



Doctoral Thesis in Land and Water Resources Engineering

Hydrogeochemistry of arsenic, fluoride, and other trace elements in groundwater in northern Tanzania

Occurrence, distribution and impacts on
drinking water quality

FANUEL JOSEPHAT LIGATE



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Academic Dissertation which, with due permission of the KTH Royal Institute of Technology, is submitted for public defence for the Degree of Doctor of Philosophy on Wednesday the 5th April 2023, at 2:00 PM at Room Sahara, Teknikringen 10B, KTH Royal Institute of Technology, Stockholm and Zoom link: <https://kth-se.zoom.us/j/62010864863>

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Lamboni dam, located at Kogete Village, Kenyamanyori ward in Tarime Town Council, Mara region, Tanzania (1.36075°S, 34.38475°E) is a source of potable water supply to the community around Tarime town. Apart from this source, most of the people use groundwater from privately owned deep and/or shallow wells whose quality is generally not well known by the users.

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DEDICATION

*To
My Parents
and
My Siblings*

“Water and its availability and quality will be the main pressures on, and issues for, societies and the environment under climate change.” (IPCC, 2007)

SAMMANFATTNING

Förekomsten av arsenik (As), fluorid (F⁻) och andra spårämnen (TE) med potentiell toxicitet i grundvattnet är ett globalt miljöproblem. Enligt den nationella kartläggningsdatabasen för vattenresurser kommer omkring 76 % av dricksvattenförsörjningen i Tanzania från grundvattenkällor. I norra Tanzania står grundvattnet för mer än 80 % av dricksvattenförsörjningen. Även om grundvattnets stora betydelse i norra Tanzania, grundvattenkvalitet med avseende på geogena föroreningar är inte optimalt förstått. Denna studie fokuserade på att uppskatta grundvattenkvaliteten med hjälp av analytiska, geokemiska modellerings-, statistiska och GIS-teknik som utfördes för att belysa grundvattnets kemiska kvalitet för att säkerställa dricksvattenförsörjning i Tanzania. Fluor etablerades som den främsta geogena grundvattenföroreningen i norra Tanzania, särskilt i avrinningsområden Pangani och Internal Drainage Basin, delar av Östafrikanska gravsänkesystemet (East Africa Rift Valley-system, EARV). Cirka 8 % och 57.6 % av vattenproverna från Geita och Sanya alluvial slätt har visat F⁻ koncentration över WHO:s riktlinjer (1.5 mg/L) för dricksvatten. Den höga F⁻ koncentrationen i grundvattnet härrör från F-rika mineraler och askavlagringar från de granitiska och alkaliska vulkaniska moderbergarterna. Konsumtionen av förhöjda koncentrationer av F⁻ i grundvatten har orsakat omfattande tand-, skelett- och förlamande fluoros bland lokala befolkning. I guldfälten i Lake Victoria Basin (LVB) rapporterades As som den främsta förekommande geogena föroreningen med konsekvent hälsoproblem bland befolkning i området. Arsenik koncentrationen i 50 % och 82 % av grundvattenproverna från Tarime respektiv Geita översteg WHO:s riktlinjer (10 µg/L). Den höga koncentrationen av As i grundvattnet från LVB var starkt förknippad med naturliga geokemiska processer såväl som guldbrytningsaktiviteter. Resultat från geokemisk modellering visade att As-mobilisering påverkades av oxidativ och/eller reduktiv upplösning av As-innehållande sulfidmineraler respektive As-innehållande järnmineraler från moderbergarterna. Koncentration av andra spårämnen så som aluminium, krom, kobolt, koppar, järn, mangan, nickel och zink var under WHO:s riktlinjer för dricksvatten. Den rumsliga variationen av As och F⁻ koncentrationen från dricksvattentäkter var relaterade till de olika grundvattennivåerna, djupet till brunnskärm och kontakttid för grundvattnets interaktion med de As och F⁻ innehållande mineralerna i berg under grundvattenflödet. Dessutom bevattningstvatten från de F⁻ förorenade grundvatten som används från borrade brunnar utgör risker för att förorena de grunda akvifererna som är lättillgängliga för konsumtion av människor och husdjur. De nuvarande WHO rekommenderade riktlinjerna för 10 µg As/L och 1.5 mg F⁻/L intag för människor är öppna för ytterligare epidemiologisk granskning, särskilt med tanke på kronisk/långvarig exponering i regionen. Den föreliggande studien belyser behovet av storskaliga utredningar för hydrogeokemiska och mänskliga hälsorisker när det gäller geogena föroreningar i regionen. Resultaten bidrar till de lokala, regionala och globala initiativen mot hållbart utnyttjande av grundvattenresurser i enlighet med Sustainable Development Goal (SDG) 6 för universell tillgång till rent vatten och sanitet för alla.

Nyckelord: Arsenik; Fluorid; Grundvatten; Viktoriasjön; Riskbedömning; Sanya alluvial slätt; Tanzania.

IKISIRI

Utokeaji wa aseniki (As), floride (F⁻), na elementi nyingine (IEs) zenye sumu kwenye maji yaliyopo ardhini ni suala mtambuka la kimazingira duniani. Kwa mujibu wa kanzidata ya taifa ya upatikanaji wa rasilimali maji, takribani 76% ya maji ya kunywa yanayosambazwa nchini Tanzania hupatikana kwenye vyanzo vya maji yaliyopo ardhini. Katika upande wa kaskazini mwa Tanzania maji yaliyopo ardhini hutumika kwa zaidi ya 80% kwa ajili ya kunywa. Licha ya umuhimu wa maji hayo kaskazini mwa Tanzania, ubora wake kuhusiana na uchafu wa kijiojeniki bado haujafahamika vizuri. Utafiti huu ulijikita kukadiria ubora wa maji yaliyopo ardhini kwa kutumia uchambuzi, modeli ya jiochemikali, kitakwimu, na Mifumo ya Taarifa za Kijiografia (GIS) ili kuelewa zaidi ubora wa kiochemikali wa maji yaliyopo ardhini katika kiunzi cha usambazaji wa maji ya kunywa nchini Tanzania. Floridi iliripotiwa kama kichafuzi kikuu cha kijiojeniki cha maji yaliyopo ardhini kaskazini mwa Tanzania hususani katika bonde la Pangani, ambayo ni sehemu ya ukanda wa bonde la ufa la Afrika Mashariki. Takribani 8% na 57.6% ya sampuli za maji yaliyokusanywa Geita na kwenye uwanda wa aluvia ya Sanya yameonesha ukolezi wa F⁻, zaidi ya kipimo cha mwongozo wa shirika la afya duniani, (WHO) ambacho ni 1.5mg/L kwa maji ya kunywa. Ukolezi mkubwa wa F⁻ katika maji yaliyopo ardhini huanzia kwenye madini yenye F⁻ nyingi na tope la umajivu kutoka kwenye miamba mikuu ya kivolkano ya graniti na alikali. Matumizi ya maji yaliyopo ardhini yenye kiwango kikubwa cha F⁻ yamechangia udhoofu wa meno na mifupa. Katika migodi ya dhahabu kwenye Bonde la Ziwa Victoria (LVB), As iliripotiwa kama kichafuzi kikuu cha kijiojeniki cha masuala ya kiafya. Ukolezi wa As kwa 50% na 82% katika sampuli za maji yaliyopo ardhini kutoka Tarime na Geita mtawalia zilizidi mwongozo wa WHO (10 µg/L). Kiwango kikubwa cha As kwenye maji yaliyopo ardhini kutoka LVB kilihusishwa sana na michakato asilia ya kiochemikali pamoja na shughuli za uchimbaji wa dhahabu. Matokeo ya modeli ya jiochemikali yamebainisha kuwa ujitokezaji wa As ulichochea na uoksidishaji na/au uyeyukaji wa taratibu wa madini ya sulfidi na chuma mtawalia yenye As kutoka kwenye miamba mikuu. Elementi nyingine (aluminiumu, kromiamu, kobalti, shaba, chuma, manganizi, nikeli na zinki zilionekana kuwa chini ya kiwango kilichopendekezwa katika muongozo wa maji ya kunywa uliotolewa na WHO. Ubadilikajabadilikaji wa kimazingira wa ukolezi wa As na F⁻ kutoka kwenye vyanzo vya maji ya kunywa kutoka ardhini ilihusianishwa na ngazi mbalimbali za maji yaliyopo ardhini, vina na muda wa kuchanganya maji yaliyopo ardhini na miamba ya madini ya As na F⁻ kwenye vyanzo vya maji. Aidha, umwagiliaji wa maji yaliyotoka kwenye visima vilivyochafuliwa na F⁻ huweka uwezekano wa kuvichafua vyanzo vya maji vyenye vina vifupi ambavyo hufikiwa kirahisi kwenye shughuli za kibinadamu na matumizi ya nyumbani. Mapendekezo ya sasa ya mwongozo wa WHO ya 10 µg As/L na 1.5 mg F⁻/L kwa ajili ya matumizi ya binadamu yanahitaji tafiti za kitabibu zaidi, hasa kwa kuzingatia matumizi ya muda mrefu ya maji ya kunywa. Utafiti huu unadokeza mahitaji makubwa ya kuchunguza madhara ya haidrojiochemikali pamoja na afya za binadamu kuhusu uchafu wa kijiojeniki katika eneo husika. Matokeo ya utafiti huu yanachangia kwenye jitihada za kitaifa, kikanda na kidunia kuhusu matumizi sahihi ya rasilimali maji yaliyopo ardhini kwa kuzingatia Lengo namba 6 la Maendeleo Endelevu (SDG 6) kwa ajili ya upatikanaji wa maji safi na salama kwa watu wote.

Istilahi muhimu: Aseniki; Bonde la Ziwa Victoria; Floridi; Maji yaliyopo ardhini; Tanzania; Tathmini ya hatari; Uwanda wa Aluvia ya Sanya.

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Fanuel Josephat Ligate
Stockholm, April 2023

LIST OF ABBREVIATION

AA3	AutoAnalyser3
ABE	Architecture and the Built Environment
AGM	Artisanal Gold Mining
AI	Artificial Intelligence
AT	Average Time
BIC	Banded Iron Formation
BH	Borehole
BW	Body Weight
CBE	Charge Balance Error
CCME	Canadian Council of Ministers of the Environment
CDI	Chronic Daily Intake
CM	Correlation Matrix
CR	Cancer Risk
CSF	Cancer Slope Factor
DAFWAT	Development of affordable adsorbent for fluoride and arsenic removal from drinking water sources in Tanzania
DI	Daily Intake
DOC	Dissolved Organic Carbon
EARV	East African Rift Valley
EF	Exposure Frequency
GCLA	Government Chemist's Laboratory Agency
GDEM	Global Digital Elevation Model
GWB	Geochemist's Workbench
HI	Hazard Index
HQ	Hazard Quotient
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
IPCC	Intergovernmental Panel on Climate Change
IS	Ionic Strength
LVB	Lake Victoria Basin
NBS	National Bureau of Statistics
PBWO	Pangani Basin Water Office
PCA	Principal Component Analysis
PRB	Pangani River Basin
RfD	Reference Dose
SDG	Sustainable Development Goal
Sida	Swedish International Development Cooperation Agency
SI	Saturation Index
SSA	Sub Saharan Africa
TBS	Tanzania Bureau of Standards
TE	Trace Elements
UNICEF	United Nations Children's Fund
UN SDG	United Nations Sustainable Development Goal
US EPA	United State Environmental Protection Agency

WB	World Bank
WHO	World Health Organization
WQI	Water Quality Index

LIST OF APPENDED PAPERS

This dissertation was developed based on the following four papers:

- I. **Ligate, F.J.**, Ijumulana, J., Ahmad, A., Kimambo, V., Irunde, R., Mtamba, J.O., Mtalo, F. & Bhattacharya, P. 2021. Groundwater resources in the East African Rift Valley: Understanding the geogenic contamination and water quality challenges in Tanzania. *Scientific African* 13: e00831, <https://doi.org/10.1016/j.sciaf.2021.e00831>
- II. Ijumulana, J., **Ligate, F.**, Irunde, R., Bhattacharya, P., Ahmad, A., Tomašek, I., Maity, J.P. & Mtalo, F. 2022. Spatial variability of the sources and distribution of fluoride in groundwater of the Sanya alluvial plain aquifers in northern Tanzania. *Science of The Total Environment* 810: 152153. <https://doi.org/10.1016/j.scitotenv.2021.152153>
- III. **Ligate, F.**, Lucca, E., Ijumulana, J. Irunde, R., Kimambo, V., Bhattacharya, P., Mtalo, F., Ahmad, A., Hamisi, R. & Maity, J.P. 2022. Geogenic contaminants and groundwater quality around Lake Victoria goldfields of Northwestern Tanzania. *Chemosphere* 307: 135732. <https://doi.org/10.1016/j.chemosphere.2022.135732>
- IV. **Ligate, F.J.**, Ijumulana, J., Irunde, R., Kimambo, V., Hamisi R., Maity J.P., Mtamba J.O., Mtalo F. & Bhattacharya, P. 2023. Hydrogeochemistry and spatial variability of arsenic and fluoride co-occurrence in groundwater from Geita district in Lake Victoria Basin, northwest Tanzania. *Groundwater for Sustainable Development* (GSD-D-23-00042, Manuscript in revision)

Author's contribution to papers

I contributed to the papers included and appended in the thesis as follows:

- I. Conceptualization of the idea, consultation of relevant literature and institutions, writing the first draft and subsequent revisions with input from the co-authors, and management of the submission process.
- II. Contribution to the formulation of content, data processing, analysis, modeling, and revising of the manuscript with input from the co-authors.
- III. Participation in the fieldwork sampling campaign, data analysis, interpretation, writing the first draft, and revision of the manuscript. Also managed the submission and publication process.
- IV. Development of the research design and methodology with the co-authors, data collection, analysis, and modeling. Wrote the first draft of the manuscript and revised it together with co-authors. Managed the submission process.

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LIST OF OTHER RELEVANT PAPERS NOT APPENDED TO THIS THESIS

- I. Ijumulana, J., **Ligate, F.**, Bhattacharya, P., Mtalo, F. & Zhang, C. 2020. Spatial analysis and GIS mapping of regional hotspots and potential health risk of fluoride concentrations in groundwater of northern Tanzania. *Science of The Total Environment* 735: 139584. <https://doi.org/10.1016/j.scitotenv.2020.139584>
- II. Ijumulana, J., **Ligate, F.**, Irunde, R., Bhattacharya, P., Maity, J. P., Ahmad, A. & Mtalo, F. 2021. Spatial uncertainties in fluoride levels and health risks in endemic fluorotic regions of northern Tanzania. *Groundwater for Sustainable Development* 14: 100618. <https://doi.org/10.1016/j.gsd.2021.100618>
- III. Irunde, R., Ijumulana, J., **Ligate, F.**, Maity, J.P., Ahmad, A., Mtamba, J., Mtalo, F. & Bhattacharya, P. 2022. Arsenic in Africa: Potential sources, spatial variability, and the state of the art for arsenic removal using locally available materials. *Groundwater for Sustainable Development* 18: 100746. <https://doi.org/10.1016/j.gsd.2022.100746>
- IV. Kimambo, V., **Ligate, F.J.**, Ijumulana, J., Maity, J.P., Jong, R., Ahmad, A., Hamisi, R., Mtamba, J.O., Mtalo, F. & Bhattacharya, P. 2023. Optimization of fluoride removal using calcined bauxite: Adsorption isotherms and kinetics. *Groundwater for Sustainable Development* 21: 100922. <https://doi.org/10.1016/j.gsd.2023.100922>
- V. **Ligate, F.J.**, Kumar, R., Ijumulana, J., Irunde, R., Kimambo, V., Hamisi, R., Maity, J.P., Mtamba, J.O., Mtalo, F. & Bhattacharya, P. 2023. Health risk evaluation of arsenic and fluoride in groundwater from Geita district in Lake Victoria Basin, northwest Tanzania. (Manuscript, under preparation)

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ABSTRACT

The occurrence of arsenic (As), fluoride (F⁻), and other trace elements (TEs) with potential toxicity in groundwater is a global environmental concern. According to the National water resource mapping database, about 76 % of the drinking water supply in Tanzania is abstracted from groundwater sources. In northern Tanzania groundwater accounts for more than 80 % of the drinking water supply. Albeit the importance of groundwater in northern Tanzania, its quality concerning geogenic contaminants is not optimally understood. The present study focused on estimating the groundwater quality using analytical, geochemical modeling, statistical, and GIS techniques which were carried out to better understand the chemical quality of groundwater in the framework of safe drinking water supply in Tanzania. Fluoride was established as the principal geogenic groundwater contaminant in northern Tanzania, particularly in the Pangani and internal drainage basins, parts of the East Africa Rift Valley (EARV) system. About 8 % and 57.6 % of the water samples collected from Geita and Sanya alluvial plain have indicated F⁻ concentration above the WHO guidelines value (1.5 mg/L) for drinking water. The high F⁻ concentration in groundwater originates from F⁻ rich minerals and ash deposits from the granitic and alkaline volcanic parent rocks. The consumption of elevated concentrations of F⁻ in groundwater has been responsible for dental, skeletal, and crippling fluorosis. In the Lake Victoria basin (LVB) goldfields, As was reported to be the main geogenic contaminant of health concern. The concentration of As in 50 % and 82 % of the groundwater samples from Tarime and Geita respectively exceeded the WHO guidelines (10 µg/L). The high concentration of As in groundwater from the LVB was highly associated with natural geochemical processes as well as gold mining activities. Results from geochemical modeling revealed that As mobilization was influenced by oxidative and/or reductive dissolution of As-containing sulfide and iron minerals, respectively from the parent rocks. The concentrations of other TEs (aluminum, chromium, cobalt, copper, iron, manganese, nickel, and zinc) were observed below the WHO drinking water guideline. The spatial variability of As and F⁻ concentration from drinking groundwater sources was associated with the different groundwater levels, screened depths, and contact time of groundwater interaction with the As and F⁻ containing rock minerals in the aquifers. Furthermore, irrigation water sourced from the F⁻ contaminated boreholes poses risks of contaminating the shallow aquifers that are easily accessible for human and domestic animals' consumption. The current WHO recommended guidelines of 10 µg As/L and 1.5 mg F⁻/L intake for humans are open to further epidemiological scrutiny, especially considering chronic/long-term exposure in the region. The present study highlights the need for large-scale hydrogeochemical and human health risk investigations concerning geogenic contaminants in the region. The findings contribute to the local, regional, and global initiatives toward sustainable exploitation of groundwater resources in conformity with the Sustainable Development Goal (SDG) 6 for universal access to safe water and sanitation for all.

Keywords: Arsenic; Fluoride; Groundwater; Lake Victoria basin; Risk assessment; Sanya alluvial plain; Tanzania.

1. INTRODUCTION

1.1. Background

Water is an important component of the ecosystem and an essential requirement for sustainable human development. Groundwater and surface water have been used concurrently or as substitutes for one another since early human civilization. The social and economic development of any nation is attributed to the sufficient and sustainable availability of water resources. The deterioration of freshwater resources in terms of quality and quantity from natural and human-induced causes is a worldwide concern. The global vulnerability of freshwater resources has been realized and included in the United Nations Sustainable Development Goals (UN-SDGs). Sustainable Development Goal 6 is dedicated entirely to clean water and sanitation, whereby target 6.1 emphasizes the “achievement of global and equitable access to safe and affordable drinking water for all by 2030”. The right to safe and clean water is also recognized as an essential component for the realization of human rights globally (Salman, 2012).

Groundwater provides drinking water for millions of people globally. In Africa, more than 400 million (about 29 %) people depend entirely on groundwater for water supply. In Sub-Saharan Africa (SSA), it is estimated that groundwater serves as a source of drinking water supply to two third of the rural population (Addison et al., 2020). Groundwater caters to more than 80% of the rural and peri-urban populations in Tanzania. The impact of climate change on the reliability of surface water and rainfall will increase the importance of groundwater resources to the people’s livelihood in Sub-Saharan Africa. The dependence on groundwater could be attributed to its resilience, ubiquitousness, and abundance (Onipe et al., 2020). A significant proportion of town dwellers also use groundwater for drinking and other household activities (Macdonald et al., 2009).

The composition of groundwater varies in terms of dissolved and suspended inorganic

constituents originating from parent rock minerals in the lithosphere through hydrogeochemical processes and from the atmosphere, hydrosphere, and cryosphere through natural and artificial recharge. The water-rock interaction in the aquifers mainly determines the chemical quality of groundwater. Under favorable physicochemical conditions, inorganic elements dissolve and precipitate in water through chemical reactions. Some of the dissolved elements are essential for healthy well-being, while others are potentially toxic to human beings, other organisms, and the environment at large. The chemical contaminants in groundwater are attributable to both geogenic and anthropogenic sources. Furthermore, groundwater can be anthropogenically contaminated by domestic, industrial, and agricultural (pesticides and herbicides) chemicals. Arsenic and F are naturally occurring elements in groundwater with detrimental health impacts on humans (Table 1).

The quality of groundwater in Africa has a significant concern. It is estimated that about 300 million people in Africa have no access to safe drinking water (Makoba & Muzuka, 2019). This is attributed to climate change, population growth, and contamination from both geogenic (Addison et al., 2020; Kassenga & Mato, 2008; Vuhahula et al., 2009) and anthropogenic sources (Elisante & Muzuka, 2015; Nkotagu, 1996a, 1996b) which increasingly threatens the quantity and quality of potable water. Elevated concentrations of As, F, and other elements (TEs), including mercury (Hg), manganese (Mn), copper (Cu), iron (Fe), uranium (U), and molybdenum (Mo) in northern Tanzania have been sporadically reported (Kaseva et al., 2018; Kitalika et al., 2018; Marwa et al., 2018; Tomasek et al., 2021) and other regions of Africa (Akpulu & Normanyo, 2017; Bretzler et al., 2017; Bretzler et al., 2019; Rango et al., 2013; Smedley, 1996; Straaten, 2000). This level of contamination should be a major concern for Tanzania and other African countries that rely on groundwater.

The presence of elevated concentrations of geogenic contaminants in groundwater poses

Table 1. Major groups of groundwater quality problems (Ravenscroft, 2022).

Type of problem	Possible causes	Examples of contaminants of concern
Naturally occurring contaminants	Chemical evolution of groundwater and mineral solutions (can be exacerbated/aggravated by human-induced activities such as mining and over-abstraction)	Arsenic, fluoride, iron, manganese, magnesium, selenium, and other inorganic species
Saltwater Intrusion	Saline groundwater water intrusion by flowing in the direction of fresh groundwater aquifers due to excessive abstraction	Sodium chloride
Aquifer pollution	Poor protection of vulnerable aquifers from humans induces discharges and leachates from domestic, agricultural, and industrial activities	Pathogens (bacteria and viruses), organic pollutants, pesticides, phosphate, nitrate, heavy metals
Well-head contamination	Inappropriate wells design/construction may lead to the direct entrance of polluted surface water or shallow groundwater	Pathogens such as bacteria and viruses

significant health risks to the population that depends on groundwater, especially for drinking purposes (Bundschuh et al., 2017; Karunanidhi et al., 2021). In Tanzania and globally, the presence of elevated concentrations of As, F, and other trace elements (TEs) jeopardize the provision of safe drinking water to the community through government and private sector initiatives (Bundschuh et al., 2013; Nilkarnjanakul et al., 2022; Scanlon et al., 2023; Tomasek et al., 2021). Although the evaluation and periodic monitoring of water quality are supposed to be part of any groundwater development project in the region, it is acknowledged that information about the quality of groundwater in Sub-Saharan Africa is scarce (Gowing et al., 2020; Oke & Fourie, 2017; Rieger et al., 2016; Rivett et al., 2018; Rwiza et al., 2016). This scarcity of groundwater quality baseline information hinders a comprehensive understanding of groundwater quality in Sub-Saharan Africa. This knowledge gap should not be understated owing to its direct economic, health, and environmental impacts on the country.

Hydrogeochemical investigations provide the basis for the understanding of groundwater characteristics that are needed for the

sustainable utilization of groundwater and human protection from the consumption of harmful chemicals through drinking water (Haghnazar et al., 2021; Maity et al., 2021; Ormachea Muñoz et al., 2015). In the present study As, F, and other trace elements (TEs) including aluminum (Al), chromium (Cr), cobalt (Co), Cu, Fe, Mn, Mo, Nickel (Ni), and Zinc (Zn), were investigated. Properly understanding the hydrogeological conditions and various geochemical processes concerning releasing these elements into groundwater is important for the effective mitigation, management, protection, and sustainable exploitation of groundwater resources.

1.2. Aquifer types, characteristics, and groundwater potential

Groundwater can be abstracted from confined and unconfined aquifers (Table 2). Confined aquifers are usually less permeable, with a low groundwater flow rate and limited dissolved oxygen. The aquifer is less prone to surface processes (rainfall, runoff, irrigation). Owing to their limited permeability, confined aquifers are less prone to contamination from pollutants emanating from the surface. However, due to the slow flow rate, there is high interaction of groundwater with the parent rocks in the aquifers which leads to

Table 2. The major aquifer types in Tanzania.

Type of aquifer	Recharge type	Groundwater quantity	quality andReferences
Unconsolidated aquifers consisting mainly of alluvial deposits (normally unconfined) e.g., the volcano-pyroclastic and alluvium deposits of the Kate basin and Sanya Bsin in Kilimanjaro	Rainfall and Infiltration from lakes and rivers	Generally, good water quality except for aquifers in the coastal plains subjected to saline intrusion. Over-abstraction can lead to saline intrusion from the ocean, a common case in coastal regions such as Dar es Salaam. Decreasing borehole yield has been observed in Sanawari area, Arusha.	(Comte et al., 2016; Mjemah et al., 2010; Mtoni et al., 2013)
Consolidated aquifers (The coastal sedimentary and Karoo sandstone aquifer	Rainfall and infiltration from lakes and rivers	Good water quality with the challenges of saline and nitrate intrusion from the ocean and municipal wastes, respectively, intrusion of manure and fertilizers from urban agriculture, household wastes from pit latrines, septic tanks, household drainage	(Comte et al., 2016; Mtoni et al., 2011; Sappa et al., 2013; Sappa & Luciani, 2014)
Basement complex aquifers (usually discontinuous and confined) e.g., the Fractured aquifers of the Makutupora basin in Dodoma	Recharged occurs through weathered and fractured zones, joints, and faults	Groundwater quantity may vary depending on the rate of abstraction; for example, parts of the water level in Makutupora basin are declining. Groundwater quality also may vary subject to the intrusion of contaminants from both natural and anthropogenic sources such as nitrates from domestic sewages.	(Kashaigili, 2013; Rwebugisa, 2008; Seddon et al., 2021)

groundwater being highly mineralized with natural inorganic chemicals such as As, F⁻, Fe, Mn, and Zn (Sappa et al., 2013).

The permeability of unconfined aquifers is higher, and they are easily accessible by surface runoff through infiltration. The recharge of unconfined aquifers from the surface is high, hence, they can easily be contaminated by surface pollutants. The common pollutants from the surface are nitrate, phosphate, and microbes. Aquifer recharge can be used to deduce the confinement of aquifers and can provide a

clue for the prediction of groundwater quantity and quality. The water-rock interaction process is important for groundwater quality. A typical example is the case of volcanic rock materials in the northern part of Tanzania which contains fluoride minerals. The interaction of the rocks with groundwater results in a high concentration of fluoride in groundwater (Kaseva et al., 2018; Makoba & Muzuka, 2019). Nevertheless, the aquifer characteristics in terms of recharge, exploitation, and management are not

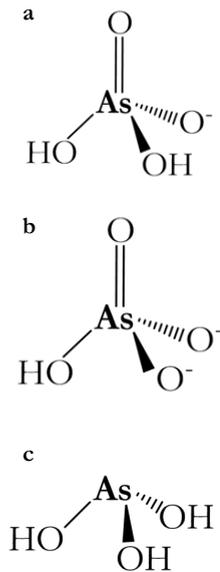


Figure 1. Molecular geometry of the dominating inorganic As species; As (V) (a and b) and As (III) (c) species.

optimally explored in Tanzania. However, with the increase in population and changing climate scenarios, groundwater exploitation for drinking, agriculture, and industrial activities will increase in the future (Comte et al., 2016; Gudaga et al., 2018; Mosha et al., 2022).

1.3. Arsenic and fluoride in groundwater

Arsenic and fluoride are among the most naturally occurring harmful chemicals due to their extent of human exposure and serious health impacts on a global scale. The major route of exposure is through drinking water contaminated by those elements, humans can also get exposed by eating food prepared with contaminated water. Geogenic As and F⁻ in groundwater result mainly from geochemical processes in the aquifers (Polya et al., 2019; Yan et al., 2021).

1.3.1. Hydrogeochemistry and mobilization of arsenic in the environment

Arsenic (As) is the 33rd element (metalloid) located in group 15 of the periodic system. It

has five electrons in the outermost shells of the s^2p^3 electronic configuration, hence it can exist in two oxidation states (+3 and +5). It occurs naturally combined with Oxygen, Sulfur, and Iron. Examples of As-containing minerals include arsenopyrite (As_2S_3), arsenolite (As_2O_3), scorodite ($FeAsO_4 \cdot 2H_2O$) (Quino-Lima et al., 2020; Smedley, 2002).

In groundwater, the presence of As is associated with leaching and dissolution processes from arsenic-containing parent rocks, soil, and sediment, arsenic can also be leached through infiltration processes from As-containing anthropogenic sources such as wood preservatives, pesticides, and metal ores (Bhattacharya et al., 1997; Maity et al., 2011; Ormachea Muñoz et al., 2015). The prevalent forms of As in the aquatic environment are trivalent arsenic [arsenite (As (III))] and pentavalent arsenic [arsenate (As (V))] from the H_3AsO_3 and H_3AsO_4 oxoacids, respectively. The acid dissociation constants (K_a) presented as the negative logarithm (pK_a) for the H_3AsO_3 is 9.29 while for H_3AsO_4 are 2.26, 6.76, and 11.29 (Fig. 1).

The geological formations that are associated with iron (reductive dissolution) and sulfide minerals (sulfide oxidation), as well as volcanic and alluvial bedrocks (alkali desorption) and geothermal processes are known for the release of arsenic from parent rocks and sediments into groundwater (Nilkarnjanakul et al., 2022). Local hydrogeology and geochemical characteristics of the aquifers and their interaction with water are important for the mobilization of As in a given area (Bundschuh et al., 2013).

The total concentration and speciation forms of arsenic (As (V) and As (III)) are highly dependent on the redox conditions of the aquifers (Fig. 2). Oxidation of different As-containing minerals solubilizes As and renders it available in groundwater. Mining, agricultural activities, and pumping of wells affect the redox conditions in the aquifers.

The major chemical reactions governing the availability of As in groundwater sources are adsorption-desorption, ion exchange, oxidation-reduction, and precipitation. Other factors include biological activities, the

Table 3. Typical geochemical mechanisms responsible for the release of arsenic in groundwater aquifers.

Process	Geochemical Condition	Geological environment	Example of countries	Reference
Reductive dissolution	Neutral pH (~7)	Glacial deposits	Bangladesh,	(Chakraborty et al., 2015; Halder et al., 2012; Sracek et al., 2021)
	Reducing groundwater condition	Holocene floodplains	India, Pakistan, Cambodia, Vietnam, China, Nepal, Botswana, Cameroon	
Sulfide oxidation	Low levels of NO ₃ ⁻ and SO ₄ ²⁻	Parent rock rich in sulfide mineralization	Tanzania, Ghana, Burkinafaso, Thailand, India, Finland, Canada, USA, Mexico	(Ahoulé et al., 2015; Drahota et al., 2021; Irunde et al., 2022)
	High SO ₄ ²⁻ content		Usually associated with gold and tin minerals	
Alkali desorption	Slightly alkaline pH (~7)	Volcanic and alluvial bedrocks	Argentina, Spain, USA, China, Bangladesh	(Ahmed et al., 2004)
	Oxidizing groundwater condition		Low level of Fe	
Geothermal processes	High groundwater temperature	Geothermal activity associated with volcanic activities.	Bolivia, Chile, Peru, Ecuador, New Zealand, Italy,	(Ormachea Muñoz et al., 2015; Quino Lima et al., 2020; Quino Lima et al., 2021)
	High Cl ⁻ content			

content of organic matter, particle sizes, and acidity/basicity (Herath et al., 2016; Nriagu et al., 2007) (Table 3).

Two main conditions govern the favorable mechanisms for the release of As in groundwater in the aquifers: (i) at high pH (above 8.5) and oxidizing conditions when the pH is high, there is also a high concentration of OH⁻ ions in solutions, this condition leads to the competition between As and OH⁻ ions to adsorb to the available sites on the surface of minerals. The high pH leads to the dissolution of As (V) species from oxide mineral and (ii) under reducing aquifer conditions, usually, groundwater

environments are more reducing than surface water environments. The main mechanisms for the dissolution and mobilization of As are the reduction of AsO₄ to AsO₃ and the reductive dissolution of As containing Fe and Al hydroxides and sulfide minerals. Reducing conditions in the aquifer systems are attributed to the presence of microorganisms, which normally use reduced carbon (organic carbon) as an electron donor and oxygen as an electron acceptor to complete the redox reaction (Hamon et al., 2004).

The main mechanisms explaining As mobilization under reducing conditions are (i) reduction of AsO₄ to AsO₃ in a soil which

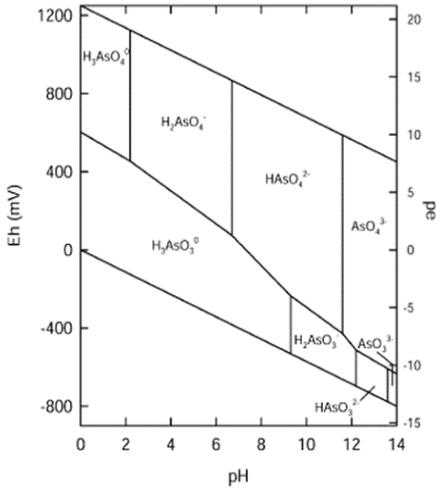
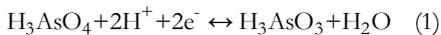


Figure 2. Eh-pH diagram for aqueous As species for the As-H₂O systems. The activity of water is unit; T = 25°C and P = 0.101 MPa activities of the soluble As species are 10⁻⁶. As (V) is predominant under oxic and suboxic while As(III) is predominant under anoxic conditions (Smedley, 2002).

sorbs AsO₃ less than AsO₄; (ii) reductive dissolution of Fe (III) hydroxides that release the previously bound As, either as AsO₄ or as AsO₃, and (iii) an increase of pH that releases AsO₄ (Hamon et al., 2004) (equation 1).



Where Eh⁰ (0.56V) is the standard reduction potential with reference to the H⁺/H₂ reduction reaction. For a given molecular species, the reduction potential is the net result of all reactions necessary for that redox transformation. High reduction potential shows that the oxidized species in each redox reaction is a strong oxidant (Fig. 2). Speciation by visual MINTEQ shows that at pH 6, the reduction of AsO₄ to AsO₃ is thermodynamically feasible at Eh=100 mV. Therefore, speciation modeling further confirms the dominance of the H₂AsO₄⁻ and HAsO₄²⁻ oxyanions in an oxidizing environment, whereas the more reduced environment is dominated by the neutral species H₃AsO₃ (Smedley, 2002; Verbeek et

al., 2017; Verbeek et al., 2020). In addition to the inorganic species, a proportionally small amount of arsenic can naturally be found in the organic compounds that are formed through the biomethylation process of the available inorganic species by microorganisms, algae, and plants to form methylated organic compounds in natural waters (and soil) (Gorny et al., 2015; Smedley & Kinniburgh, 2002; Verbeek et al., 2017).

The distribution of inorganic As forms in aquatic and soil environments is strongly dependent on the adsorption reactions with metal hydroxides of Iron and Aluminum. AsO₄ species undergo adsorption reactions with Iron and Aluminum hydroxides through ligand exchange with the reactive surfaces containing OH/OH₂ groups. Bidentate inner-sphere complexation to goethite (Fe³⁺O(OH)) and monodentate and bidentate complexation to ferrihydrite (Fe₂O₃ · xH₂O), AsO₃ can form complexes with Fe and Al (oxy) hydroxides through inner-sphere complexation mechanisms (van Genuchten & Peña, 2016; Waychunas et al., 1993).

The adsorption-desorption behavior of As species through which they are enriched in the groundwater systems from different minerals varies considerably with the pH conditions; at a small range slightly below neutral pH (6-6.5), the adsorption of AsO₄ on ferrihydrite is stronger than AsO₃, at higher pH values, AsO₃ is strongly adsorbed than AsO₄. At a relatively bigger range of pH (5 - 7), a similar preference and mechanism are followed. Overall, the adsorption of AsO₄ decreases with an increase in pH, whereas the adsorption of AsO₃ decreases with increasing pH from 5 to 9 (Dixit & Hering, 2003). The pH dependence adsorption mechanisms of AsO₄ and AsO₃ on aluminum (oxy)hydroxides are similar to that of adsorption on ferrihydrites, however, the strength of the adsorption trend is a wider range of all pH values below 8 (Appelo & Postma, 2005; Arai et al., 2001). Ionic strength (IS) is another property that affects the adsorption of AsO₄ and AsO₃ such that the strength of adsorption of AsO₄ increases with the increase of IS, whereas the

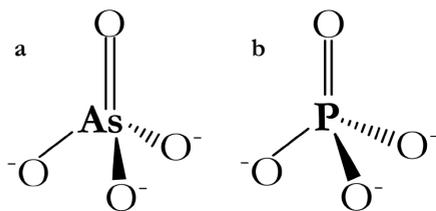


Figure 3. Molecular geometry of AsO_4^{3-} (a) and PO_4^{3-} (b).

adsorption AsO_3 decreases with increasing IS (Arai et al., 2001).

The mobilization of As in the environment is also affected by competing ions. The competition takes the form of preferential adsorption on reactive surfaces. In the solution, the ions compete for adsorption onto specifically charged surfaces or by affecting the electrostatic forces on the charged surfaces (Gómez et al., 2006; Stollenwerk, 2003). The chemistry of As (especially AsO_4) in water (and soil) systems is mainly affected by PO_4^{3-} (P(V)) anions, due to the competitive and electrostatic interaction. The competition arises from the structural similarities between the two anions (Fig. 3), AsO_3 reactions are less affected by PO_4^{3-} ions (Smith et al., 2002).

Other anions such as HCO_3^- and SO_4^{2-} generally have less competitive adsorption effects; the strength of competing ions follows the order; PO_4^{3-} , SO_4^{2-} , and HCO_3^- (Appelo et al., 2002; Gustafsson, 2001; Gustafsson, 2006; Stollenwerk, 2003).

1.3.2. Arsenic toxicity and human health problems

Arsenic is among the toxic elements known to significantly impair groundwater quality globally. The health effects due to chronic exposure to arsenic are latent and irreversible (Feitosa et al., 2021). Hence the exposed population is at risk of developing serious health consequences of chronic diseases from drinking groundwater with elevated concentrations of As. The toxicity of As is dependent upon its chemical species, whereby inorganic As (III) is generally considered to be 60 times more toxic than As

(V). The inorganic compounds of arsenic are reported to be more than 100 times more toxic than the organic forms such as monomethylarsonic acid (MMAA) and dimethylarsonic acid (DMAA), methylation of arsenic can be regarded as a detoxification process in humans and other organisms (Jain & Ali, 2000; Zhao et al., 2010) (Fig. 4).

The main route of human exposure to As is through drinking water, eating As-contaminated foodstuff, dermal absorption, and inhalation (Mondal et al., 2021). Each compound of As species exhibit different chemical and bioavailability properties leading to the complexity of the kinetics and metabolism studies of As in human and other organisms. In the human body, biotransformation between inorganic As (III) and As (V) is enzymatically mediated due to the possibilities of transformation between the two species; exposures to both could lead to similar toxicological effects (Stollenwerk, 2003).

The toxicity effects of As on human includes the competition of AsO_4 and PO_4 during ADP to ATP phosphorylation and the substitution of AsO_4 with PO_4 in DNA molecules. Furthermore, AsO_3 can inhibit enzymatic activities in cells by binding to an enzyme hydroxyl (-OH) or sulfhydryl (S) groups (Mandal & Suzuki, 2002).

Symptoms for long-term chronic As exposure include but are not limited to skin lesions (parakeratosis and hyperkeratosis), melanosis, squamous cell carcinoma, and arsenical pigmentation. Epidemiological studies reported the linkage of skin cancer to other visceral organs, such lungs, bladder, intestine, and blood vessels, and inhibition of cognitive development in children (Ahsan & Steinmaus, 2013; Feitosa et al., 2021; Souza Neto et al., 2020). Also, some studies have reported that arsenic exposure results in an increased risk of non-carcinogenic effects such as diabetes, chronic lung diseases, neurological effects, and cerebrovascular diseases, therefore the pathological effect due As exposure and numerous and complex (Kapaj et al., 2006; Smith et al., 2000).

According to the UNICEF-WHO (Sharp et al., 2018), about 140 million people in at least

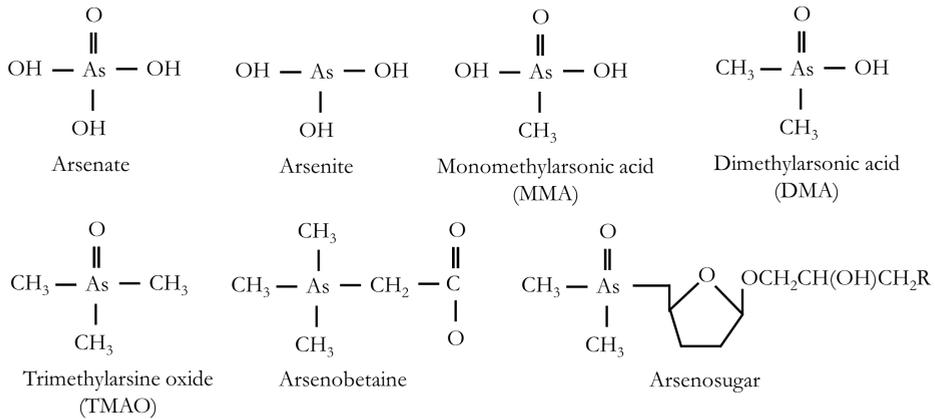


Figure 4. Inorganic and organic compounds of arsenic found in the environment. The inorganic compounds are more potent and toxic than the organic compounds.

70 countries consume drinking water with arsenic concentrations above the WHO guideline value of 10 $\mu\text{g/L}$. In Tanzania, more than 12M people live within the LVB where the current study was undertaken, and a good proportion of them, predominantly within the lake Lake Victoria goldfields are at risk of As exposure, however, there is a limited number of epidemiological studies published (Nyanza et al., 2019). Several African countries have reported groundwater pollution from As, they include Tanzania, Ghana, Botswana, South Africa, Ethiopia, and Kenya (Ahoulé et al., 2015; Huntsman-Mapila et al., 2006; Outa et al., 2020; Rango et al., 2013; Sracek et al., 2021; Taylor et al., 2005).

1.3.3. Hydrochemistry and mobilization of fluoride in the environment

Fluoride is the most electronegative and reactive halogen in the periodic table, it is

abundantly and ubiquitously available in the earth's crust. Owing to its strong reactivity, fluoride is primarily ionically bonded to other elements and is very rarely available in elemental form (Hossain & Patra, 2020). The dissolution of fluoride-bearing minerals, including apatite, biotite, fluorite, hornblende, and muscovite, is the main source of fluoride in groundwater (Mwiathi et al., 2022). The hydrogeochemical mechanisms of dissolution of such minerals involve ion exchange, adsorption-desorption, and evaporation processes (Fuoco et al., 2021; Luo et al., 2018). The possible geochemical reactions for the fluoride enrichment in groundwater from the solid matrices are presented in equations 2-6 below (Kumar et al., 2019).

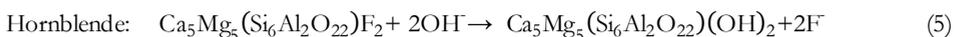
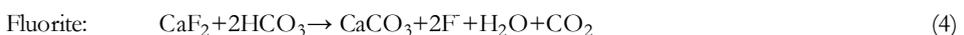




Figure 5. Typical cases of (a) dental and (b) skeletal fluorosis resulting from consumption of groundwater containing elevated concentration of fluoride (Kaseva, 2006).

13.4. Impacts of fluoride on groundwater quality

An estimated 200 million people in more than 25 countries are exposed to high fluoride concentrations through drinking water (Ijumulana et al., 2021; Kimambo et al., 2019). The presence of a high concentration of fluoride in both groundwater and surface water is mainly governed by the hydrogeochemical processes occurring when water moves through the fluoride-containing rocks, which include fluorite (CaF_2), fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), cryolite (Na_3AlF_6), sellaite (MgF_2), villiaumite (NaF) and Topaz ($\text{Al}_2(\text{SiO}_4)\text{F}_2$) (Addison et al., 2020; Vithanage & Bhattacharya, 2015).

Depending on the local geology, under favorable conditions such as pH and sufficient concentration of calcium and bicarbonate ions, F^- leaches into the water. Furthermore, unmanaged fluoride-containing materials from anthropogenic sources also contribute to the F^- enrichment in water (Rezaei et al., 2017). Globally, more than 250 million people in more than 25 countries are exposed to high fluoride-containing drinking water (Kumar et al., 2016; Kumar et al., 2019; Maity et al., 2021; Patel et al., 2015; Vithanage & Bhattacharya, 2015). In Africa, many countries; Algeria,

Benin, Botswana, Cameroon, Egypt, Ethiopia, Ghana, Kenya, Malawi, Morocco, South Africa, Sudan, Tanzania, Togo, Tunisia Zimbabwe, and Uganda, have reported elevated fluoride concentrations in drinking water (Addison et al., 2020; Kimambo et al., 2019; Rango et al., 2013).

Within the East Africa Rift Valley (EARV), about 80 million people exhibit endemic fluorosis conditions ranging from dental, skeletal, and crippling fluorosis when exposed to fluoride concentrations of 1.5-4 mg/L, 4-10 mg/L, and >10 mg/L, respectively, mainly through drinking water (Bennett et al., 2021; Ghiglieri et al., 2010; Ghiglieri et al., 2011; Ijumulana et al., 2021; Kaseva et al., 2018; Rango et al., 2012; Rango et al., 2014). More than 2 million people in Tanzania, particularly within the Pangani River Basin (PR(Thole, 2013)B), the Internal Drainage Basin (IDB), and the Lake Victoria Basin (LVB), are at risk of developing all forms of fluorosis because about 80% of the drinking water is from groundwater sources most of which are naturally contaminated with fluoride (Bennett et al., 2021; Ijumulana et al., 2021; Kaseva et al., 2018; Mbabaye et al., 2018; Tomasek et al., 2021).

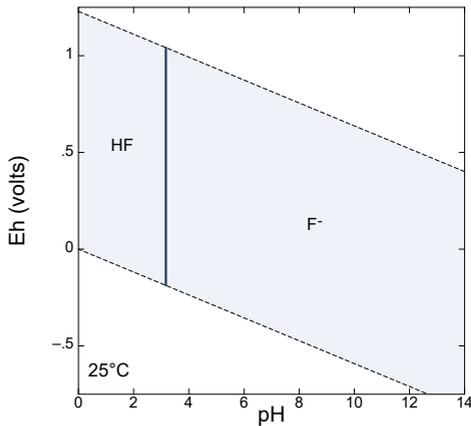


Figure 6. Eh-pH diagram for F. Only one species exists in an aqueous form. The activity of water is unit; $T = 25\text{ }^{\circ}\text{C}$ and $P = 0.101\text{ MPa}$.

13.5. Fluoride toxicity and human health problems

Fluorosis is a prominent health problem associated with the consumption of water with elevated fluoride concentration (above 1.5 mg/L) recommended by WHO (WHO, 2022) guidelines for drinking water in northern Tanzania. In the EARV, about 80 million people are affected with fluorosis, ranging from dental, skeletal, and crippling fluorosis (Fig. 5), resulting from exposure to F^- concentrations of 1.5-4 mg/L, 4-10 mg/L, and >10 mg/L, respectively, mainly through drinking water (Ghiglieri et al., 2010; Kaseva et al., 2018; Rango et al., 2017; Tomasek et al., 2021).

More than 2 million people in Tanzania, particularly within the Pangani Drainage Basin (PDV), the Internal Drainage Basin (IDB), and the Lake Victoria Basin (LVB), are at risk of developing all forms of fluorosis, as about 80% of the drinking water is sourced from groundwater, most of which are naturally contaminated with F^- (Jumulana et al., 2021; Makoba & Muzuka, 2019; Thole, 2014). Communities in the regions within the EARV have been exposed to fluoride for more than half a century (Kitalika et al., 2018; Mbabaye et al., 2018; Thole, 2013). Rural communities are especially more susceptible

to both dental and skeletal fluorosis because they mostly depend on groundwater for drinking which is the main route of exposure so far reported in the area (Ligate et al., 2021; Nakaya et al., 2023).

13.6. Other trace elements

Groundwater characteristics vary considerably with the geological condition of a given area, and so do the composition and proportion of chemical elements. Groundwater contains a wide range of essential and potentially toxic trace elements, such as Al, Mn, Co, U, Cr, Fe, Ni, and Zn. The toxicity levels and health risks associated with overconsumption and/or underconsumption of most of these elements are known globally, and both experimental and epidemiological investigations are conducted along with human civilization and technological advancement.

Other trace elements (TEs) which have potential health concerns for humans based on the WHO guidelines for drinking water quality include Barium (Ba), Boron (B), Cr, Selenium (Se), and Uranium (U) (WHO, 2017). Properly understanding the hydrogeological conditions and various geochemical processes concerning the release of these toxic elements into groundwater is important for the effective mitigation, management, protection, and sustainable exploitation of groundwater resources (Bempah & Ewusi, 2016; Bhattacharya & Bundschuh, 2015; Bundschuh et al., 2017).

1.4. Geochemical modeling of arsenic and fluoride

Geochemical codes are useful in studying the geochemistry of elements. They can offer a better understanding of different geochemical processes occurring in both liquid and solid phases. Therefore, they have been used for the prediction of behavior and mobility of elements, including As and F in different aquifers.

Geochemical models are usually based on adsorption mechanisms (Fig. 6) and speciation (Fig. 7) of different elements at the interphase of solid-liquid matrix and hence can be used to predict their mobility and fate in the environment. pH and redox-dependent

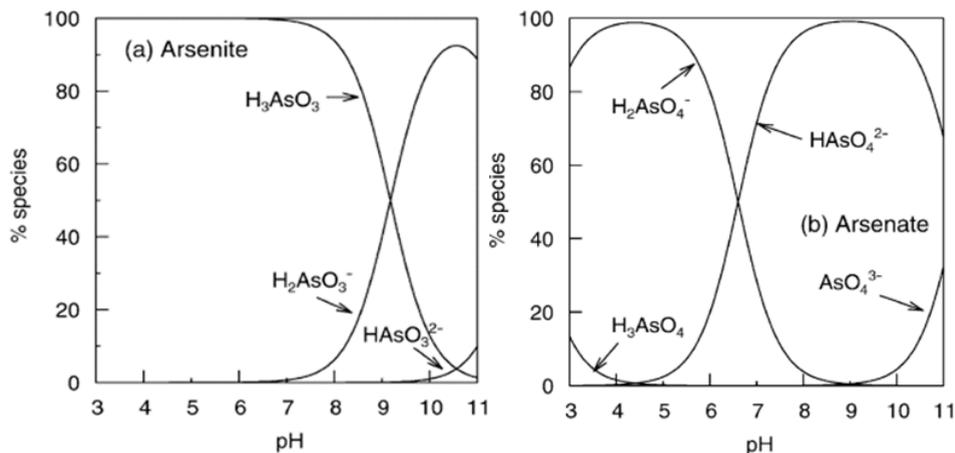


Figure 7. Speciation of (a) arsenite and (b) arsenate as a function of pH. The ionic strength in both cases are 0.01 M (Smedley, 2002).

sorption studies have been reported for As, F, and other elements, including Cu, Pb, Mn, and Fe (Dixit & Hering, 2003; Gustafsson, 2001).

1.5. Drinking water criteria and compliance with TBS and WHO

Considering the toxic effects of the inorganic compounds of As, F, and other TEs on humans, different regulatory bodies and countries have set guideline limit values for TEs concentration in drinking water.

The provisional WHO and TBS guideline limit for As concentration in drinking water is 10 $\mu\text{g/L}$ (Table 4). Elsewhere, the maximum permissible concentrations are lower than the WHO guidelines; notable examples include Australia and Canada, where the maximum permissible concentrations are 7 $\mu\text{g/L}$ and 5 $\mu\text{g/L}$, respectively. In the Netherlands, the ambition to lower the maximum permissible concentration up to 1 $\mu\text{g/L}$ was set in 2016 (Ahmad et al., 2020; Ramsay et al., 2021). The problem for humans becomes very challenging, especially when exposure routes other than drinking water (food, air, and skin) are considered. In Tanzania, the compliance of drinking water quality by most of the groundwater sources which are privately owned is difficult to monitor due to lack of information of their existence.

2. RESEARCH IDENTIFICATION

2.1. Rationale

The access to sufficient and safe drinking water in Tanzania is menaced by geogenic contamination, among other challenges. The increasing population impacts on the economy and climate change, along with variable geological settings, are exacerbating the safe drinking water quality. Most of the communities in urban, peri-urban, and rural areas in Tanzania depend on groundwater (boreholes, hand-dug wells, and shallow wells) as their main source of water for drinking and other household uses. About 75% of the Tanzania aquifer system is dominated by crystalline complexes with variable ages and compositions. Most of the basement aquifers are underlain by Precambrian parent rocks; these rocks are strongly associated with high levels of As and F. The levels of groundwater contamination with As, F, and other TEs in groundwater sources are alarming in Northern Tanzania. The occurrence of these inorganic contaminants is associated with the variation of the hydrogeological and geochemical conditions. The dominant geochemical factors include dissolution, ion exchange, redox potential, pH, and weathering of carbonate and other minerals. The study area has a significant gap in the baseline

Table 4. Drinking water standards guideline values of selected geogenic chemical parameters with health significance based on TBS and WHO (WHO, 2022).

Parameter	Unit	TBS	WHO	Significance and health effects
Arsenic	µg/L	10	10	Essential in small concentrations and toxic at concentrations above guidelines
Barium	mg/L	1000	700	Not an essential element for human nutrition
Boron	mg/L	-	2400	Usually occurs in concentration below health concern
Chromium	µg/L	50	50	Carcinogenic to humans at a concentration above the guideline
*Fluoride	mg/L	4	1.5	Essential for tooth health at low concentrations. Causes dental and skeletal fluorosis at higher concentration
Uranium	µg/L	-	30	Radioactive May cause nephritis in human
Selenium	µg/L	50	40	An essential element at low concentration
Iron	µg/L	-	-	Essential at low concentration. May Affect the aesthetic (acceptability) value of water at higher concentrations. Not of health concern at concentrations leading to drinking water acceptability.
Manganese	µg/L	-	80	Affect the aesthetic (acceptability) value of water

*The volume of water intake and consumption from other sources should be considered for establishing national guideline standards.

information about water quality. A proper understanding of the geochemistry (sources, mobility, and fate) and distribution (mapping) of geogenic contaminants in the groundwater aquifers is required. It is also imperative that before the exploration of the aquifers for safe drinking water abstraction, delineation of the associated human health risks of As and F⁻ pollution in groundwater needs to be conducted in the region and the entire country.

The present study involved the characterization of the hydrogeochemistry, spatial distribution, and health risk assessment of As, F⁻, and other TEs in groundwater sources in northern Tanzania.

The analytical data and geochemical constants were used in visual MINTEQ and Geochemist's Workbench (GWB) geochemical codes to better understand the geochemical behavior of As, F⁻, and other TEs in aquifer systems. The Geographical Information Systems (GIS) technology was

further employed to understand the spatial variability of physicochemical parameters and concentration of As and F⁻ in groundwater. Results were then used for discussion of the safety of drinking water from groundwater sources in the study area. The provisional guidelines are usually available such as those provided by the WHO, specific continents/countries, and sometimes specific regions within the same country. In this thesis, the TBS and WHO standard guidelines for both As (10 µg/L) and F⁻ (1.5 mg/L) were adopted as a reference for the suitability of groundwater for human consumption. The study is within the framework of the application of scientific data to improve the understanding of groundwater quality for the sustainable, safe drinking water supply to the community.

2.2. Objectives and research questions

2.2.1. General objective

The overall objective of this study was to improve the understanding of the occurrence

and distribution of As, F⁻, and other TEs and their impacts on drinking water quality through hydrogeochemical investigation of groundwater in the northern Tanzanian aquifer systems.

2.2.2. Specific objectives

The specific objectives were to:

- Review of chemical quality of groundwater in Tanzania mainland (*Paper I*)
- Assess groundwater F⁻ distribution in the Sanya alluvial plain of the Pangani Water Basin (PWB) in northern Tanzania (*Paper II*)
- Investigate the groundwater chemical quality in the Lake Victoria drainage basin goldfields (*Paper III*)
- Investigate the extent of the co-occurrence of As and F⁻ and its impact on groundwater quality in Lake Victoria Basin (*Paper IV*)

2.2.3. Research questions

The specific objectives were achieved through the following research questions:

- i. What is the status of chemical water quality in mainland Tanzania? (*Paper I*)
- ii. What are the main geogenic contaminants of significant health concern in groundwater sources in Tanzania? (*Paper I*)
- iii. What are the factors contributing to the elevated concentration of fluoride

in groundwater sources along the Sanya alluvial plain? (SAP) (*Paper II*)

- iv. What are the geogenic contaminants in groundwater sources used for drinking purposes in the Lake Victoria goldfields? (*Paper III*)
- v. What is the extent of As and fluoride co-occurrence and spatial variability in groundwater sources in Geita district? (*Paper IV*)
- vi. How does As and F⁻ contamination vary in space in drinking water sources in Geita district? (*Paper IV*)

2.3. Scope of the study

This study is limited to geogenic contamination of drinking water with a focus on As, F⁻ and other TEs in northern Tanzania. Water samples were collected from sources that were used for drinking, other household activities, and irrigation. Measurements of physicochemical parameters and inorganic constituents in water samples were done in situ and the laboratories respectively.

2.4. Thesis structure

The thesis is organized into six sections: Section 1, gives the general introduction and an outline of the background of the research problem. Section 2 highlights the research problem, and the significance of the study, and states the objectives (Fig. 8) and scope of the study. Section 3 describes the study area in terms of its geographical location, geology, and hydrogeology. Section 4 explains the methodology and methods of field

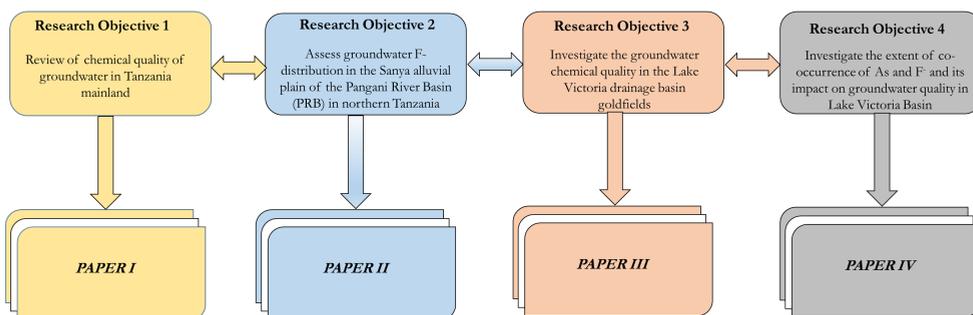


Figure 8. Concept diagram of research objectives and research papers.

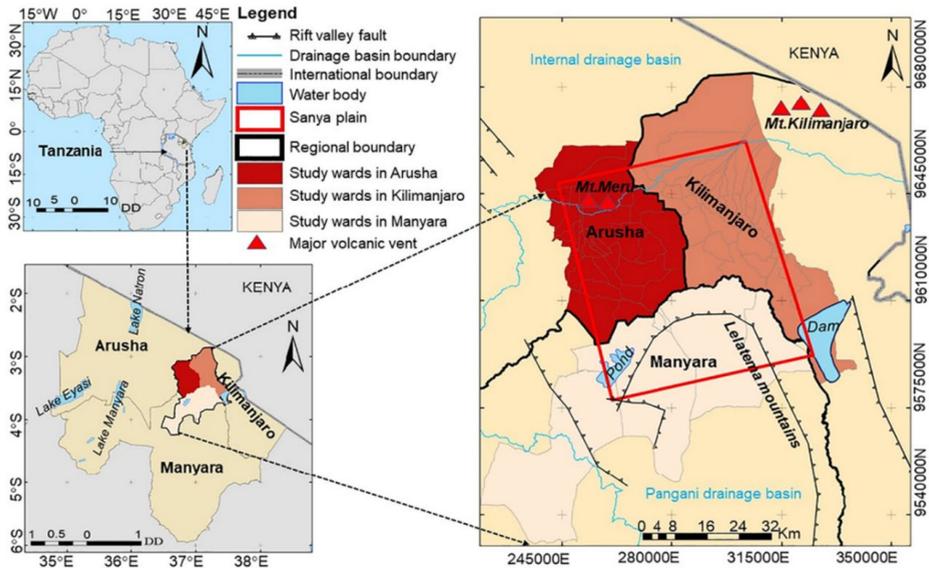


Figure 9. Geographical area and sampling locations in the Sanya Alluvial Plain (SAP). (Paper I and II).

investigations, laboratory analysis, data analysis, and geochemical modeling. Results and discussions are presented in Section 5. Section 6 provides conclusions of the study and outlook in terms of research and practice.

3. STUDY AREA

3.1. General description

The study area in the present research lies within two major drainage basins in northern Tanzania: The Pangani River Basin (PRB) and The Lake Victoria Basin (LVB). The PRB covers an area of 43650 km² between 36°20'E, 02° 55'S and 39° 02' E, 05°40' S in the northeastern part of Tanzania. The Sanya alluvial plain (SAP) located within the PRB, covers parts of Arusha, Kilimanjaro, and Manyara administrative regions in Arumeru, Siha, and Hai and Simanjiro districts respectively (Fig. 9). The area is covered by a huge range of vegetation types such as woodland, shrubland, and scattered trees. According to the national bureau of statistics (NBS), about 1 million people live within the SAP (NBS, 2018), with the main activity being agriculture and pastoralism.

Owing to the fertility of the volcanic soils and accessible groundwater from shallow aquifers, most people are involved with irrigated agricultural activities and both sedentary and nomadic livestock keeping. Groundwater is especially used as a principal source for drinking and irrigation. The subsurface (boreholes (BH) shallow wells (SW) and hand-dug wells) and spring water are the main source of drinking water in the area. The climate in the area is variable depending on the topography and geological settings, whereby the central lowland part is drier than the northern high land areas. There are both confined and unconfined aquifers with variable yields of water and usually discharge water into the Pangani river towards the Indian Ocean. The shallow unconfined aquifers have a depth of 1 to 5 to the groundwater level, and the unconfined aquifers are relatively deeper with a depth to groundwater in the range from 6 to 30 m below the surface (Ghiglieri et al., 2010; Ghiglieri et al., 2011) with the yield of up to 175,000 L/h. The average annual temperature is about 27°C and varies considerably, especially during the dry and

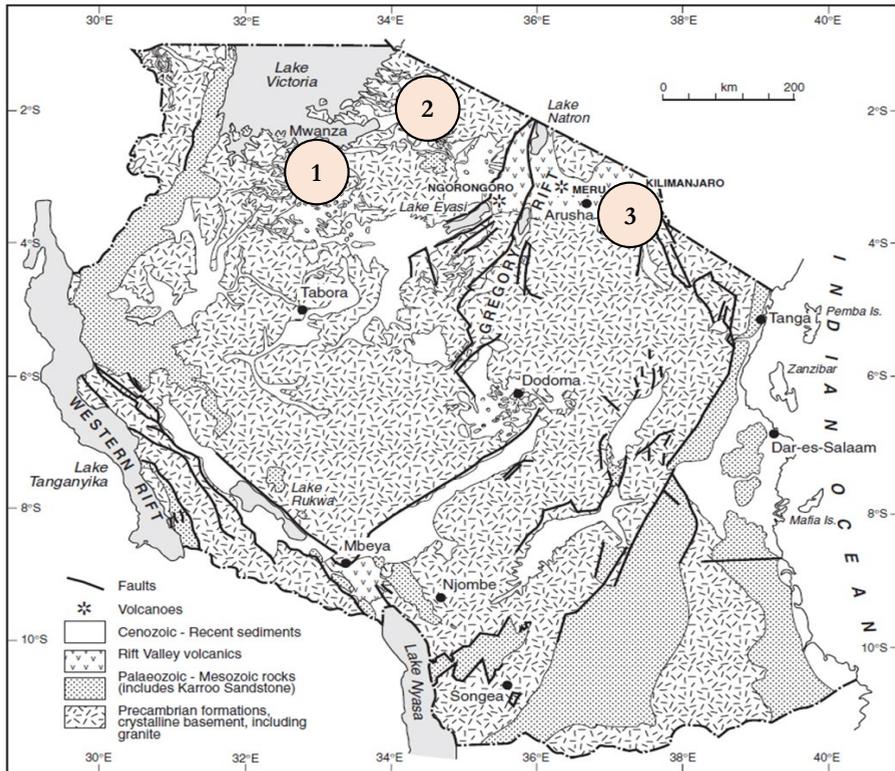


Figure 11. Geological Map of Tanzania (BGS, 2000) with sampling Districts: 1. Geita; 2. Tarime; 3. Hai and Siha.

wet seasons. The average annual rainfall ranges from 500 to 1930 mm in PRB (Tilya & Mhita, 2007).

The Lake Victoria Basin (LVB) covers an area of about 251,000 km², extending between 1°N3°S and 30°36°E on the northwestern Tanzanian. The present study focused on two districts (Geita and Tarime) in the LVB (Fig. 10). The daily activities of the people in the study sites within the LVB are agriculture and artisanal and small-scale gold mining (AGM). The study sites are characterized by an equatorial hot and humid climate with an average annual temperature of 27°C and rainfall ranging from 750 to 2300, with long rains from March to May and short rains from October to December (FDMT, 2016).

In all the study sites substantial groundwater sources were suspected of containing elevated concentrations of As, F⁻, and other

TEs that could lead to potential health risks to the community. (Almås & Manoko, 2012; Mbabaye et al., 2018; Nyanza et al., 2019; Tomasek et al., 2021). Nyanza (Nyanza et al., 2019) reported potential public health problems among pregnant women who depend on drinking water with elevated As and mercury among communities where artisanal gold mining (AGM) activities are in full swing in the Geita district. Groundwater is used for drinking, other household activities, and irrigation but is prone to elevated levels of TEs.

3.2. Geology and hydrogeology

The SAP is composed of volcano-sedimentary rocks that are Cenozoic in nature, as old as Miocene to Pliocene. The volcanic rocks and alluvial deposits are prominent in the area. Mount Meru, where most groundwater aquifers are emanating is a

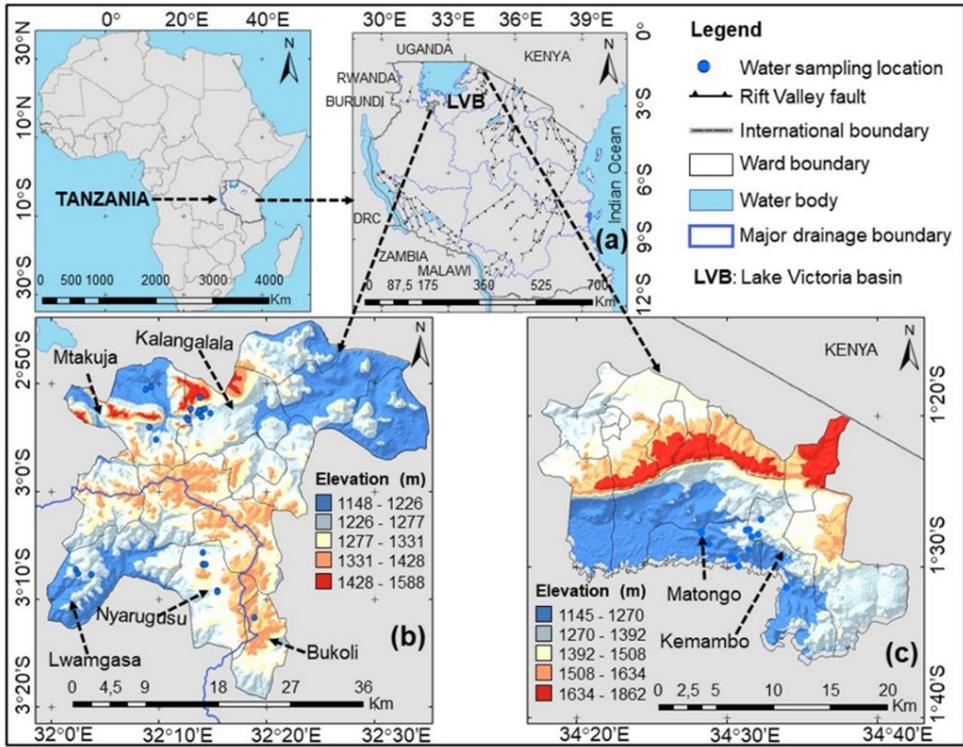


Figure 10. Geographical area and sampling locations in the (a) LVB. Two sampling sites were involved, (b) Geita and (c) Tarime (Paper I, III and IV).

volcanic mountain within the EARV with the main faults of the rift valley in the northwest of the SAP. The major aquifer systems comprise volcanic formations. Perched aquifers can be found within sedimentary formations. The volcanic and sedimentary formations influence the aquifer characteristics regarding recharge, discharge, and groundwater quality (Fig. 11). The SAP can be grouped into four groups of hydrogeological formations: The main cone, lahars, mantling ash, and Meru west group. Lahars are mostly found connected to sedimentary formations, containing phonolite, feldsparphyric, and feldspar phenocrysts. The aquifers associated with lahars are fractured and porous and have substantial permeability. The main cone group is mainly composed of volcanic materials of different ages. The major aquifers in these formations have significant permeability, high yields, and short residence

time of groundwater. The mantling ash consists of pumice and tuff deposits, with very fine-grained and clayish soil, the aquifers have limited permeability and characteristically low yield of groundwater. The Meru west group formation consists predominantly of nephelinite lavas and phonolite clasts, the contain fractured aquifers with high groundwater yield. The less common sedimentary formation consists of lacustrine sediments and fine-grained alluvial soils with low transmissivity. The aquifers in these formations are perched but with a relatively low groundwater yield (Ghiglieri et al., 2011).

The geology of the two study sites in the LVB is heterogeneous and dominated by the migmatite-granitoid-meta-sediment complex (miNA) and volcano-sedimentary complex (Greenstone Belt with banded iron formation (BIF) (gsNA). The study areas are also

Table 5. Summary of the data collection campaign.

Sampling Phase	Period	Sampling Location/Districts	Type of Water Source	Outputs
Phase I (40 water samples)	October 2016	Geita and Tarime	Boreholes, dug wells Springs, and streams	Paper III Conference abstract Policy Brief
Phase 2 (23 water samples)	March 2018	Siha and Hai	Boreholes and springs	Paper II Conference abstract Policy brief
Phase 3 (88 water samples)	August 2018	Geita	Boreholes Dug Wells Springs Stremas	Paper IV Conference abstract Policy brief
Phase 4 (13 water samples)	December 2020	Siha and Hai	Boreholes and springs	Paper II Conference abstract Policy brief

composed of other lithostratigraphic units including young alluvial and eluvial sediments (aQ). The sediments dominate the low-lying terrains in the northeast and southwest of the Geita and Mara study sites, respectively (Fig. 11). Furthermore, the detrital clastic sediments (cNP) dominate the southern section of the Mara site while the young volcanic lavas (alkali basalts, phonolite, and nephelinite) (vN-Q) characterize most of the east section. The principal water-bearing formations in the LVB are composed of the weathered and fractured basement rocks of the Precambrian Craton together with the Tertiary-Quaternary unconsolidated sediments (Fig. 11). In both sites, the miNA and gsNA lithostratigraphic units overlie the large proportion of the Precambrian Craton. In addition, the aQ overlies parts of the Tertiary-Quaternary unconsolidated sediments in the northeast and southwest of the Geita and Mara sites, respectively. The eastern section of the Tertiary-Quaternary unconsolidated sediments is overlain by heterogeneous rock formations, which may result in uncertainty in tracing the sources of geogenic contaminants in this hydrogeological environment. The groundwater potential depends on the degree and depth of the weathered zone, resulting in discontinuous aquifers with low to moderate

productivity ranging between 0.5 - 2 L/s, particularly in shallow aquifers in most rural settings of Sub-Sahara Africa (Macdonald et al., 2009). The groundwater recharge occurs through fractured zones and faults, especially in the Precambrian Craton. The perched shallow aquifer systems usually occur in the unconsolidated materials overlying the weathered bedrock and their exploitation is through hand-dug wells. However, the productivity of these shallow wells is typically low and affected by seasonal variability. The thick deposits of alluvial and lacustrine quaternary sediments, with gravel and sand, occur close to the southern and eastern shores of Lake Victoria and the high-yield aquifers (5 - 20 L/s) have developed in these formations (Cook et al., 2016; Henckel et al., 2016).

4. MATERIAL AND METHODS

4.1. Literature review

The present study involved a survey of literature to establish the status of contamination of groundwater from geogenic sources in mainland Tanzania (Fig. 10). The literature surveyed included peer-reviewed articles textbooks, reports, and grey literature.

The works of literature were accessed from scientific databases such as Web of Science, Scopus, Google Scholar, PubMed, and

Table 6. Water quality parameters used for calculation of CCME-WQI.

Parameter	Unit	Measured value	Standard value (WHO, 2017)
pH	-	6.9	8.5
EC	µS/cm	550	300
alkalinity	mmol/L	3.5	200
Na ⁺	mg/L	47	200
Ca ²⁺	mg/L	45	75
Mg ²⁺	mg/L	14.4	30
Cl ⁻	mg/L	21.7	250
NO ₃ ⁻	mg/L	21.8	50
SO ₄ ²⁻	mg/L	35.5	250
F	mg/L	0.56	1.5
As	mg/L	0.0467	0.01
Ba	mg/L	0.1346	1.3
B	mg/L	0.0208	2.4
U	mg/L	0.0017	0.03
Mn	mg/L	0.117	0.2
Cd	mg/L	0.0005	0.003
Pb	mg/L	0.002	0.01
Cr	mg/L	0.0011	0.05
Fe	mg/L	0.701	3
Ni	mg/L	0.012	0.07
Cu	mg/L	0.08	2
Zn	mg/L	0.0896	4

websites from both international and local institutions (WHO, world bank, UN-Water, FAO, UNESCO, Ministry of Water). Several key terminologies were used including but not limited to water quality, drinking water, groundwater, geogenic contaminants, inorganic contaminants, transboundary water basin, aquifers, East African Rift Valley, arsenic, fluoride, saltwater intrusion, etc. Both primary and secondary data were used for analysis.

4.2. Field investigation

To investigate the hydrogeochemistry of groundwater in the study area, the present investigation involved four phases of the sampling campaign (Table 5). During phase one, a total of 40 water samples were collected from various sources including BH (>25 m), SW (<25 m) (MacDonald et al., 2012) dug wells, and surface water (streams

and springs) bodies; 15 Samples were collected from Tarime and 25 water samples were collected from Geita in October 2016 (Paper III). In the second phase 88 groundwater and surface water samples were collected in August 2018 from boreholes, dug well, and surface water bodies (streams and springs) in Geita (Paper IV). The third and fourth phases were conducted in March 2018 and December 2020 and involved the collection of water samples from 14 boreholes and 9 springs along the Sanya Alluvial Plain (SAP) in the PRB (Paper II). Sampling locations were selected based on the preliminary information about the accessibility of the water sources, the functionality of the hand pumps, and locations to ensure wide coverage of the representative samples for the study. In all phases in situ measurements of physicochemical parameters including pH,

Table 7. Spatial data sources used in the SAP study area (Adapted from paper II).

Source of data	Description of the type of spatial data
Pangani Basin Water Office (PBWO)	Complete drilling reports of 14 BH in the SAP. Bore Holes were drilled in 2011 for irrigation purposes. Boundaries of the Pangani and Internal Drainage basins
Field Survey in northern Tanzania	The concentration of F ⁻ from 14 BH and 9 springs during the sampling campaign in 2018 and 2020. Surface elevations for the sources of water samples (14 BH and 9 Springs)
National Bureau of Statistics (NBS), Tanzania	Boundaries of Region, Districts, and Wards and population data based on the 2012 Nation census report
Survey and Mapping Division (SMD), Ministry of Land House and Human Settlements Development, Tanzania	Coordinates from National control points (T305, T311, and T312) Standard topographical maps at 1:50,000 scale
Global Digital Elevation Model (GDEM)	Open-source elevation data (30 m resolution) accessed from https://gisdata.mn.gov/dataset/-elev-30m-digital-elevation-model
Open Source DivaGIS Portal	Shapefiles for African country's boundaries downloaded from the Free Spatial Data/DIVA-GIS (diva-gis.org)

water temperature (I), electrical conductivity (EC), redox potential (Eh), and fluoride (F⁻) were obtained by using Hach® potable water quality multimeter (HQ40D) calibrated on the field before measurement.

The Hach Arsenic low range test kit (0-500 µg/L) was used at each water source for the in-situ estimation of the amount of total inorganic As from water samples. The hatch arsenic test method involves the reduction of inorganic As to arsine gas, the liberated arsine gas reacts with mercury bromide impregnated onto the test strip paper to form a mixture of arsenic and mercury halogens. The halogens subsequently discolor the test strip the degree that is proportional to the concentration of arsenic in the sample. Usually, the color changes from white to yellow to tan to brown (Anawar et al., 2003; Stolze et al., 2022). Speciation of As was carried out in the field by using disposable cartridges (Disposable Cartridges®, Metal Soft Centre, USA). In the typical procedures for As speciation, 50 mL of groundwater was passed through a cartridge packed with 2.5 g of selective adsorbent called aluminosilicate at the flow rate of about 50 mL per minute using a 50 mL syringe. As (V) in water samples was adsorbed by the aluminosilicate and As (III)

was retained in the filtrate. The average recovery of As (III) in the filtrate was 95% (recovery range is 93-104%) (EPA, 2017; Lucca, 2017). The pH of water samples was within the range of 4-9, such range was an ideal for effectiveness of the method. The collected filtrate was then collected and transported to the laboratory for analysis using using Perkin Elmer Inductively coupled plasma-Optical Emission Spectrometry (ICP-OES). Groundwater samples collected for laboratory analysis included: (a) 500 mL filtered (using Sartorius 0.45 µm filters) for analysis of major anions; (b) 500 mL filtered and acidified using a few drops of 70% nitric acid (HNO₃) to pH less than 4 for laboratory analysis of major cations and trace elements including As (EPA, 2017). All field instruments were calibrated as per the manufacturer's guidelines.

4.3. Laboratory analysis

The water samples collected for laboratory analysis included: (a) 500 mL filtered (using Sartorius 0.45 µm filters) for analysis of major anions, (b) 500 mL filtered and acidified using a few drops of 70% Nitric Acid (HNO₃) to pH less than 4 for laboratory analysis of major cations, heavy metals and trace

Table 8. Water quality classification based on CCME-WQI (Adapted from Paper III).

CCME-WQI	Water quality	Description
95-100	Excellent	Water quality is protected with a virtual absence of threat or impairment; conditions very close to natural or pristine levels.
80-94	Good	Water quality is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels.
65-79	Fair	Water quality is usually protected but occasionally threatened or impaired; conditions sometimes depart from natural or desirable levels
45-64	Marginal	Water quality is frequently threatened or impaired; conditions often depart from natural or desirable levels.
0-44	Poor	Water quality is almost always threatened or impaired; conditions usually depart from natural or desirable levels.

elements including As and, (c) 75 mL filtered and acidified and HNO_3 for As speciation (using Disposable Cartridges®, Metal Soft Centre). The total alkalinity was estimated by using a Mettler Toledo Titrator. The concentration of major anions such as Cl^- , NO_3^- , SO_4^{2-} , and HCO_3^- were measured using Dionex DX-120 Ion Chromatography (IC) equipped with an IonPacAS14 column and a Dionex ASRS suppressor at the Department of Sustainable Development Environmental Science and Engineering (SEED) Laboratory at KTH Royal Institute of Technology in Sweden and the Government Chemist's Laboratory Agency (GCLA) in Tanzania.

Major cations, namely Ca^{2+} , Na^+ , K^+ , Mg^{2+} , As, and other trace elements (TEs), including As, were analyzed using Perkin Elmer Inductively coupled plasma Mass Spectrometry (ICP-MS) at the Department of Environmental Science laboratory at Linköping University Sweden and GCLA in Tanzania. The SEAL Analytical Autoanalyzer 3 (AA3) was used to measure the concentration of PO_4^{3-} at the SEED in Sweden.

In situ parameters (T, pH, EC, Eh, TDS) were measured at each sampling point immediately after sample collection. Estimation of major ions and trace elements were done by adopting the American Public Health Association (APHA, 1998) standard procedures. The geographic information like coordinates and elevation were recorded by a

hand-held global positioning (GPS) receiver Mobile Mapper 20, alongside the functionality and depth of the wells.

4.4. Accuracy precision, and quality control

The precision and accuracy of field measurements were observed by using field blanks and taking replicate measurements. The accuracy and precision of field and laboratory analysis were regularly verified by the laboratory's internal quality control. The quality assurance of results of major ions analysis involved the use of laboratory blank reagents and checked through the calculation of the Charge Balance Error (CBE), whereby most samples were within the acceptable range of $\pm 10\%$, data from samples with CBE greater than $\pm 10\%$ were excluded in subsequent analysis. The blank samples (control) of both field and laboratory analyses were prepared and analyzed according to the standard procedures. The accuracy of the measurement was checked by using certified reference material (NIST SRM 1640a-the trace elements in natural water). the recovery for the analysed TEs was within the acceptable range of 95-105% in accordance with the US EPA standard guidelines (EPA, 2007). In all cases, replicate analysis was performed to check the reproducibility of the analysis and the precision and accuracy of the results. In all cases, replicate analysis was performed to check the precision of the

Table 9. Summary of the methods described in Papers I - IV

Specific Objective	Method of data acquisition	Data analysis	Paper
Review of chemical quality of groundwater in mainland Tanzania	Literature survey by using different keywords including but not limited to water quality, drinking water quality, aquifers, geogenic contaminants, East African Rift Valley, groundwater, transboundary water basin, fluoride removal, and As remediation. Oral interviews	Statistics	<i>I</i>
Assess groundwater F ⁻ distribution in the Sanya alluvial plain of the Pangani Water Basin (PWB) in northern Tanzania	Collection of groundwater samples In situ measurement of physicochemical parameters (T, pH, EC, Eh) and F ⁻ Laboratory analysis of major ions and trace elements in water samples	Statistics Geospatial analysis	<i>II</i>
Investigate the groundwater quality in the Lake Victoria drainage basin goldfields	Collection of groundwater samples In situ measurement of physicochemical parameters (T, pH, EC, Eh) and As Laboratory analysis of major ions and trace elements in water samples	Statistics Water quality index modeling Spatial analysis Geochemical modeling	<i>III</i>
Determine the extent of the co-occurrence of As and F ⁻ and its impact on groundwater quality in Geita district within the Lake Victoria Basin	Collection of groundwater samples In situ measurement of physicochemical parameters (T, pH, EC, Eh), As and F ⁻ Laboratory analysis of major ions and trace elements in water samples	Statistics Geochemical modeling Geospatial analysis	<i>IV</i>

results. The results in terms of elemental concentration (meq) from analytical measurements were initially validated by calculating the ionic balance (CBE) by using the following formula (equation 7):

$$CBE = \left(\frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \right) \times 100\% \quad (7)$$

The calculated value of CBE was within the range of $\pm 10\%$, which suggests that the analytical measurement errors were small and within the acceptable range for the dissolved main inorganic constituents (*Papers II, III, and IV*).

4.5. Data Analysis

Statistical analysis, Hydrogeochemical analysis, Geochemical modeling, and Spatial

Analysis were used in the present study (*Papers I, II, III, and IV*) (Table 9)

4.5.1. Descriptive statistics

The IBM SPSS Statistics (Version 28.0.) software package was used to perform different statistics. The multivariate analyses were used to characterize and visualize data by correlation matrix (CM), principal component analysis (PCA), and hierarchical cluster analysis (HCA). The PCA and HCA were applied to classify water samples into different groups based on their water chemistry. The variance and correlation, and transformation of variables into smaller sets are called Principal Components (PC) (*Papers I, II, III, and IV*).

The factor analysis was used to describe the groundwater chemistry based on the

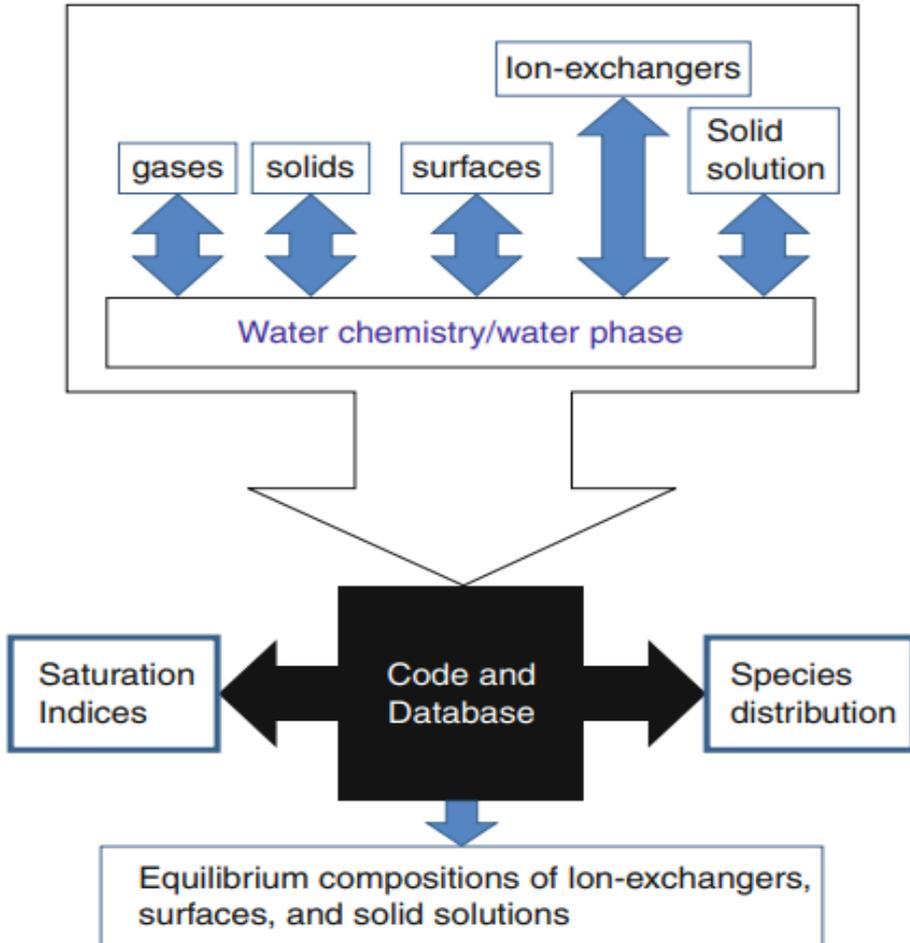


Figure 13. Geochemical modeling of environmental samples (Zhu 2012).

hydrogeochemical parameters. 18 hydrogeochemical parameters were used for factor analysis, and data were converted to dimensionless to reduce the influence of measurement units of individual parameters, normalization was done to a mean value of zero and standard deviation of one (Liu et al., 2003) using equation 8:

$$Z_i = \frac{X_i - X_m}{S_i} \quad (8)$$

Where Z_i is the i th value of the normalized variable Z , X_i is the i th value of the parameter X , X_m is the mean value of variable X and S is the standard deviation.

The PCA was applied to lower the dimensionality and maintain the variability of the data. It follows a multivariate statistical technique to reveal the relationship among environmental variables. In this technique, the raw data are reduced into new inter-correlated variables called principal components (PC) that simplified the description of the correlation among different parameters. The relationship between the different geochemical parameters in groundwater samples from the study sites was determined from the correlation matrix (CM) and PCA. The water sources with similar geochemical characteristics were determined graphically

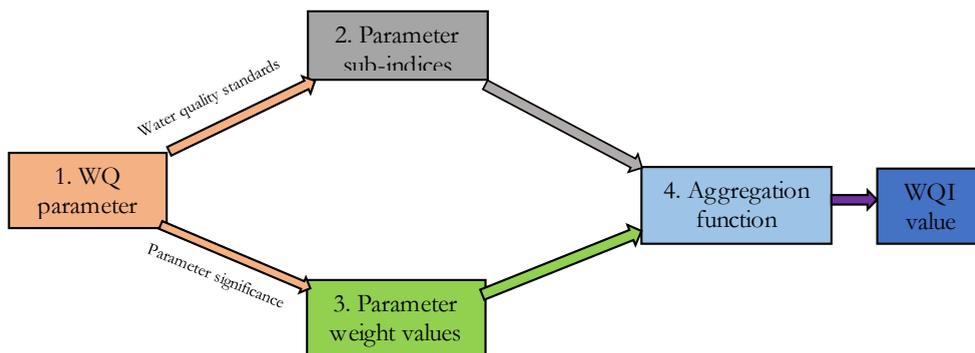


Figure 12. Schematic representation of the procedures for evaluation of water quality by using WQI (Uddin et al., 2021).

using the selected PC scores, (Ormachea Muñoz et al., 2016; Wold et al., 1987).

To assess the relationship between different physicochemical parameters, major elements, and trace elements, the PC matrix, and PCA were computed through varimax rotation, where the eigenvalue was greater than one using the Kaiser normalization.

4.5.2. Spatial analysis

Spatial data analysis was done using data that were collected in 2018 (*Paper IV*) and 2021 (*Paper II*). In *paper II*, the geographical Information System (GIS) was used to characterize the effects of various parameters including the depth of boreholes, screening depth, topography, soil types, and agricultural irrigation practices on the occurrence, distribution, and spatial variability of F⁻ in the SAP in Hai District. In *papers, III and IV*, GIS techniques were used to study the occurrence and distribution of As and F⁻ and other TEs in the LVB. Two phases were involved for the spatial analysis study in the SAP, in phase one the spatial distribution of F⁻ concentration was investigated and phase two concerned the monitoring of the impact of spatial variability of sources of F⁻ on the occurrence and distribution of dissolved F⁻ in the SAP, Table 7 present the spatial data sources for the SAP study area. The QGIS 2.2.5042 and ESRI ArcGIS were used for the compilation of spatial data and mapping. The Geoda 1.14.0 was used for the spatial analysis of the concentration of F⁻ in the study area.

The classical exploratory data analysis and visualization were done by using RStudio 1.2.5042.

4.6. Water quality index

The water quality index (WQI) is a mathematical expression used for describing water quality based on physical, chemical, and biological parameters. The most used parameters include pH, temperature, EC, total dissolved solids (TDS), hardness, alkalinity, selected anions, and cations (Table 6). Since its first development in the United States of America (USA) by Horton in 1965, the water quality index has been used as a basis for the development of other numerical expressions for drinking water quality evaluation. In this study, the Canadian Council of Ministers of the Environment Water Quality Index (CCME-WQI) (Fig. 12) was used due to its versatility, high adaptability to various water uses, low sensitivity to missing data, and simplicity to measure. Furthermore, since its endorsement by the United Nations Environmental Program (UNEP) in 2007, the CCME-WQI has received high acceptance and is used by many countries globally (Lumb et al., 2011). CCME-WQI involves three factors that are denoted by F1, F2, and F3 for the first, second, and third factors respectively. F1 addresses the scope for assessing the extent of non-compliance with water quality guidelines across the selected period, F2 is concerned with the frequency of deviation of

the tested or observed value from the acceptable limits, F3 describes the amplitude of deviation by which the objectives are not achieved. Using equation 9, the three factors are combined as the sum of the three vectors (scope, frequency, and amplitude) to produce a single WQI value (Fig. 12).

$$\text{CCME-WQI} = 100 - \left[\frac{\sqrt{F1^2 + F2^2 + F3^2}}{1.732} \right] \quad (9)$$

The F1, F2, and F3 are computed by using the equations 10-12 below:

$$F1 = \left(\frac{\text{Number of failed parameters}}{\text{Total number of parameters}} \right) \times 100 \quad (10)$$

$$F2 = \left(\frac{\text{Number of failed tests}}{\text{Total number of tests}} \right) \times 100 \quad (11)$$

$$F3 = \left(\frac{\text{nse}}{0.01(\text{nse}) + 0.01} \right) \quad (12)$$

Where 'nse' is the normalized sum excursion, it represents the collective amount by which the individual test values do not meet the compliance and is calculated by using the following expression (equation 13).

$$\text{nse} = \left(\frac{\sum_i^n \text{excursion}_i}{\text{Total number of tests}} \right) \quad (13)$$

The excursion is calculated in two ways (equations 14 and 15).

If a test value is below the objective value:

$$\text{excursion}_i = \left(\frac{\text{failed test value}_i}{\text{objective}_j} \right) \quad (14)$$

If a test value is above the objective:

$$\text{excursion}_i = \left(\frac{\text{objective}_j}{\text{failed test value}_i} \right) - 1 \quad (15)$$

The factor 1.732 in equation 9 is a constant called the normalizing factor. The numerical result from the above expression gives a

CCME-WQI value between 0 to 100 that falls within the range of the state of water quality, whereby zero indicates very poor water quality and 100 indicates excellent water quality (Table 8) (Uddin et al., 2021).

4.7. Geochemical modeling

The Geochemist's Workbench (GWB 2021) software was used to create the Piper diagram, Durov diagrams, Ion Balance, and water types. The saturation indices (SI) (equation 16) and aqueous As and F⁻ species distribution were calculated by using the geochemical software Visual MINTEQ (<https://vminteq.lwr.kth.se/download/>) (Gustafsson, 2022) (Papers III and IV). The calculated saturation indices were used to thermodynamically predict the precipitation and/or dissolution processes of minerals.

$$\text{SI} = \text{Log} \left(\frac{\text{IAP}}{\text{K}} \right) \quad (16)$$

Where K is the equilibrium constant for a given dissolution reaction and IAP is the ion activity product. When the SI > 0, a given mineral precipitates because the aqueous solution is supersaturated with respect to that mineral; When SI < 0, the aqueous solution is undersaturated with respect to the mineral and the mineral will dissolve; When SI=0, the mineral is at equilibrium with the aqueous solution (Fig. 13).

4.8. Health risk assessment

Health risk assessment of As and F⁻ entails an evaluation of the probability/likelihood of occurrence of any given probable magnitude of the harmful health impact over a given period (Bempah & Ewusi, 2016). Human health risks from individual contaminants are usually best classified as carcinogenic and non-carcinogenic (Mohammadi et al., 2019).

In the present study, non-carcinogenic health risks from As and F⁻ were evaluated by considering ingestion as an exposure route. Assessment of health risks due to exposure to elevated concentrations of As and F⁻ through drinking water, the chronic daily intake (CDI) (mg/kg/day) was calculated using equation 17. Two population groups, adults, and children were considered.

Table 10. Summary of parameters and assumed values for exposure assessment.

Parameter	Unit	Value
The concentration of TEs in groundwater samples (C)	µg/L	
Daily intake (DI)	L/day	2 for adults 1 for children
Exposure frequency (EF)	day/year	365
Exposure duration (ED)	years	30 for adults 8 for children
Body Weight (BW)	Kg/Person	70 for adults 20 for children
The period over which the dose is averaged (AT)	day	25550 for adults 3650 for children

$$CDI_{\text{ingestion}} = \frac{C \times DI \times EF \times ED}{BW \times AT} \quad (17)$$

Where C is the concentration of As and F (mg/L), DI is the average daily intake rate which is estimated to be 2 L/day for adults and 1.5 L/day for children (WHO, 2017), EF is the annual exposure frequency, ED is the duration of human exposure, BW is the average body weight (assumed to be 70 kg and 18 kg for adults and children, respectively), and AT is the average time. The parameters and assumed values in the calculation of CDI through drinking water are given in Table 10.

4.8.1. Non-carcinogenic health risks

The probability of non-carcinogenic health risk due to exposure to As and F through drinking water was estimated by using the hazard quotient (HQ), a ratio of the estimated CDI (mg/kg/day) through contaminated drinking water to the oral reference dose (RfD) (mg/kg/day) for the selected population groups using equation 17. The RfD shows the daily exposure to which humans could be continuously exposed over a lifetime with no appreciable risks of harmful effects on their health. The total potential health risks referred to as hazard index (HI) (equation 19) from exposure to As and F is obtained from the summation of all HQs using equation 18, following the EPA guidelines for health risk assessment (Bamuwamye et al., 2015)

$$HQ = \frac{CDI}{RfD} \quad (18)$$

$$HI = \sum HQ_{As} + HQ_F \quad (19)$$

Where RfD is the oral reference dose of As (0.0003 mg/Kg/day) and F (0.06 mg/Kg/day) obtained from the United States Environmental Protection Agency (US EPA) database of Integrated Risk Information System (IRIS; www.epa.gov/iris). When HI < 1 implies no appreciable risks associated with harmful effects that may occur during a lifetime, the possibility of developing non-carcinogenic health impact may occur in the exposed population when HI > 1 (Mohammadi et al., 2019; Yousefi et al., 2018).

4.8.2. Carcinogenic health risks

According to USEPA, carcinogenic health risks (CR) refer to the incremental probability of an individual to develop cancer over the cause of life due to exposure to a potential cancer-causing agent. In the present study, equation 20 was used to estimate the CR. In this case, the carcinogenic health risks due to exposure to As were estimated based on the cancer slope factor (CSF) of 1.5 mg/Kg/day that was adopted from the USEPA screening levels (Rockafellow-Baldoni et al., 2018). The risk level of 1×10^{-6} (1 per 1,000,000 chances of developing cancer because of drinking water contaminated with As) was considered the point of excess cancer risks, for 70 years. Thus, all values below the risk

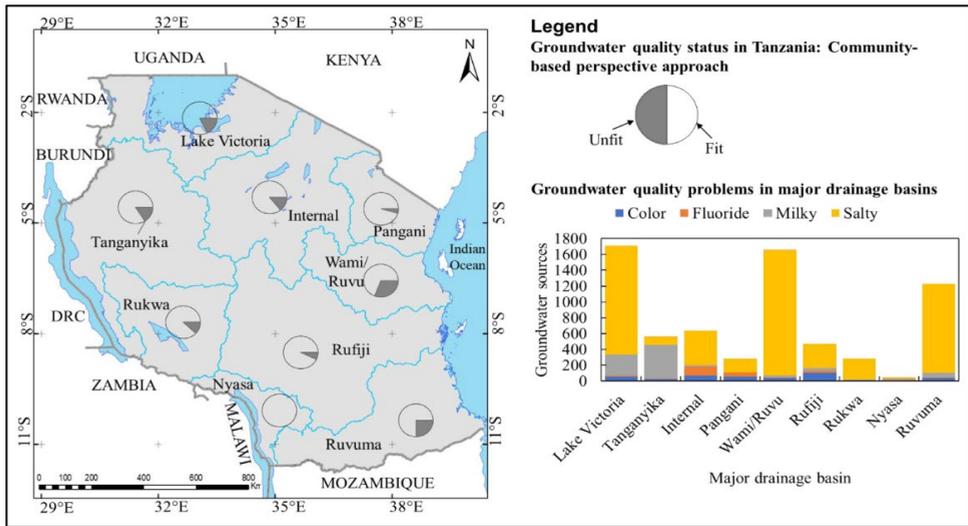


Figure 14. A map of mainland Tanzania, showing major drainage basin and the community-based perspective on groundwater quality and the potential drinking water quality problems. (Adapted from Paper I).

levels were considered safe. The borderline range of risks

as per EPA is 1×10^{-4} to 1×10^{-6} (EPA, 2019). A carcinogenic risk level of 1×10^{-4} is considered to pose health hazards hence my need for intervention (Alidadi et al., 2019; Saha et al., 2017).

$$CR = CDI \times CSF \quad (20)$$

5. RESULTS AND DISCUSSION

5.1. Geogenic contaminants and groundwater quality in mainland Tanzania

Substantial discrepancy in groundwater quality monitoring data have been observed, especially regarding geogenic contaminants in Tanzania. Despite the discrepancy in groundwater quality information, the presence of F^- was recognized as the principal geogenic groundwater contaminant over several decades, in the northern part of Tanzania, particularly in the Pangani and Internal drainage basins, parts of the EARV system. Unusually, the high F^- concentration in groundwater originates from the interaction between water and F^- rich minerals such as fluorite (CaF_2), fluorapatite

($Ca_5(PO_4)_3F$), cryolite (Na_3AlF_6), sellaite (MgF_2), villiumite (NaF) and Topaz ($Al_2(SiO_4)F_2$), and ash deposits from the granitic and alkaline volcanic parent rocks. The main mechanism of F^- enrichment in groundwater is water-rock interaction in the aquifers.

Groundwater salinity is prominent, especially in coastal and central regions of the country. Salinity, turbidity, and color were the major drinking water quality issues based on the community perspectives. The elevated concentration of F^- in groundwater was responsible for serious human health effects such as dental, skeletal fluorosis, and crippling fluorosis in northern Tanzania.

In the Lake Victoria basin, As was reported to be the main geogenic contaminant of health concern around the major gold mining areas (Ligate et al., 2022; Lucca, 2017). The release of As from iron and sulfide-bearing minerals through reductive dissolution and sulfide oxidation respectively were responsible for As enrichment in groundwater.

Arsenic was reported elsewhere to cause serious health effects, however, epidemiological studies on the health effect

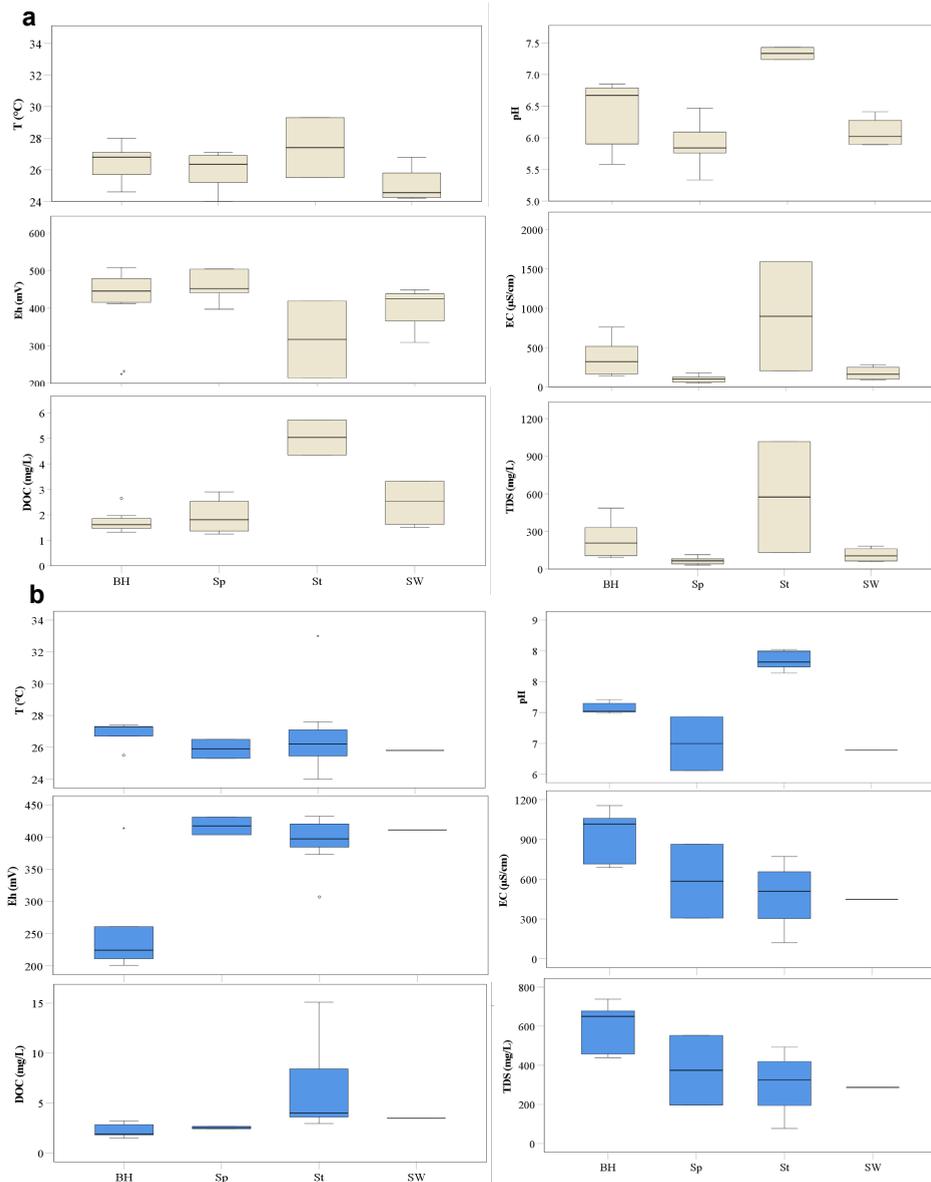


Figure 15. Variations of temperature (T), pH, redox potential (Eh), electrical conductivity (EC), dissolved organic carbon (DOC) and total dissolved solids (TDS) in the bore holes (BH), shallow wells (SW), Springs (Sp), and Streams (St) in water samples from (a) Geita and (b) Tarime. All parameters, except T and Eh , show high variability in both types of water sources. This could have been attributed to the heterogeneity of parent rock materials through which water infiltrates in the aquifers. (Adapted from Paper III).

were limited. Hydrogeological characteristics of the aquifers and groundwater quality

should be further investigated to provide a better understanding of the geochemistry of

Table 11. Statistical summary of physicochemical parameters, major ions, and heavy metals in groundwater samples collected from Geita and Tarime. Field and laboratory data were compared with the WHO drinking water guidelines (WHO, 2017). Comments are given based on the WHO recommendations.

Parameter	Unit	Min.	Media n	Max.	Mean	Standard Deviatio n	WHO (2017)
Physicochemical Parameters							
pH		5.33	6.90	8.37	6.90	0.80	6.5-8.5
T	°C	23.40	26.55	33.00	26.57	1.76	n/a
EC	µS/cm	49.80 201.0	398.00	4040.00	550.29	604.94	400
Eh	Mv	0	422.80	508.20	403.17	75.82	n/a
alkalinity	mmol/L	0.28	2.47	10.80	3.50	3.18	n/a
Major ions and redox species							
Na ⁺	mg/L	3.54	28.90	494.86	47.41	71.13	200
K ⁺	mg/L	0.24	2.69	79.40	5.41	10.80	50
Ca ²⁺	mg/L	1.75	27.53	429.57	44.64	62.22	75
Mg ²⁺	mg/L	0.55	7.39	62.27	14.41	14.35	50
Cl ⁻	mg/L	0.76	12.78	104.92	21.73	24.20	250
NO ₃ ⁻	mg/L	0.04	5.81	139.99	21.81	30.53	50
HCO ₃ ⁻	mg/L	16.84	150.55	659.04	213.75	194.05	n/a
SO ₄ ²⁻	mg/L	0.09	2.47	619.21	35.53	93.66	250
PO ₄ ³⁻	mg/L	3.00	13.77	624.21	58.76	115.81	n/a

As, F⁻, and other TEs of human health (Fig. 14).

5.2. Groundwater hydrogeochemistry

5.2.1. Physicochemical characteristics

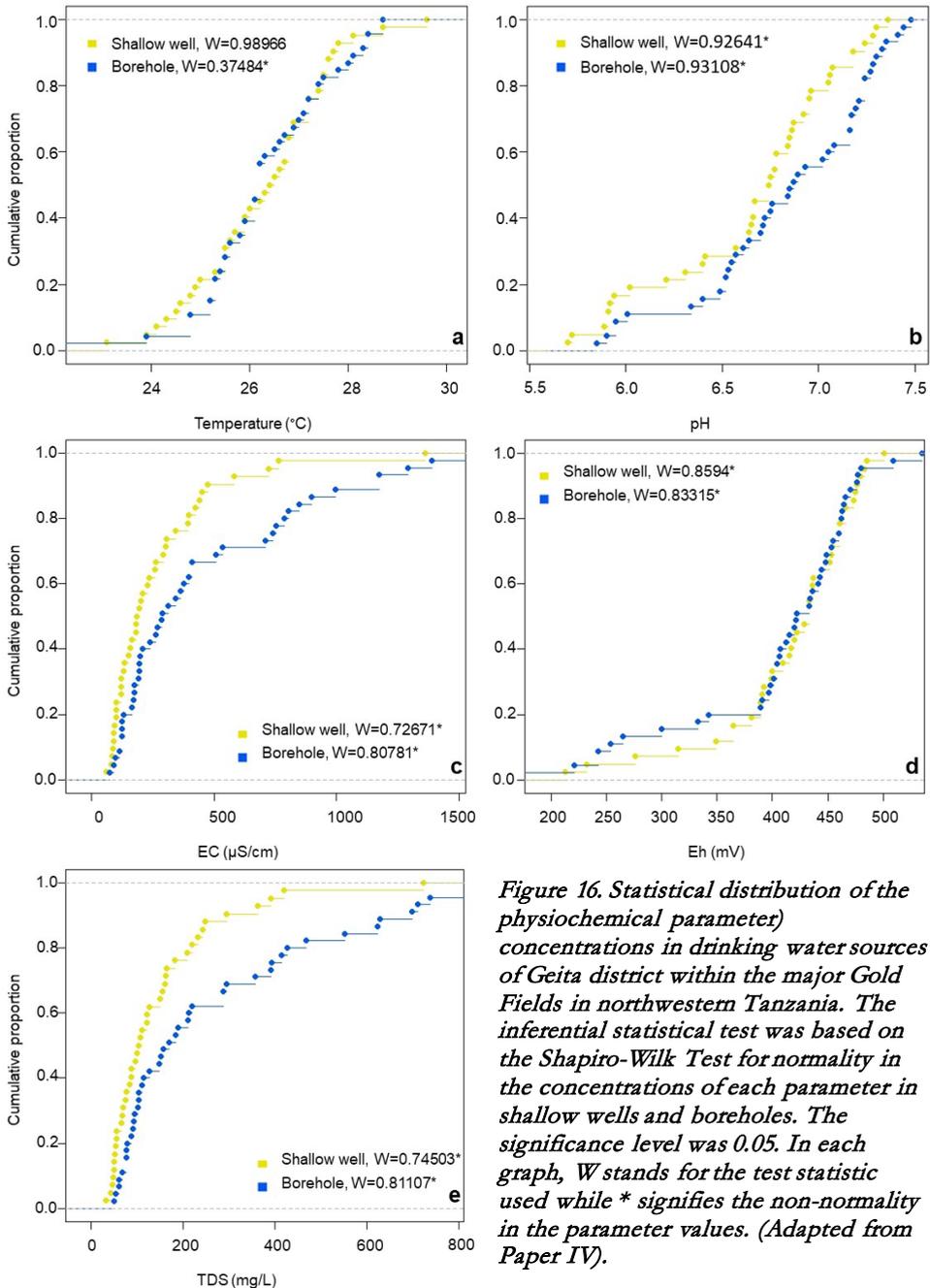
The physicochemical parameters measured *in situ* from BH and SW showed some degrees of variability. Table 11 shows a summary of statistics for physicochemical parameters. The temperatures were observed ranged from 23.1 °C to 29.6 °C (mean = 26.3 °C) and from 23.9 °C to 28.7 °C (mean = 26.5 °C) in SW and BH samples, respectively. However, the temperature variation was noticed insignificant ($p > 0.05$) between SW and BH samples during the dry season. This is a normal range in the study area which is part of the tropical climate (Serdeczny et al., 2016). It is important to mention that temperature is an important parameter owing to its influence on geochemical processes/reactions and microbial activities in the environment.

The pH ranged from 5.7 to 7.4 (mean = 6.7) in SW and from 5.9 to 7.5 (mean = 6.9) in the

BH. The pH significantly influences water quality in terms of aesthetic and chemical qualities. The pH variability significantly affects the mobility and the competitive adsorption of As in groundwater. At relatively higher pH (>8), the enrichment of F⁻ in groundwater is favored through ion-exchange reactions with OH⁻. On the other hand, the presence of sufficiently high concentrations of HCO₃⁻ and Na⁺ also favor the release of F⁻ in groundwater from various mineral phases in the aquifers (Singh et al., 2011).

In groundwater, the pH is mainly controlled by the chemical species in both the water and solid matrix. In surface water, the composition of water is determined by many factors both from natural (e.g., decomposition of organic matter) and anthropogenic sources; these, in turn, can affect the pH of water (Tibebe et al., 2022).

The mean EC value was observed to be 550.29 µS/cm (range: 49.80-4040.00), where the WHO and TBS recommend the provisional guideline values are 400 µS/cm



*Figure 16. Statistical distribution of the physiochemical parameter concentrations in drinking water sources of Geita district within the major Gold Fields in northwestern Tanzania. The inferential statistical test was based on the Shapiro-Wilk Test for normality in the concentrations of each parameter in shallow wells and boreholes. The significance level was 0.05. In each graph, W stands for the test statistic used while * signifies the non-normality in the parameter values. (Adapted from Paper IV).*

and 300 mg/L for EC and TDS, respectively, for drinking water.

The EC and TDS varied considerably depending on the type of water source. Generally, the variation of TDS and EC was

similar in both SW and BH. High TDS and EC levels affect the taste and color of the water, too salty and brownish/brackish, respectively. On the other hand, extremely low TDS and EC values could be explained

Table 12. Statistical summary of trace elements in ground water samples collected from Geita and Tarime. Field and laboratory data were compared by the WHO drinking water guidelines (WHO, 2017). Comments are given based on the WHO recommendations

Element	Unit	Min.	Median	Max.	Mean	Standard Deviation	WHO (2017)
F	mg/L	0.09	0.28	2.44	0.56	0.58	1.5
As	µg/L	0.00	20	300.00	46.70	68.61	10
Al	µg/L	9.98	29.41	8516.94	470.69	1345.07	900
Li	µg/L	0.25	2.12	49.40	6.00	9.02	na
Ba	µg/L	9.92	68.35	2472.48	134.62	335.41	1300
B	µg/L	1.94	13.53	193.58	20.78	31.46	2400
Ti	µg/L	0.15	1.14	25.43	3.25	5.03	n/a
V	µg/L	0.06	3.01	24.28	4.87	5.52	n/a
U	µg/L	0.01	0.41	14.24	1.70	3.15	30
Zr	µg/L	0.01	0.054	4.74	0.54	1.12	n/a
Sr	µg/L	22.12	241.94	2550.10	337.97	432.51	n/a
Si	µg/L	3.82	21.37	47.20	23.25	11.21	n/a
Co	µg/L	0.04	0.29	34.05	2.65	7.24	n/a
Mn	µg/L	1.06	29.34	1421.65	116.99	274.52	200
Mo	µg/L	0.03	0.38	8.65	1.64	2.44	n/a
Cd	µg/L	0.00	0.01	23.05	0.45	3.13	3
Pb	µg/L	0.03	0.20	43.58	2.10	6.63	10
Cr	µg/L	0.04	0.13	27.12	1.11	3.90	50
Fe	µg/L	2.56	12.67	9223.37	701.42	2016.96	300
Ni	µg/L	1.68	1.28	525.87	11.79	71.33	70
Cu	µg/L	0.75	1.99	268.17	8.25	36.19	2000
Zn	µg/L	0.54	12.67	3742.09	89.61	506.84	4000

by the low concentration of essential minerals such as Ca, Na, Mn, and Se.

Overall, the average EC and TDS values were below the guideline values as prescribed by WHO and TBS for drinking water purposes. The TDS followed the same trend, ranging from 31.8 to 722.9 mg/L. As per salinity classification, Kumar et al. reported that the TDS levels in all water samples showed non-saline water types (Kumar et al., 2022). Both TDS and EC are dependent upon the dissolved salts/minerals in the water (Fig. 15, Fig. 16).

Although no direct human health effect is associated with EC and TDS in drinking water, high and extremely low levels of TDS and EC may render the drinking water

objectionable to consumers resulting from unpleasant color and taste.

The dissolved organic carbon (DOC) was observed to range from 1.14 to 8.68 mg/L (mean=5.05 mg/L) in water samples from Tarime and from 1.25 to 7.58 mg/L (mean=4.41 mg/L) in water samples from Geita (Fig. 15). The DOC indicated the availability of organic matter in the water samples. The measured DOC in surface water samples was generally higher than in groundwater samples, this could have been attributed to runoff from agricultural fields and other natural processes on the earth's surface.

The microbial degradation of organic matter influences the geochemistry of As and other

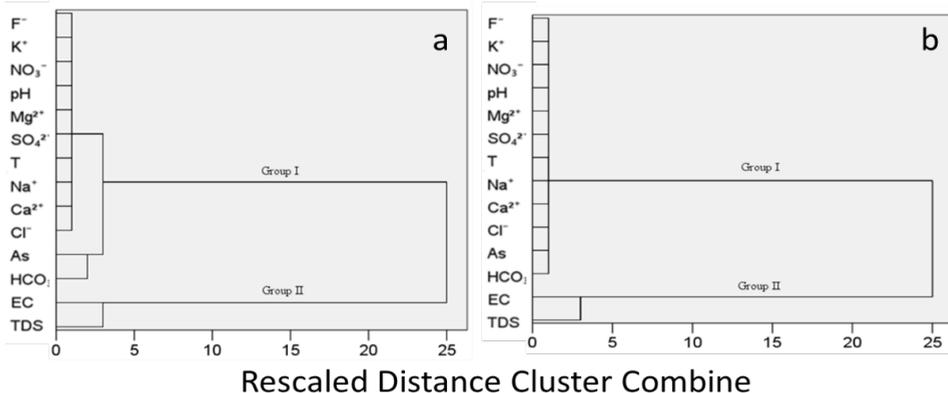


Figure 17. Dendrogram of the characteristics for the physicochemical parameters, major ions, As and F of groundwater samples from: (a) SW with depth <25 m and (b) BH with depth >25 m (Adapted from Paper IV).

TEs. Microbial activities consume the available dissolved oxygen and create the reducing environment that in turn could promote the mobilization of TEs such as As, Mn and Zn (Anawar et al., 2003).

5.2.2. Occurrence and distribution of major ions

The major ion chemistry of groundwater from various drinking water sources were summarized in Table 11. Considerable variations in the concentration of major ions were observed in different water sources. Ca^{2+} and Na^{+} are the most abundant cations, ranging between 1.75 – 429.57 mg/L (mean: 44.64) and 3.54– 494.86 mg/L (mean: 47.41), respectively. Mg^{2+} is the third predominant cation, with concentrations ranging between 0.55 and 62.27 mg/L (mean: 14.41).

Potassium was the least prevalent major cation in water, ranging from 0.24 to 79.40 mg/L (mean: 5.21) (Table 11). The variation of major cation concentrations can be described by the type of source rocks, weathering, and subsequent dissolution processes. The variability of Ca^{2+} and Mg^{2+} is similar, with samples from Geita town having relatively low concentrations compared to those from Geita rural. The concentration of Na^{+} in groundwater samples ranged from 3.5 to 494.8 mg/L (mean: 47.41 mg/L).

The calculated $\text{Na}^{+}/\text{Cl}^{-}$ ionic ratio indicated that the concentration of Na^{+} was higher than that of Cl^{-} in most samples, this could have been attributed to the dissolution of Na^{+} from silicate minerals. The K^{+} concentration in the water samples ranged from 0.03 to 35.57 mg/L, with a mean value of 5.41.

The concentration of Cl^{-} was in the range of 0.03 to 105.7 mg/L (mean: 21.73 mg/L). The Cl^{-} enrichment in groundwater can be originating from both geogenic and anthropogenic sources, especially for the wells that were not properly protected from sewage and domestic wastewater (Ligate et al., 2022). The enrichment of SO_4^{2-} in groundwater is typically from geogenic sources. The WHO guideline recommended permissible limit for drinking water is 150 mg $\text{SO}_4^{2-}/\text{L}$. From the water samples, the recorded concentration of SO_4^{2-} ranged from 0.09 to 619.21 mg/L (mean: 35.51 mg/L), which is below the WHO guideline value.

The groundwater NO_3^{-} was noticed in the range of 0.04 and 139.99 mg/L, respectively (mean: 21.81). NO_3^{-} is typically associated with anthropogenic sources. The concentration between 3.1 and 10 mg/L provides an indication of pollution emanating from various anthropogenic activities (Patel et al., 2015).

5.2.3. Occurrence and distribution of arsenic and fluoride

The water chemistry and geochemical modeling revealed that the occurrence of elevated concentrations of As and F⁻ was exhibited due to water-rock interaction. The fluoride-bearing minerals (associated with volcanic rocks and soils), such as fluorite, apatite, biotite, and hornblende, were possibly responsible for the contamination process.

The groundwater chemistry varied significantly in both BH and SW. The dendrogram (Fig. 17) shows two groups of water quality parameters in the groundwater samples from both SW and BH samples in the Geita region. Group I represent the correlation of different parameters, namely pH and T, major ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, SO₄²⁻, NO₃⁻, Cl⁻) and trace elements (As and F⁻), while Group II is represented by EC and TDS. It can thus be deduced that, As and F⁻ enrichment in groundwater is associated with multiple physicochemical reaction in the aquifers.

The predominant water types were Ca-Na-Cl - SO₄²⁻ type and Na-Cl type in both the well categories (Fig. 18, Fig. 19). The correlation matrix (Table 13) and PCA (Fig. 21) shows a significant correlation coefficient (α), greater than 0.05, and an eigenvalue greater than 1 among all the major ions in the data sets. The cumulative variation of the two major PCs (PC1 and PC2) was explained by 61.9% of the total variance in groundwater chemistry from 40 water samples. The PC1 accounted for 34.2% of the total variance. The variables with the positive loadings in the PC1 were B, Cd, Ba and Pb, Cr, Mn, Ni, Cu, and Zn. as explained by the factor loading between 0.5 and 0.9. On the other hand, PC2 was explained by 27.7% of the total variance; the parameters with positive loadings in this component included pH, EC, As, HCO₃⁻, Cl⁻, F⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺, and U based on the factor loading values between 0.5 and 0.9. The positive loading of these parameters' concomitant with the low positive loading of Fe indicates that the association of As and other TEs are controlled through the complex mechanisms through the dissolution of CO₃²⁻/HCO₃⁻ phases, ion exchange, and

silicate weathering. Other parameters not explained by PC1 and PC2 had loading factor values <0.5 hence smaller variations between them.

The correlation between different parameters and factors, based on the rotation angle of vectors relative to each other and the degree of association among the variables are presented in Table 13 and Figure 21. A good correlation ($r = 0.53$) of Arsenic with Na⁺ was observed. Fluoride showed good correlation with pH ($r = 0.54$), and Mn ($r = 0.11$), Fe ($r = 0.21$), Na⁺ ($r = 0.43$) and Ca²⁺ ($r = 0.33$). Considering the factor loading scores for PC1 and PC2, water samples from Geita and Tarime exhibited similar nature of correlation such that there were small variations of concentration of major ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻, SO₄²⁻) and TEs. About 28% and 80% of water samples from Geita and

Tarime had As concentration above the WHO guideline value of 10 $\mu\text{g/L}$ for safe drinking.

The dissolved concentrations of other redox species, such as Fe and Mn influence the availability of As and other TEs in drinking water. The pH range between 5.3 to 8.4 (mean = 6.9) could affect the aqueous chemistry of As hence rendering As available in solution, on the other hand, PO₄³⁻ affects As binding to reactive sites due to its electrostatic interactions between AsO₄³⁻ and PO₄³⁻ resulting from structural similarities and hence competition on the available sites. The correlation between As and PO₄³⁻ is presented in Table. 13 where a weak correlation ($r = 0.11$) was observed, similar observations have been reported by other literature about the small effects of PO₄³⁻ on the As adsorption in an aqueous medium (Smith et al., 1993; Verbeeck et al., 2020).

For factor analysis, four factors were considered (Fig. 21) based on an eigenvalue greater than 1; the obtained factors were explained by 76.69% of the total hydrogeochemical variation in groundwater samples. As, pH, EC, DOC, Cl⁻, Na⁺, Mg²⁺, K⁺, and Ca²⁺ shows a positive correlation in factor loading 1. Factor 2 indicates that As is negatively correlated with important parameters such as DOC, PO₄³⁻, F⁻ and Mn²⁺.

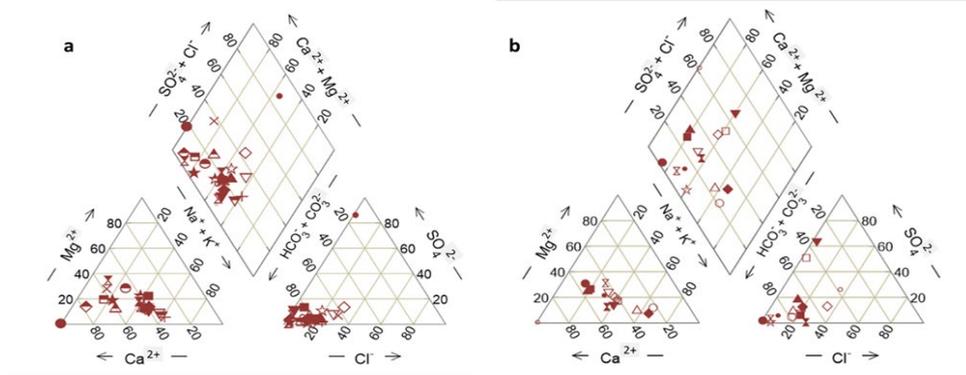


Figure 18. Variation of the characteristic of water, based on samples from (a) Geita and (b) Tarime. The dominant water type in both locations is $\text{Ca}^{2+} - \text{HCO}_3^-$, showing strong influence of carbonate minerals on the composition of water (Adapted from Paper III).

In factor 3, pH, As, DOC, and Mn shows negative loadings relative to other parameters. Factor 4 indicates positive loading for Eh, As, DOC, PO_4^{3-} , NO_3^- and negative loading for pH, EC, HCO_3^- , F, Cl, Mg^{2+} , Ca^{2+} , Mn, and Fe (Fig. 21).

The percentage variance in the four extracted loading factors were 37.68%, 19.88%, 11.38%, and 7.76% for factor 1, factor 2, factor 3, and factor 4, respectively. The correlation of As with other parameters has also been explained using bivariate plots (Fig 22) where a relatively weak correlation is observed between As and Fe ($R^2 = 0.15$), Mn ($R^2 = 0.02$), HCO_3^- ($R^2 = 0.01$), PO_4^{3-} ($R^2 = 0.01$), these parameters were selected based on their importance on the adsorption and desorption reaction of As in the environment. Important geochemical conditions such as redox and pH could be important for the mobilization and distribution of As and other elements from the parent rock minerals.

5.2.4. Occurrence and distribution of other trace elements

The concentrations of other TEs (Al, Cr, Co, Cu, Fe, Mn, Ni, and Zn) in water samples were below the drinking water quality guidelines based on WHO guidelines for drinking water (WHO, 2022). The concentration of Al ranged between 11.57 and 1252.54 $\mu\text{g/L}$ (mean = 161.12 $\mu\text{g/L}$ for

BH and from 13.35 to 2047.63 $\mu\text{g/L}$ (mean = 315.56 $\mu\text{g/L}$) in SW and BH, respectively. B values ranged from 4.17 to 138.32 (mean = 20.32) in SW and from 1.94 to 17.22 (mean = 8.45) in BH. Barium concentrations varied between 26.14 and 478.11 $\mu\text{g/L}$ (mean = 150.01 $\mu\text{g/L}$) in SW, while the concentrations were lower in the BH samples with concentrations in the range of 18.12 to 164.28 $\mu\text{g/L}$ (mean = 71.59 $\mu\text{g/L}$). Cu values were from 0.89 to 268.17 (mean: 29.96) in SW and from 0.75 to 13.015 (mean: 4.56) in BH. The total dissolved Fe concentration varied from 205.37 to 722.88 $\mu\text{g/L}$ (mean = $\mu\text{g/L}$). Fe is the most important cation associated with the geochemistry of As in the aquifers because under favorable redox conditions, As may precipitate or dissolve, controlling its availability in drinking water. Li concentration ranged from 0.42 to 21.38 (mean = 7.3) (Table 12).

The values for Mn, Ni, and Zn were in the range of 1.06 to 1303.16 (mean= 190.10), 0.29 to 525.86 (mean = 53.86), and 5.61 to 3742.09 (mean = 391.89) respectively, in SW and 2.01 to 761.46 (mean 170.82), 0.28 to 6.86 (mean = 1.95) and 0.28 to 6.86 (mean = 1.95) respectively in BH. The correlation matrix (CM) (Table 13) showed a considerable correlation among trace elements at the correlation coefficient (α) greater than 0.05. The cumulative coefficient for the two principal components (PC), PC1 and

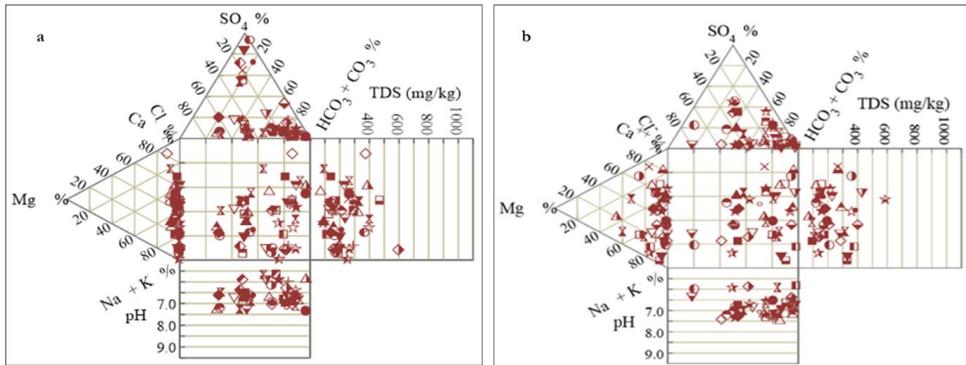


Figure 19. Durov diagram showing hydrochemical facies and the distribution of major ions and TDS for water samples from (a) BH and (b) SH in the Geita region (Adapted from Paper IV).

PC2, in groundwater samples from Geita was explained by 89.61 % and 84.32 % of the total variance in SW and BH respectively. The PC1 contributed 77.30 and 64.31 in SW and BH, respectively. The geological setting and geochemical processes can explain the observed variation of range and correlation of concentrations TEs.

5.2.5. Spatial analysis of F in the Sanya alluvial plain

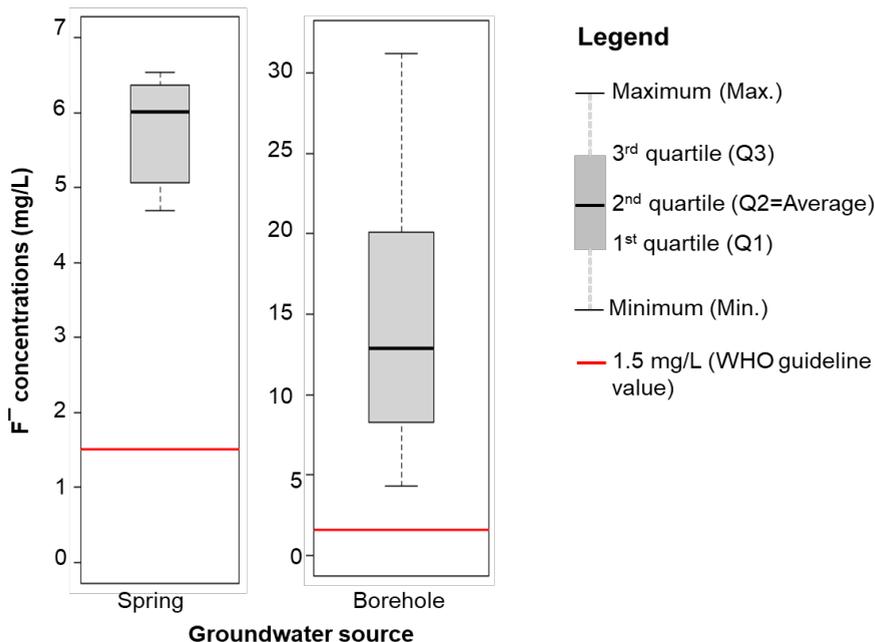
Variable concentrations of F were observed ranging from 0.10 to 32.00, 0.20 to 75.00, and 0.80 to 63.00 mg/L in the upper SAP, along the Sanya river valley and across the Sanya floodplain (along Kikuletwa river) (Fig. 20). The minimum and maximum recorded values within the SAP were observed to increase downstream along the Sanya river valley, this could have been attributed to the contact time of interaction between the F⁻ bearing volcanic rocks, soils, and sediments. The volcanic soils and ashes are well reported to be among the important sources of high F concentrations (Ghiglieri et al., 2011; Ijumulana et al., 2022; Vithanage & Bhattacharya, 2015). Considering the WHO (WHO, 2022) guidelines values for drinking water most of the water samples had concentrations higher than the allowable limit and were from sources located within the Sanya floodplain. Therefore, contact time was established to be one of the factors for the variability of F concentration in groundwater aquifers (Nakaya et al., 2023).

Exploratory data analysis results (Table 14, Fig. 18), show that F concentration varied from 4.0 to 7.0 mg/L in springs and from 4.0 to 32 mg/L in BH, implying that all groundwater sources had concentrations above the WHO (WHO, 2022) guidelines of 1.5 mg/L for drinking water and therefore not suitable for human consumption.

Boreholes showed high variability of F concentration. The relatively low F concentration in samples collected from springs could be attributed to the presence of shallow aquifers and short contact time. Irrigated agricultural practices act as secondary sources of variability of F concentration in the groundwater aquifer system of SAP especially when water from the high F concentration containing BH is used for irrigation.

5.2.6. Spatial analysis of As, F and other water quality parameters in Geita

The global Moran's I statistic indicated the clustering process in some of the drinking water quality parameters. The univariate local Moran's I statistical method identified and mapped significant spatial patterns in each parameter. In this context, the significant spatial patterns included drinking water sources with similar concentrations occurring in some places within the study area. The spatial variability was reported for parameters with significant spatial patterns; the drinking water sources with high pH dominated the northern part of the study area (Fig. 23a). The



Source	F ⁻ concentrations (mg/L)							
	Min.	Max.	Q1	Median	Q3	IQR	Mean	s.d
Borehole	4.29	31.25	8.28	12.90	20.10	11.82	14.23	8.27
Spring	4.70	6.46	5.02	5.39	6.25	1.23	5.55	0.65

Figure 20. Statistical distribution of F⁻ concentrations in springs and BH along Sanya River channel and within river Sanya floodplain respectively (Adapted from Paper II).

lithological layers in this part included the volcano-sedimentary complex (Greenstone Belt with BIF) and the migmatite-granitoid-meta-sediment complex in the south and north sections, respectively. On average, the slope in the two sections was relatively flat, with the lowest slopes dominating the north section. On the other hand, the drinking water sources with low pH dominated the southern part of the study area. Most drinking water sources in this part were in the volcano-sedimentary complex (Greenstone Belt with BIF), at relatively steep slopes where small-scale and artisanal gold mining activities are in full swing. For the EC (Fig. 23b) and TDS (Fig. 23c), the drinking water sources with high values dominated the northern part of the study area within the migmatite-granitoid-meta-sediment complex. On the other hand,

most of the drinking water sources with low values are concentrated in the volcano-sedimentary complex (Greenstone Belt with BIF) mainly in the relatively elevated slopes characterized by the high population density and small-scale mining activities. The Eh did not demonstrate apparent distinct spatial patterns (Fig. 23c) except for the high spatial pattern that dominated the southern part of the studied area. The northern section demonstrated the most heterogeneous part as envisaged by many high values in the neighborhood of low values.

The spatial distribution of K⁺ (Fig. 23d), in the drinking water sources, showed that high concentrations were scattered in the study area where most of them (7 out of 10) occurred in the volcano-sedimentary

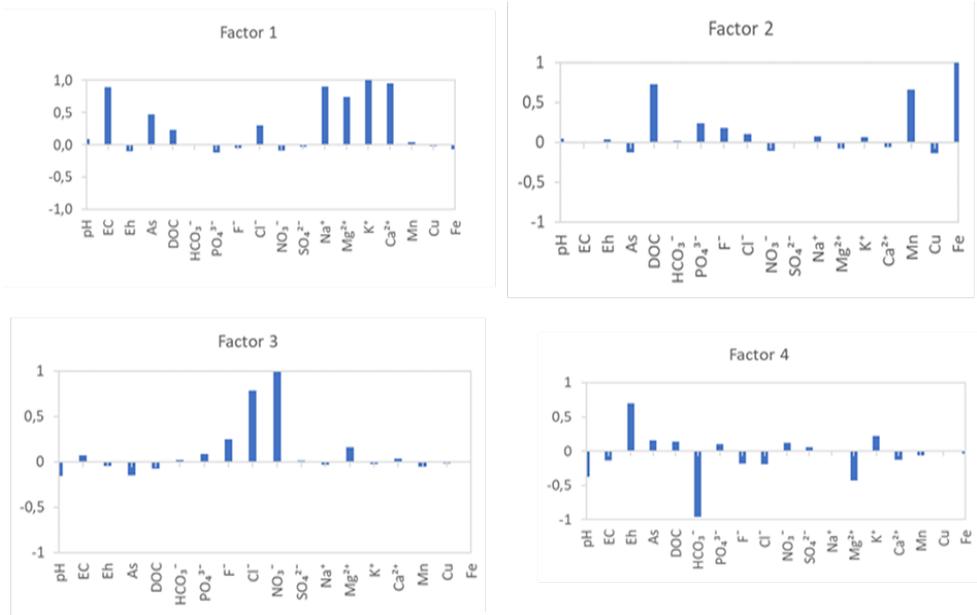


Figure 21. Factor loadings for different hydrogeochemical parameters for 38 water samples, loading value ≥ 0.5 indicates a significant influence of the corresponding parameters to the characteristics of water (Adapted from Paper III).

complex (Greenstone Belt with BIF). The drinking water sources with relatively low concentrations dominated the north and south of the study area. The low concentration values in the northern section were mainly in the lowlands, whose lithology is mainly dominated by the migmatite-granitoid-meta-sediment complex together with alluvial and eluvial sediments.

Both F⁻ (Fig. 24a) and As (Fig. 24b) showed distinct patterns of drinking water sources with high and low concentrations. Many of the drinking water sources with high concentrations of F⁻ dominated the northeast section, mainly in the lowlands underlined by the migmatite-granitoid-meta-sediment complex. Some of the drinking water sources in this setting had F⁻ exceeding the recommended guideline value of 1.5 mg/L (WHO, 2011). The pH of drinking water in this setting was also high, indicating the alkaline environment that is favorable for the mobilization of F⁻ ions in water through the water-rock interaction. Most of the drinking water sources with low F⁻ concentrations dominated parts of the volcano-sedimentary

complex (Greenstone Belt with BIF) around Geita township and in the southern section characterized by relative highlands. The pH in this section is also relatively low, signifying that complexation of F⁻ with other metals may be taking place resulting in the reduction of the aqueous concentration of F⁻ ions. Total field measured As (Fig. 24c) and As (III) measured in the laboratory (Fig. 24d), formed two distinct spatial patterns with high and low As values. Both high and low spatial patterns in As concentrations dominated the same locations to similar extents. All drinking water sources in the high spatial pattern category had values exceeding 10 µg/L, which is the maximum permissible value recommended by the WHO for drinking water. These drinking water sources with poor quality in terms of As dominated the northeast and south of the studied area.

The drinking water sources with high levels of As in the northeast were also characterized by high levels of F⁻ signifying the co-occurrence of these elements in groundwater in these settings. The drinking water sources with high As occur predominantly in the

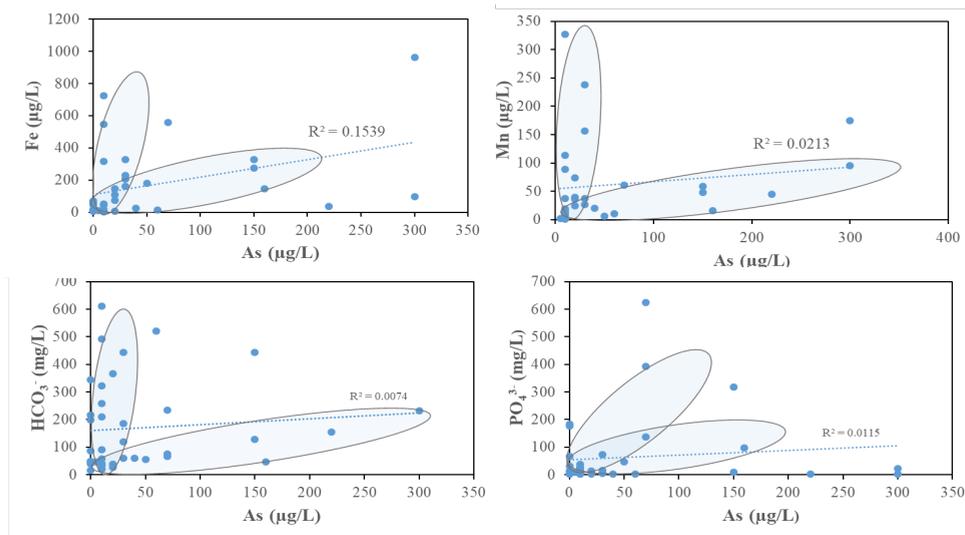


Figure 22. Bivariate plots showing the correlation between As and other redox sensitive elements (Fe and Mn) and anions HCO_3^- and PO_4^{3-} poor correlation suggest complex mechanism of arsenic and other TEs enrichment in water sample from Geita and Tarime.

southern part of the study area under intensive small-scale gold mining activities as well artisanal gold processing. The pH in this setting is low, signifying the oxidizing environment. The high levels of As in this section is a result of oxidation of the arsenopyrite exposed to the surface through small-scale mining operations.

The spatial cluster analysis results, As and F⁻ demonstrated spatial co-occurrence presenting multiple environmental health risks including human beings. In this context, co-occurrence refers to the spatial patterns in As and F⁻ dominating the same extent. The study shows the co-occurrence of As and F⁻ in the northeast section of the studied area. The environment hosting these drinking water sources is reducing in nature, as envisaged by the pH range between 6.9-8.5 values.

5.3. Geochemical modeling

Geochemical modeling of As and F⁻ was performed by computing the SI of different As and F⁻ containing minerals, including ferrihydrite, arsenopyrite, calcite, and fluorites by using Visual MINTEQ and geochemical codes. The following parameters

and species were the input to visual MINTEQ; pH Alkalinity, Temperature, major cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}), major anions (Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- and PO_4^{3-}), and the trace element elements Al, As, F⁻, Mn, Fe, and Zn. The results show that most of the As-containing minerals were oversaturated, except for scorodite, which was undersaturated. Scorodite is a common weathering product of arsenopyrite and its persistence in nature has been shown to control As concentrations in water (Rimstidt & Vaughan, 2003).

The negative SI value (Fig. 25), therefore indicates the dissolution of this mineral, giving aqueous arsenate. Once As is released into the water, it tends to be readily adsorbed on other solid phases, such as Fe, Al, Mn oxide/hydroxides, and clay minerals. The positive SI for Fe (III) oxide/hydroxides (ferrihydrite, and goethite) and Al oxide-hydroxides (gibbsite, boehmite, and diaspore) reveals that water is supersaturated with respect to these solid phases, suggesting their tendency to precipitate. Co-precipitation of As with Fe and Al oxide/hydroxides suggests that under favorable conditions, As may be

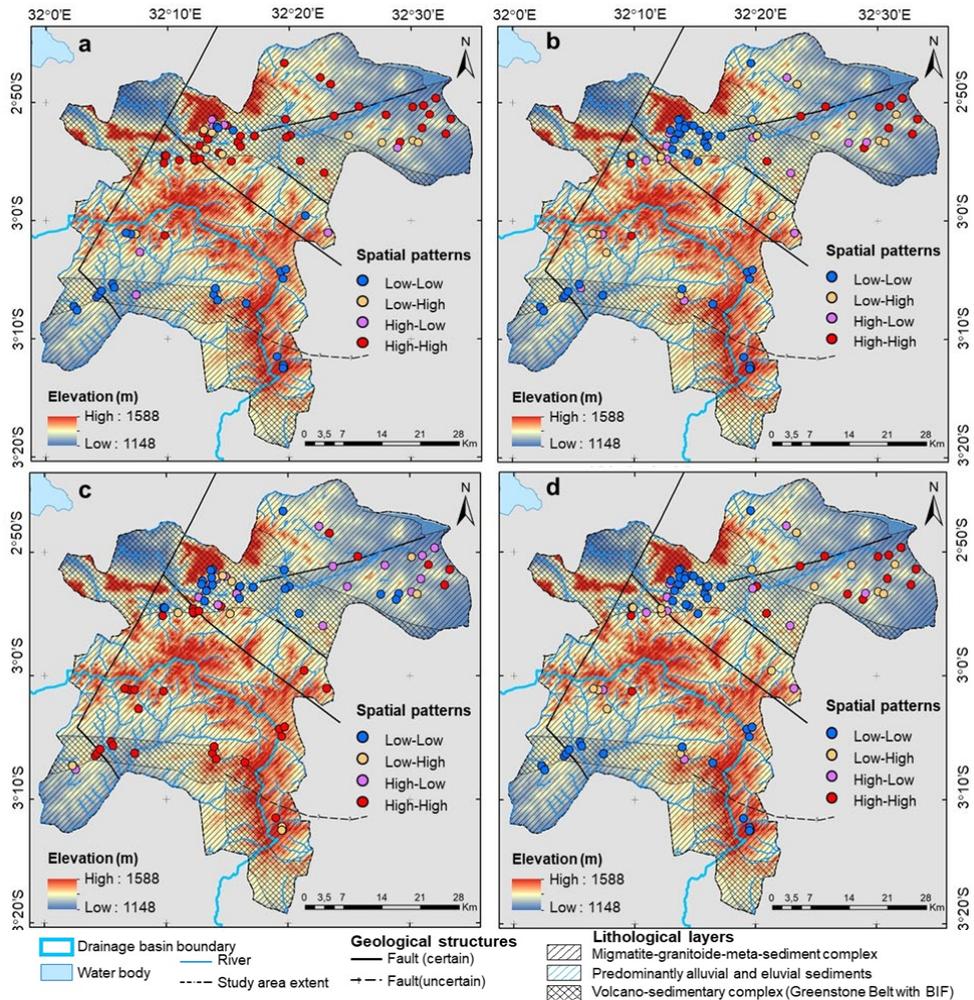


Figure 23. Spatial distribution patterns of the water quality parameters in the Geita region. a) pH; b) EC; c) Eh; d) TDS; (Adopted from Paper IV).

resealed from the complexes and contaminated drinking water.

The water samples were also over-saturated with respect to clay minerals like kaolinite, montmorillonite, and illite, which all show strong sorption behavior towards As(V) (Manning & Goldberg, 1997). On the other hand, the results show that fluorite and calcite were undersaturated (Fig 26). The presence of the undersaturated fluoride-containing mineral phases could be one of the limiting factors for the dissolved concentration of F⁻ in groundwater. The Ca-HCO₃ water type

shows very low concentrations of F⁻ as compared to the Na-HCO₃ water type because, soluble F⁻ in groundwater of the former type is independent of the dissolution of fluorite minerals. It can therefore be deduced that the extent of the solubility of fluorite and calcite minerals is responsible for the control of the presence of F⁻ in the aquifers (Rafique et al., 2009). The low solubility of calcite and high solubility of F⁻ contribute to high F⁻ concentration in groundwater; however, the contact time and flow dynamics also affect the F⁻ dissolution.

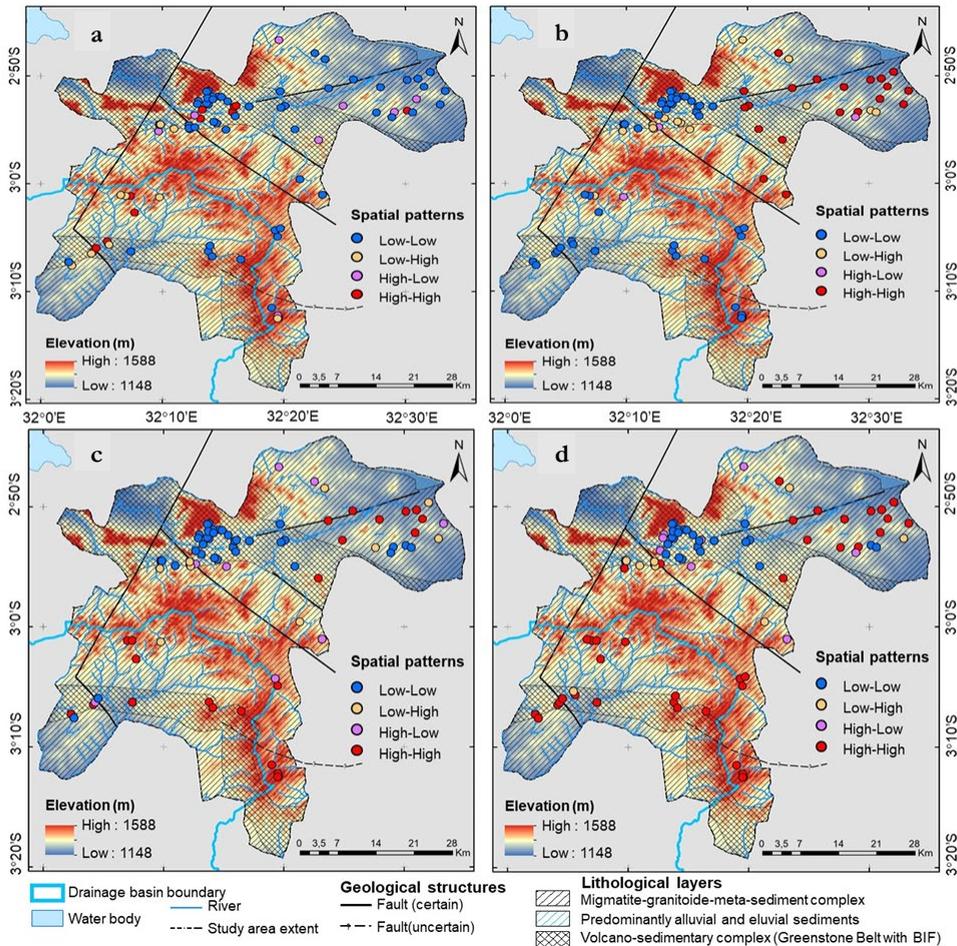


Figure 24. Spatial distribution patterns of the water quality parameters in the Geita region. a) K^+ ; b) F^- ; c) Total As (measured in the field); and d) As (III) (analyzed in the laboratory) (Adapted from Paper IV).

Fluoride enrichment is associated with Na-rich and Ca-poor alkaline groundwater whereby dissolution of fluorite and other F^- containing minerals, competitive adsorption of co-occurring anions, and cation exchange are the prevalent processes of governing water-rock interactions in the aquifers (Brunt et al., 2004; Kimambo et al., 2019; Xing et al., 2022).

Overall, the elevated concentrations of As and F^- reported in the groundwater samples of the present study are mainly from geogenic sources. The mobilization of As can also be explained by the oxidizing conditions that

favor the desorption of As from Fe-oxhydroxides (hematite and goethite). The characteristic alkaline ($pH > 7$) conditions result in negatively charged minerals surfaces which subsequently limits the adsorption of As species and makes them available in solution.

5.4. Water quality evaluation

The CCME-WQI model was used to calculate the water quality using 22 parameters (Table 6), and the obtained value was used to classify the water quality based on the values and description given in Table 8. The CCME-WQI calculated was 87.6978,

Table 14. Surveyed elevations and F⁻ concentrations at selected BH and springs in the Sanya river floodplain.

Sample location	Elevation (m)	F ⁻ 2018	F ⁻ 2020	Description
BH548	911.3654	22.5	<i>n.m</i>	Sanya Station, Ngomeni
BH542	906.9718	31.25	<i>n.m</i>	Sanya Station, Railway
BH553	901.8843	20.1	<i>n.m</i>	Sanya Station, Sokoni
BH165	889.7513	14.5	20.4	Sanya Station, DIP
BH556	881.3095	4.29	<i>n.m</i>	Cement
BH510	877.2979	6.75	5.71	Hemed
BH506	872.2323	13.3	7.61	Migungani
BH518	871.5052	8.28	<i>n.m</i>	Peter Sechu
BH511	867.5125	8.84	<i>n.m</i>	Tindigani Mrinji
BH522	861.7269	12.5	<i>n.m</i>	Kitivu Kati
NF	911.5829	<i>n.m</i>	6.25	Ngomen furrow intake
MzF	897.7978	<i>n.m</i>	6.46	Mzegazega furrow
PF	890.6827	<i>n.m</i>	6.25	Palestina furrow intake
CF	880.8719	<i>n.m</i>	5.01	Cement furrow intake
HF	876.5594	<i>n.m</i>	5.77	Hemed furrow
MgF	870.4363	<i>n.m</i>	5.11	Migungani furrow
PSF	870.8498	<i>n.m</i>	4.7	P. Sechu furrow intake
MrF	866.0505	<i>n.m</i>	5.02	Mrinji furrow intake
KKF	860.3972	<i>n.m</i>	5.39	Kitivu Kati furrow intake

n.m = not measured

which according to Table 6 falls within the range of 80-95, showing that the drinking water was good based on the measured samples and parameters considered in the calculation, it can further be described that there is a small deviation from the natural condition.

The raw measured data show that EC and As concentrations were higher than the WHO standards of 300 $\mu\text{S}/\text{cm}$ and 10 $\mu\text{g}/\text{L}$, respectively. The observed high values of EC and As could be attributed to the mining activities carried out in the study area that enhance the dissolution of As and other minerals from the parent rocks into groundwater. Despite the possible uncertainties associated with its application, the CCME-WQI model can provide useful information on the water quality status.

5.5. Health risks assessment

5.5.1. Exposure assessment

To assess human exposure, the average chronic daily intakes of As and F⁻ for adults and children in the study were calculated and

presented in table 12. The trends for chronic daily intake of As were greater than that of F⁻ in groundwater and were above the permissible limits based on US EPA IRIS guidelines.

5.5.2. Non-carcinogenic health risk

Following the USEPA methodology, the non-carcinogenic human health risks were estimated. The oral route (ingestion) was the only exposure pathway considered in the present study. The non-carcinogenic human health risks were estimated for As and F⁻ exposure. The calculated mean HQ values for As were greater than 1, showing that there are non-carcinogenic health risks associated with exposure to As. However, the values for F⁻ were within the acceptable risks suggesting that there were no non-carcinogenic health risks to both adults and children in the study area. Furthermore, the HI was computed to determine the total potential non-carcinogenic impact for As and F⁻ by summing up the HQs. The mean values of HI for adults and children were recorded to be 3.66 and 16.61, respectively.

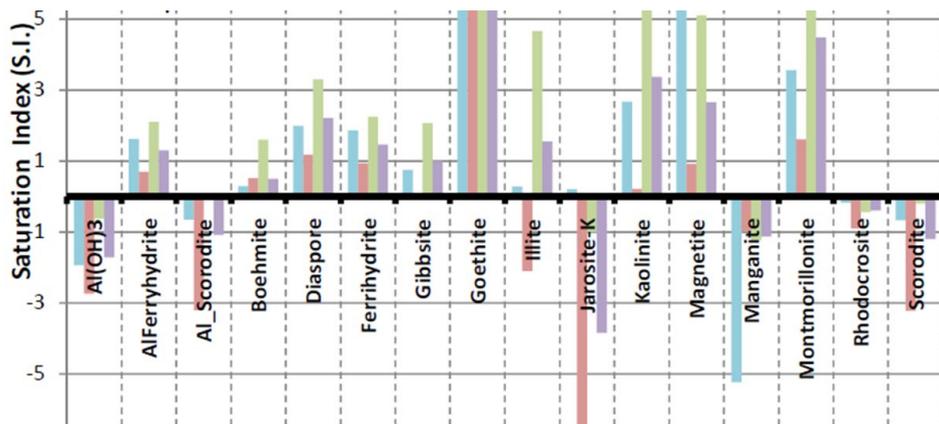


Figure 25. Saturation indices for selected minerals phases affecting the groundwater chemistry (Adapted from Paper III).

The results (Table 15) show that both the adults and children were susceptible to non-carcinogenic health risks when exposed to both As and F⁻. When considered individually, only As had an impact since the HI values for F⁻ were below 1, hence, no influence on non-carcinogenic health risks.

5.5.3. Carcinogenic health risks

The mean carcinogenic health risks due to exposure to As estimated based on consumption of drinking water from groundwater sources were 1.01 and 5.00 for children and adults, respectively. The calculated value of health risks was higher than the acceptable risks. that can lead to health problems for the exposed population. During the analyses of carcinogenic effects of As and F⁻, it was observed that As is more hazardous than F⁻ in terms of carcinogenic health risk. This analytical result provides the evidence that most cases of the cancer development for the exposed population in this study areas could be associated with prolonged drinking of As contaminated groundwater. The analyses of carcinogenic health risks results for As and F⁻ are given in Table 15.

Results from this study showed the high likelihood of potential cancer risks for both children and adults were due to As exposure through drinking water from As-contaminated groundwater sources. The

estimated CR was relatively higher for children compared to adults; therefore, children were more likely to be susceptible to cancer risk due to As exposure. Alidadi (Alidadi et al., 2019) reported that children are more vulnerable to health risks because higher consumption of water. Furthermore, the body's systems, including the immune, endocrine, reproductive, and digestive systems, are still under development and less efficient to metabolize, detoxify and excrete toxic materials. Children are more prone to be affected by toxicants than adults. When children are exposed to toxic elements from water, the impact is irreversible and leads to chronic health problems (Peek et al., 2018). Therefore, immediate intervention and control measures are required to safeguard the children and the entire population in the study area from chronic health problems due to the As exposure.

5.5.4. Risk uncertainties

The reliability and validity of the health risk assessments were limited by the factors body weight and daily variability of drinking water intake. From the perspectives of carcinogenic health risks, most of the assumptions and probability variables were adopted from the US EPA guidelines (EPA, 2019), which may offer limited application to the population in this study due to various reasons such as climate, drinking water, and eating habits.

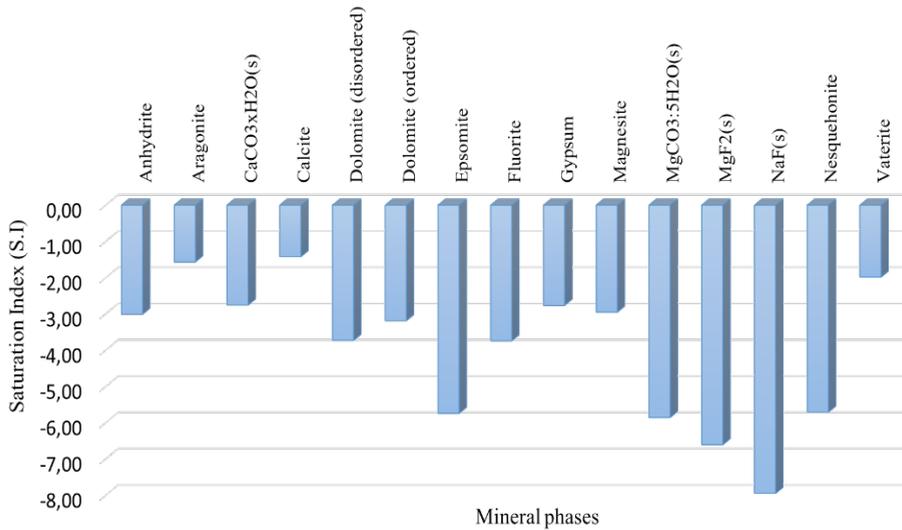


Figure 26: Saturation indices for selected mineral phases controlling the w, all minerals are undersaturated, this is reflected on the low concentrations of fluoride in the water samples.

Other exposure routes for example dermal contacts and inhalation were not considered for risk evaluation. Carcinogenic risks evaluation was applied to As and not F⁻ because there is no CSF value available for the latter. CSF value for As was constantly applied to all individuals, but in reality, there may be variability of CSF among individuals. Total As concentrations were considered for health risks estimation, but different As species have different toxicity effects. The health risks were evaluated based on the As and F⁻, however, there might be other drinking water contaminants with toxic effects on humans. Finally, specific organs (such as the brain, liver, and kidney) evaluation could provide more realistic results than application to the whole body.

5.6. Water quality compliance with TBS and WHO standard guidelines

The assessment of drinking water quality was conducted in the study area. Results of the chemical analyses of groundwater quality assessment showed that most of the population in Geita region are exposed to groundwater sources of elevated As concentration which greatly exceed WHO

and TBS (> 10 µg/L) drinking water limits. The WHO (WHO, 2017) and TBS guidelines were used for references and classification of the suitability of water for drinking purposes. About 82% and 8% of As and F⁻ samples had elevated concentrations of As and F⁻, respectively, above the recommended WHO and TBS guideline values in Geita. The maximum concentration of 290 µg/L for As was recorded at the privately owned SW in Busanda Uarabuni Village, Busanda ward, Geita District. This raises a serious alarm as most of the privately owned water wells are usually not monitored by the Government water authorities. The maximum concentration of 2.17 for F⁻ was recorded at the BH owned and managed by the community at Masumve Bumanji village, Shiloleni Ward. Overall, the recorded concentration of F⁻ showed a very low risk to human health.

The implementation of standards for drinking water quality compliance for As, F⁻, and other TEs in Tanzania is affected by several factors including the variability of source water chemistry, effectiveness of remediation technologies climatic conditions and political commitment. As a result, there

Table 15. Non-carcinogenic human health risk (HQ) for As and F

Element	HQ (adults)			HQ (children)		
	minimum	maximum	mean	minimum	maximum	mean
As	0.10	11.43	3.66	0.46	51.85	16.61
F ⁻	0.00	0.00	0.00	0.00	0.00	0.00
HI	0.10	11.43	3.66	0.46	51.85	16.61

have been several reviews of the allowable concentration of F⁻ in drinking water from 8 mg/L in 2008 to 1.5 mg/L in 2022. The occurrence of As in drinking water was discovered in the 1990s, and there is no yet clear national guideline for the same in drinking water, for research purposes, the WHO guideline concentration has been adopted. Elsewhere, for example, in the Netherlands, progress has been made to the extent of lowering As guidelines in drinking water from 10 µg/L to 1 µg/L.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

The proper assessment of the groundwater sources quality and carcinogenic health risks of As, F⁻ and other TEs from geogenic sources were evaluated using analytical chemistry, geochemical modeling and GIS spatial techniques for safe water supply to the community in the northwest Tanzania. The overall results indicate that the As and F⁻ contamination varied widely in the northwest Tanzania, with the highest risks of As concentration in the mining areas, especially in the Geita region. Due to poor and/or lack of drinking water infrastructures in urban, peri-urban, and rural areas in northern Tanzania, groundwater remains to be an important alternative and sole source of water to support the livelihoods of many households.

The present study has revealed that, under favorable geochemical conditions, As and F⁻ can be mobilized from the parent rock minerals through water-rock interaction mechanisms in the aquifer over time. This leads to the natural contamination of groundwater by As and F⁻. Human health

concerns were raised about the consumption of elevated concentrations of As and F⁻ through drinking water owing to the existence of scarce safe drinking water sources and high reliance on groundwater sources. Other TEs of human health concerns such as Mn, Fe, Al, and Zn, were also investigated and observed to be below the maximum acceptable limits for drinking water purposes based on the WHO and TBS drinking water guidelines. The presence of a considerable concentration of Fe in some of the analyzed samples could explain the complexities of As quantification in drinking water because under oxidized conditions, As has a higher affinity to ferric oxide to form complexes that can later release As under a limited oxygen environment.

The overall hydrogeochemical data shows that groundwater in the study area is suitable for human consumption, however, As and F⁻ call for further attention from researchers, policymakers, and the general public. The maximum allowable concentration of 0.01 mg As/L and 1.5 mg F⁻/L intake is open to further epidemiological dialogues, especially under chronic/long-term exposure in the region.

The present study improves understanding of the mechanisms of groundwater enrichment and mobilization of inorganic solutes including As and F⁻ in the groundwater aquifers in the study area. It also contributes to a better understanding of the hydrogeochemical insights of groundwater in the area. Health risks evaluation results due to exposure to As and F⁻ through drinking water are also important for water supply systems. Furthermore, this thesis provides important baseline information to the relevant authorities in Tanzania about drinking water

quality from groundwater sources. The challenges associated with the provision of safe drinking water to the communities are multifaced and require multiple approaches to get a sustainable solution.

The present study has shown that the combination of geochemical exploration, spatial analysis, and health risk assessment can provide the best framework for the exploration and management of groundwater resources in the study area and the country at large. The discussion and conclusions from this thesis will be helpful along with the struggle for the realization of the Tanzania Vision 2025 goal and the UN Sustainable goal 6 of ensuring universal access to safe water and sanitation, which in turn will support the national social and economic development agenda. Furthermore, the information from this thesis can help guide the actions of decision-makers toward groundwater quality management and protection.

6.2. Recommendations

To effectively manage groundwater, it is crucial to have baseline information on water quality. This thesis recommends various outlooks based on the information presented and field experience. These include further investigation into groundwater hydrogeochemistry, detailed analysis of sediments and rock samples to better understand the distribution and mobilization of elements in the solid matrix, and isotopic studies to understand the geochemical evolution of groundwater. Additionally, establishing piezometers for continuous monitoring of groundwater quantity, quality, and the spatial distribution of harmful elements such as As and F is recommended.

Leaching tests and microprobe analysis experiments should also be conducted to better understand the release mechanisms and mobility of TEs in the soil matrix and their uptake by plants and animals.

To understand the effects of chronic and cumulative exposure to harmful elements, comprehensive epidemiological and human health risk studies are necessary. Health risk assessments should also consider exposure routes other than water, such as dermal, food, and air exposure.

Improvements to the regulatory and management frameworks of groundwater abstraction and use are needed. Four important alternative approaches are recommended based on the need and available resources. These are considering alternative safe drinking water sources, blending water with low and high concentrations of TEs, rainwater harvesting with remineralization, and the development of sustainable treatment technology. Long-term monitoring plans for groundwater quality and quantity should consider the impact of climate change. Relevant authorities should also ensure data availability on groundwater users for effective water resources management and safe water supply to the community.

The use of artificial intelligence (AI) for groundwater quality monitoring is recommended as it can improve efficiency, reduce costs and provide valuable insights for groundwater management. However, it should be noted that AI is not a substitute to human expertise and therefore it ought to be used in conjunction with the traditional and locally available methods.

7. REFERENCES

- Addison, M. J., Rivett, M. O., Robinson, H., Fraser, A., Miller, A. M., Phiri, P., Mleta, P., & Kalin, R. M. (2020). Fluoride occurrence in the lower East African Rift System, Southern Malawi. *Sci Total Environ*, 712, 136260. <https://doi.org/10.1016/j.scitotenv.2019.136260>.
- Ahmad, A., van der Wens, P., Baken, K., de Waal, L., Bhattacharya, P., & Stuyfzand, P. (2020). Arsenic reduction to <1microg/L in Dutch drinking water. *Environ Int*, 134, 105253. <https://doi.org/10.1016/j.envint.2019.105253>.
- Ahmed, K. M., Bhattacharya, P., Hasan, M. A., Akhter, S. H., Alam, S. M. M., Bhuyian, M. A. H., Imam, M. B., Khan, A. A., & Sracek, O. (2004). Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. *Applied Geochemistry*, 19(2), 181-200. <https://doi.org/10.1016/j.apgeochem.2003.09.006>.
- Ahou l, D. G., Lalanne, F., Mendret, J., Brosillon, S., & Ma ga, A. H. (2015). Arsenic in African Waters: A Review. *Water, Air, & Soil Pollution*, 226(9). <https://doi.org/10.1007/s11270-015-2558-4>.
- Ahsan, H., & Steinmaus, C. (2013). Invited commentary: use of arsenical skin lesions to predict risk of internal cancer: implications for prevention and future research. *Am J Epidemiol*, 177(3), 213-216. <https://doi.org/10.1093/aje/kws366>.
- Akpalu, W., & Normanyo, A. K. (2017). Gold Mining Pollution and the Cost of Private Healthcare: The Case of Ghana. *Ecological Economics*, 142, 104-112. <https://doi.org/10.1016/j.ecolecon.2017.06.025>.
- Alidadi, H., Tavakoly Sany, S. B., Zarif Garaati Oftadeh, B., Mohamad, T., Shamszade, H., & Fakhari, M. (2019). Health risk assessments of arsenic and toxic heavy metal exposure in drinking water in northeast Iran. *Environ Health Prev Med*, 24(1), 59. <https://doi.org/10.1186/s12199-019-0812-x>.
- Alm s,  . R., & Manoko, M. L. (2012). Trace Element Concentrations in Soil, Sediments, and Waters in the Vicinity of Geita Gold Mines and North Mara Gold Mines in Northwest Tanzania. *Soil and Sediment Contamination*, 21, 135-159. <https://doi.org/10.1080/15320383.2012.649372>.
- Anawar, H. M., Akai, J., Komaki, K., Terao, H., Yoshioka, T., Ishizuka, T., Safiullah, S., & Kato, K. (2003). Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes. *Journal of Geochemical Exploration*, 77(2-3), 109-131. [https://doi.org/10.1016/s0375-6742\(02\)00273-x](https://doi.org/10.1016/s0375-6742(02)00273-x).
- APHA. (1998). *Standard Methods for the Examination of Water and Wastewater* (20th Edition ed.). American Public Health Association, American Water Works Association and Water Environmental Federation.
- Appelo, C., & Postma, D. (2005). *Geochemistry, Groundwater and Pollution* (2nd ed.). A.A. Balkema Publishers.
- Appelo, C. A. J., Weiden, M. J. J. V. d., Tournassat, C., & Charlet, L. (2002). Surface Complexation of Ferrous Iron and Carbonate on Ferrihydrite and the Mobilization of Arsenic. *Environmental Science & Technology*, 36(14), 3096-3103. <https://doi.org/10.1021/es010130n>.
- Arai, Y., Elzinga, E. J., & Sparks, D. L. (2001). X-ray Absorption Spectroscopic Investigation of Arsenite and Arsenate Adsorption at the Aluminum Oxide-Water Interface. *J Colloid Interface Sci*, 235(1), 80-88. <https://doi.org/10.1006/jcis.2000.7249>.
- Bamuwamy, M., Ogwok, P., & Tumuhairwe, V. (2015). Cancer and Non-cancer Risks Associated With Heavy Metal Exposures from Street Foods: Evaluation of Roasted Meats in an Urban Setting. *Journal of Environment Pollution and Human Health*, 3(2), 24-30. <https://doi.org/10.12691/jephh-3-2-1>.
- Bempah, C. K., & Ewusi, A. (2016). Heavy metals contamination and human health risk assessment around Obuasi gold mine in Ghana. *Environ Monit Assess*, 188(5), 261. <https://doi.org/10.1007/s10661-016-5241-3>.

- Bennett, G., Van Reybrouck, J., Shemsanga, C., Kisaka, M., Tomašek, I., Fontijn, K., Kervyn, M., & Walraevens, K. (2021). Hydrochemical Characterisation of High-Fluoride Groundwater and Development of a Conceptual Groundwater Flow Model Using a Combined Hydrogeological and Hydrochemical Approach on an Active Volcano: Mount Meru, Northern Tanzania. *Water*, 13(16). <https://doi.org/10.3390/w13162159>.
- BGS. (2000). *User Guide: Africa Groundwater Atlas Country Hydrogeology Maps, Version 1.1*. <https://www2.bgs.ac.uk/africagroundwateratlas/index.cfm>.
- Bhattacharya, P., & Bundschuh, J. (2015). Groundwater for sustainable development – cross cutting the UN sustainable development goals – editorial. *Groundwater for Sustainable Development*, 1(1-2), 155-157. <https://doi.org/10.1016/j.gsd.2016.04.004>.
- Bhattacharya, P., Chatterjee, D., & Jacks, G. (1997). Occurrence of Arsenic-contaminated Groundwater in Alluvial Aquifers from Delta Plains, Eastern India: Options for Safe Drinking Water Supply. *International Journal of Water Resources Development*, 13(1), 79-92. <https://doi.org/10.1080/07900629749944>.
- Bretzler, A., Lalanne, F., Nikiema, J., Podgorski, J., Pfenninger, N., Berg, M., & Schirmer, M. (2017). Groundwater arsenic contamination in Burkina Faso, West Africa: Predicting and verifying regions at risk. *Sci Total Environ*, 584-585, 958-970. <https://doi.org/10.1016/j.scitotenv.2017.01.147>.
- Bretzler, A., Stolze, L., Nikiema, J., Lalanne, F., Ghadiñi, E., Brennwald, M. S., Rolle, M., & Schimmer, M. (2019). Hydrogeochemical and multi-tracer investigations of arsenic-affected aquifers in semi-arid West Africa. *Geoscience Frontiers*, 10(5), 1685-1699. <https://doi.org/10.1016/j.gsf.2018.06.004>.
- Brunt, R., Vasak, L., & Groffioen, J. (2004). *Fluoride in groundwater: Probability of occurrence of excessive concentration on global scale* (SP 2004-2).
- Bundschuh, J., Maity, J. P., Mushtaq, S., Vithanage, M., Seneweera, S., Schneider, J., Bhattacharya, P., Khan, N. I., Hamawand, I., Guilherme, L. R. G., Reardon-Smith, K., Parvez, F., Morales-Simfons, N., Ghaze, S., Pudmenzky, C., Kouadio, L., & Chen, C. Y. (2017). Medical geology in the framework of the sustainable development goals. *Sci Total Environ*, 581-582, 87-104. <https://doi.org/10.1016/j.scitotenv.2016.11.208>.
- Bundschuh, J., Maity, J. P., Nath, B., Baba, A., Gunduz, O., Kulp, T. R., Jean, J. S., Kar, S., Yang, H. J., Tseng, Y. J., Bhattacharya, P., & Chen, C. Y. (2013). Naturally occurring arsenic in terrestrial geothermal systems of western Anatolia, Turkey: potential role in contamination of freshwater resources. *J Hazard Mater*, 262, 951-959. <https://doi.org/10.1016/j.jhazmat.2013.01.039>.
- Chakraborty, M., Mukherjee, A., & Ahmed, K. M. (2015). A Review of Groundwater Arsenic in the Bengal Basin, Bangladesh and India: from Source to Sink. *Current Pollution Reports*, 1(4), 220-247. <https://doi.org/10.1007/s40726-015-0022-0>.
- Comte, J.-C., Cassidy, R., Obando, J., Robins, N., Ibrahim, K., Melchioly, S., Mjemah, I., Shauri, H., Bourhane, A., Mohamed, I., Noe, C., Mwega, B., Makokha, M., Join, J.-L., Banton, O., & Davies, J. (2016). Challenges in groundwater resource management in coastal aquifers of East Africa: Investigations and lessons learnt in the Comoros Islands, Kenya and Tanzania. *Journal of Hydrology: Regional Studies*, 5, 179-199. <https://doi.org/10.1016/j.ejrh.2015.12.065>.
- Cook, Y. A., Sanislav, I. V., Hammerli, J., Blenkinsop, T. G., & Dirks, P. H. G. M. (2016). A primitive mantle source for the Neoproterozoic mafic rocks from the Tanzania Craton. *Geoscience Frontiers*, 7(6), 911-926. <https://doi.org/10.1016/j.gsf.2015.11.008>.
- Dixit, S., & Hering, J. G. (2003). Comparison of Arsenic(V) and Arsenic(III) Sorption onto Iron Oxide Minerals: Implications for Arsenic Mobility. *Environmental Science and Technology*, 37(18). <https://doi.org/10.1021/es030309t>.
- Drahota, P., Peresta, M., Trubac, J., Mihaljevic, M., & Vanek, A. (2021). Arsenic fractionation and mobility in sulfidic wetland soils during experimental drying. *Chemosphere*, 277, 130306. <https://doi.org/10.1016/j.chemosphere.2021.130306>.

- Elisante, E., & Muzuka, A. N. N. (2015). Occurrence of nitrate in Tanzanian groundwater aquifers: A review. *Applied Water Science*, 7(1), 71-87. <https://doi.org/10.1007/s13201-015-0269-z>.
- EPA, U. (2017). *Groundwater sampling* (SESDPROC301-R4).
- EPA, U. S. (2007). US EPA Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). In.
- EPA, U. S. (2019). *Updated Problem Formulation and Systematic Review Protocol for the Inorganic Arsenic IRIS Assessment*, EPA/635/R-19/049, 2019. U.S. Environmental Protection Agency. https://cfpub.epa.gov/ncea/iris_drafts/recordisplay.cfm?deid=343951.
- FDMT. (2016). Flood & Drought Management Tools. Retrieved 12 15, from <http://fdmt.iwlearn.org/en>.
- Feitosa, M. M., Alvarenga, I. F. S., Jara, M. S., Lima, G., Vilela, F. J., Resende, T., & Guilherme, L. R. G. (2021). Environmental and human-health risks of As in soils with abnormal arsenic levels located in irrigated agricultural areas of Paracatu (MG), Brazil. *Ecotoxicol Environ Saf*, 226, 112869. <https://doi.org/10.1016/j.ecoenv.2021.112869>.
- Fuoco, I., Apollaro, C., Criscuoli, A., De Rosa, R., Velizarov, S., & Figoli, A. (2021). Fluoride Polluted Groundwaters in Calabria Region (Southern Italy): Natural Source and Remediation. *Water*, 13(12). <https://doi.org/10.3390/w13121626>.
- Ghiglieri, G., Balia, R., Oggiano, G., & Pittalis, D. (2010). Prospecting for safe (low fluoride) groundwater in the Eastern African Rift: the Arumeru District (Northern Tanzania). *Hydrology and Earth System Sciences*, 14(6), 1081-1091. <https://doi.org/10.5194/hess-14-1081-2010>.
- Ghiglieri, G., Pittalis, D., Cerri, G., & Oggiano, G. (2011). Hydrogeology and hydrogeochemistry of an alkaline volcanic area: the NE Mt. Meru slope (East African Rift – Northern Tanzania). *Hydro Earth Syst. Sci. Discuss.*, 8, 8255-8289. <https://doi.org/10.5194/hessd-8-8255-2011>.
- Gómez, J. J., Lillo, J., & Sahún, B. (2006). Naturally occurring arsenic in groundwater and identification of the geochemical sources in the Duero Cenozoic Basin, Spain. *Environmental Geology*, 50(8), 1151-1170. <https://doi.org/10.1007/s00254-006-0288-z>.
- Gorny, J., Billon, G., Lesven, L., Dumoulin, D., Made, B., & Noiriel, C. (2015). Arsenic behavior in river sediments under redox gradient: a review. *Sci Total Environ*, 505, 423-434. <https://doi.org/10.1016/j.scitotenv.2014.10.011>.
- Gowing, J., Walker, D., Parkin, G., Forsythe, N., Haile, A. T., & Ayenew, D. A. (2020). Can shallow groundwater sustain small-scale irrigated agriculture in sub-Saharan Africa? Evidence from N-W Ethiopia. *Groundwater for Sustainable Development*, 10. <https://doi.org/10.1016/j.gsd.2019.100290>.
- Gudaga, J. L., Kabote, S. J., Tarimo, A. K. P. R., Moshia, D. B., & Kashaigili, J. J. (2018). Effectiveness of groundwater governance structures and institutions in Tanzania. *Applied Water Science*, 8(2). <https://doi.org/10.1007/s13201-018-0721-y>.
- Gustafsson, J. P. (2001). Modelling competitive anion adsorption on oxide minerals and an allophane-containing soil. *European Journal of Soil Science*, 52, 639-653.
- Gustafsson, J. P. (2006). Arsenate adsorption to soils: Modelling the competition from humic substances. *Geoderma*, 136(1-2), 320-330. <https://doi.org/10.1016/j.geoderma.2006.03.046>.
- Gustafsson, J. P. (2022). *Visual MINTEQ Program Version 3.1*. Retrieved December 2022 from <http://vminteq.com>.
- Haghnazar, H., Johannesson, K. H., Gonzalez-Pinzon, R., Pourakbar, M., Aghayani, E., Rajabi, A., & Hashemi, A. A. (2021). Groundwater geochemistry, quality, and pollution of the largest lake basin in the Middle East: Comparison of PMF and PCA-MLR receptor models and application of the source-oriented HHRA approach. *Chemosphere*, 288(Pt 1), 132489. <https://doi.org/10.1016/j.chemosphere.2021.132489>.

- Halder, D., Biswas, A., Bhattacharya, P., Bhowmick, S., Mandal, U., Chatterjee, D., & Nriagu, J. (2012). Arsenic exposure and health risk from consumption of brown rice in rural Bengal, India. *Arsenic in the Environment Understanding the Geological and Medical Interface of Arsenic*, Cairns, Australia.
- Hamon, R. E., Lombi, E., Fortunati, P., Nolan, A. L., & Mclaughlin, M. J. (2004). Coupling Speciation and Isotope Dilution Techniques To Study Arsenic Mobilization in the Environment. *Environmental Science and Technology*, 38, 1794-1798.
- Henckel, J., Poulsen, K. H., Sharp, T., & Spora, P. (2016). Lake Victoria Goldfields. *Episodes*, 39(2), 135-154. <https://doi.org/10.18814/epiugs/2016/v39i2/95772>.
- Herath, I., Vithanage, M., Bundschuh, J., Maity, J. P., & Bhattacharya, P. (2016). Natural Arsenic in Global Groundwaters: Distribution and Geochemical Triggers for Mobilization. *Current Pollution Reports*, 2(1), 68-89. <https://doi.org/10.1007/s40726-016-0028-2>.
- Hossain, M., & Patra, P. K. (2020). Hydrogeochemical characterisation and health hazards of fluoride enriched groundwater in diverse aquifer types. *Environ Pollut*, 258, 113646. <https://doi.org/10.1016/j.envpol.2019.113646>.
- Huntsman-Mapila, P., Mapila, T., Letshwenyo, M., Wolski, P., & Hemond, C. (2006). Characterization of arsenic occurrence in the water and sediments of the Okavango Delta, NW Botswana. *Applied Geochemistry*, 21(8), 1376-1391. <https://doi.org/10.1016/j.apgeochem.2006.05.003>.
- Ijumulana, J., Ligate, F., Irunde, R., Bhattacharya, P., Ahmad, A., Tomasek, I., Maity, J. P., & Mtalo, F. (2022). Spatial variability of the sources and distribution of fluoride in groundwater of the Sanya alluvial plain aquifers in northern Tanzania. *Sci Total Environ*, 810, 152153. <https://doi.org/10.1016/j.scitotenv.2021.152153>.
- Ijumulana, J., Ligate, F., Irunde, R., Bhattacharya, P., Maity, J. P., Ahmad, A., & Mtalo, F. (2021). Spatial uncertainties in fluoride levels and health risks in endemic fluorotic regions of northern Tanzania. *Groundwater for Sustainable Development*, 14. <https://doi.org/10.1016/j.gsd.2021.100618>.
- Irunde, R., Ijumulana, J., Ligate, F., Maity, J. P., Ahmad, A., Mtamba, J., Mtalo, F., & Bhattacharya, P. (2022). Arsenic in Africa: Potential sources, spatial variability, and the state of the art for arsenic removal using locally available materials. *Groundwater for Sustainable Development*, 18. <https://doi.org/10.1016/j.gsd.2022.100746>.
- Jain, C. K., & Ali, I. (2000). Arsenic: Occurrence, Toxicity and speciation techniques *Water Research*, 34(17), 4304-4312.
- Kapaj, S., Peterson, H., Liber, K., & Bhattacharya, P. (2006). Human health effects from chronic arsenic poisoning--a review. *J Environ Sci Health A Tox Hazard Subst Environ Eng*, 41(10), 2399-2428. <https://doi.org/10.1080/10934520600873571>.
- Karunanidhi, D., Subramani, T., Roy, P. D., & Li, H. (2021). Impact of groundwater contamination on human health. *Environ Geochem Health*, 43(2), 643-647. <https://doi.org/10.1007/s10653-021-00824-2>.
- Kaseva, M. E. (2006). Contribution of trona (magadi) into excessive fluorosis--a case study in Maji ya Chai ward, northern Tanzania. *Sci Total Environ*, 366(1), 92-100. <https://doi.org/10.1016/j.scitotenv.2005.08.049>.
- Kaseva, M. E., Mayige, C., Salukele, F., Mkongo, G., & Sangeti, E. M. (2018). Spatial Distribution of Fluoride Concentration in Drinking Water Sources in Northern Tanzania. *Journal of Civil and Environmental Research*, 10, 41-51.
- Kashaigili, J.J. (2013). Groundwater Availability and Use in Sub-Saharan Africa: Tanzania, Groundwater Availability and Use in Sub-Saharan Africa: A review of 15 Countries 195-215 (International water management institute (IWMI), Colombo, Sri Lanka 2013).

- Kassenga, G., & Mato, R. (2008). Arsenic contamination levels in drinking water sources in mining areas in Lake Victoria Basin, Tanzania, and its removal using stabilized ferralsols. *International Journal of Biological and Chemical Sciences*, 2(4), 389-400. <http://www.ajol.info>.
- Kimambo, V., Bhattacharya, P., Mtalo, F., Mtamba, J., & Ahmad, A. (2019). Fluoride occurrence in groundwater systems at global scale and status of defluoridation – State of the art. *Groundwater for Sustainable Development*, 9. <https://doi.org/10.1016/j.gsd.2019.100223>.
- Kitalika, A. J., Machunda, R. L., Komakech, H. C., & Njau, K. N. (2018). Fluoride Variations in Rivers on the Slopes of Mount Meru in Tanzania. *Journal of Chemistry*, 2018, 1-18. <https://doi.org/10.1155/2018/7140902>.
- Kumar, G., Rao, K., Yadav, A., Kumar, M., & Dora, H. (2022). Multivariate statistical analysis approach to assess groundwater quality in two selected mandals of Vizianagaram district, Andhra Pradesh, India. *Journal of the Indian Chemical Society*, 99(5). <https://doi.org/10.1016/j.jics.2021.100338>.
- Kumar, M., Das, N., Goswami, R., Sarma, K. P., Bhattacharya, P., & Ramanathan, A. L. (2016). Coupling fractionation and batch desorption to understand arsenic and fluoride co-contamination in the aquifer system. *Chemosphere*, 164, 657-667. <https://doi.org/10.1016/j.chemosphere.2016.08.075>.
- Kumar, S., Singh, R., Venkatesh, A. S., Udayabhanu, G., & Sahoo, P. R. (2019). Medical Geological assessment of fluoride contaminated groundwater in parts of Indo-Gangetic Alluvial plains. *Sci Rep*, 9(1), 16243. <https://doi.org/10.1038/s41598-019-52812-3>.
- Ligate, F., Ijumulana, J., Ahmad, A., Kimambo, V., Irunde, R., Mtamba, J. O., Mtalo, F., & Bhattacharya, P. (2021). Groundwater resources in the East African Rift Valley: Understanding the geogenic contamination and water quality challenges in Tanzania. *Scientific African*, 13. <https://doi.org/10.1016/j.sciaf.2021.e00831>.
- Ligate, F., Lucca, E., Ijumulana, J., Irunde, R., Kimambo, V., Mtamba, J., Ahmad, A., Hamisi, R., Maity, J. P., Mtalo, F., & Bhattacharya, P. (2022). Geogenic contaminants and groundwater quality around Lake Victoria goldfields in northwestern Tanzania. *Chemosphere*, 307(Pt 2), 135732. <https://doi.org/10.1016/j.chemosphere.2022.135732>.
- Liu, C.-W., Lin, K.-H., & Kuo, Y.-M. (2003). Application of factor analysis in the assessment of groundwater quality in a blackfoot disease area in Taiwan. *Science of the Total Environment*, 313(1-3), 77-89. [https://doi.org/10.1016/s0048-9697\(02\)00683-6](https://doi.org/10.1016/s0048-9697(02)00683-6).
- Lucca, E. (2017). *Geochemical Investigation of Arsenic in Drinking Water Sources in Proximity of Gold Mining Areas within the Lake Victoria Basin, in Northern Tanzania* [MSc, KTH Royal Institute of Technology]. Stockholm, Sweden.
- Luo, W., Gao, X., & Zhang, X. (2018). Geochemical processes controlling the groundwater chemistry and fluoride contamination in the Yuncheng Basin, China-An area with complex hydrogeochemical conditions. *PLoS One*, 13(7), e0199082. <https://doi.org/10.1371/journal.pone.0199082>.
- MacDonald, A. M., Bonsor, H. C., Dochartaigh, B. É. Ó., & Taylor, R. G. (2012). Quantitative maps of groundwater resources in Africa. *Environmental Research Letters*, 7(2). <https://doi.org/10.1088/1748-9326/7/2/024009>.
- Macdonald, A. M., Calow, R. C., Macdonald, D. M. J., Darling, W. G., & Dochartaigh, B. É. Ó. (2009). What impact will climate change have on rural groundwater supplies in Africa? *Hydrological Sciences Journal*, 54(4), 690-703. <https://doi.org/10.1623/hysj.54.4.690>.
- Maity, J. P., Nath, B., Chen, C. Y., Bhattacharya, P., Sracek, O., Bundschuh, J., Kar, S., Thunvik, R., Chatterjee, D., Ahmed, K. M., Jacks, G., Mukherjee, A. B., & Jean, J. S. (2011). Arsenic-enriched groundwaters of India, Bangladesh and Taiwan—comparison of hydrochemical characteristics and mobility constraints. *J Environ Sci Health A Tox Hazard Subst Environ Eng*, 46(11), 1163-1176. <https://doi.org/10.1080/10934529.2012.598711>.

- Maity, J. P., Vithanage, M., Kumar, M., Ghosh, A., Mohan, D., Ahmad, A., & Bhattacharya, P. (2021). Seven 21st century challenges of arsenic-fluoride contamination and remediation. *Groundwater for Sustainable Development*, 12. <https://doi.org/10.1016/j.gsd.2020.100538>.
- Makoba, E., & Muzuka, A. N. N. (2019). Water quality and hydrogeochemical characteristics of groundwater around Mt. Meru, Northern Tanzania. *Applied Water Science*, 9(5). <https://doi.org/10.1007/s13201-019-0955-3>.
- Mandal, B. K., & Suzuki, K. T. (2002). Arsenic round the world: a review. *Talanta*, 58, 201-235.
- Manning, B. A., & Goldberg, S. (1997). Adsorption and Stability of Arsenic(III) at the Clay Mineral-Water Interface. *Environmental Science and Technology*, 31(7), 2005-2011. <https://doi.org/https://doi.org/10.1021/es9608104>.
- Marwa, J., Lufingo, M., Noubactep, C., & Machunda, R. (2018). Defeating Fluorosis in the East African Rift Valley: Transforming the Kilimanjaro into a Rainwater Harvesting Park. *Sustainability*, 10(11). <https://doi.org/10.3390/su10114194>.
- Mbabaye, G. K., Minja, R. J., Mtalo, F. W., Legonda, I., & Mkongo, G. (2018). Fluoride occurrence in domestic water supply sources in Tanzania: A case of Arumeru District Arusha Region. *Tanzania Journal of Science*, 44(3), 72-92.
- Mjemah, I. C., Van Camp, M., Martens, K., & Walraevens, K. (2010). Groundwater exploitation and recharge rate estimation of a quaternary sand aquifer in Dar-es-Salaam area, Tanzania. *Environmental Earth Sciences*, 63(3), 559-569. <https://doi.org/10.1007/s12665-010-0723-z>.
- Mohammadi, A. A., Zarei, A., Majidi, S., Ghaderpoury, A., Hashempour, Y., Saghi, M. H., Alinejad, A., Yousefi, M., Hosseingholizadeh, N., & Ghaderpoori, M. (2019). Carcinogenic and non-carcinogenic health risk assessment of heavy metals in drinking water of Khorramabad, Iran. *MethodsX*, 6, 1642-1651. <https://doi.org/10.1016/j.mex.2019.07.017>.
- Mondal, D., Rahman, M. M., Suman, S., Sharma, P., Siddique, A. B., Rahman, M. A., Bari, A., Kumar, R., Bose, N., Singh, S. K., Ghosh, A., & Polya, D. A. (2021). Arsenic exposure from food exceeds that from drinking water in endemic area of Bihar, India. *Sci Total Environ*, 754, 142082. <https://doi.org/10.1016/j.scitotenv.2020.142082>.
- Mosha, D. B., Gudaga, J. L., Gama, D., & J, K. J. (2022). Valuing groundwater use: Resolving the potential of groundwater in the Upper Great Ruaha River Catchment of Tanzania. In V. Re, R. L. Manzione, T. A. Abiyi, A. Mukherji, & A. MacDonald (Eds.), *Groundwater for Sustainable Livelihoods and Equitable Growth* (1st ed., pp. 392). CRC Press. <https://doi.org/https://doi.org/10.1201/9781003024101>.
- Mtoni, Y., Mjemah, I. C., Bakundukize, C., Van Camp, M., Martens, K., & Walraevens, K. (2013). Saltwater intrusion and nitrate pollution in the coastal aquifer of Dar es Salaam, Tanzania. *Environmental Earth Sciences*, 70(3), 1091-1111. <https://doi.org/10.1007/s12665-012-2197-7>.
- Mtoni, Y., Mjemah, I. C., Van Camp, M., & Walraevens, K. (2011). Enhancing Protection of Dar es Salaam Quaternary Aquifer: Groundwater Recharge Assessment. In *Advances in the Research of Aquatic Environment* (pp. 299-306). https://doi.org/10.1007/978-3-642-19902-8_35.
- Mwiathi, N. F., Gao, X., Li, C., & Rashid, A. (2022). The occurrence of geogenic fluoride in shallow aquifers of Kenya Rift Valley and its implications in groundwater management. *Ecotoxicol Environ Saf*, 229, 113046. <https://doi.org/10.1016/j.ecoenv.2021.113046>.
- Nakaya, S., Takada, R., Yasumoto, J., Masuda, H., Yoshitani, J., Shinjo, R., Lugodisha, I., & Komakech, H. (2023). Effect of groundwater residence time on geogenic fluoride release into groundwater in the Mt. Meru slope area, Tanzania, the Great Rift Valley, East Africa. *J Contam Hydrol*, 253, 104125. <https://doi.org/10.1016/j.jconhyd.2022.104125>.
- NBS. (2018). *Tanzania in Figures 2017*. <https://www.nbs.go.tz/index.php/en/tanzania-in-figures/433-tanzania-in-figures-2017>.

- Nilkarnjanakul, W., Watchalayann, P., & Chotpantararat, S. (2022). Spatial distribution and health risk assessment of As and Pb contamination in the groundwater of Rayong Province, Thailand. *Environ Res*, 204(Pt A), 111838. <https://doi.org/10.1016/j.envres.2021.111838>.
- Nkotagu, H. (1996a). The groundwater geochemistry in a semi-arid, fractured crystalline basement area of Dodoma, Tanzania. *African Journal of Earth Science*, 23(4), 593-606.
- Nkotagu, H. (1996b). Origins of high nitrate in groundwater in Tanzania. *Journal of African Earth Sciences*, 22, 471-478. [https://doi.org/10.1016/0899-5362\(96\)00021-8](https://doi.org/10.1016/0899-5362(96)00021-8).
- Nriagu, J. O., Bhattacharya, P., Mukherjee, A. B., Bundschuh, J., Zevenhoven, R., & Loeppert, R. H. (2007). Arsenic in soil and groundwater: an overview. In *Arsenic in Soil and Groundwater Environment - Biogeochemical Interactions, Health Effects and Remediation* (pp. 3-60). [https://doi.org/10.1016/s1875-1121\(06\)09001-8](https://doi.org/10.1016/s1875-1121(06)09001-8).
- Nyanza, E. C., Bernier, F. P., Manyama, M., Hatfield, J., Martin, J. W., & Dewey, D. (2019). Maternal exposure to arsenic and mercury in small-scale gold mining areas of Northern Tanzania. *Environ Res*, 173, 432-442. <https://doi.org/10.1016/j.envres.2019.03.031>.
- Oke, S. A., & Fourie, F. (2017). Guidelines to groundwater vulnerability mapping for Sub-Saharan Africa. *Groundwater for Sustainable Development*, 5, 168-177. <https://doi.org/10.1016/j.gsd.2017.06.007>.
- Onipe, T., Edokpayi, J. N., & Odiyo, J. O. (2020). A review on the potential sources and health implications of fluoride in groundwater of Sub-Saharan Africa. *J Environ Sci Health A Tox Hazard Subst Environ Eng*, 55(9), 1078-1093. <https://doi.org/10.1080/10934529.2020.1770516>.
- Ormachea Muñoz, M., Bhattacharya, P., Sracek, O., Ramos Ramos, O., Quintanilla Aguirre, J., Bundschuh, J., & Maity, J. P. (2015). Arsenic and other trace elements in thermal springs and in cold waters from drinking water wells on the Bolivian Altiplano. *Journal of South American Earth Sciences*, 60, 10-20. <https://doi.org/10.1016/j.jsames.2015.02.006>.
- Ormachea Muñoz, M., Garcia Aróstegui, J. L., Bhattacharya, P., Sracek, O., Garcia Moreno, M. E., Kohfahl, C., Quintanilla Aguirre, J., Hornero Diaz, J., & Bundschuh, J. (2016). Geochemistry of naturally occurring arsenic in groundwater and surface-water in the southern part of the Poopó Lake basin, Bolivian Altiplano. *Groundwater for Sustainable Development*, 2-3, 104-116. <https://doi.org/10.1016/j.gsd.2016.04.002>.
- Outa, J. O., Kowenje, C. O., Plessl, C., & Jirsa, F. (2020). Distribution of arsenic, silver, cadmium, lead and other trace elements in water, sediment and macrophytes in the Kenyan part of Lake Victoria: spatial, temporal and bioindicative aspects. *Environ Sci Pollut Res Int*, 27(2), 1485-1498. <https://doi.org/10.1007/s11356-019-06525-9>.
- Patel, K. S., Sahu, B. L., Dahariya, N. S., Bhatia, A., Patel, R. K., Matini, L., Sracek, O., & Bhattacharya, P. (2015). Groundwater arsenic and fluoride in Rajnandgaon District, Chhattisgarh, northeastern India. *Applied Water Science*, 7(4), 1817-1826. <https://doi.org/10.1007/s13201-015-0355-2>.
- Peek, L., Abramson, D. M., Cox, R. S., Fothergill, A., & Tobin, J. (2018). Children and Disasters. In *Handbook of Disaster Research* (pp. 243-262). https://doi.org/10.1007/978-3-319-63254-4_13.
- Polya, D. A., Sparrenbom, C., Datta, S., & Guo, H. (2019). Groundwater arsenic biogeochemistry – Key questions and use of tracers to understand arsenic-prone groundwater systems. *Geoscience Frontiers*, 10(5), 1635-1641. <https://doi.org/10.1016/j.gsf.2019.05.004>.
- Quino-Lima, I., Ramos-Ramos, O., Ormachea-Munoz, M., Quintanilla-Aguirre, J., Duwig, C., Maity, J. P., Sracek, O., & Bhattacharya, P. (2020). Spatial dependency of arsenic, antimony, boron and other trace elements in the shallow groundwater systems of the Lower Katari Basin, Bolivian Altiplano. *Sci Total Environ*, 719, 137505. <https://doi.org/10.1016/j.scitotenv.2020.137505>.

- Quino Lima, I., Ramos Ramos, O. E., Ormachea Muñoz, M., Chambi Tapia, M. I., Quintanilla Aguirre, J., Ahmad, A., Maity, J. P., Islam, M. T., & Bhattacharya, P. (2021). Geochemical mechanisms of natural arsenic mobility in the hydrogeologic system of Lower Katari Basin, Bolivian Altiplano. *Journal of Hydrology*, 594. <https://doi.org/10.1016/j.jhydrol.2020.125778>.
- Rafique, T., Naseem, S., Usmani, T. H., Bashir, E., Khan, F. A., & Bhangar, M. I. (2009). Geochemical factors controlling the occurrence of high fluoride groundwater in the Nagar Parkar area, Sindh, Pakistan. *J Hazard Mater*, 171(1-3), 424-430. <https://doi.org/10.1016/j.jhazmat.2009.06.018>.
- Ramsay, L., Petersen, M. M., Hansen, B., Schullehner, J., van der Wens, P., Voutchkova, D., & Kristiansen, S. M. (2021). Drinking Water Criteria for Arsenic in High-Income, Low-Dose Countries: The Effect of Legislation on Public Health. *Environ Sci Technol*, 55(6), 3483-3493. <https://doi.org/10.1021/acs.est.0c03974>.
- Rango, T., Kravchenko, J., & Jeuland, M. (2012). Groundwater Quality and Its Health Impact : An Assessment of Dental Fluorosis in Rural Inhabitants of the Main Ethiopian Rift. *Environment International*, 43, 37-47.
- Rango, T., Vengosh, A., Dwyer, G., & Bianchini, G. (2013). Mobilization of arsenic and other naturally occurring contaminants in groundwater of the Main Ethiopian Rift aquifers. *Water Res*, 47(15), 5801-5818. <https://doi.org/10.1016/j.watres.2013.07.002>.
- Rango, T., Vengosh, A., Jeuland, M., Tekle-Haimanot, R., Weinthal, E., Kravchenko, J., Paul, C., & McCornick, P. (2014). Fluoride exposure from groundwater as reflected by urinary fluoride and children's dental fluorosis in the Main Ethiopian Rift Valley. *Sci Total Environ*, 496, 188-197. <https://doi.org/10.1016/j.scitotenv.2014.07.048>.
- Rango, T., Vengosh, A., Jeuland, M., Whitford, G. M., & Tekle-Haimanot, R. (2017). Biomarkers of chronic fluoride exposure in groundwater in a highly exposed population. *Sci Total Environ*, 596-597, 1-11. <https://doi.org/10.1016/j.scitotenv.2017.04.021>.
- Ravenscroft, P. a. L., L. (2022). *Seeing the Invisible: A strategic report on groundwater quality*. <http://hdl.handle.net/10986/37197>.
- Rezaei, M., Nikbakht, M., & Shakeri, A. (2017). Geochemistry and sources of fluoride and nitrate contamination of groundwater in Lar area, south Iran. *Environ Sci Pollut Res Int*, 24(18), 15471-15487. <https://doi.org/10.1007/s11356-017-9108-0>.
- Rieger, K., Holm, R. H., & Sheridan, H. (2016). Access to groundwater and link to the impact on quality of life: A look at the past, present and future public health needs in Mzimba District, Malawi. *Groundwater for Sustainable Development*, 2-3, 117-129. <https://doi.org/10.1016/j.gsd.2016.07.002>.
- Rimstidt, J. D., & Vaughan, D. J. (2003). Pyrite oxidation: a state-of-the-art assessment of the reaction mechanism. *Geochimica et Cosmochimica Acta*, 67(5), 873-880. [https://doi.org/10.1016/s0016-7037\(02\)01165-1](https://doi.org/10.1016/s0016-7037(02)01165-1).
- Rivett, M. O., Miller, A. V. M., MacAllister, D. J., Fallas, A., Wanangwa, G. J., Mleta, P., Phiri, P., Mannix, N., Monjerezi, M., & Kalin, R. M. (2018). A conceptual model based framework for pragmatic groundwater-quality monitoring network design in the developing world: Application to the Chikwawa District, Malawi. *Groundwater for Sustainable Development*, 6, 213-226. <https://doi.org/10.1016/j.gsd.2018.01.005>.
- Rockafellow-Baldoni, M., Spayd, S. E., Hong, J. Y., Meng, Q., Ohman-Strickland, P., & Robson, M. G. (2018). Arsenic Exposure and Cancer Risk Reduction with Local Ordinance Requiring Whole-House Dual-Tank Water Treatment Systems. *Hum Ecol Risk Assess*, 24(5), 1256-1267. <https://doi.org/10.1080/10807039.2017.1411779>.
- Rwebugisa, R. A. (2008). Groundwater recharge assessment in the Makutupora basin , Dodoma Tanzania., *Master of Science*.

- Rwiza, M. J., Kim, K. W., & Kim, S. d. (2016). Geochemical Distribution of Trace Elements in Groundwater from the North Mara Large-Scale Gold Mining Area of Tanzania. *Groundwater Monitoring and Remediation*, 36, 83-93. <https://doi.org/10.1111/gwmr.12152>
- Saha, N., Rahman, M. S., Ahmed, M. B., Zhou, J. L., Ngo, H. H., & Guo, W. (2017). Industrial metal pollution in water and probabilistic assessment of human health risk. *J Environ Manage*, 185, 70-78. <https://doi.org/10.1016/j.jenvman.2016.10.023>.
- Salman, S. M. A. (2012). The Human Right to Water—Challenges of Implementation. 106th Annual Meeting (American Society of International Law).
- Sappa, G., Ferranti, F., Ergul, S., & Ioanni, G. (2013). Evaluation of the groundwater active recharge trend in the coastal plain of Dar es Salaam (Tanzania). *Chemical and Pharmaceutical Research*, 5(12), 548-552..
- Sappa, G., & Luciani, G. (2014). Groundwater management in Dar Es Salam coastal aquifer (Tanzania) under a difficult sustainable development. *WSEAS Transactions on Environment and Development*, 10.
- Scanlon, B. R., Fakhreddine, S., Rateb, A., de Graaf, I., Famiglietti, J., Gleeson, T., Grafton, R. Q., Jobbagy, E., Kebede, S., Kolusu, S. R., Konikow, L. F., Long, D., Mekonnen, M., Schmied, H. M., Mukherjee, A., MacDonald, A., Reedy, R. C., Shamsudduha, M., Simmons, C. T., . . . Zheng, C. (2023). Global water resources and the role of groundwater in a resilient water future. *Nature Reviews Earth & Environment*. <https://doi.org/10.1038/s43017-022-00378-6>.
- Scharp, C., Sargsyan, H., Polo, F., Johnston, R., & De France, J. (2018). *Guidance on the Investigation and Mitigation of Arsenic Contamination*. United Nations Children’s Fund (UNICEF), http://www.unicef.org/wes/http://www.who.int/water_sanitation_health.
- Seddon, D., Kashaigili, J. J., Taylor, R. G., Cuthbert, M. O., Mwihumbo, C., & MacDonald, A. M. (2021). Focused groundwater recharge in a tropical dryland: Empirical evidence from central, semi-arid Tanzania. *Journal of Hydrology: Regional Studies*, 37. <https://doi.org/10.1016/j.ejrh.2021.100919>.
- Serdeczny, O., Adams, S., Baarsch, F., Coumou, D., Robinson, A., Hare, W., Schaeffer, M., Perrette, M., & Reinhardt, J. (2016). Climate change impacts in Sub-Saharan Africa: from physical changes to their social repercussions. *Regional Environmental Change*, 17(6), 1585-1600. <https://doi.org/10.1007/s10113-015-0910-2>.
- Smedley, P. (1996). Arsenic in rural groundwater in Ghana: Part special issue: Hydrogeochemical studies in sub-saharan Africa. *Journal of African Earth Sciences*, 22(4), 459-470. [https://doi.org/10.1016/0899-5362\(96\)00023-1](https://doi.org/10.1016/0899-5362(96)00023-1).
- Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17, 517-568. [https://doi.org/10.1016/S0883-2927\(02\)00018-5](https://doi.org/10.1016/S0883-2927(02)00018-5).
- Smedley, P. L. a. K. D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17(2002), 517-568. [https://doi.org/10.1016/S0883-2927\(02\)00018-5](https://doi.org/10.1016/S0883-2927(02)00018-5).
- Smith, A. H., Arroyo, A. P., Mazumder, D. N. G., Kosnett, M. J., Hernandez, A. L., Beeris, M., Smith, M. M., & Moore, L. E. (2000). Arsenic-Induced Skin Lesions among Atacameño People in Northern Chile despite Good Nutrition and Centuries of Exposure. . *Environmental Health Perspectives*, 108(7), 617–620. <https://doi.org/https://doi.org/10.2307/3434881>.
- Smith, E., Naidu, R., & Alston, A. M. (2002). Chemistry of inorganic arsenic in soils: II. Effect of phosphorus, sodium and calcium on arsenic sorption. *Journal of Environmental Quality*, 31, 557 – 563.
- Smith, W. R., Markham, M. W., & Robinson, W. W. (1993). *Treating of waste water with bauxite to remove phosphates from the waste water* (United States of America Patent No. U. S. Patent.

- Souza Neto, H. F., Pereira, W., Dias, Y. N., Souza, E. S., Teixeira, R. A., Lima, M. W., Ramos, S. J., Amarante, C. B. D., & Fernandes, A. R. (2020). Environmental and human health risks of arsenic in gold mining areas in the eastern Amazon. *Environ Pollut*, 265(Pt B), 114969. <https://doi.org/10.1016/j.envpol.2020.114969>.
- Sracek, O., Křibek, B., Mihaljevič, M., Ettler, V., Vaněk, A., Penížek, V., Veselovský, F., Bagai, Z., Kapusta, J., & Sulovský, P. (2021). Mobility of Mn and other trace elements in Mn-rich mine tailings and adjacent creek at Kanye, southeast Botswana. *Journal of Geochemical Exploration*, 220. <https://doi.org/10.1016/j.gexplo.2020.106658>.
- Stollenwerk, K. G. (2003). Geochemical Processes Controlling Transport of Arsenic in Groundwater: A Review of Adsorption. In A. H. Welch & K. G. Stollenwerk (Eds.), *Arsenic In Ground Water*. Springer. https://doi.org/https://doi.org/10.1007/0-306-47956-7_3.
- Stolze, L., Battistel, M., & Rolle, M. (2022). Oxidative Dissolution of Arsenic-Bearing Sulfide Minerals in Groundwater: Impact of Hydrochemical and Hydrodynamic Conditions on Arsenic Release and Surface Evolution. *Environ Sci Technol*, 56(8), 5049-5061. <https://doi.org/10.1021/acs.est.2c00309>.
- Straaten, P. v. (2000). Human exposure to mercury due to small scale gold mining in northern Tanzania. *The Science of the Total Environment*, 259, 45-53.
- Taylor, H., Appleton, J. D., Lister, R., Smith, B., Chitamwebwa, D., Mkumbo, O., Machiwa, J. F., Tesha, A. L., & Beinhoff, C. (2005). Environmental assessment of mercury contamination from the Rwamagasa artisanal gold mining centre, Geita District, Tanzania. *Sci Total Environ*, 343(1-3), 111-133. <https://doi.org/10.1016/j.scitotenv.2004.09.042>.
- Thole, B. (2013). Ground Water Contamination with Fluoride and Potential Fluoride Removal Technologies for East and Southern Africa. In *Perspectives in Water Pollution*. <https://doi.org/10.5772/54985>.
- Thole, B. (2014). Initial fluoride concentration and loading capacity in defluoridation with bauxite, gypsum, magnesite and their composite. *Journal of Water, Sanitation and Hygiene for Development*, 4(2), 200-205. <https://doi.org/10.2166/washdev.2014.025>.
- Tibebe, D., Zewge, F., Lemma, B., & Kassa, Y. (2022). Assessment of spatio-temporal variations of selected water quality parameters of Lake Ziway, Ethiopia using multivariate techniques. *BMC Chem*, 16(1), 11. <https://doi.org/10.1186/s13065-022-00806-0>.
- Tilya, F. F., & Mhita, S. M. (2007). Frequency of Wet and Dry Spells in Tanzania. *Climate and land degradation*.
- Tomasek, I., Mouri, H., Dille, A., Bennett, G., Bhattacharya, P., Brion, N., Elskens, M., Fontijn, K., Gao, Y., Gevera, P. K., Ijumulana, J., Kisaka, M., Leemakers, M., Shemsanga, C., Walraevens, K., Wragg, J., & Kervyn, M. (2021). Naturally occurring potentially toxic elements in groundwater from the volcanic landscape around Mount Meru, Arusha, Tanzania and their potential health hazard. *Sci Total Environ*, 807(Pt 1), 150487. <https://doi.org/10.1016/j.scitotenv.2021.150487>.
- Uddin, M. G., Nash, S., & Olbert, A. I. (2021). A review of water quality index models and their use for assessing surface water quality. *Ecological Indicators*, 122. <https://doi.org/10.1016/j.ecolind.2020.107218>.
- van Genuchten, C. M., & Peña, J. (2016). Antimonate and arsenate speciation on reactive soil minerals studied by differential pair distribution function analysis. *Chemical Geology*, 429, 1-9. <https://doi.org/10.1016/j.chemgeo.2016.03.001>.
- Verbeeck, M., Hiemstra, T., Thiry, Y., & Smolders, E. (2017). Soil organic matter reduces the sorption of arsenate and phosphate: a soil profile study and geochemical modelling. *European Journal of Soil Science*, 68(5), 678-688. <https://doi.org/10.1111/ejss.12447>.
- Verbeeck, M., Thiry, Y., & Smolders, E. (2020). Soil organic matter affects arsenic and antimony sorption in anaerobic soils. *Environ Pollut*, 257, 113566. <https://doi.org/10.1016/j.envpol.2019.113566>.

- Vithanage, M., & Bhattacharya, P. (2015). Fluoride in the environment: sources, distribution and defluoridation. *Environmental Chemistry Letters*, 13(2), 131-147. <https://doi.org/10.1007/s10311-015-0496-4>.
- Vuhahula, E. A. M., Masalu, J. R. P., Mabelya, L., & Wandwi, W. B. C. (2009). Dental fluorosis in Tanzania Great Rift Valley in relation to fluoride levels in water and in 'Magadi' (Trona). *Desalination*, 248(1-3), 610-615. <https://doi.org/10.1016/j.desal.2008.05.109>.
- Waychunas, G. A., Rea, B. A., Fuller, C. C., & Davis, J. A. (1993). Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochimica et Cosmochimica Acta* 57, 2251-2269.
- WHO. (2017). *Guideline for drinking-water quality*. W. H. Organization.
- WHO. (2022). *Guidelines for drinking-water quality*.
- Wold, S., and, K. E., & Geladi, P. (1987). Principal Component Analysis. *Chemometrics and Intelligent Laboratory Systems*, 2, 37-52.
- Xing, S., Guo, H., Wu, P., Hu, X., Zhao, Z., & Yuan, Y. (2022). Distribution and formation processes of high fluoride groundwater in different types of aquifers in the Hualong-Xunhua Basin. *Earth Science Frontiers*, 29(3). <https://doi.org/10.13745/j.esfsf.2022.1.34>.
- Yan, X., Chen, X., Tian, X., Qiu, Y., Wang, J., Yu, G., Dong, N., Feng, J., Xie, J., Nalesnik, M., Niu, R., Xiao, B., Song, G., Quinones, S., & Ren, X. (2021). Co-exposure to inorganic arsenic and fluoride prominently disrupts gut microbiota equilibrium and induces adverse cardiovascular effects in offspring rats. *Sci Total Environ*, 767, 144924. <https://doi.org/10.1016/j.scitotenv.2020.144924>.
- Yousefi, M., Ghoochani, M., & Hossein Mahvi, A. (2018). Health risk assessment to fluoride in drinking water of rural residents living in the Poldasht city, Northwest of Iran. *Ecotoxicol Environ Saf*, 148, 426-430. <https://doi.org/10.1016/j.ecoenv.2017.10.057>.
- Zhao, F. J., McGrath, S. P., & Meharg, A. A. (2010). Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. *Annu Rev Plant Biol*, 61, 535-559. <https://doi.org/10.1146/annurev-aplant-042809-112152>