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Full Length Research Paper

A Comparative Hydrogeochemical Study of Granitic Fractured and Alluvial Channel Aquifer Systems

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Abstract

Hydrogeochemical investigations were carried out with the aim of assessing the geochemical water composition and processes governing groundwater hydrochemistry in Alluvial Aquifer of the Modder River catchment in Southern Africa and the granitic fractured Aquifer of Pallisa District in eastern Uganda. This was based on chemical analyses of water samples from existing wells and new boreholes in the two study areas. From the analyses, there were significant variations in the quality composition of groundwater. The calculated SAR, Na% and RSC values indicated that the water is of good quality and is suitable for drinking and irrigation purposes except for a few locations. Na and HCO_3 are dominant with respect to the chemical composition of the groundwater. Detailed studies of the hydrogeochemical processes in the alluvial and granitic aquifer systems also shown that dissolution of silicate weathering, dolomite and calcite minerals, ion exchanges as well as anthropogenic influence in a lesser extent are the dominant hydrogeochemical processes that control groundwater quality. The increase in salinity is related to the dissolution of minerals in the host rocks and the evaporative concentration of solutes.

Keywords: Hydrogeochemistry, Granitic fractured, Alluvial channel aquifer, WISH, PHREEQC model, Pallisa District, Modder River catchment.

INTRODUCTION

Hydrogeochemical processes in groundwater are largely controlled by the physical and chemical interactions that occur between the groundwater and the aquifer materials. Hydrogeochemical processes are responsible for the seasonal, temporal and spatial variations of groundwater chemistry and quality (Rajmohan and Elango, 2004). In alluvial channel aquifers that typically consist of unconsolidated sediments, groundwater hydrogeochemical processes are mainly influenced by the mineralogy of sediments that interacts with the infiltrating water. Alluvial aquifers located along the major rivers of the Southern Africa Karoo basin typically comprises of unconsolidated calcrete, clay, silts and sand deposits. According to Woodford and Chevallier (2002), Quaternary deposits are a major characteristic along main rivers of the Karoo basin. Calcrete sediments at shallow depth are a common phenomenon close to river channels in semi-arid to arid climates. The study site 1 is characterised by arid to semi-arid conditions. The formation of calcretes close to river channels can also be related to shallow water tables and high infiltration rates that contribute to the precipitation of leached carbonates and dolomite minerals in the groundwater (Parsons and Abrahams, 1994). In the riparian zones, evapotranspiration can also contribute to mineral precipitation in the vadose zone when the aquifer has a shallow water table. Dissolution of calcite and dolomite minerals influence the groundwater chemistry and may also create preferential flow paths for groundwater recharge at the surface and within the deposits. Ion exchange reactions involving Na^+ and Ca^{2+} often dominate geochemical processes in detrital sedimentary aquifers (Cardona *et al*., 2004). Agricultural

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chemicals such as fertilizers and pesticides have been noted as significant contaminant sources for alluvial aquifers (Kelly, 1997). It is upon such a background that this study was aimed to investigate the hydrogeochemical processes and their contribution to the overall water quality. The study utilizes the conventional Piper diagram, bivariate plots and PHREEQC model (Parkhurst and Appelo, 1999) to analyze groundwater chemistry data obtained during sampling runs conducted in February, May and August of 2011.

Case study sites

Study site 1

It is located in Modder River catchment area, downstream of the Krugersdrift Dam which is situated about 30 km from the city of Bloemfontein, in the Free State Province of South Africa (Figure 1). Modder River is a seasonal river in which the majority of the flow occurs during rainy seasons. The study area is surrounded by farms that are mainly characterised by summer and winter crop production. In general, the study area is characterised by arid to semi-arid climate (weatherSA, 2011) with long periods of low rainfall events. The area is generally dry and on average receives about 600 mm of rainfall per annum. The rainfall is often associated with heavy thunderstorms. During the rainy season of water year (2010-2011), the study area received about 680 mm of rainfall (Figure 2). February and June 2011 were characterized by extremely high rainfall amounts in excess of 150 mm which resulted in flooding events. The riparian vegetation alongside the Modder River banks comprises of tall thorn trees, small Bushveld shrubs and thick grasses.

Study site 2

Pallisa District lies within the Kyoga Basin and is located in the eastern part of Uganda. It is of approximately 1 585 km^2 in area and is bordered by Kumi District from the north, Budaka District to from the east, Butaleja District from the south-east, Namutumba District from the south, Kaliro District from the west. The chief town is Pallisa and its coordinates are 01^o 1''N, 33^o 43''E (Figure 1). Pallisa District is located between latitude 33^o 25''E and 34^o 09''E and Longitude 0^o 50''N and 01^o 25''N. There are small towns of Kabwangasi, Kamuge, Kibuku and Butebo within Pallisa district. The topography slopes gently from the east to the west with land surface elevations ranged from 1 200 m asl in the eastern part to 1 000 m asl in the south-western part (Figure 2). Most of the land is used for small scale agricultural farming while wetlands, woodland, bush land, grassland, deciduous plantations and urban areas represent about 30% of the land surface. The average temperatures range between 20 and 30 ^{o}C, with minor daily temperature variations. The mean annual minimum temperature is 18 ^{o}C and the mean annual maximum temperature is 32^{o}C. The weather conditions are characterized by bi-modal rainfall system controlled by the Inter-Tropical Convergence Zones (ITCZ) (Nyende, 2007), where the mean annual precipitation is of about 1 250 mm/year.

Geohydrological properties

For Study site 1, the groundwater mainly flows within the gravel-sand channel deposits which are typically characterised by high hydraulic conductivity properties (Washington State Department of Ecology, 1994-2011)**.** The hydraulic conductivity of the aquifers spatially varies depending on the sorting of the channel deposit aquifer materials and the amount of silt and clay present in the deposits. In other words, the sorting of gravel-sand aquifer materials and the silt-clay content has great influence on the aquifer hydraulic properties. Although high hydraulic conductivities of the gravel-sand deposits are good for groundwater yields, it can also accelerate contaminant migration. Groundwater recharge of the shallow alluvial cover aquifers occurs locally through normal and preferential infiltration as enhanced by the dense vegetation that often characterises riparian zones. Surface runoff and drainage from the terrestrial land also assist in the accumulation of water on the lower riparian zone thus enhancing the infiltration of water into the shallow alluvial cover aquifer system. Because of shallow water table conditions, the recharge process is often quick. The local recharged groundwater of the alluvial cover aquifer typically has short residence time (characterised by a shallow water table (< 3 mbgl) which implies that recharging waters takes a short time to reach the water table). High hydraulic properties of the channel deposits facilitate fast groundwater movement which consequently discharges into the river system. Geochemically, the shallow local groundwater system would be characterised by low Total Dissolved Solids (TDS) because of limited time in contact with the non-saline aquifer materials. Coarse-grained alluvial channel aquifers can be approximated by a homogeneous porous media when estimating hydraulic and transport parameters. However groundwater and transport flow in the sediments is greatly controlled by aquifer material architecture (Zappa *et al*., 2006). It is therefore important to understand the effects that the physical properties of channel deposits has on the spatial variation of measured aquifer parameters. The influence that physical and chemical properties of geological material have on the spatial variation of geo-hydrological properties is collectively referred to as “heterogeneity”.

In study area 2, water is extracted from both the fractured bedrocks and from the overlying weathered

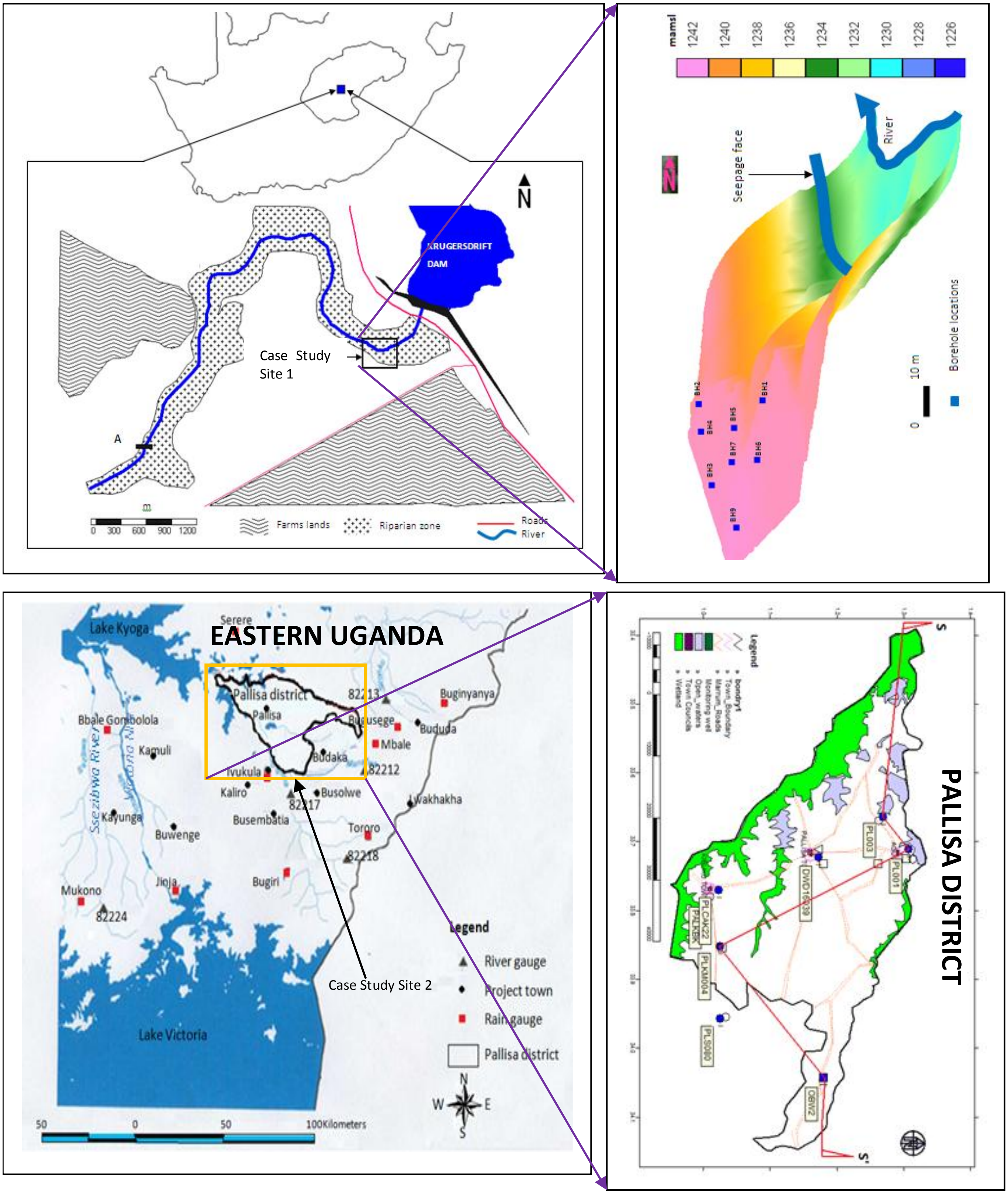


Figure 1. Location of the two study sites, Modder River Catchment in Bloemfontein and Pallisa District within the Kyoga Basin in eastern Uganda.

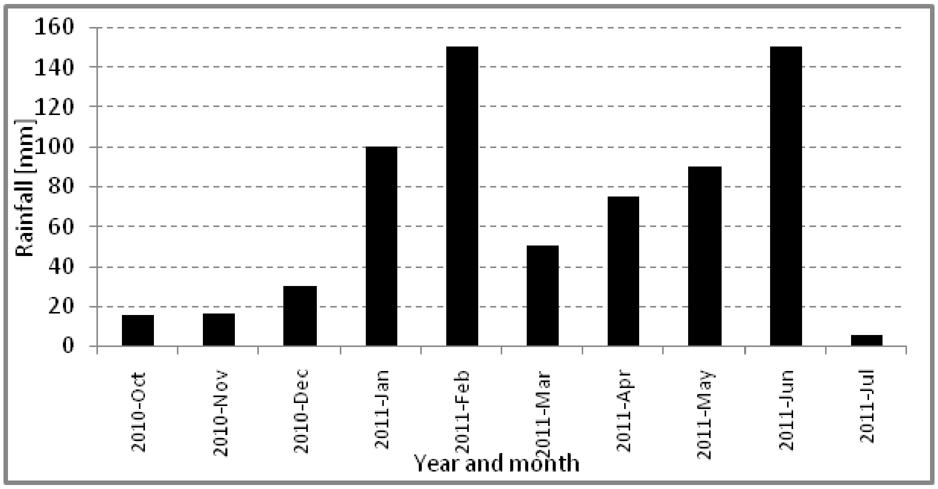


Figure 2. Monthly rainfall recorded during water year (oct.2010-sep.2011).

regolith (BH PL003; BH OBW2). The regolith aquifer is seen increasingly as a usable resource which aid agencies are seeking to develop on grounds of favourable yields and lower cost than the deeper groundwater (BH PL004) (Figure 3).

The regolith layer has an upper horizon of clayey sediment which is effective at filtering out some surface-derived pollutants (e.g. bacteria) and in restricting the entry of air to the underlying aquifers. This has some implications for the degree of aeration of the aquifers and groundwater chemistry. The basement aquifer has poor permeability (Chilton PJ and Foster SSD, 1993; 1995), but is variably fractured. The development of fractures is crucial for the availability and yield of groundwater; hence the productivity of the aquifer is highest at the shallowest levels. According to Briggs et al. (1989), the high rainfall and temperature of tropical climates serve to increase the rate at which chemical weathering processes occur as a result of hydrolysis, oxidation and dissolution. The geopetal imprint of long-term deep weathering and erosional unloading was identified in the vertical heterogeneity of the fractured-bedrock and weathered-mantle aquifers; the horizontal heterogeneity is lithologically controlled. The two units form an integrated aquifer system in which the more transmissive (5-20 m^2/d) (Nyende, 2013a) and porous weathered mantle provides storage to underlying bedrock fractures ($T \approx 1\ m^2/d$). The thickness and extent of the more productive weathered-mantle aquifer are functions of contemporary geomorphic processes.

METHODS

Groundwater sampling for site 1

For study site 1, a total of 16 groundwater and two river samples were collected during three sampling events in February, May and August and December 2011. Six of the groundwater samples were obtained from boreholes (terrestrial aquifer) while one of the samples was obtained from the seepage water flowing out at the contact plane between the overlying unconsolidated sediments and the shale bedrock at the river bank. Samples from the boreholes were collected in clean polyethylene bottles using a low flow pump at an abstraction rate of 0.30 l/s. Temperature and electrical conductivity (EC) were continuously monitored in the purged water. Samples were only obtained after the stabilization of temperature and EC. Figure 1 shows the location of boreholes from which the groundwater samples were collected. River samples were collected downstream and up stream of the alluvial channel aquifer.

Inorganic groundwater chemistry analyses were conducted by the Institute for Groundwater Studies (IGS) laboratory of the Free University in South Africa. The samples were analysed for major and minor ions; and silicon. The validity of the analytical measurements of the ions was determined by calculating the ionic balance error within the range of ± 5%. Saturation indices of quartz, calcite and dolomite as the most dominant and major minerals respectively were calculated using PHREEQC model (Parkhurst and Appelo, 1999).

XRD and X-Ray analysis for site 1

The X-ray fluorescent spectrometry (XRF) and X-ray diffractometry (XRD) analysis was performed on randomly selected geological logs to determine the presence and absolute quantities of mineral species and major oxide elements in the geological samples. Six samples representative of the soil, calcrete, clay-silt, gravel-sand and shale formation were selected for the analysis. Hundred grams of disturbed samples were

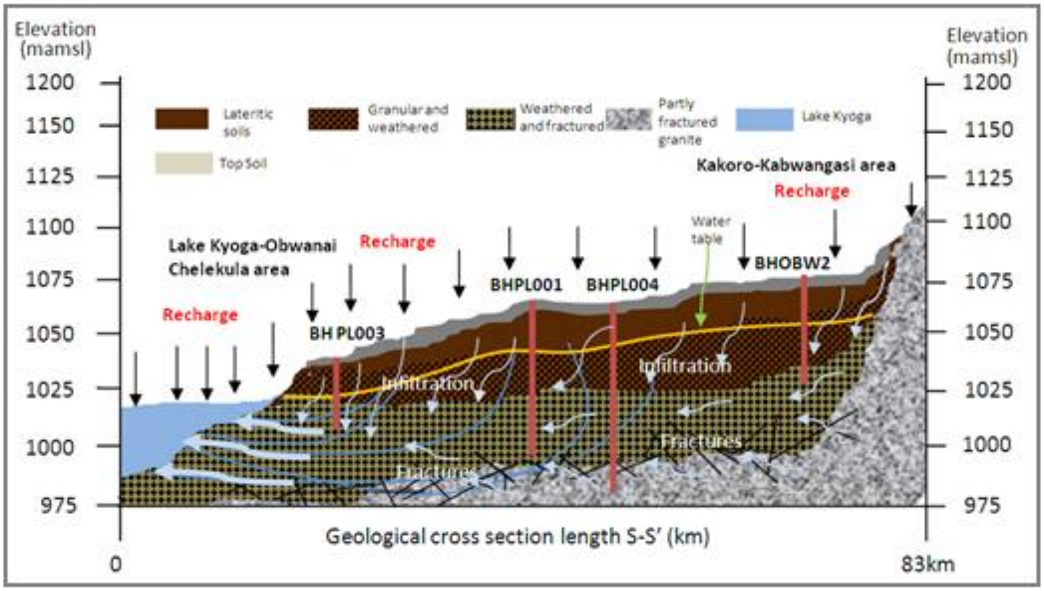


Figure 3. Schematic hydrostratigraphic units of the Kabwangasi - Kakoro-Lake Kyoga exaggerated cross-sectional conceptual geological model of groundwater flow in Pallisa District, eastern Uganda (approximate scales).

randomly collected from calcrete, alluvium-silt, clay and gravel-sand formations of the boreholes drilled into the alluvial channel aquifer. The logs from different boreholes were then mixed to obtain a representative sample of the lithology. The XRF and XRD analysis was conducted by the Geology laboratory of the Free State University in South Africa.

Groundwater sampling for site 2

For the study site 2, groundwater sampling was carried out in 2010 - 2011. In order to study the variation of groundwater quality in the study area, groundwater and soil samples were collected with the help of the Directorate of Water Resources Department, Entebbe and Kyambogo University twice a year during wet and dry periods, from July - October 2010 and December 2010 - March 2011. Samples were collected during the driest part of the year to avoid dilution by infiltration and the wettest part when dilution had taken place under the recharge activity. Water and soil samples were collected in such a way that they represented different types of lithologic units, (i.e. from different topographic levels), human impact and different climatic conditions. A total of 176 groundwater samples were collected from existing 56 sampling stations that included two newly drilled deep and four shallow wells. The boreholes are used for domestic water supply. Plastic sampling bottles were rinsed with distilled water before being used to sample. The bottles were tightly sealed, stored in ice box in the field (at 4°C) and taken to the Government laboratory at Wandegeya in Kampala for analysis. The sample preservation and analysing techniques were in accordance with the standard test procedures. The collected groundwater samples were analysed for major ions such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-} and SO_4^{2-}. Sensors were used for on-the-spot field water quality measurement of TDS, electrical conductivity (EC), pH and temperature. Alkalinity was measured (by Gran-titration) within 12 hours at a field laboratory. Trace elements such as lead and arsenic were not analysed, due to limitations of standards and reagents. Field measurement of pH is essential for meaningful interpretation of the results, especially for groundwater modelling, since loss of CO_2 could take place between the well head and the laboratory, thus leading to a pH rise. EC is a key parameter in both surveys and monitoring, since it enables the quick detection of spatial or temporal changes in the groundwater. Total hardness was calculated using the WISH computer software. In order to study the quality of groundwater, the chemical data were evaluated in terms of its suitability for domestic, agriculture and drinking purposes. The analysed data not only could be used for the classification of water for utilitarian purposes but also for ascertaining the various factors on which the chemical characteristics of water depend. Boreholes were pumped until stable readings for the parameters were obtained. Water samples were also collected in yellow high density polyethylene bottles except for samples for the analyses of hydrogen and oxygen isotope ratios. In the field, two filtered (0.45 µm cellulose nitrate membrane filter) samples (one part was acidified to pH = 1 with ultra-pure HNO_3 in new pre-flushed PE bottles and the other not acidified) were then taken for laboratory analysis for the determination of cations as described by Edmunds (1996b). Concentrations of cations in water and the rock samples were determined by Atomic Absorption Spectroscopy (AAS); following dissolution of the rock sample powders in 2N HCl. Analyses of anions were carried out on a Dionex DX120 ion chromatograph. The detailed hydrochemical characteristics of potable groundwater, including variations in concentrations of major cations and anions, are described in US 201:1994 and US 43:1999 for drinking water quality.

RESULTS

The groundwater chemistry analysis results have been used to identify and describe the hydrogeochemical processes governing the groundwater evolution and their contribution on the overall groundwater quality.

Table 1 shows the maximum and minimum concentrations of major and other important ions in ground- water samples collected from the aquifer.

The Ca^{+2} and Mg^{+2} concentrations in the all the groundwater samples exceed the SANS (1996) drinking water quality target values of 32 and 30 mg/l respectively. Abundance of the major ions is in the following order: $HCO_3^- > Na^+ > Cl^- > Mg^{+2} > Ca^{+2} > SO_4^{-2} > K^+$. Sodium and HCO_3^- are the most dominant cation and anion with an average contribution to total cations and anions of at least 60 % and 80 % respectively. Based on the Piper diagram (Figure 4); the groundwater is classified as a Na^+-HCO_3^- water type.

Table 2 shows the major elements oxides and minerals detected by XRF and XRD analysis. The XRF analysis (Table 2) shows that the alluvial channel deposits are dominated by silicates, aluminum and iron oxides. Magnesium, calcium and potassium oxides in the unconsolidated channel deposits occur in relatively small contents of above 1 %. The clay-silt formation has the greatest abundance of the calcium major oxide in excess of 11 %. Anhydrite constitutes about 43 % of the fines.

The XRD analysis (Table 2) shows that quartz is the super dominant mineral in all samples of the channel deposits sediments that were analysed. Calcite was detected as a minor mineral in the gravel-sand and shale but is the dominant mineral constituent of the clay-silt formation. Dolomite and magnetite occurs in the calcrete deposits as major minerals.

The distribution of the major ion composition in Pallisa District is shown in Figures 5 and 6 by Piper Tri - linear diagrams. From Figures 5 and 6, it can be seen that most wells in saprolite, fractured and granite layers are mainly dominated by Ca+Mg, Na+K, CO_3+HCO_3, Ca-HCO_3^--SO_4 or HCO_3-Cl+SO_4 - waters.

Water samples from the basement rocks are typically low in Mg, Cl, SO_4, and high in Ca. Hence, they are of Ca-HCO_3, or Ca-HCO_3- type, with a few of Mg-Ca-HCO_3 type. Water samples from sandstone are Na-Ca-Mg-HCO_3, Mg-Ca-HCO_3 and Na-HCO_3 - types. Others have Ca-Mg-Na+K and are not dominant in any type. The Piper diagrams also show overlapping hydrochemical characteristics of borehole water for the dry and wet seasons. Groundwater in Pallisa is generally of Ca-[Mg]-HCO_3 - type. This type of water is typical of shallow groundwater systems in crystalline areas. With increasing depth an increase in magnesium is observed.

DISCUSSION

The discussion seeks to identify and describe the possible hydrogeochemical processes contributing to the formation of a Na^+-HCO_3^- groundwater type (Figure 7). Attention has also been placed on levels of nitrates as nitrogen NO_3^-(N) in the groundwater given the proximity of the alluvial channel aquifer to agricultural farming activities. Identification of the important hydrogeochemical process in a groundwater system is not a unique exercise mainly because different reactions and weathering process can result in similar type of ions being present in the groundwater. The task of identifying the major hydrogeochemical processes is more of a diagnostic in nature. Two optional approaches can be used, firstly one can use the concentrations of the ions detected in groundwater to work backwards and try to identify their origins. On the other hand, it is also possible to start by identifying the minerals and major element oxides of the aquifer materials and then comparing their predicted potential influence on the groundwater quality to the measured ions. The relative nature of the exercise calls for the use of complimentary lines of evidence to identify and understand hydrogeochemical processes as demonstrated in this paper.

Hydrogeochemical processes

Carbonate system

The carbonate systems of the site only consist of bicarbonate (HCO^-_3) ion that constitutes more than 80 % of the total anion in the groundwater system (Figure 5). The weathering and dissolution of calcite and dolomite minerals that were detected in the unconsolidated deposits is the main sources of HCO^-_3, calcium (Ca^{+2}) and magnesium (Mg^{+2}) ions in the groundwater system. The carbonate mineralogy of calcretes is mainly dominated by calcite and dolomitic minerals (Parsons and Abrahams, 1994). Although calcium (Ca^{2+}) often dominates in calcrete minerals, calcite rich in magnesium (Mg^{+2}) has also been reported in the Kalahari region of Southern Africa (Watts, 1980). The presence of HCO^-_3, Ca^{+2} and Mg^{+2} in the groundwater system can therefore be explained using the processes

Table 1. Maximum and minimum concentrations of major ions and other important ions measured in the groundwater during the monitoring period, also shown in the table is the South African National Standards (SANS 1996) of drinking water quality target concentrations.

Ions	Minimum [mg/l]	Maximum [mg/l]	SANS 1996 [mg/l]
Na^+	82.90	209.60	≤ 100
K^+	4.75	8.23	≤ 50
Ca^{+2}	32.50	56.40	≤ 32
Mg^{+2}	40.09	82.80	≤ 30
Cl^-	48.84	107.00	≤ 100
SO_4^{-2}	20.02	74.83	≤ 200
F^-	0.25	0.73	≤ 1
NO_3^- (N)	0.00	0.82	≤ 6
HCO_3^-	365.00	613.00	-[a]
Si^{+4}	19.05	23.93	-

[a]- no standard available

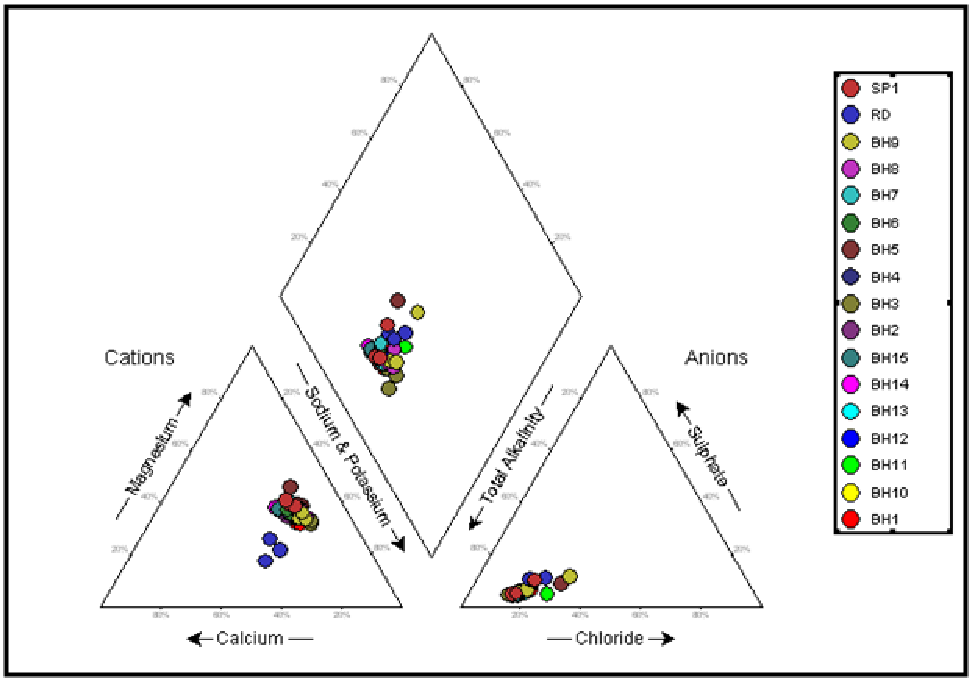


Figure 4. Groundwater and river samples plot on a piper diagram; groundwater samples are encircled by the dashed oval while the bold oval encircles the river water samples.

Table 1. Major minerals detected in alluvial aquifer materials; XX-dominant (>40% per volume), X-major (10-40% per volume), xx-Minor (2-10% per volume) and x-accessory (1-2% per volume).

		Major minerals detected in the channel deposits and their relative % content					
Sample description	**Depth [m]**	**Quartz**	**Calcite**	**Dolomite**	**Magnetite**	**Pyrite**	**Gypsum**
Soil	0-1	XX	<x		x	<x	
Calcrete	1-3	XX		xx	xx		<x
Clay-silt	3-5	XX	X		x		
Gravel-sand	5-8	XX	xx				
Shale	8-12	XX	xx		<x		

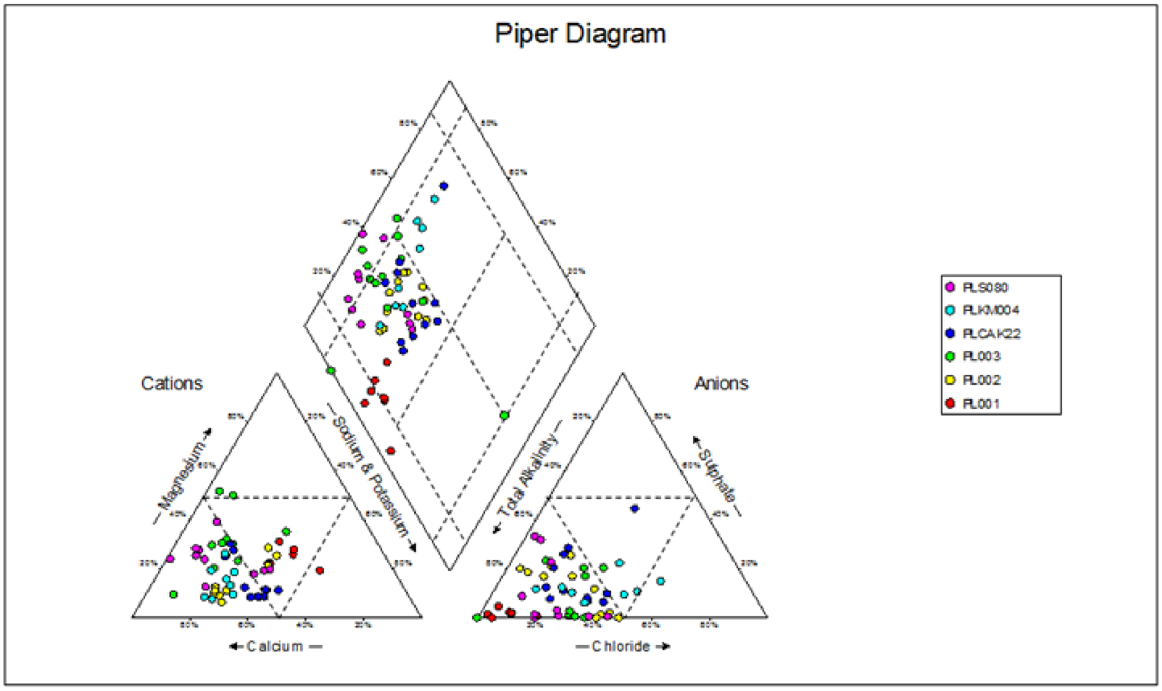


Figure 5. Piper Tri-linear diagram showing hydrochemical facies of groundwater during the wet season in the different boreholes of Pallisa District in eastern Uganda.

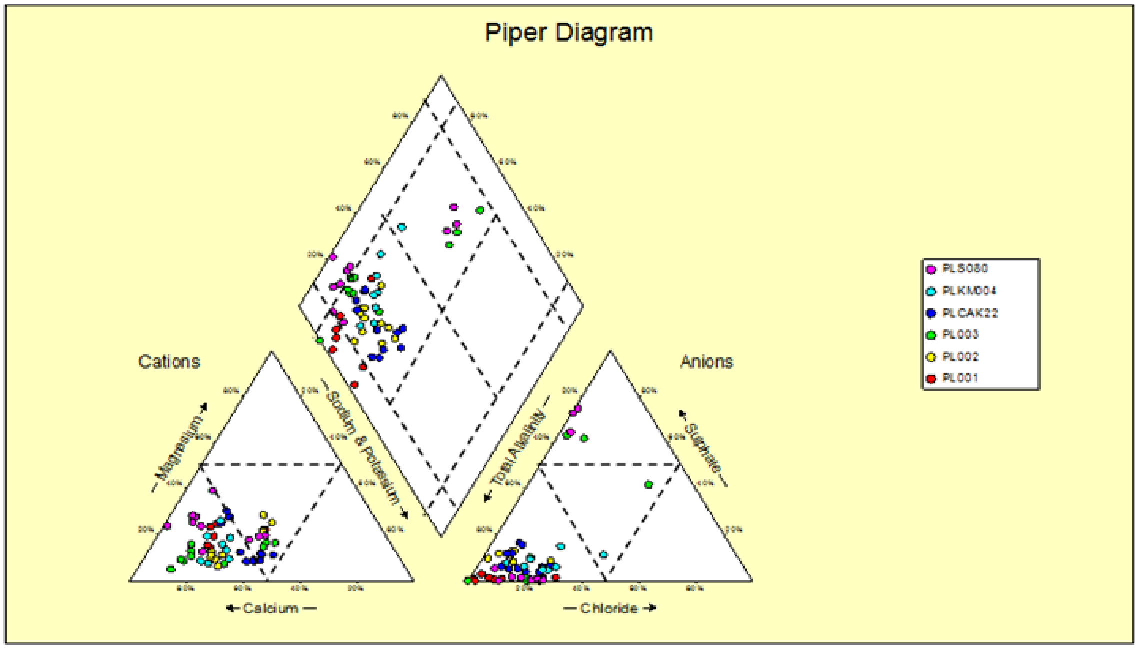


Figure 6. Piper Tri-linear diagram showing hydrochemical facies of groundwater during the dry season in the different boreholes of Pallisa District in eastern Uganda.

of the carbonate system. A flow diagram in Figure 7 provides the following stages below:

Stage 1: Carbon dioxide (CO_2) in the soil medium reacts with the infiltrating rain water to form carbonic acid (H2CO3). Elevated levels of CO_2 are generally expected in the soil at the site from the respiration of organic matter.

Stage 2: Infiltrating recharging waters rich in $H_2CO_3^-$ interacts with calcrete reacting with calcite ($CaCO_3$) and dolomite $CaMg(CO_3)_2$ minerals within the deposits. The reaction leads to the dissolution of calcite and dolomite minerals, thus providing Ca^{+2}, Mg^{+2} and HCO_3^- ions in the groundwater.

Stage 3: is controlled by cation exchange reactions

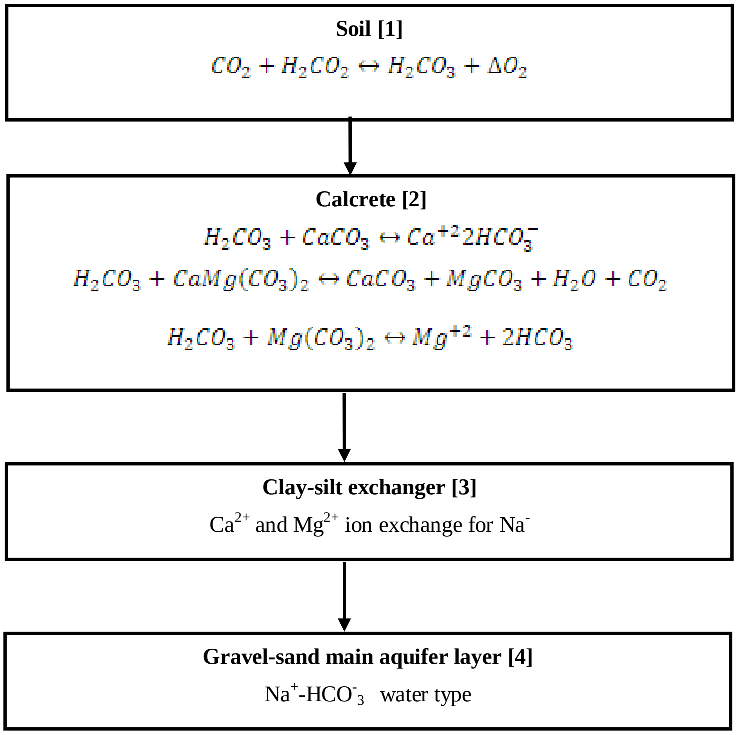


Figure 7. A flow diagram showing the idealised carbonate system reactions that occur during the recharge process as the water passes through the aquifer media of different chemical and physical properties.

where Ca^{+2} and Mg^{+2} exchanges for Na^+ on alluvium silt-clay sediments. The silt-clay sediment absorbs Ca^{+2} and Mg^{+2} while Na^+ is released into the groundwater solution. Although no practical tests were conducted to test the occupation of the exchanger sites, the study seeks to assess the possible contribution of ion exchange process to the elevated Na^+ based on theoretical understanding and field results

Stage 4: defines the existing groundwater type from the preceding reactions in stages 1 to 3. The process typically takes place during groundwater recharge where Ca^{+2}, Mg^{+2} and HCO^-_3 ions often flushes salt water out of the aquifer. The resulting groundwater in the gravel-sand main aquifer layer is Na^+-HCO_3^- type.

Nitrates as nitrogen NO_3^-(N)

Studies have also established a correlation between strong exposure to nitrates in drinking water and the incidence of gastric and intestinal cancer (Cissé and Mao, 2008). It is therefore imperative to assess the evolution of NO_3^-(N) in a typical alluvial channel aquifer.

However the low saturated hydraulic conductivities in the vadose zone gives infiltrating recharging waters sufficient time to go through denitrification thereby reducing the NO_3^-(N) levels in the water that reaches the alluvial channel aquifer.

Sodium

High Na^+ concentrations in the groundwater system can be attributed to ion exchange and silicate weathering. Multiple evidences on bi-variate plots to infer the contribution of the ion exchange geochemical process on the enrichment of Na^+ concentrations are presented.

Ion exchange

The Na^+ against Cl^- plot shows that all groundwater samples at the site 1 are located above the 1:1 evaporation line (Figure 8) implying that Halite (NaCl) is not the main source of Na^+ in the groundwater water. The shifting of the groundwater plots from the 1:1 line is due to increased Na^+ concentration and the ion exchange process can be used to explain the effect.

The plot of Ca^{2+} + Mg^{2+} versus SO_4^{2-} + HCO_3^- will be close to the 1:1 line if dissolutions of calcite, dolomite and gypsum are the dominant reactions in a system (Guler et al., 2002). The groundwater sample plots on the right side of the 1:1 line (Figure 9) and according to Fisher and Mulican (1997), ion exchange process tends to shift the sample plots to right. The shift to the right of the 1:1 line is due to the decrease of Ca^{2+}+ Mg^{2+} cations as they leave the groundwater system to occupy the sediments exchange site left by Na^+.

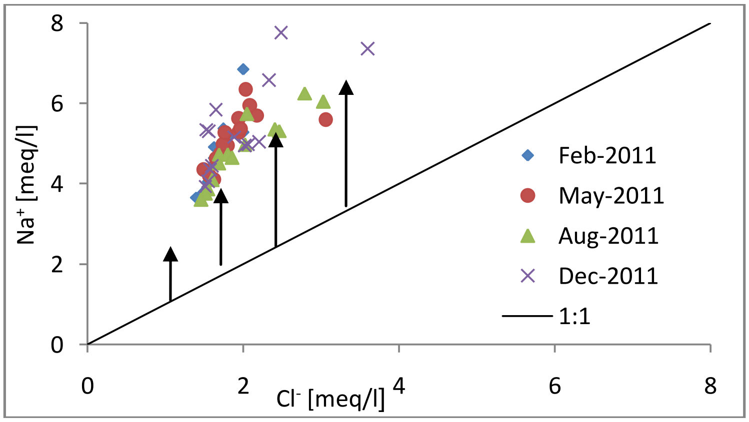


Figure 8. Bivariate plot of Na^+ against Cl^- at the study site; black arrows indicate the contribution of the ion-exchange process and deviation from the 1:1 evaporation line; meq/l– meq/l.

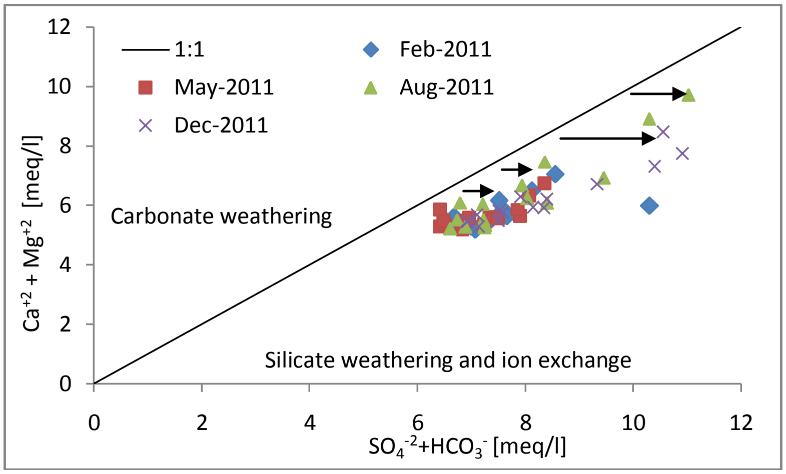


Figure 9. Bi-variate plot showing (Ca^{2+}+Mg^{2+}) against (SO_4^{2-}+HCO^-_3) for the groundwater samples from the alluvial channel aquifer and terrestrial aquifer.

A plot of (Ca^{2+}+Mg^{2+}-SO_4^{2-}-HCO_3^-) against (Na^+-Cl^-) was used to assess the existence of ion exchange reactions in the groundwater systems. By subtracting chloride from sodium chloride (considering that Cl^- is a conservative ion, and assuming that all Cl^- comes from precipitation), groundwater that are not influenced by ion exchange will plot close to zero on this axis.

Figure 10 a-d shows a plot of (Ca^{2+}+Mg^{2+}-SO_4^{2-}-HCO_3-) against (Na^+-Cl^-) for the groundwater samples from boreholes drilled into the alluvial channel aquifer and terrestrial regional aquifer.

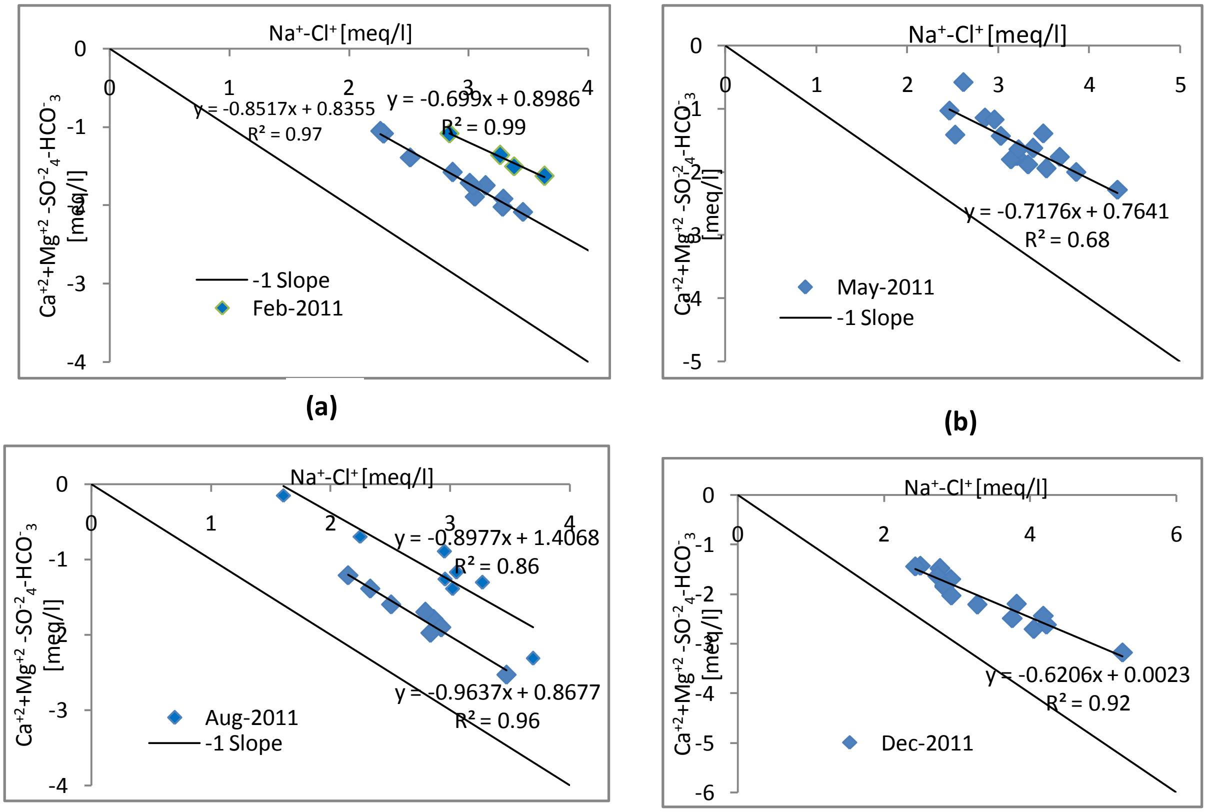
Linear regression plots on Figure 10(a-d) shows that groundwater samples fit into lines that have gradients between -0.69 and -0.96. The gradients of the lines are generally close to -1 and are characterised by a goodness fit of (r^2) ranged between 0.68 and 0.99, thus enhancing evidence about the occurrence of ion exchange in the alluvial aquifer. The two different slopes on the (Ca^{+2}+Mg^{+2}-SO_4^{-2}-HCO_3^-) against (Na^+-Cl^-) plot of February 2011 (Figure 10, a) and August 2011 (Figure 11, c) implies that there might be two levels of ion exchange in the groundwater system. There is however no field evidence to ascertain the existence of different levels of ion exchange.

Silicate weathering

The unconsolidated channel deposits at the site are rich in silica as they formed at least 60 % of the total compositions major oxide elements. In general, silica is one of the most abundant oxides in the earth's crust. High silica concentration in groundwater (> 20 mg/l, Table 1) is derived from silicate weathering (Equation 4).

$$\underset{\text{(Albite)}}{2NaAlSi_3O_8}+2H_2CO_3+9H_2O \rightarrow \underset{\text{(Kaolinite)}}{Al_2Si_2O_5(OH)_4}+2Na^++4H_4SiO_4+2HCO^-_3 \quad (4)$$

Based on (Equation 4), silicate weathering can also increase the concentration of $HCO3^-$ and Na^+ in the ground water. The contribution of silicate weathering on the increase of ground Na^+ can be also explained by the



(a) (b) (c) (d)

Figure 10. Relationship between (Ca^{+2}+Mg^{+2}-SO_4^{-2}-HCO_3^-) against (Na^+-Cl^-) for groundwater sampled in February 2011 (a), May 2011 (b), August 2011(c) and December 2011 (d).

trends shown on scatter plots on Figure 8 to Figure 10.

Saturation indices

Saturation indices for quartz, dolomite and calcite were determined using the Phreeqc hydrogeochemical model (Parkhusrt and Appelo, 1999). The calculations were conducted using thermodynamic data contained in the database of the Phreeqc for Windows software. Mineral equilibrium calculations for groundwater are useful in predicting the presence of reactive minerals in the groundwater system and estimating mineral reactivity.

Figure 11 shows the relationship between the saturation indices of calcite and dolomite minerals for the groundwater samples collected during the monitoring period. Calcite and dolomite saturation are all positive indices and plot in quadrant A which implies that the groundwater had sufficient residence time for supersaturation to occur. The saturation index of calcite is lower than of the dolomite ($SI_{dolomite}/SI_{calcite} \geq 2$); hence the later is most likely to precipitate first. The groundwater is supersaturated with respect to quartz which is the most dominant mineral in the channel deposits. Groundwater samples have low concentrations of SO_4^{-2} in the range of 20-53 mg/l, thus the water is undersaturated with respect to gypsum (SI < -1.5). No gypsum minerals were detected in the channel deposits and hence the most likely source of SO_4^{-2} is the old waters.

Sulphate and chloride

Figure 12 shows a scatter plot of chloride against sulphate ions. High correlation between chloride and sulphate ions can be a reflection of similar processes that are affecting the two ions. In shallow alluvial channel aquifers along the riparian zones, sulphate and chloride ions in groundwater can be both enriched due to the evapotranspiration process. Scanlon and Goldsmith RS (2009) reported high correlation (r = 0.85) of total sulfate and chloride inventories in profiles beneath natural ecosystems.

Groundwater quality

The groundwater quality is evaluated based on its suitability for drinking, agricultural, and domestic use

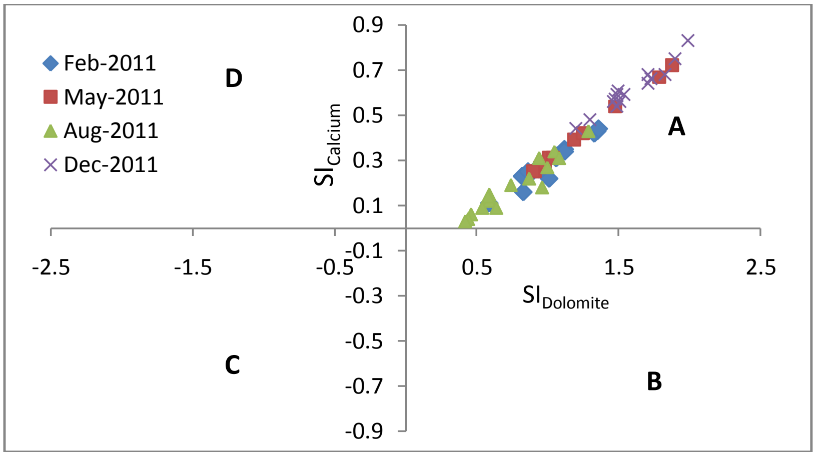
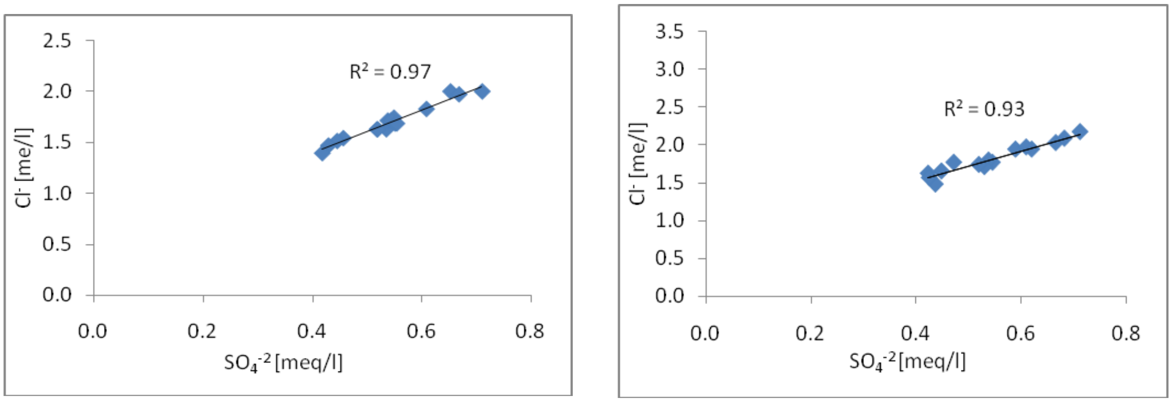
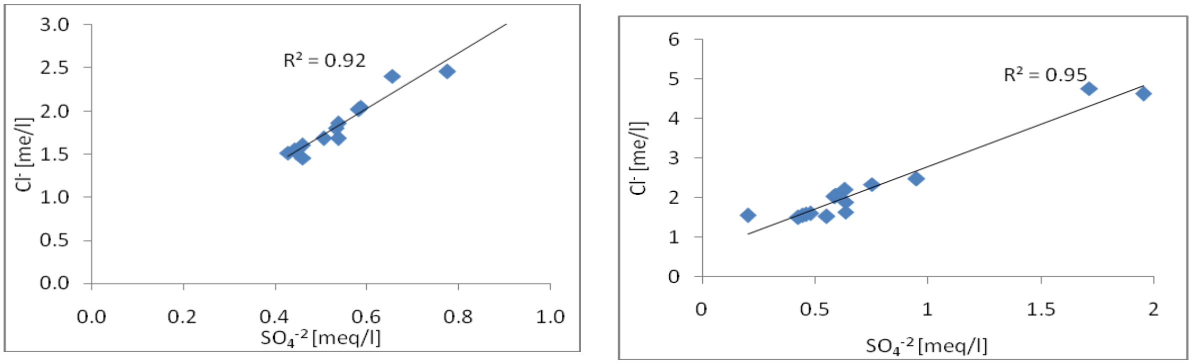


Figure 11. Relationship between the saturation indices for calcium/calcite and dolomite; quadrants define: A-Dolomite and calcite supersaturation, B-Dolomite undersaturation and calcite supersaturation, C-dolomite and calcite undersaturation; and D-dolomite supersaturation and calcite undersaturation.



(a) Feb -2011

(b) May -2011



(c) August -2011

(d) December-2011

Figure 12. Scatter diagrams showing Cl^- against SO_4^{-2} plots for groundwater samples collected in: (a) February, (b) May 2011, (c) August and (d) Dec 2011.

using local and international guidelines. The possible influence that that hydrogeochemical processes has on the overall groundwater is described and explained. High concentrations of Na^+ above the (SANS 1996) limit concentration of ≤ 100 mg/l is due to the ion exchange and silicate weathering hydrogeochemical process. Ca^{+2} and Mg^{+2} exceeded the target levels of 32 mg/l and 30 mg/l respectively in the groundwater samples. The

Table 2. Classification of groundwater based on hardness (Sawyer and McMcartly 1967).

Total hardness as $CaCO_3$ [ppm]	Water class	Number samples
0-75	Soft	0
75-150	Moderate Hard	0
150-300	Hard	53
> 300	Very Hard	15

calcite weathering and dissolution processes are responsible for high Ca^{+2} and HCO_3^-. Dissolution and weathering of dolomite minerals in the sedimentary deposits contributes to high Mg^{+2} concentrations.

Hardness

Classification of groundwater based on total hardness shows that 81 % of the water is hard. The total hardness value ranges from 240 mg/l-500 mg/l. The seepage groundwater sample has the highest total hardness and is mainly attributed to the accumulation of Ca^{+2} and Mg^{+2} cations along the flow path to the discharging zone. Table 3 shows the classification of groundwater based on the total hardness for the samples collected during the monitoring period.

It is worth to point out that the total hardness is above the World Health Organization (WHO) (1993) standard of 100 mg/l. Although the total hardness exceed the international target water quality concentration levels, it does not constitute a serious threat because the hardness is only temporary. According to WHO (2010), water with hardness above 200 mg/l has potential to cause scale deposition in the water distribution system, heating and boiling equipment. On the hand, soft water (hardness < 100 mg/l) often result in the corrosion of pipes and this can lead to dissolving of heavy metals from the pipes in the drinking water (National Research Council, 1977).

Irrigation water quality

The suitability of groundwater for irrigation requirements is often determined using the Sodium Adsorption Ratio (SAR) parameter mainly because it can quantify the potential effects of alkali and sodium hazard on crops (Arumugam and Elangovan, 2009). Figure 13 (for site 1) shows the classification of groundwater based on salinity and alkalinity hazard of irrigation (US Salinity Laboratory Staff, 1954).

The groundwater is characterised by high salinity (C3) and would suit soils with improved drainage to flush out the salts. From an irrigation requirement point of view, the groundwater has generally low Na^+ concentration and there is less risk of harmful Na^+ effects. High HCO_3^- concentration in the groundwater also has great potential to precipitate out of the calcium carbonate thereby increasing SAR in the groundwater. Total bicarbonate levels in the groundwater ranges from 373-613 mg/l and has a major contribution on elevated calcite and dolomite saturation indices.

The conductivity values ranges from 150 - 370 mS/m (SA Drinking water). The large variation in EC is mainly attributed to lithologic composition and anthropogenic activities prevailing in this region. Normally, irrigation water with an EC of < 70 mS/m causes little or no threat to most crops while EC > 300 mS/m may limit their growth (Tijani, 1994). Figure14.

Based on the WISH classification for South African Drinking waters (2005) (for site 2) and the US Laboratory classification (modified after Richards, 1954) (see Figure 15) the salinity hazard for water samples in Pallisa District is low (2.2%), medium (21.7%), high (34.8%) and very high (41.3%). Most of the groundwater samples belong to high salinity hazard (C3) as per the salinity hazard classification in the study area. Nineteen samples plotted in very high salinity (C4 field), sixteen samples plotted in the high salinity hazard category (C3) while ten of the samples belong to the medium salinity hazard category (C2) and one in low salinity zone (C1).

Groundwater that falls in the low (C1) and medium salinity hazard class (C2) can be used in most cases without any special practices for salinity control. However, water samples that fall in the high salinity hazard class (C3) may have detrimental effects on sensitive crops and adverse effects on many plants. Such areas require careful management practices. Very high salinity water (C4) is not suitable for irrigation under ordinary conditions but may be used for salt tolerant plants on permeable soils with special management practices (Figure 15).

Trace elements

Table 4 (for site 1) shows the maximum and minimum concentrations of trace elements analysed in the groundwater. The concentration levels of Fe^{2+} and Al^{3+} trace elements in the groundwater are all below SANS (1996) limit values. Manganese exceeded the water quality limit value of (0.05 mg/l) in the groundwater samples and can be attributed to sources of manganese oxides in the sediments. In general, trace elements in groundwater are often dissolved in very small quantities,

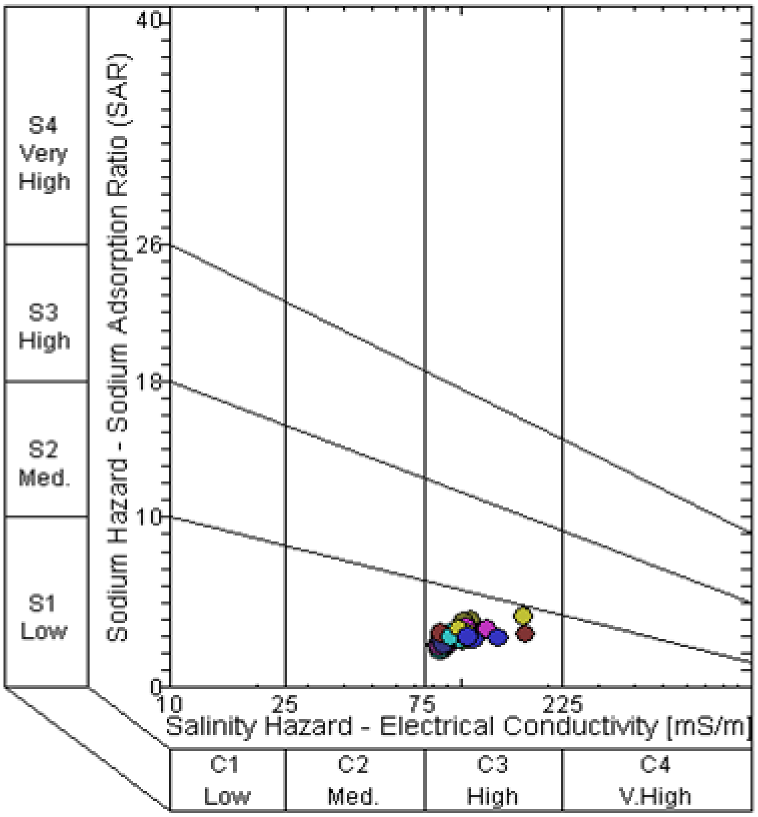


Figure 13. Classification of groundwater based on salinity and alkalinity hazard of irrigation requirements for study site 1.

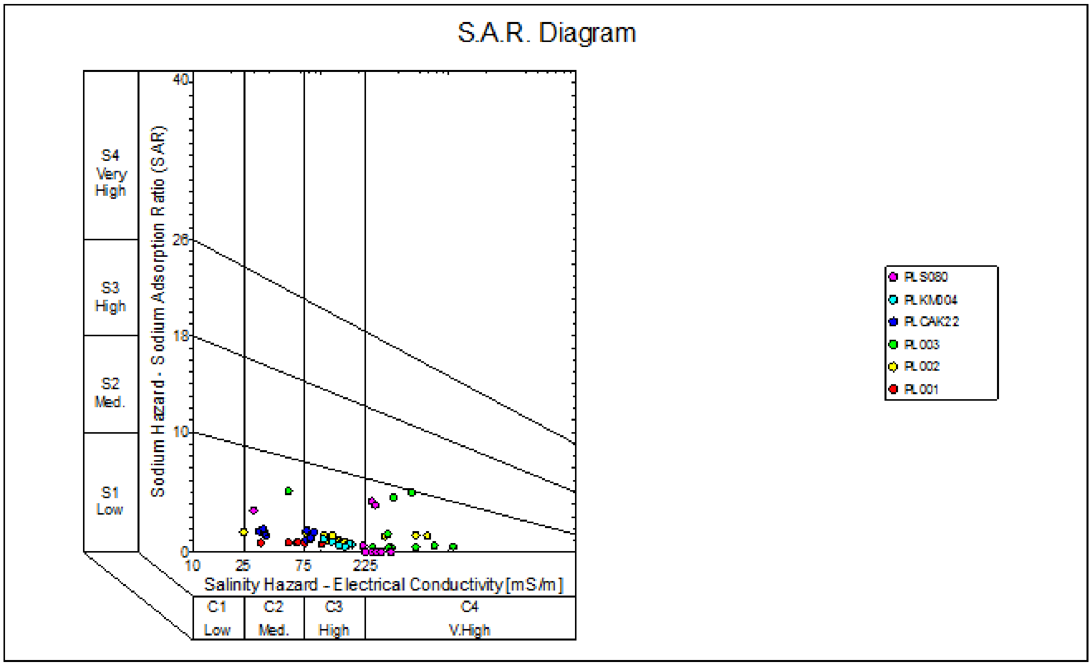


Figure 14. Groundwater classification for the different boreholes sampled during the wet and dry seasons in Pallisa District.

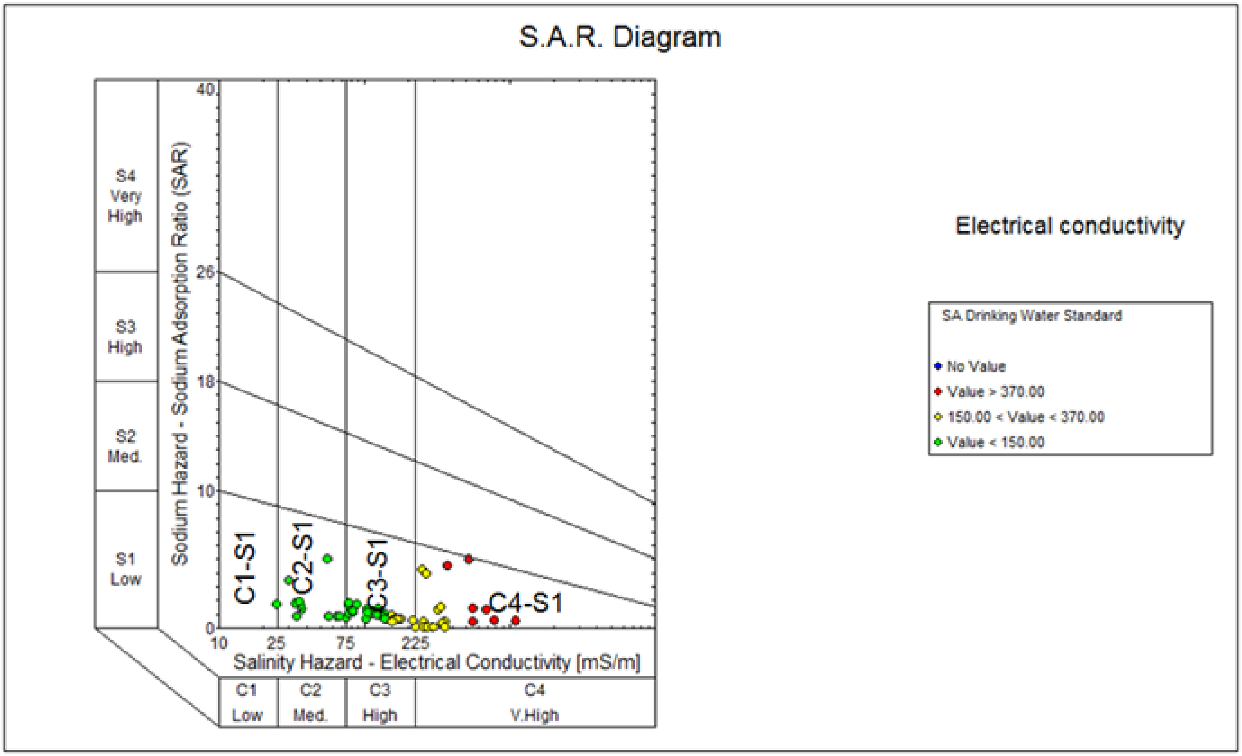


Figure 15. Salinity diagram for classification of irrigation waters (after Lukas, 2003; modified and adapted from Richard, 1954; Wilcox, 1948 and 1995).

Table 4. Maximum and minimum concentrations of trace elements analysed in the groundwater.

Ions	Minimum [mg/l]	Maximum [mg/l]	(SANS 1996) [mg/l]
Fe^{+2}	0.002	0.067	≤ 0.1
Mn^{+2}	0.006	0.090	≤ 0.05
Al^{+3}	0.008	0.049	≤ 0.15

typically less than 1 mg/l (USGS 1993). The presence of Mn^{2+}, Fe^{2+} and Al^{3+} in low concentrations is due to the dissolution of natural tracer elements from the aquifer sediments under anaerobic conditions into the groundwater.

The hydrogeochemical investigation and analysis shows that there is no distinction between the groundwater chemistry of deep and shallow boreholes. The results of this investigation can be used to ascertain the existence of one aquifer system as had been observed during borehole drilling. During groundwater abstraction at the site, water comes from the high transmissivity gravel-sand deposits which are conceptually the main aquifer yielding layer. The groundwater samples from the seepage zone also exhibit similar hydrogeochemical trend to the rest of the groundwater samples collected from the boreholes. It is therefore evident that the shallow alluvial channel aquifer is losing groundwater into the river, thereby making the river a “gaining” one.

In addition, the discussion based on the study site 2 made it possible to collate available groundwater data and information in Pallisa District. This information has been used to assess the groundwater resources in the Kyoga basin. The boreholes within the interior of Pallisa District and the groundwater sampled from shallower depth are of a much better quality. No microbiological analyses were performed on the samples, but a H_2S test was used in the field and it gave an indication that some forms of bacteria are present. The shallow aquifer has modern age waters (Nyende, 2013b) and is rapidly recharged by precipitation that is prone to contamination by activities on the ground surface such as poor sanitation practices, overgrazing and farming practices including application of fertilizers. The source for this could be probably the extensive use of on-site sanitation systems (mostly the pit latrines) in many parts of the rural areas of Pallisa district. The investigation indicates that among major cations, Ca^{+} is generally dominant representing on average 64.11% of all the cations. The order of anions abundance is $HCO_3^{-} > Cl^{-} > SO_4^{2-}$.

Based on TDS, 46% of water samples are suitable for drinking purposes. Salinity diagrams reveal that except for the southern parts of study area; most of the groundwater samples are not suitable for irrigation purposes under normal condition. The salinity hazard for water wells is classified as medium, high and some show very high salinity. Alkali hazard also is classified from low hazard to very high. Therefore, salinity is the principal concern in irrigated agriculture in Pallisa area. The fluoride levels reflect the distribution of granite rather than the contamination sources. Geochemical data in Pallisa area indicates that the polluted sources degrade the groundwater quality along the downgrading zone.

CONCLUSION

The investigations of the hydrogeochemical processes in an alluvial channel and fractured granitic aquifers located in Karoo basin of Southern Africa and eastern Uganda respectively were aimed at a comparative study in identifying and describing the groundwater evolution and its contribution to the groundwater quality. The XRF and XRD analyses were performed on representative geological samples to identify and quantify the major elements oxides and minerals in the sediments. The XRF and XRD analysis of geological samples shows that the channel deposits are dominated by SiO_2 element oxides and quartz minerals thus high concentrations of Si were found in the groundwater. Samples of groundwater were collected in July–October 2010, December 2010-March 2011, May 2011, August 2011 and December 2011. The study utilized the conventional piper diagram, bi-model plots, WISH Program and PHREEQC hydrogeochemical model to analyze groundwater chemistry data. Detailed studies of the hydrogeochemical processes in the alluvial and granitic fractured aquifer systems show that dissolution of dolomite and calcite minerals, and ion exchanges are the dominant hydrogeochemical processes that controls the groundwater quality.

The major conclusions obtained from the research conducted at the two study sites are:

- The groundwater quality of the alluvial channel aquifer is largely controlled by calcite and dolomite dissolutions, silicate weathering and ion exchange hydrogeochemical processes.
- The investigation revealed that the alluvial channel aquifer groundwater has evolved from Ca^{2+}-Mg^{2+}-HCO_3^- recharge waters that go through ion exchange with Na^+ in the clay-silt sediments to give a Na^+-HCO_3^- water type.
- Calcrete deposits are the source of Ca^{2+}, HCO_3^- and Mg^{2+} ions, while the clay-silt provides Na^+ cation exchange sites for Ca^{2+} which was detected in the sediments.
- The hydrogeochemical investigation shows no distinction between the groundwater chemistry of deep and shallow boreholes which imply the existence of one aquifer system or of two connected aquifers have mixed groundwater.
- The groundwater chemistry of the alluvial channel aquifer and terrestrial aquifer is controlled by the interactions of recharging waters and minerals of the aquifer material, rather than by a chemical evolution of water along general directions of local groundwater flow and seasonal variations.
- The study shows the potential usefulness of simple bivariate plots as a complimentary tool to the conventional methods for identification and analyzing groundwater hydrogeochemical processes. The plots simplify analysis of the groundwater chemistry processes and should be used to complement conventional tools.
- The spatial variation in chemical, hydraulic and solute transport properties is attributed to aquifer heterogeneity which is largely depended on lithology and the formation processes.
- The boreholes plotting in the freshwater region have a Ca^{2+}~~/~~ -Mg^{2+}-HCO_3^- major ion composition. This is characteristic of freshly recharged groundwater that has equilibrated with CO_2 and soluble carbonate minerals under open system conditions in the soil zone and;
- The water from boreholes located in the inland area of recharge is fresher than the ones located in the discharge area ~~of~~ (boreholes near Lake Kyoga).

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