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The potential of water resources contamination around a large-scale gold mine

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**THE POTENTIAL OF WATER RESOURCES CONTAMINATION
AROUND A LARGE-SCALE GOLD MINE**

Musiba Masamba Musiba

**A Dissertation Submitted in Partial Fulfilment of the Requirements for the Degree of
Master's in Hydrology and Water Resources Engineering of the Nelson Mandela African
Institution of Science and Technology**

Arusha, Tanzania

May, 2022

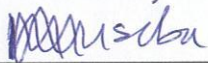
ABSTRACT

This study used the hydro-chemical properties and isotopic signatures of water to understand the main sources of deterioration of water quality around the North Mara gold mine in Tarime District, Mara Region. The chemical and isotopic signatures of the surface and groundwater were used in understanding the origin, flow pattern, residence times, and vulnerability to pollution. Most samples that were located downstream, western side of the mine tailings dam were slightly acidic with pH as low as 4.6 and enriched with stable isotopes. Most samples with elevated concentrations of Na^+ , Cl^- , SO_4^{2-} and NO_3^- could not be isotopically linked with the local geochemistry, but the observed water chemistry was controlled by evaporation and anthropogenic effects. The Piper trilinear diagram showed Ca and Mg cations dominance, while bicarbonates and sulfates dominated the anions. The heavy metals, Pb and Hg levels (mean 70.29 and 17.95 $\mu\text{g/L}$, respectively) were all higher than the levels recommended in both the World Health Organization (WHO) and Tanzanian drinking water guidelines. The low pH values and elevated concentrations of cyanides, heavy metals, and metalloids were probably associated with mining activities. The radioactive isotope results indicated the vulnerability of the water to recent contamination that could be attributed to near-surface anthropogenic activities. Moreover, stable isotopic studies indicated the pollutants-carrying water flow pattern was from the eastern to the western side of the study area. Lowland samples had higher tritium activities than the highland ones. Therefore, the present study concludes that groundwater recharge from recent local precipitation may have an impact on the sources studied and the use of shallow dug out wells should be minimized.

DECLARATION

I, Musiba Masamba Musiba, do declare to the Senate of Nelson Mandela Africa 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.

Musiba Masamba Musiba



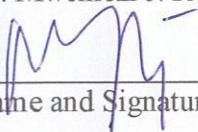
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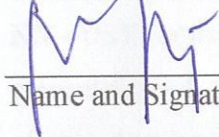
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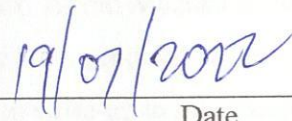
CERTIFICATION

The undersigned certifies that have read and hereby recommend for acceptance by the Senate of the Nelson Mandela African Institution of Science and Technology, the dissertation titled "*The Potential of Water Resources Contamination around a Large-Scale Gold Mine*" in partial fulfillment of the requirements for the award of the Master's degree in Hydrology and Water Resources Engineering of the Nelson Mandela African Institution of Science and Technology.

Dr. Mwemezi J. Rwiza



Name and Signature of Supervisor



Date

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DEDICATION

This dissertation is dedicated to:

My Lovely Parents

My mother Weseja Kitundu and my late father Masamba Musiba (R.I.P)

My wife

Epifania Robert

My children

Purity, Esperance, Leonel and Alegria

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LIST OF ABBREVIATIONS AND SYMBOLS

μS/cm	Micro Siemens per Centimetre
AMD	Acid Mine Drainage
EC	Electrical Conductivity
EWURA	The Energy and Water Utilities Regulatory Authority
GML	Global Meteoric Line
GPS	Global Positioning System
LMWL	Local Meteoric Water Line
MEWES	Materials, Energy, Water and Environmental Sciences
mg/L	Milligrams per Litre
NM-AIST	The Nelson Mandela African Institution of Science and Technology
NMGM	North Mara Gold Mines
SMCL	Secondary maximum Contaminant Level
TDS	Total Dissolved Solids
TU	Tritium Units
TZS	Tanzania Standards
USEPA	United States Environmental Protection Agency
V-SMOW	Vienna Standards Mean Ocean Water
WHO	World Health Organization
WISE-futures	Water Infrastructure and Sustainable Energy futures

CHAPTER ONE

INTRODUCTION

1.1 Background of the Problem

In many developing countries, like Tanzania, the inaccessibility of drinking water remains a serious concern that needs immediate action. The demand for domestic use and economic development is increasing despite the deterioration in quantity and quality (Vaux, 2011). In Tanzania, one of the environmental impacts comes from the expansion of mining activities. Large-scale mining expansion that emerged in the late 1990s, mostly around the Lake Victoria goldfields, has resulted in significant socio-economic changes. For example, within two to three decades village lands have been turned into small towns, regardless of the little rural settlement planning. These abrupt changes, among other things, have the potential to cause pressure on the water resources around the mine areas.

Water pollution has been highly linked to large- and small-scale mining operations. When this is coupled with natural and other anthropogenic factors, pollution of ground and surface water sources is accelerated. Other environmental impacts related to large-scale mining operations include lowering of the water table due to excessive water use in ore processing, and disruption of groundwater flow through excavation (Maliganya *et al.*, 2013; Ouyang & Elsworth, 1993). These processes, if not checked, can affect the hydrochemistry of surface water as well as groundwater that form an important part in the hydrological cycle. In addition to mining operation, the increased human settlements in and around the mines, has triggered other environmental pollution challenges that result from domestic wastes. Therefore, understanding how natural or human-related activities affect the surface and groundwater, remains one of the important aspects for water quality and its suitability.

Normally, for classification and assessment of water quality, the most common major ions such as: Na^+ , K^+ , Mg^{2+} , SO_4^{2-} , HCO_3^- , Ca^{2+} , and Cl^- , are considered. However, studies for the characterization of the hydro-chemical properties of both surface water and groundwater around the large-scale mining operations are limited. Despite the environmental impacts known to occur around mining areas, only a few studies have been published on elevated levels of trace and heavy metals from water sources, soil, and biological systems (Almås & Manoko, 2012; Bitala *et al.*, 2009; Dimitriou & Zacharias, 2006; Rwiza *et al.*, 2016; Taylor *et al.*, 2005). Therefore, it

is imperative to encourage the carrying out of studies related to the distribution of water pollutants in and around the large-scale mine operations of Tanzania.

In addition to hydro-chemical studies, it is also imperative to assess the vulnerability of water resources to contamination. Such environmental assessments are usually done by estimating the age and the groundwater flow path (Bowell *et al.*, 1995; Dimitriou & Zacharias, 2006). These estimations usually serve in understanding the pattern of transport of pollutants and groundwater movement rates for assessing the vulnerability of groundwater systems to contamination ([ENREF 21](#)Hinkle, 2009). The knowledge on contamination distribution helps to determine the groundwater susceptibility to near-surface contamination.

Furthermore, the deployment of environmental isotopes helps in the determination of groundwater residence time and flow patterns (Hamutoko *et al.*, 2017; Yeh *et al.*, 2011). The ^2H and ^{18}O are stable isotopes which can be deployed to estimate the flow of groundwater, enabling to allocate the water origin and how it mixes with other water types. On the other hand, the radioactive isotopes such as tritium, can assist the process of estimation of water residence time (Kendall & Doctor, 2003). The tritium radioactivity (half-life 12.43 years), measured in tritium units (TU), can thus predict groundwater recharge from local and recent precipitation (Lucas & Unterweger, 2000).

The current study applied isotopic signatures and hydrochemical characteristics of surface water and groundwater samples to determine the water quality and assess groundwater contamination vulnerability. The spatial distribution of pollution was evaluated by analyzing various water resources' hydrochemical composition. The knowledge and basis of the water flow patterns, and residence time were determined by the spatial distribution of groundwater isotopes. Additionally, the stable and radioisotopes assisted in arriving at a conclusion regarding the vulnerability of groundwater to contamination.

1.2 Statement of the Problem

The problem is limited knowledge about the sources and distribution of pollutants due to mine operations and other anthropogenic activities. Less is known in many areas in sub-Saharan Africa about how the economic sectors can be detrimental to the natural environment. Due to zero or limited knowledge, the governments and other actors find it difficult to solve environmental problems related to activities such as mining and mineral processing. This is because there is limited data on which to base mitigation decisions on. The extensive generation of toxic

pollutants due to economic activities is a problem that needs to be solved. The miners, mining companies, the Government of Tanzania and other stakeholders in the mining sector would like to tame pollution in the mining areas. But these stakeholders lack studies that indicate the extent of the problem. This is why this study was conducted – to reduce the knowledge gap related to mining pollution and pollution patterns, thereof, for informed decision-making.

1.3 Rationale for the Study

The rationale for this study is based on the recognition of the importance of water resources both in quantity and quality amidst increasing demand. Water sources around mining areas is considered important considering recurrent grievances concerning pollution. So the rationale is for considering availability of alternative sources of water around North Mara Gold Mine (NMGM) to avoid impacts of pollution. The use isotopes both stable and radioactive, serve their application in determining groundwater origin and processes of water mixing while the radioactive ones can assess the groundwater dynamics (Kendall & Doctor, 2003). Understanding timescales of groundwater and how it is transported remains of paramount importance to understanding and controlling its quality to avoid pollution. In this context, spatial information about the groundwater system in question is needed and hence the subject of groundwater dating remains a practical area of research and application. Using isotopes in hydrological studies are very rare in our country and need further application

1.4 Research Objectives

1.4.1 General Objective

The general objective of this study was to assess the isotopic and hydrochemical characteristics of surface water and groundwater in order to delineate the sources and distribution of pollutants associated with mining operations.

1.4.2 Specific Objectives

In the present study, three specific objectives were covered as follows:

- (i) To assess the extent to which surface water and groundwater pollution may be attributable to mining operations.

- (ii) To determine the vulnerability of surface water and groundwater to pollution related to both natural and anthropogenic activities prevalent in the study area.

1.5 Research Questions

To address adequately the specific objectives outlined above, the following research questions were used:

- (i) To what extent are mining operations contributing to surface water and groundwater pollution?
- (ii) How are surface water and ground water vulnerable to natural and anthropogenic pollution?

1.6 Significance of the Study

Understanding pollutant sources and pathways in geological formations can be useful in assisting the efforts geared for avoiding the negative effects in environmental systems. The findings in the current study can be put to use in monitoring efforts, locating new boreholes, planning land use, and evaluating remediation activities. Using isotopes to understand contaminant transport assists in the assessment of pollution of water, demarcating the most vulnerable zones, and effectively managing, and remediating pollution. Such efforts can minimize clashes between the mining operators and agencies for environmental management.

Communities, livestock, wildlife, and other environmental compartments have been detrimentally affected by pollution around mining operations. Owing to this, the present study may help in the efforts geared to avoiding the use of degraded water sources and could help in the community efforts locate their water wells in the safer zones. Identifying the affected (or potentially affected) waters by pollution and ascertaining the vulnerability to pollution can help the local efforts to design the physical protective mechanisms, find alternative water sources, and may be used as a tool to compel authorities to take appropriate measures for avoidance of future pollution.

1.7 Delineation of the Study

Hydrochemical and isotope analysis research is a relatively broad field. The analysis presented in this dissertation is not intended to be comprehensive over the entire field. Rather, it focuses

on specific ions and isotopes that directly influence the water quality and make it easy to understand the water residence time. Both analyses are relevant to the operationalization of planning and management interventions to reduce the impacts of pollution in the study area. The area of study was confined within 10 km from the mining sites and only 19 sampling points were identified. The number of sampling points chosen were limited by the budget for analysis cost and the study timeframe. However, the chosen sampling points were a good representation of the study area, covering places where most of the population within the North Mara Gold Mines (NM-GM) dwell. Sampling was conducted during the month of April, which features the rainy period in that region.

CHAPTER TWO

LITERATURE REVIEW

2.1 Surface and Groundwater Pollution in Mine Operations

Mining and mineral processing operations have the potential of causing water resources pollution. Despite the fact that the intention for mining is to meet the demand for minerals resources and to improve the quality of living, if unchecked, it can produce effluents that contain toxic chemicals with the potential to deteriorate the quality of water resources (Hogsden & Harding, 2011). The impacts of the deterioration of water quality can be widespread pollution into surface and groundwater systems downstream. Geologically, the higher elevations in a catchment could be the groundwater recharge sites too. This means that a high concentration of pollutants at higher elevations can be transported downstream.

In most cases, mining activities include both open-pit and underground mining works. Both of these operations involve a significant extraction of groundwater to create depressions in which the operations take place. Morris *et al.* (2003) summarized the sources, pollution pathways, and potential impacts on the receiving end of the environment (Table 1).

Table 1: Groundwater problems arising from mining activities

Mining process, activity, or consequence	Potential effects on subsurface if design inadequate	Resultant environmental problem
Mine drainage	Return of mine water	Pollution to surface and groundwater due to acid mine drainage (AMD)
Mine gas generation	Migration through strata	Mine gas emission at the surface
Tailings dams	Seepage of effluents	Pollution plumes
Waste rock dumps	Leachate rich acid and metal	Pollution plumes below tailings

Morris *et al.* (2003)

2.2 Mining-related Pollution in Africa

The mining industry produces large quantities of waste, which remain a critical concern especially in large-scale gold-producing countries such as Ghana and South Africa. According to Chuhan-Pole *et al.* (2017), in sub-Saharan Africa, gold mining is the second largest contributor

to the region's exports whereby Mali, Ghana, Tanzania and South Africa were in the world's top 20 gold producing countries by 2013. Despite its importance to the economy, the large-scale and artisanal gold mining activities are clad with pollution issues. The effects are manifested by the ubiquity of heavy metals related to gold ore such as arsenic, lead and mercury (specifically from artisanal mining), cyanide discharge and air pollution among others.

The impact of pollution from mining operations has the potential to disturb the earth's health systems. However, the exposure and health effects of mining activities are sometimes closely linked to the lifestyle of an individual (Tolonen, 2015). Aragón and Rud (2015) reported air pollution in Ghana associated with high incidences of cough while von der Goltz and Barnwal (2014) reported children stunting incidences in communities living nearby mining areas. Similar cases have been reported in Nigeria in which the assessment of pollution related to the levels of heavy metals in surface and groundwater reported higher concentrations than the WHO standards (Okegye & Gajere, 2015). These pollutants usually reach surface water and groundwater systems in the aquifer zone through fractured areas/pores and infiltration (Idris *et al.*, 2014). The impact on local communities could also be linked to the level of awareness of the local community. In South Africa, the pollution threats from the mining industry to the local communities' health were reported to be exacerbated due to recklessness in abiding by governing laws and regulations (Kamunda *et al.*, 2016).

2.3 Pollution in Tanzania's Gold Mine Operations

Large-scale gold production in Tanzania started in 1998 and since then it has become the third-largest gold exporter amongst African countries after Ghana and South Africa (Almås & Manoko, 2012). Although the large-scale gold mine operations contribute to the country's economy, they can threaten the environment and cause serious health risks to nearby communities. In Tanzania, for example, Chuhan-Pole *et al.* (2017) reported impacts to communities after discovering high levels of mercury from hair samples and breast milk collected from miners in the artisanal mining areas. Similarly, Bitala *et al.* (2009) reported heavy metals, cyanide and other trace elements pollution from water which were suspected to be originating from tailing dams containing waste rocks. Other impacts from Hg accumulation were discovered in livestock such as ducks, cattle and fowl (Chibunda & Janssen, 2009; Kinabo & Lyatuu, 2009). Arsenic and other trace metals were also found in samples taken from human and in plants near gold mining communities in Tanzania (Evjen, 2011).

2.4 Use of Environmental Isotopes in Pollution Studies

2.4.1 Stable Isotopes of Oxygen and Hydrogen

Hydrogen and oxygen like other chemical elements have isotopes. Protium (^1H) and deuterium (^2H) are the most stable isotopes of Hydrogen while tritium (^3H) is the radioactive isotope. The stable isotopes of oxygen are ^{16}O , ^{17}O and ^{18}O (Yurtsever & Araguas, 1993). The ^{18}O and ^2H are heavy stable isotopes of oxygen and hydrogen, respectively while ^{16}O and ^1H light stable isotopes of oxygen and hydrogen. Some chemical, physical and biological processes can affect the ratio between heavy and light isotopes in the natural water system (Miljević & Golobočanin, 2007). The variations in isotopic content of these stable isotopes which occur naturally infer their applicability in hydrology. This is because each effect on isotopes causes a unique characteristic of precipitation which makes various water sources to be temporarily and locally marked with a certain characteristic isotopically (Fig. 1). The composition of isotopes in water is expressed in a universal standard by comparing to an internationally accepted standard of ocean water known as Standard Mean Ocean Water (SMOW).

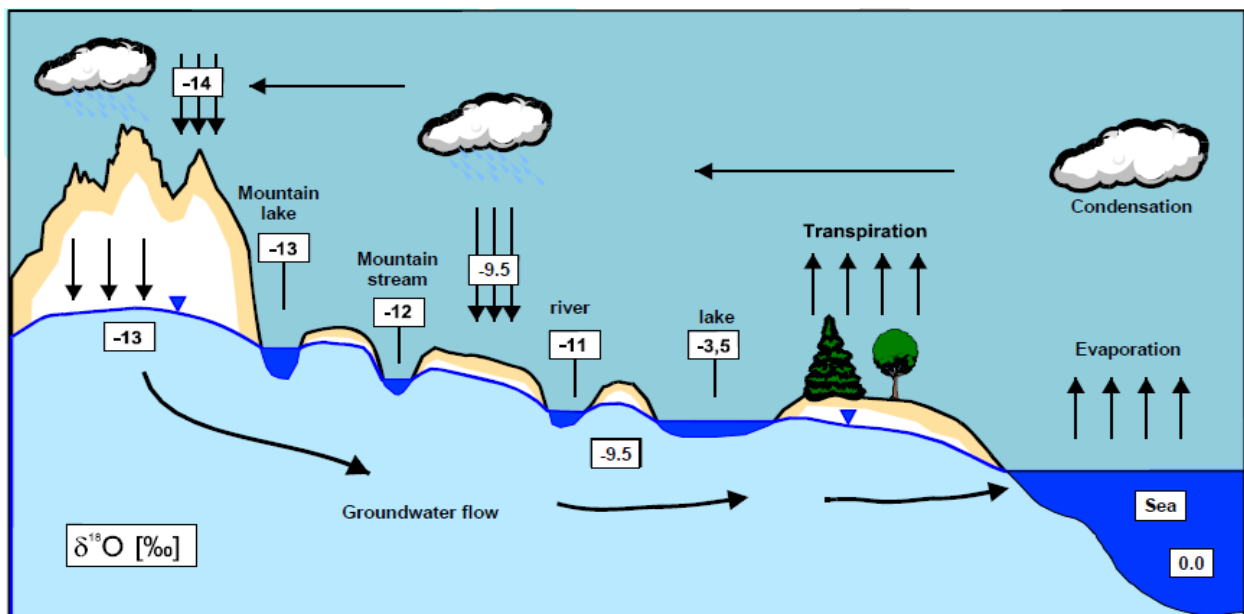


Figure 1: Fractionation of Isotopes in hydrological cycle (www.hydroisotop.de)

Generally, the meteoric water has a characteristic isotopic signature which provides a basis for delineation of areas of groundwater recharge (Gat, 1971). Thus, water that has recharged at different times, locations, or followed different flow paths will be isotopically distinct. The resulted uniqueness can create a spatial relationship with distinctive isotopic signatures of water collected from different sources. It can therefore identify the possible direction of groundwater. If the stable isotope compositions are plotted against a local meteoric water line (LMWL), the

resulting graph can explain the origin of water, i.e whether the water is from distant sources or local precipitation (Pelig-Ba, 2009).

The isotopes of ^2H and ^{18}O can determine the source of recharge and the amount of evaporation the water has undergone before recharge. The variation in natural waters shows a linear relation as a consequence of evaporation and their behaviours during the fractionation processes are similar (Yurtsever & Araguas, 1993). The equation derived in this relationship was first given by Craig (1961) (using annual average values of ^{18}O and ^2H) as given in Equation 1. The stable isotope content of water $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ is expressed by convention as parts per thousand deviations relative to the Vienna Standard Mean Oceanic Water (VSMOW) standard. The delta (δ) notation, commonly used to report isotope concentration, is defined as:

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \text{ (‰)} \quad (1)$$

Where: R_{sample} and R_{standard} refer to the isotopic ratios $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ in samples and standards, respectively. The δ value can be positive or negative. The δ positive value means that sample has more heavy isotopes than the standard and the sample is therefore enriched (isotopically heavier) and vice versa (Clark & Fritz, 1997).

Analysis of isotopic signatures of ^2H and ^{18}O in wells relative to standards were conducted by Tandia *et al.* (1998) to determine groundwater flow direction with the potential of transporting contaminants around Peninsula of Dakar Region, Senegal. The results showed that the eastern part samples of the peninsula water were depleted isotopically than those from the western part. This rendered a conclusion that the flow of groundwater was from the eastern to the western part of the Peninsula.

Similarly, Shivanna *et al.* (1998) employed isotopic signatures techniques for assessing the groundwater vulnerability to pollution. A sample for analysis was collected from local precipitation, surface water, shallow groundwater and deeper groundwater. The results showed that surface water ^2H , ^{18}O and ^3H isotopic values were more negative compared to precipitation samples. But the plot of $^2\text{H} - ^{18}\text{O}$ values from shallow groundwater fell on an evaporation line similar to that of surface waters. These similarities indicated that the shallow aquifers were receiving recharge from recent local precipitation and that fresh and modern water was more polluted than the old deeper water samples. The locally recharged recent water concluded to be more vulnerable to immediate near-surface pollution.

2.4.2 Radioactive Isotopes of Tritium

Tritium, a radioactive isotope like carbon-14, having a half-life of 12.4 years is used in isotopes hydrology as a transient environmental tracer for the determination of groundwater age (Plummer & Friedman, 1999), and it can also predict the flow direction (Rozanski *et al.*, 1991). Having the concentration of tritium especially in its initial inputs, like in precipitation forms a basis for interpreting its concentrations in groundwater and understanding the residence time of groundwater (Fontes, 1983). Tritium declines across different groundwater sources through the decay process which can guide for finding the age, direction, and even groundwater linear velocity (Rozanski *et al.*, 1991). It is measured in picocuries per litre (pCi/L) or tritium units (1 TU = 3.19 pCi/L).

Variations in tritium isotopic composition can be used to date groundwater recharge because groundwater tritium concentrations reflect atmospheric tritium levels when the water was last in contact with the atmosphere. The direct incorporation of ^3H into precipitation molecules of water was due to atmospheric testing of thermonuclear weapons which were done between 1952 and the 1960's. However, tritium is naturally produced in low concentrations due to atmospheric interaction with cosmic rays produced by the solar wind. But due to water exchange with oceans, its half-life being short and having no continuation of its release from thermonuclear testing of weapons, the concentration has been decreasing (Plummer & Friedman, 1999). So, its presence in groundwater can be used to confirm the water that was recharged after 1950s or water with mixtures of pre-and post-1950s. Additionally, due to easy measurement of tritium makes it to have a very wide spectrum of applications to waters with a residence time of fewer than 50 years (Fontes, 1983). According to Kendall and Doctor (2003), by 2003 the waters from precipitation before 1953 would have not more than 0.1– 0.4 TU. So detectable or higher concentrations of tritium in present water will signify waters derived since 1953.

2.5 Impact of Groundwater Age on Water Quality

The knowledge of groundwater age is essential in the estimation of rates of groundwater movement and how pollutants are transported (Hinkle, 2009). It can therefore be useful in water quality assessment since the groundwater age can predict which pollutants the water might contain (Lindsey *et al.*, 2019). In addition to its application in hydrology, the information on water residence time can be used to assess the potential risk of pollution for given water resources. It is studied that recent anthropogenic contaminants have a higher chance of entering

young groundwater than the old ones (Plummer & Friedman, 1998). However, the geochemical processes due to groundwater oxidation or reduction reactions with rocks in the aquifer and the contained minerals can strongly impact the quality of groundwater (Borch *et al.*, 2009). Therefore, major ions concentrations will likely be increasing with groundwater residence times which may also complement environmental tracers in relative age estimation in understanding the groundwater dynamics (Morgenstern *et al.*, 2010).

The younger groundwater is usually said to be as old as few decades and normally available in shallow, unconfined aquifers which are characterized by high recharge rates and its recharges have a high possibility to be driven by precipitation or irrigation water (McMahon *et al.*, 2011). On the contrary, low recharge rates, thicker aquifers and where the confining units separate aquifers, groundwater could be thousands of years old. However, the confining units may form a local scale flow systems in which groundwater circulation normally dominates at shallow depths (Toth, 1963). The discharge from such systems usually supports flows to surface water and groundwater when the topography is at higher elevations (Buttle, 1998). These water systems, although can provide a considerable supply of water for use, have a high chance of susceptibility to contamination (Phillips & Castro, 2003).

2.6 Groundwater Vulnerability Assessment

Groundwater vulnerability assessment is considered as a new scientific approach which was applied for the first time in the late 1960s (Vías *et al.*, 2006). The concept, together with pollution risk, requires the passage of pollutants from the origin through the pathway to the target such as water to be protected (Nguyet & Goldscheider, 2006). According to Dimitriou and Zacharias (2006) the three aspects deemed important for assessment of vulnerability, are the pollutant travel time from the origin to the target, the attenuation along its pathway, and the residence time of pollution at the target. Holman *et al.* (2005) did a vulnerability assessment and found that the presence of a pollutant in groundwater depended on the amount and timing of surface loadings of such pollutant. Dimitriou and Zacharias (2006) employed isotopes to make a groundwater vulnerability map which indicated that lowland has relatively high natural protection due to long residence time in the aquifer which also lessens interaction of water bodies. This reveals that physically the environment can render protection to the aquifers for a certain level which depends mainly on the hydro-geomorphologic status. In fact, other classical scientific approaches as used by Gemitzi *et al.* (2014) are regarded ineffective in tracing groundwater flow and identification of areas of recharge while environmental tracers, such as e.g. $\delta^{18}\text{O}$, $\delta^2\text{H}$ and tritium, are perfect

tools to assess the vulnerability by identifying the water time scales and sources of groundwater systems.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The study was conducted in the mining areas located in a region of northern Tanzania. North Mara Gold Mines (NMGM) is located in the Tarime District of the Mara Region. It lies between latitude $1^{\circ} 25' 50''$ south of Equator, and longitude $34^{\circ} 33' 51''$ east (Fig. 2). The geology in the vicinity is composed primarily of metavolcanic, metasedimentary rocks and Archean granite which dominate the Greenstone terranes. The rock underlying is primarily pyrite (FeS_2), while a small section is composed of arsenopyrite (FeAsS), galena (PbS) and sphalerite ($(\text{Zn}, \text{Fe})\text{S}$) (Bowell *et al.* 1995). The catchment area is especially around Lake Victoria Goldfields which are within sulphide ore rich in gold. The mining operation involves the two main underground mine and open-pit mine namely, Nyabigena and Nyabirama, respectively.

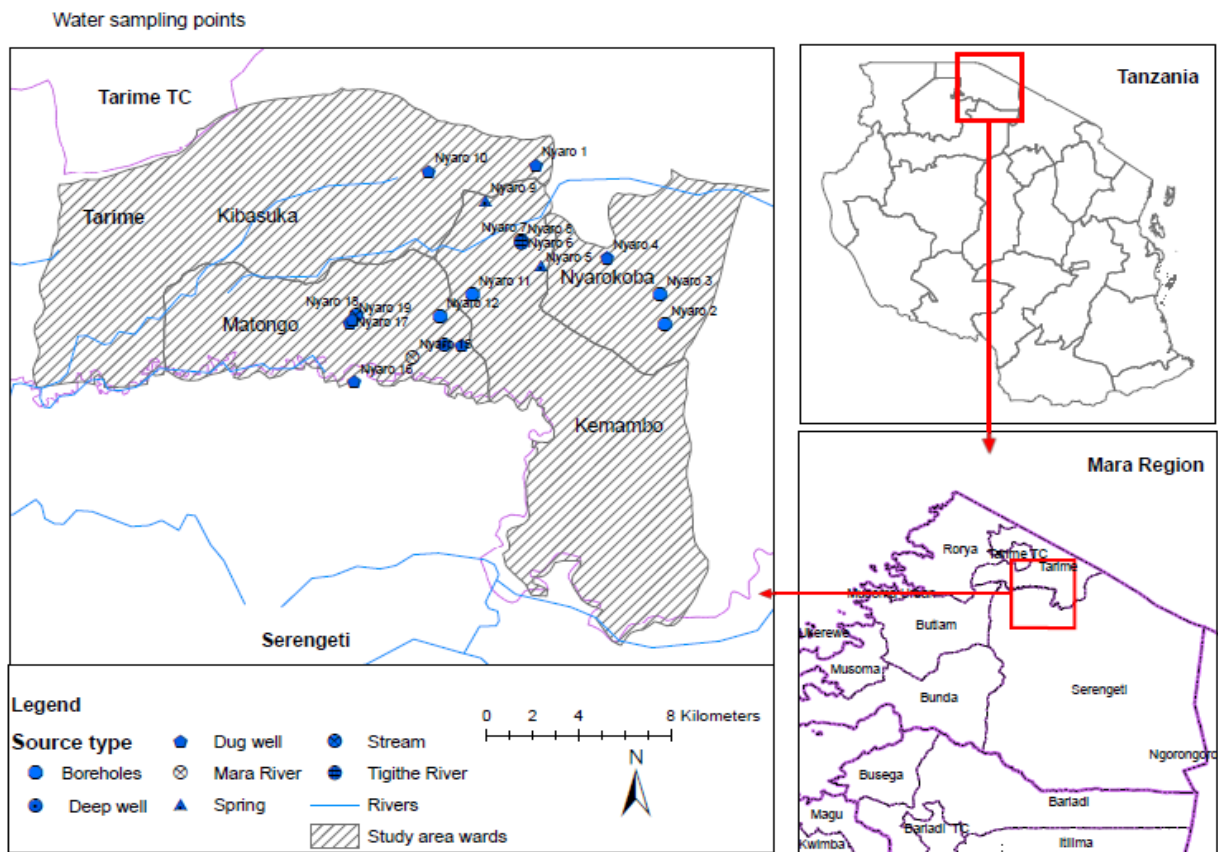


Figure 2: A Tanzania map (top right corner) indicating the location of the Lake Victoria Greenstone Zone (bottom right) and sampling sites locations (left)

3.2 Sample Collection and Analysis

The total of 19 water samples were collected from various drinking and general water sources within and around the two mining communities in April 2019. From each sampling point, 5 samples were collected for statistical quality assurance, which make a total of 95 samples. Water samples were collected from hand dug-out wells, boreholes, springs and surface water. Both water sources used for domestic consumption. Four samples were collected from the Rivers namely, Mara River, the Tigithe River and an unnamed small stream at the sub-village of Kwinyunyu passing near the tailings dam of Nyabirama open pit mine.

The sample bottles were rinsed with deionized water two times before sampling. A 1000 mL polypropylene bottle was used to collect water samples, filtered and preserved with 0.5 mL of concentrated nitric acid to maintain pH 2.0. Samples for nitrate analysis were preserved by sulfuric acid. The samples were kept in the cool box with ice packs to maintain the temperature of 4°C before transporting them to the Nelson Mandela African Institution of Science and Technology (NM-AIST) laboratory for preservation and analysis. The samples were stored in the refrigerator maintained at 4°C until the completion of analyses.

For analysis of stable isotopes of hydrogen and oxygen, 100–250 mL high-density polypropylene (HDPE) bottles were used to collect samples, while for tritium isotope analysis 50 mL HDPE bottles were used. For prevention of evaporation, the HDPE bottles were sealed prior to laboratory analysis. The sampling point coordinates were recorded by using a handheld GPS unit and the nearby landmarks characteristics were also recorded. The ScichemTech SCT-THER-PEN-6 (multiparameter device) was used to record on site data, such as pH, dissolved oxygen (DO), temperature, total dissolved solids (TDS) and electrical conductivity (EC).

Furthermore, the major ions analyses were conducted in the Nelson Mandela African Institution of Science and Technology (NM-AIST) and the Ngurdoto Defluoridation Research Center laboratories, both located in Arusha, Tanzania. The NO_3^- , CO_3^{2-} , HCO_3^- , SO_4^{2-} , Cl^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions were analyzed. The analyses of Ca and Mg were done by using ISO 6059: 1984 – EDTA (0.05 N) titration method. Sodium Ion – Selective Electrode Method used for Na and K analysis, while the AWWA/APHA: 4500-Cl-B Argentometric Method used for Cl^- analysis. The alkalinity in water by Titrimetric Method (titration with 0.01N H_2SO_4) was used to analyze CO_3^{2-} and HCO_3^- . NO_3^- and SO_4^{2-} were analyzed by the use of spectrophotometric methods.

The stable and radioactive isotopes analyses were performed by using a ThermoScientific MAT 253 Stable Isotope Ratio Mass Spectrometer at the University of Waterloo Isotope Laboratory (Ontario, Canada). The isotopic values are represented per mil (‰) in δ -values relative to international Vienna Standards Mean Ocean Water (V-SMOW), represented by Equation (1). The values are precision measured within $\pm 0.20\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.8\text{‰}$ for $\delta^2\text{H}$ as required by the V-SMOW standards. Tritium amounts were obtained by using the liquid scintillation counting (LSC) procedures. The amount was obtained direct (not enriched) by a detection limit of 6.0 ± 6.0 TU at 2 sigma, in tritium units (TU).

The WFX-210 (Beijing Rayleigh Analytical Instrument Corporation) atomic absorption spectroscopy (AAS) was used for the analysis of heavy metals and metalloids. Before analysis the samples underwent a wet acid digestion by using diacid mixture 9:4 (v/v) (nitric acid: hydrochloric acid). A revised Phenolphthalein Method was used for the analysis of cyanide. The standard solutions were prepared in the same acid matrix to run the analytical blanks. The soaking of laboratory plastic and glassware overnight was performed using a 10% HNO_3 solution and then rinsed with deionized water before analytical procedures were performed. Both samples were analyzed in triplicate, and the results were obtained after averaging the data. The calculations were performed by the use of the Microsoft Excel 2015 Version.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Hydro-chemical composition of water sources

4.1.1 Groundwater and Surface Water pH

The results for 19 sampling points are presented in Table 2. Most samples had pH values between 6.3 and 8.5. The water $\text{pH} < 7$ is normally considered acidic while $\text{pH} > 7$ is considered as basic while $\text{pH} = 7$ is neutral. However, it is very rare for water in natural environments to have exactly neutral condition. Surface water systems have the normal pH range between 6.5 and 8.5 while groundwater systems have a range between 6 and 8.5. In addition, samples from points Nyaro4, Nyaro5, Nyaro7, Nyaro9 and Nyaro10 with pH 6.41, 6.30, 4.60, 6.20 and 6.39 had pH values below 7.0. These samples with low pH values were collected within a km in the vicinity of the mine tailings dam of Nyabigena mine. However, other samples with $\text{pH} > 7.0$ were also collected in the vicinity of both mine sites.

The leakage from effluent control ponds and mine waste dumps could be contributing to the low pH values in boreholes (Nyaro 7, 9, 10 and 19). Nyaro7 is located very close to the tailings dam and Tigithe River. Nyaro 6 and Nyaro 8 samples were collected from Tigithe River near the tailings dam of Nyabigena underground mine. Nyaro19 was collected within a kilometre from Nyabirama tailings dam and waste rock dump. The waste rock dump has the probability of having elevated concentrations of pyritic materials from sulphide ores. The material could be oxidizing to produce ferrous and sulphuric acid which contaminates water sources.

Tanzanian drinking water standards, set the lower limit and upper limit of pH to be 6.5 and 8.5, respectively (EWURA, 2014). The WHO international standards for pH values for surface and groundwater systems are in a close range between 6.0 and 8.5 (WHO, 2011). The 32% of the samples equivalent to six (6) water samples had pH values which are slightly below the limit allowed for Tanzanian guidelines. These pH values were obtained from samples collected mostly from shallow dug-out wells and spring water located closest to mine sites. This is the indication that mining activities are contributing to lower surface and groundwater pH in the area.

Slight alkaline in nature ($\text{pH} = 8.3\text{--}8.6$) were collected from surface water Tigithe River, Mara River, stream water and groundwater from boreholes in the Eastern side of the study site. High pH values signify dominance of dissolved HCO_3^- than that of CO_3^{2-} , ions known most for their

effect on natural water pH. Naturally, the possible sources of bicarbonate include the presence of organic matter that is oxidized to produce carbon dioxide, which promotes the dissolution of minerals (Laar *et al.*, 2011). The levels of water pH in most sampling points were within the Tanzanian standards for drinking water. Few samples with pH below 6.5 may accelerate heavy metals enrichment, migration and distribution in water resources (Wang *et al.*, 2016). These make water sources more susceptible to pollution.

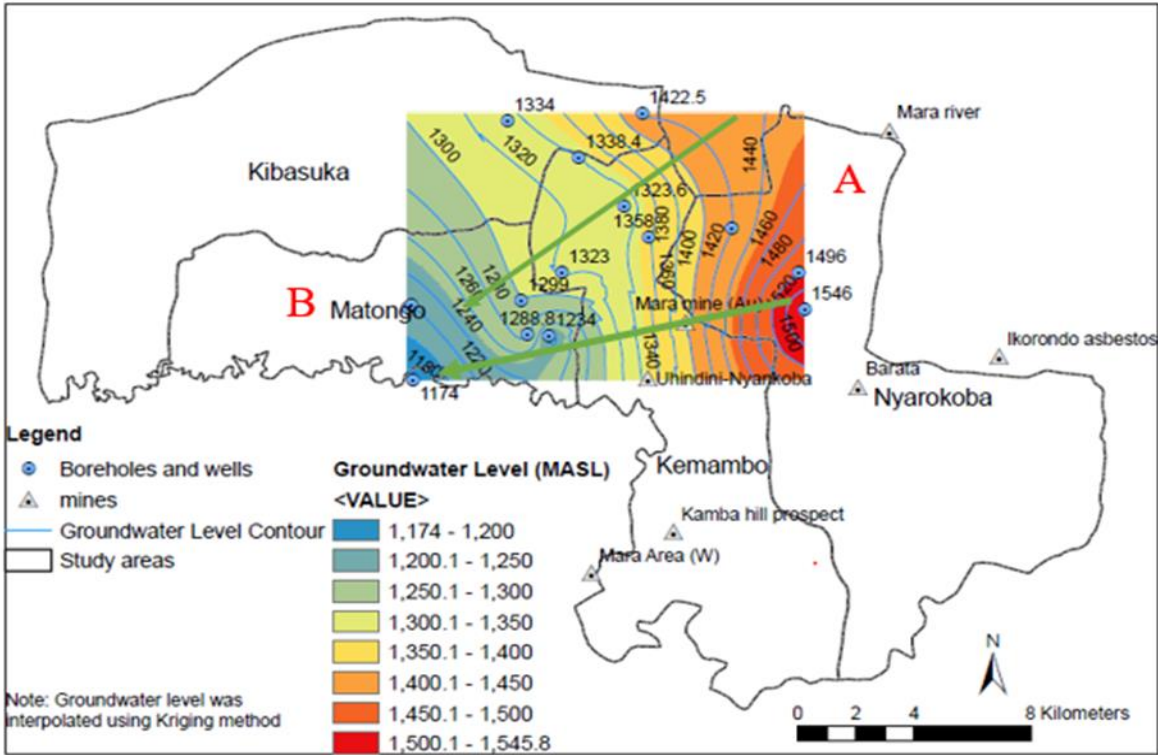


Figure 3: The groundwater contour line shows the groundwater flow direction

Table 2: Hydro chemical and Isotopic composition of waters samples from the North Mara gold mine

Sample point	$\delta^{18}\text{O}$	$\delta^2\text{H}$	^3H	pH	EC	*TDS	*Na ⁺	*K ⁺	*Ca ²⁺	*Cl ⁻	*CO ₃ ⁻	¹ HCO ₃ ⁻	*SO ₄ ²⁻	*NO ₃ ⁻	*Mg ²⁺
Nyaro1**	-3.02	-10.22	N.M	7.26	712	356	73	4.4	43.4	7	0.55	324.4	11	11.4	16.6
Nyaro2**	-3.37	-14.50	<6.0	8.18	676	338	120	5.2	10.3	21	4.53	318.4	6	2.7	5.1
Nyaro3**	-2.69	-7.35	<6.0	6.68	164	82	19	7.9	10.1	18	0.02	45.0	1	24.1	6.6
Nyaro4***	-2.76	-8.03	N.M	6.41	151	76	18	6.4	9.7	16	0.01	55.0	0	7.3	2.8
Nyaro5***	-2.42	-7.33	N.M	6.33	142	71	20	6.7	15.6	8	0.01	57.0	1	14.7	4.9
Nyaro6****	-0.96	-0.30	N.M	8.36	349	175	28	6.5	16.6	11	2.00	92.9	28	1.5	8.1
Nyaro7**	-1.79	-2.96	9.0	4.60	1388	698	210	19	94.5	190	0.00	0.0	136	10.6	47.7
Nyaro8****	-1.14	-0.38	N.M	6.70	430	216	37	8.2	37.2	22	0.04	77.0	62	10.1	6.0
Nyaro9***	-2.00	-3.27	11.5	6.20	226	114	19	5.5	10.8	9	0.01	52.0	15	19.1	5.4
Nyaro10**	-2.60	-9.01	7.0	6.39	179	90	21	5.4	7.9	10	0.01	63.0	7	7	6.2
Nyaro11**	-3.00	-11.55	<6.0	7.00	837	418	44	11	43.8	32	0.25	264.7	9	9.3	24.3
Nyaro12**	-1.78	-1.57	<6.0	7.76	1030	515	99	32	113.4	88	1.14	209.8	100	34.6	1.51
Nyaro13***	-2.21	-4.22	<6.0	7.12	773	387	74	1.9	45.5	56	0.22	174.8	65	15.4	11.5
Nyaro14**	-2.37	-5.55	<6.0	6.54	595	298	36	7.8	42.4	14	0.03	80.0	140	19.8	6.6
Nyaro15****	-2.70	-11.74	N.M	7.31	992	496	71	1.8	55.97	22	0.55	286.4	12	214	4.33
Nyaro16**	1.51	15.33	N.M	8.36	540	270	57	9.8	29.9	54	3.16	146.7	31	7.3	16.3
Nyaro17**	0.98	9.94	N.M	6.81	3456	1736	310	54	558	53	0.11	174.9	103	8.9	160
Nyaro18****	4.73	31.09	N.M	8.30	4200	2120	430	85	306.8	60	2.85	152.0	82	2	88.9
Nyaro19**	1.25	14.24	8.3	6.48	3988	1996	6.3	1.6	10.7	7	0.00	5.0	1900	50.9	8.5
Mean				7.00	1096.2	550.1	89.1	14.7	77.0	36.7	0.8	134.7	142.6	24.8	22.7
WHO standard limits				6-8.5		500-1500	500-2000	10-12	75-200	250-600		300-600	200-600	50	30-150

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ measured within a precision of $\pm 0.2\%$ and $\pm 0.8\%$, respectively according to VSMOW standards. Tritium in direct within $\pm 8\text{TU}$. * ionic concentrations and EC were measured in mg/L and $\mu\text{S}/\text{cm}$, respectively. N.M=Not measured. **boreholes, *** springs and **** surface water

4.1.2 Electrical Conductivity (EC) and Total Dissolved Solids (TDS)

The TDS and EC values variation ranged between 142–3988 $\mu\text{S}/\text{cm}$ (median 676 $\mu\text{S}/\text{cm}$) and 71–1996 mg/L (median 318 mg/L), respectively. Dugout well and shallow wells EC values ranged from 540 to 3988 $\mu\text{S}/\text{cm}$ while springs between 143 and 773 $\mu\text{S}/\text{cm}$ (Table 2). The trend of EC and TDS variation can be seen increasing from the East-West direction of the study site which signifies upstream to downward. The deterioration of water quality downstream shows the migration of pollutants along the water flow direction. Singh *et al.* (2015) classified TDS value of 500 mg/L to be desirable for drinking; 500–1000 mg/L as permissible for drinking; 3000 mg/L as not fit for drinking, although they can be acceptable for agricultural purposes and TDS greater than 3000 mg/L to be only useful for irrigation. From Table 2, 15 samples fell in the category of 'desirable for drinking, one is within the category of 'permissible limit' while all water sources fall in suitable for irrigation category.

The main contribution of TDS, EC and other ionic concentrations in water is partly connected to variations in groundwater geochemical processes and higher contribution by anthropogenic activities (Raju *et al.*, 2009). Human-related activities such as industrial discharge agriculture, domestic waste discharge, and natural processes like geological weathering may contribute to high levels of EC and TDS in natural waters (Dinka *et al.*, 2015). The observed high levels TDS from the western side of Nyabirama mine sites from the samples taken within 200 m can be attributed directly to the effluents from the mine tailings dam.

4.1.3 Ionic Compositions

The cations were dominated by sodium ion (Na^+) with values ranging between 16.3 to 430 mg/L (median 44.00 mg/L). The other ions, Calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+) ion ranged between 7.9–06.8 mg/L (median 42.40 mg/L), 1.5–160 mg/L (median 6.60 mg/L), and 1.6–85 mg/L (median 6.70 mg/L), respectively (Table 2). The cations of sodium (Na^+), dominated by 44% followed by calcium and magnesium by (38%) and (11%), respectively. The minor contribution was by potassium ion (7%). Thus, 68% of the cation chemistry of samples has the trend: $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}/\text{K}^+$ while 21% followed $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+}/\text{K}^+$.

The observed trend of ion concentration was suggested by WHO (2011), that can be principally contained in sedimentary rocks while other elements such as barium, manganese, aluminium, strontium, zinc and iron can be found in surface water and groundwater sources in various concentrations. However, according to Magos (1991), the trend of concentration can also depend

on geographical location the ranging from as low as 1 mg/L to as high as 400 mg/L. Therefore, the results for the levels of Ca^{2+} and Mg^{2+} presented in Table 2 fall in the range that is commonly found in most natural water systems. Hamutoko *et al.* (2017), concluded that the mobility and chemistry of major cations in the natural groundwater systems can be controlled by the cations exchange. However, in the study site, the use of shallow water sources and dug-out wells could be the reason for the reduced dilution effect affected by evaporation processes.

For the anionic concentrations, bicarbonate dominated the other anions ranging from 0.0 to 324.4 mg/L (median 92.89 mg/L), followed by sulphate range of 0.0–1900 mg/L (median 28 mg/L), chloride between 0–190 (mean 98.5 mg/L) and then by nitrate with a range of 1.5 – 50.9 mg/L (mean 26.2 mg/L) (Table 2). 42% of the samples salinity and hardness chemistry belonged the series of $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. The $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$, $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^-$ and $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^-$ series represented by a small percentage of 5%. Generally, 41% of the anionic chemistry is dominated by sulphate ion and 39%, followed closely by bicarbonate while 10% by chloride and 7% by nitrate ions. A high amount of sulphate ions could be linked to contamination from rocks containing sulphide minerals excavated from open-pit or underground mines, and processing chemicals. A similar study by *Bowell et al.* (1995) carried out in areas located a few kilometres south of the North Mara mining revealed water characterized by the high concentration of sulphate ions.

Chloride (Cl^-) concentrations depend on the other associated cations such as sodium, potassium and calcium chloride and its range in natural waters is usually 1 and 100 mg/L. Most commonly, chloride is present as sodium chloride in groundwater. A plot of chloride concentrations against sodium concentration is presented in Fig. 4. About 75% of the samples were used in plotting this graph as five sampling sites were found to be outliers. As can be seen from the R^2 value, chloride correlated well with sodium in the analyzed water samples ($R^2 = 0.866$). This signifies the water to test salty. Moreover, the correlation between sodium and chloride has been used to identify salinity mechanisms such as the dissolution of halite deposits and evaporation in arid and semi-arid regions (Rezaei & Hassani, 2018). In the current study, the levels of Cl^- ranged from 7 to 190 mg/L with a mean value of 36.7 mg/L (Table 1) and a median value of 21 mg/L. According to *Kumar et al.* (2020), such a high concentration of chloride in groundwater is found in areas where the temperature is high and rainfall is low. Thus, dry climate in combination with the leaching of the upper layers of soil by domestic and industrial activities together lead to the observed higher chloride concentration.

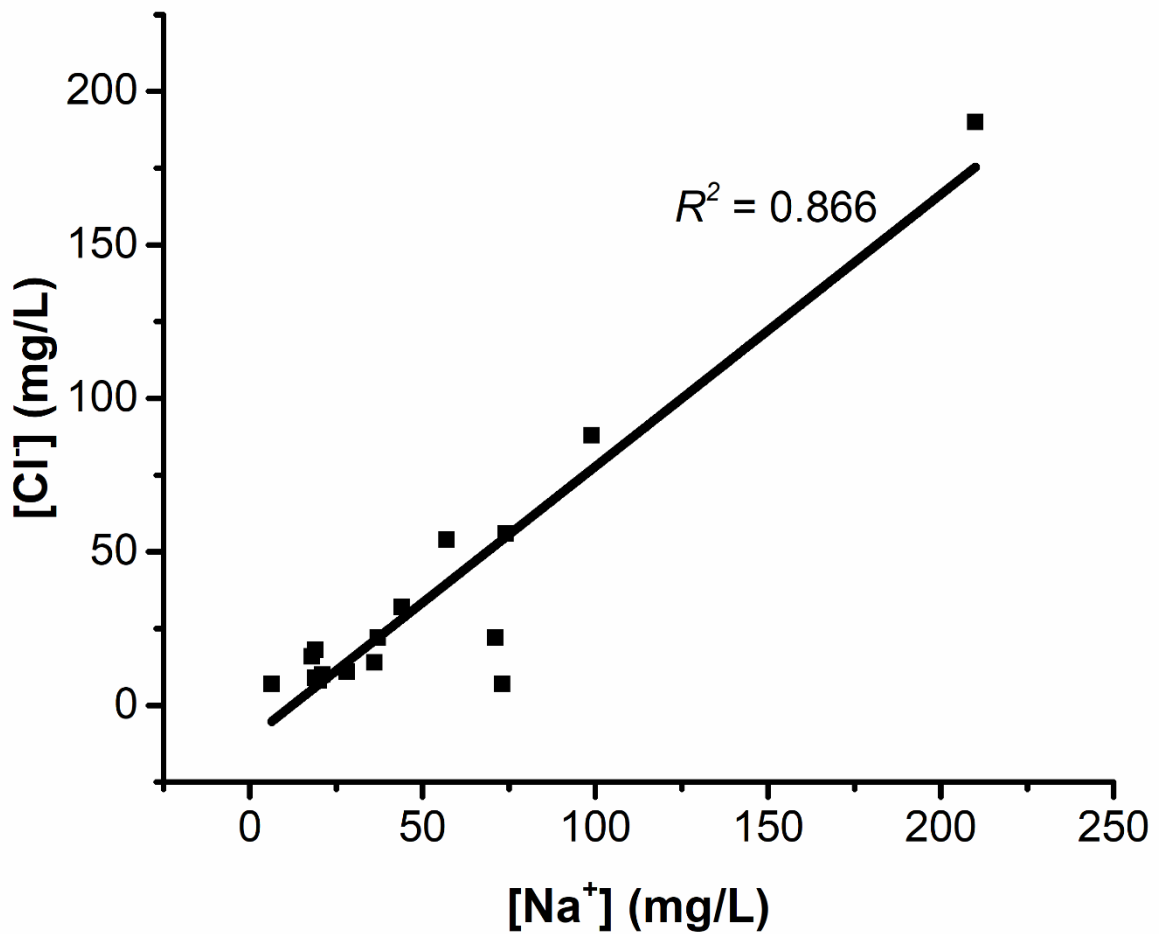


Figure 4: Chloride concentrations vs. sodium concentrations scatter plot for field data collected at the NMGGM mine sites

From the Table 4, SO_4^{2-} dominated the anionic chemistry. The SO_4^{2-} ranged from 0 to 1900 mg/L (mean = 142.6 ± 428.1), HCO_3^- ranged from 0 to 324.4 mg/L (mean = 134.7 mg/L), Cl^- ranged from 0 to 190 mg/L (mean = 36.7 mg/L) and finally NO_3^- ranged between 1.5 – 214 mg/L (mean = 24.8 mg/L) (Table 1). The 42% of the samples salinity and hardness equally belonged to $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ series. 5% showed $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$, $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^-$ and $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^-$ series. The anionic chemistry was generally, dominated by SO_4^{2-} and HCO_3^- by 41% and 39%, respectively. The minor contribution by Cl^- and NO_3^- ions by 10% and 7%, respectively. All samples, except one (Nyaro19) had concentrations of SO_4^{2-} below (250 mg/L) the secondary maximum contaminant level (SMCL) recommended by WHO for drinking water quality (WHO, 2011). The abundance of sulphate-containing materials in the natural environment contributes much to the higher levels of occurrence of SO_4^{2-} in groundwater. However, for samples with concentration as higher as 1900 mg/L downstream of the mine

tailings dams could not be linked to natural process. Thus, such levels of SO_4^{2-} in water indicated the contamination of groundwater recharge with acidic effluents discharged from the mine tailings dam and other due to atmospheric depositions.

The concentrations of NO_3^- ranged from 1.5 to 214 mg/L (mean = 24.8 mg/L) (Table 2). The higher concentrations were measured from Mara River (Nyaro15) and groundwater samples collected from most springs. The spatial distribution of NO_3^- is high in both the northern side (highland areas) and the western side (lowland areas) of the study area. The NO_3^- level as lower as 10 mg/L and an upper level of 75 mg/L is regulated to be suitable for drinking as suggested by the Tanzania Bureau of Standards (TBS). The 52% (equivalent to 10 samples), had concentrations of nitrate within the Tanzanian permissible limits, while 48% had above the permissible upper limit. The concentration of NO_3^- in water resources is usually linked by 90%, 9% and 1% to sources like agriculture, human/animal waste and lawns wastewater, respectively (Bryan & Loscalzo, 2011). Nitrate (NO_3^-) is highly soluble in water so can seep easily unfiltered with water into the soil, especially during irrigation, rainfall and crop watering activities making it occur both at the surface and groundwater at higher levels. The observed high NO_3^- , concentrations from surface water at Mara and Tigithe rivers was the indication of the anthropogenic activities' contribution.

4.1.4 Classification of Hydro-chemical Characteristics

The Piper trilinear diagram (Fig. 5) plotted some major ions from water samples. The concentrations entered in the source data file were in units of milligrams per litre. The results compared to water types classification by Ravikumar and Somashekar (2010) which showed that Ca^{2+} and Mg^{2+} dominated the water cations while SO_4^{2-} and HCO_3^- dominated the anions. This mean that the water samples could be classified to contain the sulphates and bicarbonates of Ca and Mg.

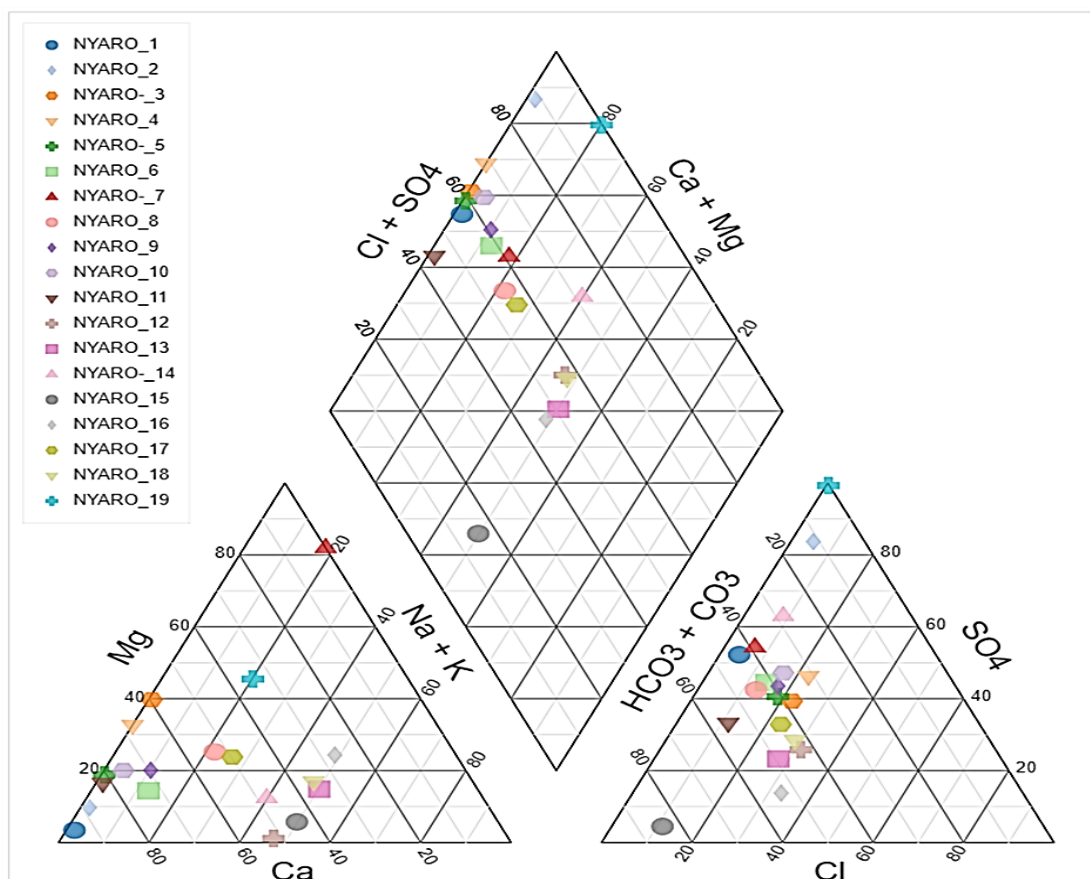


Figure 5: The Piper trilinear diagram demonstrating the hydrochemical regimes of the studied waters (Ravikumar & Somashekar, 2010)

4.2 Correlation Analysis

The coefficient of correlation (r) values are mostly used as a measure of dependence between two parameters of water and exhibit how well one variable predicts the other (Howladar *et al.*, 2014). The correlation analysis showed that the pH negatively correlated with Cl^- , Mg^{2+} , SO_4^{2-} , Hg, Pb and Cd while correlated positively with Na^+ , EC, K^+ , Ca^{2+} , As, NO_3^- , HCO_3^- and CN^- (Table 3). The relationship showed how groundwater chemistry was influenced by CO_3^{2-} and mineral dissolution of SO_4^{2-} . The correlation of EC with all other parameters except HCO_3^- and Cd was positively. The salinity in water is mostly indicated by EC. The highly significant correlation between EC and other major cations was the indication of the major cations' contribution to the dissolved salts in the water samples. The correlation results are in line with what was depicted by the hydrochemical regimes in the piper diagram (Fig. 5). The cyanide only correlated well with Pb, Na and EC. This correlation could signify that sodium cyanide and cyanide complexed with Pb, making it to be the major cyanide species in the analyzed water. Interestingly, heavy metals lacked a significant correlation with metalloids.

Table 3: Pearson correlation coefficients matrix of surface and groundwater ($n = 19$)

	pH	EC	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻
pH	1.00								
EC	0.10	1.00							
Na ⁺	0.16	0.71**	1.00						
K ⁺	0.24	0.70**	0.92**	1.00					
Ca ²⁺	0.09	0.68*	0.83**	0.82**	1.00				
Mg ²⁺	0.00	0.69*	0.83**	0.78**	0.97**	1.00			
Cl ⁻	-0.32	0.22	0.51*	0.36	0.30	0.34	1.00		
HCO ₃ ⁻	0.58*	-0.01	0.19	0.07	0.15	0.08	-0.11	1	
SO ₄ ²⁻	-0.16	0.59*	-0.12	-0.10	-0.06	-0.04	-0.09	-0.32	1.00

The values with * indicates a good correlation ($r = 0.5-0.69$) while ** means high correlation ($r > 0.7$)

4.3 The Concentration of Metals, Metalloids and Cyanides

Table 4 gave a summary of heavy metals/metalloids and cyanide concentrations in both surface and groundwater samples collected around NMGM sites. Samples collected from the stream at Kwinyunyu Village near Nyabirama tailings dam (Nyaro18) and the Mara River (Nyaro15) had high concentrations of free cyanide (CN⁻), of 20 µg CN⁻/L and 15 µg CN⁻/L, respectively. Low concentrations of cyanides usually are found in environmental waters while mining operations are the leading anthropogenic sources (Mousavi *et al.*, 2013). The level of cyanide in drinking water for health-based value is rounded to 500 µg/L as a limit by WHO. The reported values of CN⁻ were below the WHO threshold and agreed with cyanide levels reported to be normal in water from other countries such as Italy, Korea and Brazil (Jaszczak *et al.*, 2017). However, reporting the highest concentrations of cyanide near the mine tailings dam may raise an issue of concerns about the possibility of the tailings influencing the cyanide levels in water resources.

The community borehole (Nyaro7) located near the Nyabigena mine tailings dam reported the highest concentrations of Pb. Similarly, Pb values were also found high from mostly surface water and springs near the mine tailings dam. The highest concentrations > 130 and > 120 µg Pb/L, were from springs at Nyaro4 and Nyaro17 sampling points, respectively. Tigithe river samples (Nyaro 6), and unnamed stream in the Kwinyunyu sub-village (Nyaro18) reported Pb levels > 134 and 130 µg Pb/L, respectively. 84% (equivalent to 16) samples were found to contain Pb levels above 10 µg/L values recommended by WHO, while 6 samples contained Pb levels above 100 µg/L the value recommended by TBS (TBS 2005; WHO 2011). The United States Environmental Protection Agency (USEPA) defined Pb to be a toxic and hazardous substance to most forms of life even at relatively low concentrations (USEPA,1986) in Adesiyan

et al. (2018)). For human beings Pb is known to cause neurotoxin which can negatively affect the cognitive abilities of under-five children (Rwiza *et al.*, 2018). Therefore, the levels of Pb reported from surface and groundwater sources in the present study are quite alarming.

Table 4: Cyanide and selected heavy metal/metalloid ions levels in water samples collected from the NMGM of Tanzania

Sample Point	Cyanide (CN)	Mercury (Hg)	Arsenic (As)	Lead (Pb)	Cadmium (Cd)
Nyaro1	12.48	16.64	0.03	43.50	0.72
Nyaro2	7.49	11.46	0.09	3.79	0.21
Nyaro3	12.48	27.23	0.08	65.03	0.55
Nyaro4	12.48	17.82	0.02	131.48	0.80
Nyaro5	4.99	8.79	0.06	50.14	2.71
Nyaro6	9.98	18.68	0.06	134.40	1.95
Nyaro7	12.48	20.77	0.04	153.75	1.04
Nyaro8	7.49	9.21	0.02	0.30	0.03
Nyaro9	7.49	7.56	0.06	28.24	1.36
Nyaro0	4.99	33.59	0.08	72.30	0.54
Nyaro11	4.99	29.44	0.13	37.64	0.92
Nyaro12	2.50	11.69	0.08	3.97	0.61
Nyaro13	12.48	21.71	0.05	86.14	0.44
Nyaro14	5.99	15.64	0.02	49.43	0.12
Nyaro15	14.98	20.56	0.00	31.29	1.61
Nyaro16	7.49	17.96	0.02	40.32	0.90
Nyaro-17	9.98	7.86	0.01	120.36	1.29
Nyaro18	19.97	21.49	0.09	130.60	0.10
Nyaro19	13.62	22.88	0.07	152.75	1.25
Mean	9.70	17.95	0.05	70.29	0.90

The concentrations of As ranged from 'no detection' to 0.13 $\mu\text{g As/L}$ at Nyaro15 and Nyaro11 sample points, respectively. All 19 sampling sites reported As concentrations that fall within the standards of both the WHO and the TBS. The average concentration of As in the earth's crust is reported to 2 $\mu\text{g/L}$ (Ritter, 2002). Since Arsenic sources include natural weathering of geological material, gold-rich areas like NMGM whose geology consists of a small section of As-containing ores, e.g. arsenopyrite (FeAsS) and pyrite (FeS_2) may contain enriched quantity of As.

The highest values for Cd, (2.71 $\mu\text{g/L}$) were detected in samples collected from a spring water source (Nyaro 5) within 100 m from Nyabigena mine tailings dam. However, all reported concentrations of Cd were below 3 $\mu\text{g Cd/L}$ and 100 $\mu\text{g Cd/L}$ the maximum allowed limits for drinking water by WHO and TBS, respectively (TBS, 2005; WHO, 2011). According to

Adesiyan *et al.* (2018) Cd is a nonessential, highly toxic, and easily dissolved in water, can be found in unpolluted water in values less than 1 µg Cd/L and can cause adverse effects on living organisms. The reported highest Cd levels from two surface water sources (Nyaro 5 and Nyaro 6) indicate that atmospheric deposition could be the contributing source. However, the spring water source (Nyaro 5), may pose an alarming concern because its Cd level of 2.71 µg/L values was close to the limit set by WHO.

For Hg, the lowest and highest concentration of 7.56 µg/L and 33.6 µg/L collected at Nyaro 9 and Nyaro10 sampling points, respectively were both higher than 6 µg/L recommended by WHO drinking water quality guideline (Table 4). Mercury (Hg) is a toxic pollutant, which can persist in the environment and bioaccumulate in living organisms, except for severely contaminated areas, Hg concentrations are expected to be low in most raw and treated water (Ritter *et al.*, 2013). In most sub-Saharan Africa, mining areas (metal refinery e.g. gold–Au) especially by artisanal miners are the major source of Hg. The observed values in the study site give an insight that Hg was being intensively used for Au extraction and was leaching into the water resources in considerable high quantities.

4.4 Isotopic studies

4.4.1 Composition of isotopes of oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$)

The analyses for $\delta^2\text{H-H}_2\text{O}$ and $\delta^{18}\text{O-H}_2\text{O}$ compared to international Vienna Standards Mean Ocean Water (V-SMOW) after Craig (1961) are shown in Table 2. The $\delta^{18}\text{O-H}_2\text{O}$ values ranged between -3.37‰ and 4.73‰ with a mean of -1.39‰ while $\delta^2\text{H-H}_2\text{O}$ values ranged between -14.5‰ and 31.09‰ with a mean of -1.44‰ . The stable isotope compositions from surface and groundwater were plotted together with the Local Meteoric Waterline (LMWL) (Fig. 6). The data are derived from plotting the water samples, as obtained using the regression analysis and insertion of the Global Meteoric Waterline (GMWL) after Craig (1961). The GMWL relationship is given by Equation (2):

$$\delta^2\text{H} = 8 \cdot \delta^{18}\text{O} + 10 \quad (2)$$

Where δ is the isotopic enrichment factor, ^{18}O and ^2H are heavy isotopes of oxygen and hydrogen, respectively. The regression equation obtained is indicated by Equation (3) for both surface and groundwater samples.

$$\delta^2\text{H} = 5.47 \cdot \delta^{18}\text{O} + 6.137, R^2 = 0.983 \quad (3)$$

Where R^2 is the constant for linear regression.

Furthermore, most of the samples were plotted on or near the LMWL while few were plotted farther away (Fig. 6). Samples plotted closer or on the LMWL are likely to be recharged directly from local precipitation with little evaporation effects. One sample (Nyaro18) from a small stream flowing westward from Nyabirama tail dam plotted further away from the LMWL indicated higher evaporation effects. On average, the groundwater along the eastern margin is shown to be more depleted than those from the western. For example, the borehole from the eastern part (near Nyabigena underground mine), Nyaro 2 had $\delta^{18}\text{O}$, $\delta^2\text{H}$ values of -3.37‰ , -14.50‰ of, and Nyaro3 had $\delta^{18}\text{O}$, $\delta^2\text{H}$ values of -2.69‰ , -7.35‰ . These values are comparatively lower than Nyaro19 ($\delta^{18}\text{O} = 1.25\text{‰}$, $\delta^2\text{H} = 14.24\text{‰}$) and Nyaro17 ($\delta^{18}\text{O} = 0.98\text{‰}$, $\delta^2\text{H} = 9.94\text{‰}$) from the western (near Nyabirama open-pit mine). The eastern part (side A in Fig. 3) of the study site which has low (depleted) values $\delta^{18}\text{O}$ is at a higher elevation than the western part (side B in Fig. 3).

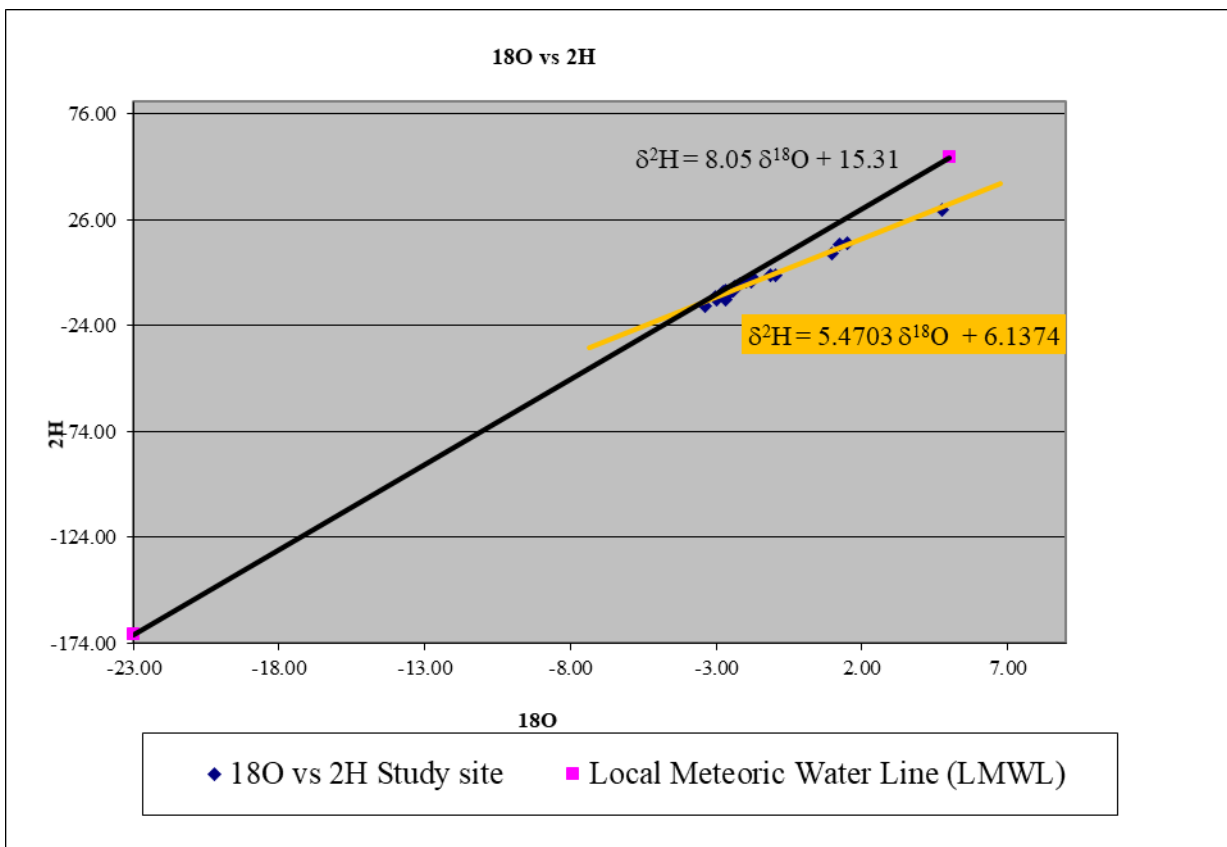


Figure 6: Graph of stable isotopes of oxygen and hydrogen. The regression line is in peach/coral color

According to Johnson *et al.* (2010), isotopically depleted groundwater indicates that the water recharged at higher altitudes and hence due to longer residence time has drastically affected by

evaporation. Low values of $\delta^{18}\text{O}$ in the eastern part indicate that the eastern part is the recharge area and water flows from east to west, resulting in differential evaporation rates. The western side downstream has higher values of $\delta^{18}\text{O}$ due to the effects of some physical and chemical processes along the flow path. The flow of water along its pathway leads to the enrichment of heavy isotopes with distance because, during evaporation, lighter isotopes leave the water surface preferentially, with the remaining water enriched with heavier isotopes (Yeh *et al.*, 2011).

As indicated that the general flow pattern of both surface and groundwater is from Eastern to the Western part around both gold mine sites, therefore the pollutants will be following the flow path regardless of the source. This can be shown by the isotopic variations of oxygen along with other physical and chemical characteristics, such as EC, Cl^- and NO_3^- , which provide supplementary information on the contaminant transport and sources. The variations in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in water discussed earlier can naturally be determined by the recharge sources and age. However, according to Bakari *et al.* (2012), in contaminated groundwater, the variations in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are also controlled by the composition of the saline and/or pollutant sources. The groundwater samples show a weak correlation (0.2) between $\delta^{18}\text{O}$ values with chloride content while both HCO_3^- and NO_3^- have a negative correlation of -0.2 and -0.1, respectively. These reflect the depleted $\delta^{18}\text{O}$ characteristics of the saline sources and other pollutants. Although the isotopic variations of $\delta^{18}\text{O}$ did not show a strong correlation concerning the nitrate concentrations values in freshwater, the high- $\delta^{18}\text{O}$ values and EC might reflect groundwater pollutants from anthropogenic sources. However, downstream mining areas, unpolluted groundwater may be discharged into the streams which can cause dilution of pollutants making the concentration decrease downstream.

4.4.2 Tritium radioactivity

Ten (10) samples were analyzed for tritium (^3H) activity. Based on ± 8.0 TU, six samples had direct tritium less than 6.0 while four samples had more than 6.0 TU. The maximum tritium activity reported was 9.0 TU. Although looking at tritium activity alone, it may not provide a final conclusion on the groundwater ages but can provide approximate information of whether the water is modern or young (< 50 years) or pre-modern (> 50 years) (Clarke *et al.*, 1976; Zouari *et al.*, 2002). However, the relative age indicated by tritium isotope is useful in concluding the water resources vulnerability from recent contamination. Morgenstern *et al.* (2010) showed that the mix of modern and sub-modern water could have tritium values between 0.8 and 4.0 TU

while modern water or young (age of < 5 to 10 years) have activities between 5.0 and 15.0 TU. This means that the modern recharged water has relatively higher tritium activities than old water. The concept is similar to Singh *et al.* (2010) classification of 1 to 4 TU tritium activity to be a mixture of old and recent water while 4.1 to 18 TU for recent water while between 18.1 and > 28.0 TU activities for thermonuclear water. The sites with depleted ^3H values will therefore belong to old groundwater while higher values of ^3H represent recharge from recent rainfall.

In the present study, 40% of the groundwater samples within the gold mining area represent recent water while 60% account for old and modern water mixtures. Modern groundwater is generally more vulnerable to contamination than old due to the introduction of anthropogenic contaminants by human activities like mining activities. The general spatial distribution of tritium is produced such that, higher elevations are dominated by lower tritium and tritium activities decrease along with groundwater flow. This makes a possibility of ^3H contamination in groundwater following recent recharge precipitation. It is evident that water pollution increases along the flow path (from side A to B in Fig. 3). The samples from the eastern side of both mines are more polluted. For example, sample points such as Nyaro 7 located within 100m from mine tail dam has values of pH of 4.6 (9 TU) and relatively high SO_4^{2-} , TDS, Cl^- , Pb^{2+} and CN^- values of 136, 698, 190, 153.7 and 1.04 mg/L, respectively.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Coupling isotopic composition with hydrochemical analysis of surface and groundwater near the NMGM in Tanzania enabled the researcher to examine water quality and vulnerability to contamination. The stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$) have provided an understanding of the water flow pattern while the major ions geochemistry provides the levels and the processes contributing to water quality deterioration. The stable isotopes analysis showed that evaporation and altitudinal effects to some extent controlled the water chemistry. The radioactive isotope of Tritium (^3H) proved to be useful to validate the vulnerability of waters to contamination from anthropogenic activities by estimating residence time. Radioactive showed that groundwater was vulnerable to recent near-surface contamination because it received recharge from recent local precipitation rather than paleoclimatic precipitation.

The hydrochemical analysis showed that most of the major ions were higher in the shallow depths of groundwater. The water quality deteriorated spatially along the water flow path downstream. The major ions in shallow groundwater and surface water sources are attributed partly to the lithogenic while the main contribution is anthropogenic activities such as domestic effluents, agriculture, and mining activities. Most samples enriched with heavy metals had low pH values (mini. = 4.6, e.g. Pb (max. = 153.8 $\mu\text{g/L}$), Cd (max. = 2.7 $\mu\text{g/L}$) and Hg (max. = 33.6 $\mu\text{g/L}$), as well as cyanide (max. = 20 $\mu\text{g/L}$) that could be linked to anthropogenic activities. 84% of water samples contained Pb levels above the levels recommended by the Tanzanian standards. Two sites recorded Cd levels (2.7 and 2 $\mu\text{g/L}$) which were close to the limit set by WHO. The general flow pattern of water-carrying pollutants was toward the west side, where the Mara River and Lake Victoria are located. These may have some implications for the possibility of loading pollutants into the two water systems which are highly important for the economy of the East African Region.

5.2 Recommendations

The use of deep boreholes and locating them at the highland areas (eastern side of the mining sites) where the levels of pollutants were found to be relatively low is highly recommended. The current study therefore discourages the use of shallow boreholes and dug wells to minimize the

risk of exposure to pollutants. More studies that utilize additional stable and radioactive isotopes in this region of East Africa are needed. This is amongst the sub-Saharan Africa region which is fastest growing and increasing in terms of the human population, industrial activities, mining activities, and agricultural activities. Thus, more studies to assess the impacts of human activities on water resources are of paramount importance.

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RESEARCH OUTPUTS

(i) Publication

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(ii) Poster Presentation