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**Hydrogeochemical Analysis and Modelling of Ground
Water in Kenya. A Critical Literature Review**

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Abstract

Purpose: Hydro geochemistry of groundwater provides a broad, more regionally extensive understanding of groundwater systems. Furthermore, this improved knowledge can be used to create more comprehensive management and conservation plans, and more equitable ground water regulations. The purpose of our study therefore is to analyze and model hydrogeochemical of groundwater in Kenya.

Methodology: The paper used a desk study review methodology where relevant empirical literature was reviewed to identify main themes and to extract knowledge gaps.

Findings: It was found that there was high concentration iron, zinc and manganese present in groundwater samples in the Sub Catchment. The close proximity of cattle kraals, pit latrines and domestic sewage effluents were found to be the factors that influence and degrade the quality of groundwater. The sanitary survey revealed that the risk to pollution for the boreholes ranged from low to medium but all the shallow wells were in the high-risk category due to the proximity of cattle kraals, pit latrines and domestic waste dumps to these wells.

Unique Contribution to Theory and Practice: The study recommended that county government should facilitate the removal of these excess ions from the borehole waters to ensure that the residents are consuming clean water since the concentrations of Na^+ , Ca^{2+} , Mg^{2+} , F^- , Cl and NO_3^- were found to be elevated in 90 % of the boreholes. Also, there is need for the county government to provide more piped water in the areas for the safety of the residents and avoid overexploitation of the boreholes.

Keywords: hydrogeochemical, analysis, modelling, ground water

1.0 INTRODUCTION

Hydrogeochemistry is the science of determining the source and time of groundwater recharge, identifying mineral make-up of aquifer materials, estimating how long water has been in an aquifer, examining how water from various sources mix and interact and evaluating what types of geochemical processes have occurred during the water's journey through the system (Bozau and van Berk, 2013; White, 2013). It is indicative of the water's origin and history of passage through underground materials which water has been in contact with, in shallow and deep-seated conditions (Chidambaram et al., 2012).

Natural and anthropogenic activities together with chemical and biogeochemical constituents considerably changes groundwater composition. Groundwater quality is mostly controlled by natural factors such as; Mineralogy, residence time, geological structures, recharge water composition and geochemical reactions that occur within an aquifer. It is also governed by anthropogenic activities such as over-pumping of the water together with agricultural and industrial processes (Appelo and Postma 2005).

Computerized geochemical models are powerful tools for understanding the chemical state of natural waters. The models are also used to predict the behavior of such waters under variety of hypothetical conditions. Chidambaram et al., (2012) and many others researchers such as Miron et al. (2015) and Liu et al. (2015) have developed a variety of geochemical models for describing and deducing the chemical behavior of complex and mixed waters.

The world total water resource is estimated to be 1.36×10^{12} m³, of which, approximately 97.2 % is salty and mainly found in oceans (Bilal. et al., 2015). This leaves a small fraction of about 2.8% as freshwater, out of which 2.2 % is available as surface water and 0.6 % as groundwater (Bilal et al., 2015). A fifth of all water used in the world is obtained from groundwater (Margat and Van der Gun, 2013). Availability of water for usage is mainly controlled by the quality of groundwater. Quality being the resultant effect of all biogeochemical processes and reactions, which have acted on water from the moment it has condensed in atmosphere to the time it's discharged by a well or spring (Aghazadeh and Mogaddam, 2010).

Trace elements exhibit a dualistic behavior in their interactions with the Earth's plants and animals. Many trace elements are vital to the growth and health of flora and fauna. Such elements are; Cu, Zn, Mn, Fe, Mo, B Se and Co, where they act as catalysts in the processes of life at low levels. However, at elevated concentrations, these essential nutrients commonly have a harmful effect. They can become toxic to organisms, including people, through both direct exposure, transportation and bioaccumulation in food chains (Palmer et al., 2011).

Elevated concentrations of trace elements in the environment occur as a result of anthropogenic activities, through mining, milling, or smelting of ores (Parsons et al., 2001). Application of agricultural fertilizers and combustion of fuels are other sources of trace elements (Kelly et al., 1996; Otero et al., 2005). Elements can also be enriched by natural processes, such as redistribution and mobilization of trace elements from host rock or regolith by surface and subsurface waters, and flooding events (Adamo et al., 2006; D'Ascoli et al., 2006; Gasparon and Matschullat, 2006).

Hydrogeochemistry of groundwater provides a broad, more regionally extensive understanding of groundwater systems. Furthermore, this improved knowledge can be used to create more comprehensive management and conservation plans, and more equitable ground water regulations

(Appelo and Postma, 2005). The hydro geochemistry of Kenya is intended to provide valuable information that would form the basis for sustainable management and conservation of groundwater. This is aimed at enhancing effective domestic, industrial and agricultural use of groundwater. In order to manage this limited resource effectively, hydrogeochemistry of groundwater is essential to establish the water types, Saturation indices and hydrogeochemical processes affecting the groundwater in Kenya.

1.2 Statement of the Problem

Diseases caused by poor quality water are of great concern, not only in Kenya but also worldwide. Kenyans are said to be at risk of dental fluorosis and serious bone defects resulting from high fluoride concentrations in drinking water which is a major contaminant in groundwater (Moraa, 2013). The levels of physico-chemical parameters of groundwater above the WHO (2011) permissible guidelines have resulted to health problems among the water users especially in rural areas of the developing countries. A significant number of serious human health problems have been reported to have occurred in such areas as a result of contamination of groundwater (WHO, 2011). For instance, excess nitrate in drinking-water has been linked to methemoglobinemia in infants, the so called 'blue-baby' syndrome. Nitrate leads to the oxidation of normal hemoglobin to methemoglobin which is unable to transport oxygen to the tissues. This may result in cyanosis (a dark blue coloration) and in some cases, asphyxiation and death (WHO, 2004) Some residents suffer from dental fluorosis which could be attributed to drinking water with high levels of fluoride during enamel formation (WHO 2011). This is an indication that the borehole water in the region could be having higher levels of some minerals than the applicable standards. Although some studies on groundwater quality have been done in the region, very little has been done on hydrogeochemical analysis and processes controlling groundwater chemistry in the area.

1.3 Significance of the Study

This study was to enable the residents to be aware of the levels of various parameters of groundwater which will enable them know the precautions to take as they use this water. The results of this study will also be useful to the County government in order to know how to treat the borehole waters and enhance safe water supply coverage in the areas. This will ensure sustainable provision of good quality water to the population and aid towards achievement of the "Kenya Vision 2030". The current status of the groundwater quality in the areas will be known with certainty by the planners, scientists, researchers, policy makers and decision makers involved in the monitoring and regulation of water quality especially the Water Resources Authority (WRA). This will aid in the management and conservation of the declining groundwater resources in the region.

1.4 Objectives of the Study

The general objective of the study was to analyze and model the hydrogeochemical quality of groundwater in Kenya.

2.0 LITERATURE REVIEW

2.1 Hydrogeochemistry of Groundwater

Hydrogeochemistry is a science of groundwater composition and properties. It studies the distribution of ground water of different properties and composition in the conditions of geologic medium, as well as causes and effects of changes in these properties (Aghazadeh et al., 2017). Groundwater hydrochemistry provides researchers with all the information needed to understand the physical processes and chemical reactions through which the groundwater undergoes, starting from rainfall, runoff, and infiltration to the roots which it passes through to reach the vadose zone and finally recharge the aquifer (Kura et al., 2016).

Land and water are critical natural resources that sustain human life and the lives of all other creatures on our planet (Selvakumar et al., 2014). Groundwater is one of the primary sources of water for human consumption, agriculture and industrial uses in any area (Selvakumar et al., 2014). Determination of physical and chemical quality of water is essential for assessing its suitability for various purposes (Selvakumar et al., 2014). Generally, the quality of groundwater depends on the composition of recharge water, the interaction between the water and the soil, the soil-gas interaction, the rock with which it comes into contact in the unsaturated zone, the residence time, and reactions that take place within the aquifer (Andrade et al., 2008; Khurshid et al., 2002; Selvakumar et al., 2014).

Groundwater quality in a region is largely determined by both natural processes (dissolution and precipitation of minerals, groundwater velocity, quality of recharge water, and interaction with other types of water aquifer) and anthropogenic activities (Andrade et al., 2008). Literature suggests that little work on this aspect has so far been done in Mbeere south groundwater (Kitetu et al., 2015; Kinuthia et al., 2009; Republic of Kenya, 2001). The natural chemical quality of groundwater is generally good, but elevated concentrations of a number of constituents can have negative effects on agricultural use as well as human health. The geochemistry of groundwater data gives crucial evidence to the geologic history of rocks and indications of groundwater recharge, movement, and storage (Thilagavathi et al., 2014).

2.2 Factors Affecting Hydrogeochemistry of Groundwater

The geochemistry of groundwater data gives crucial evidence to the geologic history of rocks and indications of groundwater recharge, movement, and storage (Walton 1970). The natural chemical quality of groundwater depends on geological as well as geographical arrangement in the region (Chandrasekar et al. 2013). Understanding factors influencing groundwater chemistry is important to prevent groundwater pollution especially in semi-arid areas where rainfall is low and water resources are limited (Osman and Al-Abri, 2014).

Mineral dissolution and precipitation are important in both natural and engineered processes because they influence water chemistry. For example, acid stimulation accelerates mineral dissolution, therefore increasing reservoir porosity and permeability. On the other hand, mineral precipitation during hydrocarbon production results in wellbore clogging. The dissolution of carbonate cap rocks can potentially result in CO₂ leakage from CO₂ storage reservoirs. Slow groundwater circulation in rocks and prolonged contact between water and rocks enhances weathering and dissolution which results in elevated element concentration (Osman and Al-Abri, 2014).

Ion exchange reactions occur when ions in water exchange with those electrostatically bound to the solid phase. They occur commonly in the presence of iron oxides, organic matters, and clay minerals with large surface area. Ion exchange reactions are important in determining natural composition in ground water. They can alter water composition and trigger other reactions including mineral dissolution and precipitation (Kumar et al., 2009).

Sorption is the adhesion of chemicals to solid surfaces. Adsorption process occurs in many natural and engineered systems. Studies of contaminated systems have shown that sorption–desorption is an important hydrogeochemical process that regulates transport and fate of inorganic and organic contaminants in natural subsurface systems. For example, metals (e.g. Cd^{2+} , Cr^{3+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} or Zn^{2+}) can become immobilized by adsorbing on sediments and soils. They can also become mobilized through desorption from the solid surface and re-enter the aqueous phase when geochemical conditions allow (Astrup et al., 2016).

2.3 Physicochemical Characteristics of Groundwater

The term physicochemical characteristic is used in reference to the property of water. This may affect its acceptability due to aesthetic considerations such as taste and color, toxicity reactions, unexpected physiological responses of laxative effect, and objectionable effects during normal uses such as curdy precipitates (WHO, 2004). The physico-chemical characteristics of groundwater are important to find out whether it is fit for drinking or some other beneficial uses (Devendra et al., 2014). Some of the physical characteristics are pH, temperature, total dissolved solids and electrical conductivity while some of the chemical properties are the major cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and Fe^{3+}) and major anions (F^- , Cl^- , SO_4^{2-} , CO_3^{2-} , and HCO_3^-).

2.4 Diseases Caused by Polluted Water

Diseases caused by poor quality water are of great concern, not only in Kenya but also worldwide. Studies done by Mashhood (2011) revealed that Polluted water can lead to blow out of water borne diseases such as typhoid, cholera, giardiasis, amoebiasis, diarrhea among others. Ombaka et al (2013) in their study on Effects of Human Activities and Seasonal Variation on Water Quality of Nkenye (Chikuu) Stream in Chuka, Kenya identified some of them as blue baby syndrome which is caused by high levels of nitrates and fluorosis which is caused by high levels of fluorides in drinking water.

According to Maiti, (1982), high chloride content in groundwater causes hypertension, osteoporosis, renal stones and asthma. Poor quality water can lead to less drinking water hence dehydration, bad smell, bad living and working conditions. It also incurs high cost of water supply due to expenses used in its treatment. Studies by the World Health Organization (WHO) indicate that more than 3.4 million people are dying every year, especially in third world countries as a result of water related diseases (WHO, 2011).

2.5 Modeling of Groundwater

The computerized geochemical models are reliable tools for understanding the chemical state of natural waters and for predicting the activities of such waters under variety of hypothetical conditions (Ramamoorthy et al., 2018). Geochemical speciation models and reactive transport models have reached an operational stage, allowing simulation of complex dynamic experiments

and description of field observations. For decades, the main focus has been on model performance but at present, the availability and reliability of thermodynamic data is the limiting factor of the models. Thermodynamic models applied to real and complex geochemical systems require much more extended thermodynamic databases with many minerals, colloidal phases, humic and fulvic acids, cementitious phases and (dissolved) organic complexing agents (Van der Lee and Lomenech, 2004).

Many different forms of models are exploited, usually dictated by the objectives of research. 'Conceptual models' are the most vital. All of us have some kind of concept of water-rock interactions. For groundwater interacting with aquifer minerals, one might conceive that most minerals would be undersaturated in the area of recharge. However, some minerals (those that dissolve fastest) would become saturated at some point down gradient, having reached their equilibrium solubility (a state of "partial equilibrium"). The conceptual model can be formalized into a set of mathematical equations using chemical principles, the "mathematical model," entered into a computer program, the "code," and predictions made to test the assumptions (and the databases) against the results from real-field data. This exercise helps to quantify and constrain the possible reactions that might occur on the subsurface (Nordstrom, 2007).

2.6 Empirical review

Akungah and Nyagetiria (2012) conducted a research study on assessment of physical and biochemical parameters of pollution in freshwater reservoirs in Kericho tea estates, Kenya. Forty depth integrated water samples were collected from each of the four dams. A total of 25 parameters were investigated over the study period to provide the baseline data for future reference in these water bodies. It was observed that Kerenga dam recorded the highest mean levels in iron (6.379mg/l), magnesium (1.479mg/l), zinc (2.472mg/l), copper (0.065mg/l), nitrates (5.47mg/l), orthophosphates (0.017mg/l), total nitrogen (14.84), total phosphorus (0.098), chlorophyll-a levels (0.055mg/l) and BOD (31.15mg/l) while Jamji record highest mean levels in silver (0.191mg/l) and suspended solids (174mg/l). Sambret dam, which was our control reservoir, recorded the lowest levels of nutrients, chlorophyll-a and highest levels of manganese (1.172mg/l). Total coliform bacteria were more prevalent in Kerenga and Jamji; faecal coliforms 99MPN/100ml, total coliform (349MPN/100ml) and total viable counts (4.6x10⁵ cfu/ml) followed by Sambret and Chagaik in that order. The results show that the levels of metals (except manganese and iron) and nitrates are below the maximum permissible levels set by WHO in drinking water. However, as regards microbial analyses, the dams were observed to be highly polluted by fecal and total coliforms and therefore not safe for domestic purposes before treatment. In addition, three of the four dams were found to be highly eutrophic regardless of the criteria used for their classification. Agricultural run-offs, domestic effluents, geo-chemical sources, municipal and urban run-off as well as leaching of nutrients were some of the possible contamination sources to the reservoirs. It was therefore proposed that nutrient containment, especially phosphorus, be given special attention.

Ebenezer, Ashun (2014) conducted a research study to determine the safety of groundwater sources and to examine the factors influencing groundwater quality. The study sought to assess the groundwater quality and to map its spatial distribution in terms of suitability for domestic purposes. Groundwater samples from 19 boreholes and 17 shallow wells were sampled from during the months of April to June 2013 and analyzed for selected physico - chemical and

microbial parameters. Standard methods were used for the analysis of groundwater samples in the laboratory. It was observed from the calculated Water Quality Index (WQI) that, 21 of the samples were in the 100 - 200 range indicating poor quality, 11 in the 200 - 300 range, indicating very poor quality and 4 samples in the above 300 range indicating unsuitable for drinking purposes. This was due to the high concentration iron, zinc and manganese present in groundwater samples in the Sub Catchment. The close proximity of cattle kraals, pit latrines and domestic sewage effluents were found to be the factors that influence and degrade the quality of groundwater. The sanitary survey also revealed that the risk to pollution for the boreholes ranged from low to medium but all the shallow wells were in the high-risk category due to the proximity of cattle kraals, pit latrines and domestic waste dumps to these wells. Groundwater in the Thirirka Sub Catchment should therefore be treated before used. The construction of wells with cement blocks with an apron and a well drainage system around these wells should be encouraged. Inhabitants of the Sub Catchment should be informed by officials of NEMA and WRMA about the status of groundwater in the Sub Catchment.

Kanyaru & Savina Mbura (2018) conducted a study sought to assess the selected physico-chemical parameters of ground water in Kamanyaki location, Tharaka Nithi County, Kenya with the following specific objectives; to determine the physico-chemical parameters of ground water during dry and wet season, to compare the levels of physico-chemical parameters of ground water during dry and wet season and to compare the levels of physico-chemical parameters of ground water with the Kenya Bureau of standards. Field survey design was used and it was accompanied by laboratory tests to analyze the level of each parameter from eight shallow wells. Plastic sample bottles of 1000ml were used to collect a total of 64 samples. The results reveal that the physico-chemical parameters during the dry season were significantly different ($P \leq 0.05$) from the wet season and the physico-chemical parameters during the dry and wet season were found to be significantly different ($P \leq 0.05$) from the recommended levels by the Kenya Bureau of Standards with the mean levels for fluoride being higher than the recommended standards in both seasons. The mean levels for fluoride during dry and wet season were found to be 5.0 mg/l and 2.9 mg/l respectively which were higher than the Kenya Bureau of Standards 1.5mg/l standards. Electrical conductivity was also found to be significantly different ($P \leq 0.05$) from Kenya Bureau of Standard which is 1400 $\mu\text{s}/\text{cm}$ in the two seasons with the mean levels of 2836 $\mu\text{s}/\text{cm}$ and 3824 $\mu\text{s}/\text{cm}$ in dry and wet season respectively. Therefore, there is need to supply clean water for domestic purposes in the study area as the ground water in the area is not safe for drinking especially due to the high levels of fluoride in the water which could have contributed to the dental discoloration among many residents in the area.

2.7 Research Gaps

A knowledge gap occurs when desired research findings provide a different perspective on the issue discussed. For instance, Akungah and Nyagetiria (2012) conducted a research study on assessment of physical and biochemical parameters of pollution in freshwater reservoirs in Kericho tea estates, Kenya. Forty depth integrated water samples were collected from each of the four dams. A total of 25 parameters were investigated over the study period to provide the baseline data for future reference in these water bodies. The results show that the levels of metals (except manganese and iron) and nitrates are below the maximum permissible levels set by WHO in drinking water. However, as regards microbial analyses, the dams were observed to be highly

polluted by fecal and total coliforms and therefore not safe for domestic purposes before treatment. On the other hand, our study aimed at analyzing and modelling the hydrogeochemical quality of groundwater in Kenya.

Secondly, a methodological gap can be identified from the research, for example, Kanyaru & Savina Mbura (2018) conducted a study sought to assess the selected physico-chemical parameters of ground water in Kamanyaki location, Tharaka Nithi County, Kenya. Field survey design was used and it was accompanied by laboratory tests to analyze the level of each parameter from eight shallow wells. Plastic sample bottles of 1000ml were used to collect a total of 64 samples. The results reveal that the physico-chemical parameters during the dry season were significantly different ($P \leq 0.05$) from the wet season and the physico-chemical parameters during the dry and wet season were found to be significantly different ($P \leq 0.05$) from the recommended levels by the Kenya Bureau of Standards with the mean levels for fluoride being higher than the recommended standards in both seasons. The mean levels for fluoride during dry and wet season were found to be 5.0 mg/l and 2.9 mg/l respectively which were higher than the Kenya Bureau of Standards 1.5 mg/l standards. Electrical conductivity was also found to be significantly different ($P \leq 0.05$) from Kenya Bureau of Standard which is 1400 $\mu\text{s}/\text{cm}$ in the two seasons with the mean levels of 2836 $\mu\text{s}/\text{cm}$ and 3824 $\mu\text{s}/\text{cm}$ in dry and wet season respectively. However, our study used desk study review methodology.

3.0 METHODOLOGY

The study adopted a desktop literature review method (desk study). This involved an in-depth review of studies related to cancer prevention practices among women in the reproductive age in Kenya. Three sorting stages were implemented on the subject under study in order to determine the viability of the subject for research. This is the first stage that comprised the initial identification of all articles that were based on hydrogeochemical analysis and modelling of ground water in Kenya. The search was done generally by searching the articles in the article title, abstract, keywords. A second search involved fully available publications on the subject on hydrogeochemical analysis and modelling of ground water in Kenya. The third step involved the selection of fully accessible publications. Reduction of the literature to only fully accessible publications yielded specificity and allowed the researcher to focus on the articles that related to hydrogeochemical analysis and modelling of ground water in Kenya which was split into top key words. After an in- depth search into the top key words (hydrogeochemical, analysis, modelling, ground water), the researcher arrived at 3 articles that were suitable for analysis.

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4.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

4.1 Conclusion

Hydrogeochemistry of groundwater is essential to establish the water types, saturation indices and hydrogeochemical processes affecting the groundwater in Kenya. It was found that there was high concentration iron, zinc and manganese present in groundwater samples in the Sub Catchment. The close proximity of cattle kraals, pit latrines and domestic sewage effluents were found to be the factors that influence and degrade the quality of groundwater. The sanitary survey revealed that the risk to pollution for the boreholes ranged from low to medium but all the shallow wells were in the high-risk category due to the proximity of cattle kraals, pit latrines and domestic waste dumps to these wells. Groundwater in the Sub Catchment should therefore be treated before used.

4.2 Recommendations

The study recommended that county government should facilitate the removal of these excess ions from the borehole waters to ensure that the residents are consuming clean water since the concentrations of Na^+ , Ca^{2+} , Mg^{2+} , F^- , Cl^- and NO_3^- were found to be elevated in 90 % of the boreholes. Also, there is need for the county government to provide more piped water in the areas for the safety of the residents and avoid overexploitation of the boreholes.

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