). It is important to note that Cd posed the highest risk at all sites in the rainy month. All other elements posed a low ecological threat. Likewise, the potential ecological risk index (R_I) values were below 150, indicating a low potential risk at all sites and for both months (Fig. 37). However, during the rainy month, R_I values were sufficiently higher than the dry month values. This was indicative of the influence of human activities, e.g., agriculture and mining, on the transport, distribution, and content of heavy metals in sediments facilitated by rainfall events in the study area (Byrne *et al.*, 2012; Chileshe *et al.*, 2019; Garcia *et al.*, 2012).

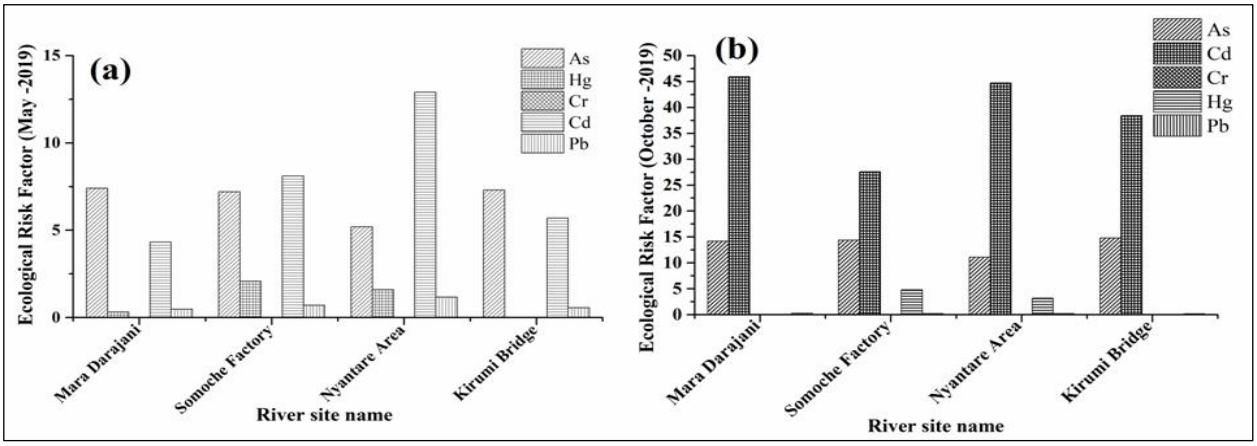


Figure 36: Ecological risk factors along the Mara River for (a) the dry month and (b) rainy month

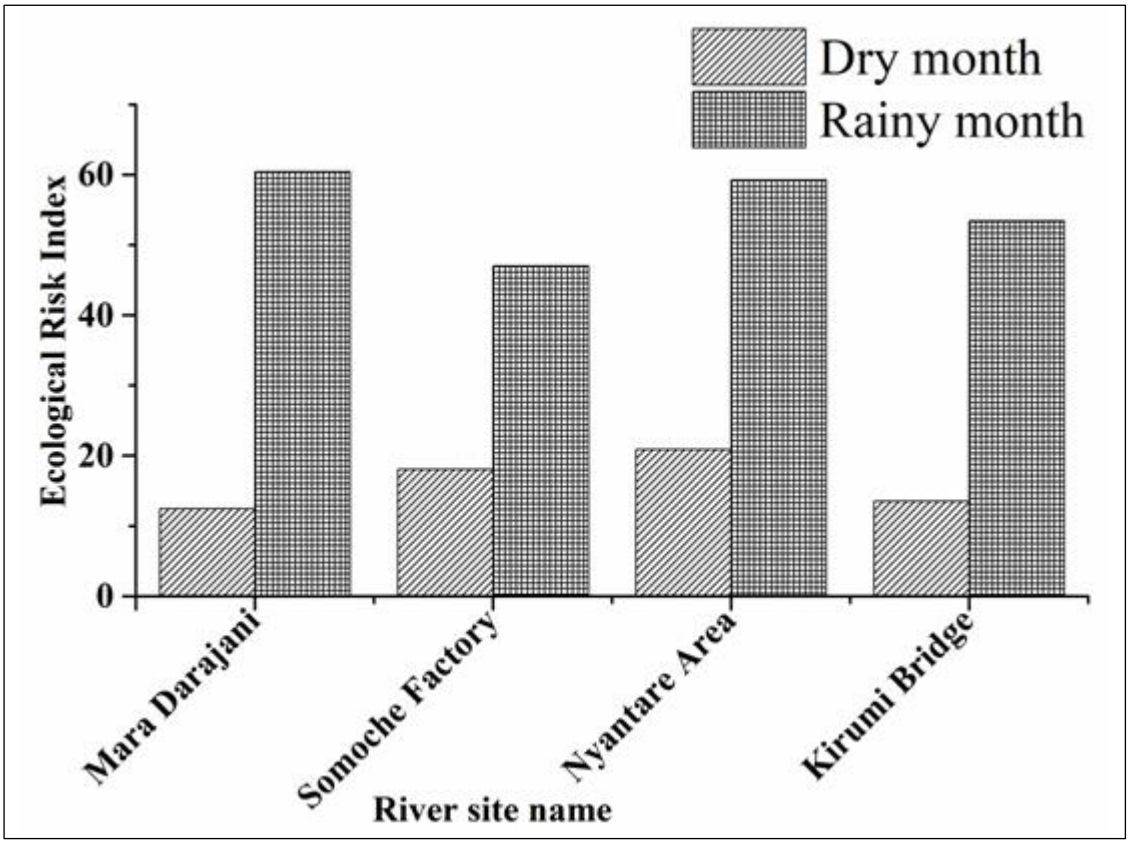


Figure 37: Potential ecological risk index along the Mara River for the dry and rainy months of 2019

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The present study revealed that As and Cd contaminations in both the dry and rainy months in sediments in the Mara River and its tributaries were above the background levels and well above the SQGs. High levels of As and Cd at Nyarwera tributary probably originated from Sirori-Simba artisanal mines. Moreover, pollution by As - Pb and Cd - Pb was significantly negatively and positively correlated in the dry month along the Mara River. The positive correlation of Cd and Pb in sediments in the Mara River during the dry month may be indicative that they originated from similar pollution sources. However, the negative correlation of As and Pb in sediments during the same month could be a revelation that different soil was involved. In the dry month, the PCA revealed that nonpoint sources of contamination of Cd, Cr and Hg in sediments at Somoche Factory, Kirumi Bridge, and Mara Darajani existed. Likewise, the PCA indicated that Pb contamination in the water at Kirumi Bridge was probably related to some traffic deposition due to its vicinity to the Musoma–Sirari highway. The present study found that As and Cd in sediments along the Mara River and its tributaries were likely to exhibit adverse ecological effects on sediment-dwelling organisms in the rainy month.

Furthermore, I_{geo} values indicated that Cd was more elevated in the dry month than in the rainy month at Somoche. However, the I_{geo} values for Cd at Nyarwera and Gurubi tributaries indicated a moderate accumulation. Contamination of Cd and As in tributaries were more elevated in the rainy month than in the dry month. The enrichment factor values indicated that, overall, As, Cd and Pb were in the range of extremely-to-severe enrichment. Indices further indicated that rainfall events might have aggravated the enrichment of heavy metals in sediments. Generally, the present study concludes that low to moderate potential ecological risks existed in the Mara River and its tributaries in May and October 2019.

5.2 Recommendations

The present study showed that all the Mara River tributaries originated from larger to small-scale gold mining areas. Mining activities are important industries for the economical growth of the country generating employment for people and raising the country. On the other hand, excessive mining activities may result in the creation of a unique mining landscape. To rescue the heavy metals disruption impact on the study area, the authors recommend; that first, effective monitoring

of mining sites by local authorities should be excised to avoid an increase in uncontrolled solid waste disposal. At mine sites, containment of all contaminated water is to be ensured using water management strategies. Wastewaters with elevated arsenic, chromium, cadmium, iron, manganese, mercury, and molybdenum, may be treated using unconventional industrial byproducts such as slags or oxidation, reduction, precipitation, adsorption, or cation exchange techniques. Secondly, governments should consider initiating monitoring conservation programs to minimize unwanted materials from mining sites.

The following recommendations are important to further this research in the future:

(i) Laboratory and field-scale toxicological studies by subjecting ecologically-sensitive organisms, e.g., *Daphnia magna,* to varied doses that mimic the concentrations found in the present study. Therefore, the present study highly recommends the use of extremely sensitive aquatic organisms to study the possible influence of pollution on the aquatic life in the Mara Basin as well as in the broader Lake Victoria Basin.

(ii) Although the present study could somehow associate heavy metal pollution with some anthropogenic inputs, further studies that use modern 'fingerprinting' techniques are advised. As such, isotopic analysis studies for samples collected from the Mara River and its tributaries would be useful in determining the exact location of heavy metal sources in water and sediments.

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APPENDICES

Appendix 1: Water Samples Digestion for Pb, Cr and Cd Determination

The water samples were digested using reagent-grade chemicals of concentrated nitric acid of 65 % and reagent water. Before digestion, the sample pH was checked to ensure that it reads at pH < 2 or needs to be adjusted. A well-mixed, acid-preserved sample of 100 mL was measured in a measuring cylinder and transferred into the empty weighed beaker. 5 mL of concentrated nitric acid (HNO3 68 %) was added to a beaker and covered with a ribbed watch glass in a fume hood. Boiling chips were added to aid boiling. Then it was evaporated in a hotplate while continuing heating with the addition of concentrated nitric acid to 20 mL volume. The sample colors were changed to a light-colored, clear solution. The beaker and the watch glass cover were washed with reagent water and filtered. The filtrate was transferred into a 100 mL volumetric flask and rinsed with 5 mL of the reagent water. The sample was cooled, diluted to the mark, and mixed thoroughly, ready for analysis. Along with this experiment, a blank sample determination was carried out. All experimental procedures described above followed the literature (APHA, 2017).

Appendix 2: Water Samples Digestion for As Determination

Digestion of water samples was done by preparation of reagent, 5% potassium persulfate solution. The solution was made by dissolving 25 g of $K_2 S_2 O_8$ in reagent water and diluted to 500 mL. The solution was stored in glass and refrigerated. During digestion, undigested 50 mL of water samples were added into a 100 mL micro-Kjeldahl flask. With the aid of a pipette, 1 mL of 2.5 N H_2SO_4 and 5 mL of 5% $K_2S_2O_8$ was added. The mixture was heated in capped containers of an autoclave at 121°C for 1 hour. After digestion, the final volume was diluted to 50 mL for arsenic determination. The sampling digestion aiming for arsenic determination followed the method described in the standard methods for examining water and wastewater (APHA, 2017).

Appendix 3: Water Samples Digestion for Hg Determination

Digestion of water samples for mercury determination was carried out using EPA method 245.1. The reagent used was mercury assayed level of solid contained not less than 0.05 mg/L. Other reagents were water reagents, nitric acid (HNO_3) with a specific gravity of 1.41, sulfuric acid (H_2SO_4) with a specific gravity of 1.84, potassium permanganate, potassium persulfate, Sodium chloride-hydroxyl ammonium chloride, and stannous chloride solutions.

A water sample of 100 mL was transferred into a B.O.D bottle. Concentrated sulfuric (H_2SO_2) and nitric (HNO_3) acids of 5 mL and 2.5 mL were added. Likewise, 15 solutions of $KMnO_4$ were added to the B.O.D bottle. The mixture was shaken until the purple color persisted for 15 minutes. Then, 8 mL of potassium persulfate solution was added to it. The mixture was thoroughly mixed again. Finally, the sample container was capped and covered with aluminium foil and heated for two hours in a water bath set at 95°C (APHA, 2017).

Appendix 4: Sediment Samples Digestion for Pb, Cr, and Cd Determination

Sediment digestion using EPA method 3050 B (SW – 846) was carried out to determine lead, chromium, and cadmium metals. However, the same techniques were used for sediment digestion to determine arsenic metals with some modification. Wet sediment samples of 2 g were transferred into the digestion vessel. Under a fume hood, 10 mL of 1:1 (HNO_3) were added to the sample, and the slurry was mixed. A watch glass was covered on top of it. The digestion machine, Kjeldahl (Avishkar International PVT LTD, Mumbai), was set to the heating temperature of 95 °C ± 5 °C and then refluxed for 10 to 15 minutes to avoid boiling. Samples were cooled; then 5 mL concentrated nitric acids were added, and the covers were replaced, followed by refluxing for 30 minutes. A brown fume was generated, and 5 mL of concentrated HNO_3 was added several times until the brown fumes stopped forming. Solutions were allowed to evaporate to approximately 5 mL without boiling (APHA, 2017).

After the sample cooled, 2 mL of water and 3 mL of 30% (H_2O_2) were added. The vessel was covered with a watch glass and returned to the heating source for warming while starting the peroxide reaction. The assembly was continued heating until bubbliness decreased then cooled. The 30% (H_2O_2) were continued added with warming until the general appearances of samples were unchanged. The acid peroxide reactions were continued heated until the volume samples were reduced to 5 mL. The sample was cooled, diluted by reagent water to 100 mL, and filtered through Whatman paper number 41 of 0.45 μm (Whatman Merck Millipore Corporation, Darmstadt, Germany), followed by centrifugation to 2,000 - 3,000 rpm to clear the supernatant. Finally, 10 mL of concentrated HCL was added to the sample, and the samples were digested to a heating source and refluxed at 95 °C ± 5 °C for 15 minutes, left to cool, and analyzed HG – AAS (APHA, 2017).

For samples digested for arsenic determination, the pretreatment method was adopted. At the final volume stage, 5 mL of concentrated hydrochloric acid was added. The addition of acid facilitated removing excess hydrogen peroxide (H_2O_2) in the solution for accurate arsenic determination (APHA, 2017).

Appendix 5: Sediment Samples Digestion for as Determination

Digestion of sediments was carried out by weighing 0.8 g of untreated wet samples and placed in a BOD bottle. A volume of 5 mL of deionized water and 5 mL of aqua regia was added to it. The mixtures were heated for two minutes in a water bath at 90 +/- 5 C. Then cooled, followed by the addition of 50 mL deionized water and 15 mL potassium permanganate solution. The solution was mixed thoroughly and placed in a water bath for 30 minutes at 90 ± 5 C. The digestion time was recorded. The solution cooled, and 6 mL sodium chloride-hydroxylamine hydrochloride solutions were added to reduce excess permanganate. Finally, the sample was transferred into a volumetric flask and diluted with deionized water to the final volume (APHA, 2017).

RESEARCH OUTPUTS

(i) Published Paper (1)

Nkinda, M. S., Rwiza, M. J., Ijumba, J. N., & Njau, K. N. (2020). Quantitative assessment of metal contamination and associated pollution risk in sediments from the Mara River in Tanzania. *Environmental Monitoring and Assessment*, 192(11), 1-16.

Nkinda, M. S., Rwiza, M. J., Ijumba, J. N., & Njau, K. N. (2021). Heavy metals risk assessment of water and sediments collected from selected river tributaries of the Mara River in Tanzania. *Discover Water*, 1(1), 1-20.

(ii) Poster Presentation