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Trace element constraints on the origin and evolution of groundwater from southwestern periphery of the Volta Lake, Ghana

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ABSTRACT

The level of trace elements in groundwater from the southernwestern periphery of the Volta Lake (Manya Krobo area) was determined and their origin assessed by estimating pH, TDS, saturated index (SI), hardness, alkalinity, hardness alkalinity ratio (HAR), groundwater acidification (Aci) and acid neutralizing capacity (ANC). Aluminum, manganese, iron and vanadium concentrations in groundwater at most areas were higher than originally anticipated (i.e. in excess of the WHO recommended guideline values) of a non-mining area. Dissolution of aquifer materials probably enhanced by moderately acidic waters is responsible for mobilization of trace elements in the groundwater in the area. The groundwater samples are generally undersaturated with respect to most of carbonate phases. Though pH showed slightly acidic waters, calculated groundwater acidification (Aci) was low (in fact, negative) and hardness alkalinity ratios (HAR) were consistently less than unity suggesting influence of weak acid probably of natural origin. The positive acid neutralizing capacity (ANC) values recorded throughout indicated a long-lasting superfluous in the acid-buffering capacity of the groundwater in the Manya Krobo area along the Volta Lake. Therefore, it is necessary to incorporate other trace metals removal techniques into borehole operations beyond removal of iron.

Introduction

Trace elements make up only 1% of naturally-occurring dissolved constituents in groundwater, but can sometimes make it unfit or unacceptable for consumption. Reactions of rainwater in the soil/rock profile during infiltration and percolation provide groundwater with its essential mineral composition. It takes up carbon dioxide, and the resultant weak acid dissolves soluble minerals. In humid climates with regular recharge, groundwater moves continuously and contact times can be relatively short with only the most readily soluble minerals being dissolved.

The concentration of some of these minerals can also be increased from polluting activities at the land surface, and it is important for management purposes to differentiate anthropogenic impacts from naturally-occurring problems; this will require investment in detailed groundwater investigation and monitoring.

In rural communities in Ghana, groundwater is a major source of year long potable water supply but without problems such as high salinity in coastal areas and mobilization of trace elements in mineral mining areas. Kaka et al (2011) found that groundwater in the Manya Krobo area along the Volta Lake were suitable for domestic and irrigation purposes based on physic-chemical parameters and major ions. In this study, the level of trace elements in groundwater from the southernwestern periphery of the Volta Lake (Manya Krobo area) was determined and their origin assessed by estimating pH, TDS, saturated index (SI), hardness, alkalinity, hardness alkalinity ratio (HAR), groundwater acidification (Aci) and acid neutralizing capacity (ANC).

Materials and Methodology

Study area

Location

The study area lies between latitudes 6.2-6.50N and Longitudes 0.3 - 0.00 W of the Greenwich Meridian. Land use in the study area is agriculture, mainly subsistence crop production and animal husbandry. Varieties of herbicides are also employed in preparing farmlands and weed controls. Inorganic fertilizer and other agrochemical are sparingly used in the area.

The undulating topography of the area ranges between 660 meters above sea level in the south-western part of Sekesua and about 50 meters above sea level at margins of the Volta Lake.

The area experiences two major seasons, namely wet and dry seasons. The rainy season exhibits double maxima: the main rainy season occurs between April and July, whilst the minor one falls between September and October of every year. The dry and warm season are experienced from November to March.

Geology and hydrogeology

The area under study is underlain by rocks of the Voltaian Super-group and the Buem structural unit (Fig. 1.) The Voltaian Super Group is made up of Neo-proterozoic to Early Cambrian, lithologically diverse platform sediments. There are few detailed geologic descriptions of sediments of the Voltaian Group sequences; subdivision of the group is difficult due to poor exposure and the lack of laterally persistent lithological marker beds or fossils (Anani, 1999). The group has generally been divided into three formations, each separated by an unconformity marked by a tillite (Fig. 2). The Lower Voltaian

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Formation consists of a massive to cross-bedded arkosic sequence.

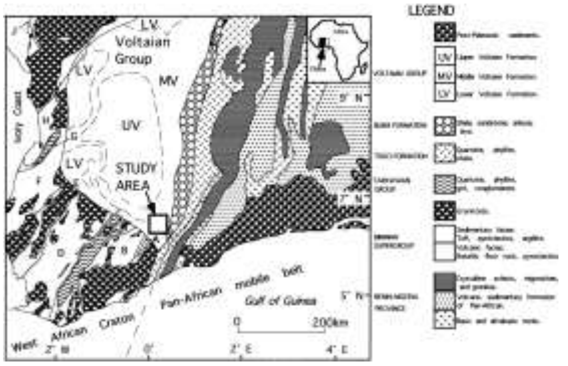

Fig. 1. Generalized geological map of the West African Craton. Modified after Ako and Wellman (1985). Belts and basins in the Birimian are defined after Leube et al. (1990) as follows: *A* = Kibi–Winneba belt; *B* = Cape Coast Basin; *C* = Ashanti belt; *D* = Kumasi Basin; *E* = Sefwi belt; *F* = Sunyani basin; *G* = Bui belt; *H* = Maluwe Basin; *I* = Bole–Navrongo belt; *J* = Lawra belt.

The Middle Voltaian Formation consists of a flyschoid sequence, and the Upper Voltaian Formation consists of a molasse sequence (Affaton et al., 1980). The Lower Voltaian Formation unconformably overlies the Birimian Supergroup.

The Middle Voltaian Formation overlies the Lower Voltaian Formation with a slight angular unconformity. Conglomeratic beds interpreted as tillites form the basal part of the Middle Voltaian Formation (Petters, 1991). Shales, siltstones and sandstones, glauconitic in part, constitute the principal lithologies of the Middle Voltaian Formation. The Upper Voltaian Formation is divided into a lower and an upper unit.

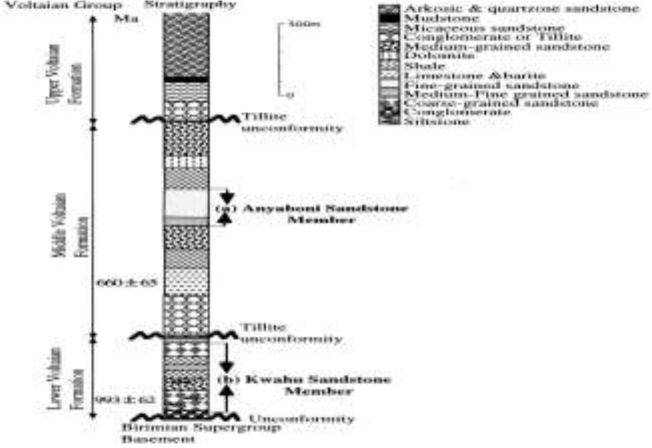

Fig. 2. Sequence of the Voltaian Group indicating horizons of both the Kwahu Sandstone Member and the Anyaboni Sandstone Member (redrawn after Cahen et al., 1984 and Petters, 1991)

The lower unit consists mostly of dirty-yellow, fine-grained, thinly bedded, micaceous, feldspathic quartz sandstones with subordinate argillite intercalations. The upper unit consists of white to whitish-yellow, massive, fine- to medium-grained, cross-bedded arkosic and quartzose sandstones. The Upper Voltaian Formation occurs as scattered outcrops in the central part of the Voltaian Basin, with an average thickness of about 400m. Hydrostratigraphic units of the Voltaian group are identified as Anyaboni and Kwahu sandstone Members (Saunders, 1970 and Anani, 1999) (Fig. 2).

A few localities in the study area are situated in the lower part of the Middle Buem Member of the Buem Formation. The Buem formation consists of a thick sequence of shale, sandstone, and volcanic rocks with subordinate limestone, tillite, grit and conglomerate. The sandstones overlie the basal beds of shale and the conglomerate and tillite overlie the sandstone. (Dapaah-Siakwan and Gyau-Boakye, 2008).

Methodology

A total of 25 groundwater samples were collected across the catchment during the periods of September, 2009. The geographical location of all sampling sites was recorded using a hand-held global positioning system (GPS) (Fig.3).

Alkalinity and physical parameters such as electrical conductivity (EC), total dissolved solids (TDS), temperature and pH of the samples were measured in the field using Hatch field titration kit and portable EC and pH meters. Boreholes were purged until stable readings for the physical parameters were obtained.

Samples were subsequently filtered through 0.45 micron membranes and collected in acid-washed, well-rinsed polyethylene bottles. Filtered and acidified (1% v/v HNO_3) samples were used for major cations and trace metals. The sulphate and nitrate ions were analyzed using a UV-Visible spectrophotometer (Shimadzu). The chloride ion concentrations in the water samples were determined by titration.

The trace elements were determined by Instrumental Neutron Activation Analysis (INAA). In this analysis, 0.5ml volume of each sample was transferred with calibrated Eppendorf tip ejector pipette (Brinkmann Instruments, Inc. Westbury New York) into pre-weighed 1.5 ml polyethylene vials to obtain a mass of 500mg. A piece of clean cotton wool (pre-weighed) was put gently into the sample in the vial, caped and heat-sealed. The cotton wool was added as a safety measure to avoid the sample spilling and spreading radioactive material in case the vial opens in the reactor or when taken out of the reactor. Irradiations were performed using the Ghana Research Reactor-1 (GHARR-1) facility at Ghana Atomic Energy Commission, Kwabenya. The elements of interest were assayed using different timing parameters, namely the irradiation time (t_i), the decay time (t_d), and the counting time (t_c). These timing parameters mainly depend on the half-life of the radionuclide produced, that is, short-lived nuclides ($t_{1/2}$ less than a few hours), medium-lived radionuclides ($t_{1/2}$ longer than several hours), and long-lived radionuclides ($t_{1/2}$ longer than several days).

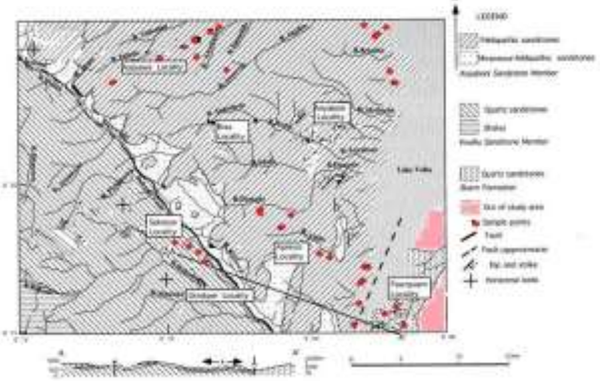

Fig.3: Sampling location map of the study area

Samples and standards were sent into one of the available inner irradiation sites with a thermal flux, 5×10^{11} $ncm^{-2}s^{-1}$ when the reactor (GHARR-1) is operated at 15kW by means of a pneumatic transfer system (rabbit system) at pressure of 65 psi. The t_i, t_c and t_d for the water samples were 2, 10 and ≤ 3 minutes respectively for Al, Ca, Mg, Mn, Cu, and V. For the medium-lived radionuclides, the samples were irradiated for 1 hour, delayed for about 24 hours and counted for 10 minutes.

Computer-based gamma-ray spectroscopy system of an N-type high purity germanium (HPGe) detector Model GR2518, a HV power supply Model 3105, a spectroscopy amplifier Model 2020, all manufactured by Canberra Industries Inc., an 8k Silena-Emcaplus multichannel analyzer (MCA) emulation software card and a 486 Micro-computer for spectrum data evaluation and analysis was used. The detector operates on a bias voltage of 3000 V and has resolutions of 0.85 keV (FWHM) and 1.8 keV (FWHM) for ^{57}Co and ^{60}Co gamma-ray energies of 122 keV and 1332.5 keV, respectively. The relative efficiency of the detector was 25%.

The qualitative analysis, which involves the identification of various elements in the samples, and the quantitative analysis of concentrations, were achieved using the gamma-spectrum software of the MAESTRO 32.

Results and Discussion

Major ion chemistry

The summary results of major ions, non-ionic parameters and trace metal concentrations measured in the 25 groundwater samples are presented in Tables 1. The suitability of groundwater for drinking and irrigation purposes based on non-ionic and major ions was vividly evaluated in Kaka et al., 2011.
Major ions revealed HCO_3 type dominated the anions and Na-K type dominated the cations during the post monsoon period of September 2009 resulting into Na–K–HCO_3-Cl (48%), Na–HCO_3 (40%) and Na–Cl (12%) facies. HCO_3^- and Na^+ dominant water normally indicates ion-exchanged waters, although the generation of CO_2 at depth can produce HCO_3^- where Na^+ is dominant under certain circumstances (Winograd and Farlekas, 1974). Based on Cl, SO_4, HCO_3 concentrations, the groundwater sources were categorized as normal chloride (92%) and normal sulphate (100%) and normal bicarbonate (56%) types.

Salinity of groundwater at the margin of Volta Lake

The salinity of the groundwater in the periphery of the Volta Lake varies from 0.4 to 1.5‰ as compared to salinity of 0.1 to 0.3‰ in high grounds distant from the Volta Lake.

Origin of saline water in sedimentary aquifers has variously been ascribed to processes of seawater intrusion, dissolution of evaporite deposits and shale-membrane filtration of meteoric water (Graf *et al.*, 1966; Carpenter, 1978; Hanor, 1979). The former process in this case may be ruled out since the study area is about 60 miles north of the sea (Gulf of Guinea). Residence of fluids in the sedimentary basins may also play crucial roles in the subsequent chemical evolution of such saline fluids. The geology of area reports patches of clay and shale at bank of the Volta Lake and these may host gypsum and rock salt. Clay and shale are hydroaluminum silicates that by themselves do not add salts to the water that comes in contact with them. However, clay and shale often contain veins and nodules of gypsum, pyrite, and rock salt. Clay and shale are impermeable and form aquicludes rather than aquifers, but because of the high solubility of gypsum and especially rock salt, groundwater in contact with clay and shale at the base of aquifers often gets saline and is of poor quality.

Trace elements

Trace element concentrations in groundwater can sometimes make it unfit or unacceptable for consumption though they constitute only 1% of naturally-occurring dissolved constituents in groundwater. Physico-chemical conditions such as temperature, pH and Eh often enhance their dissolution in aqueous systems.

The pH of the groundwater in the study area varies from 5.20 to 6.92. These could be described as moderately acidic waters. Sour tasted groundwater is a reminiscence of acidic waters, but was not pursued in this study as it is highly subjective. A major consequence of acidic waters is mobilization of trace metals. It is evident in Table 1 that there is a myriad of variation in the concentration of some trace metals in the sedimentary Voltaian.

Aluminium (Al)

Aluminium concentration was relatively high in all the boreholes in the study area. Values ranging from 4714.9 to 36982.0µg L^{-1} with mean concentration of 15686.2µg L^{-1} were obtained. Its mean concentration was relatively higher than that obtained in natural waters (0.2mg/l). Very high values were detected around the Aworwoso, Seseamang, and Akrusu Yiti areas all in the Anyaboni formation. This means that the rocks could contain much Al in these areas. It was also possible that the exceptionally high Al concentration could arise from microgibbsite passing through the filters. Pelig-Ba (1996) similarly obtained as high as 47970µg/L of Al in Voltaian terrain in the Upper West Regions of Ghana.

Aluminium forms during mineral weathering of feldspars, such as orthoclase, anorthite, albite, micas and bauxite, and subsequently ends up in clay minerals of kaolinite or soils and concentration in groundwater may also be attributed to a number of factors including the availability of dissolved organic matter (Edmunds et al., 1992). The presence of chelating agents such as fulvic and humic acids are capable of raising the solubility of Al to several orders of magnitude (Bolt and Bruggenwert, 1978).
The most abundant aluminium compounds are aluminium oxide and aluminium hydroxides, and these are insoluble in water. Aluminium oxide may be present in water in alkalic form:

$2Al_2O_3\,(s) + 6H^+\,(aq) \rightarrow Al^{3+}\,(aq) + 3H_2O\,(l)$.

The other ionic species of Al forms hydroxy complexes whose stability is dependent on pH, that is, the stability increases with rising pH of the water (Drever, 1997).

Iron (Fe)

The presence of Fe in water in high concentration usually gives aesthetic problems to water consumers. In this study, total Fe concentrations range between 260 and 2476µgL^{-1}. It is possible that some of the increase of Fe concentration could be attributed to the corrosion of pump parts as was shown by Langaneger (1987) and Pelig-Ba (1991). The contribution of Fe from the local bedrock would therefore not be overruled.

The Eh-pH diagram for the groundwater system at 25^{0}C and 1 atmosphere within the study area is presented in Fig. 4. Thermodynamic data of the dissolved Fe redox species were cited from Stum and Morgan (1991). Consistent with field observation, the samples plot in the Fe^{2+} indicating amorphous iron as the control on Fe concentration in the groundwater. The solubility of iron phases is greater when the dissolved iron species is the reduced Fe^{2+} (DeLaune and Reddy, 2005). In other words, Fe is more soluble under reducing conditions. Because most natural waters have pH values in the range 5.5-8.5, they will not contain much iron unless redox conditions are relatively reducing.

Nonetheless, boreholes with high iron concentration also have $Fe^{2+}/SO_4^{2-} > 1$ suggesting that SO_4^{2-} reduction has taken place or confirming the absence of gypsum in the area.

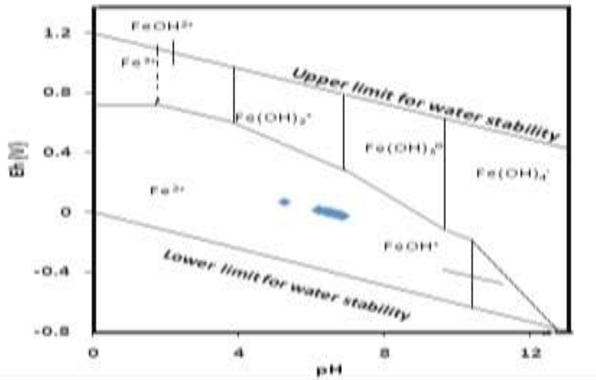

Fig. 4: Eh-pH diagram showing the stability fields of the dissolved Fe RedOx species in the water samples.

Fe^{2+} could have been derived from other sources as well. Hematite dissolution in the presence of proton (acid) is extremely slow but in the presence of organic ligands, the reaction can be fast (Appelo and Postma 1999). Though in this study the content of organic matter in the soil zone has not been measured, the upper zone of soils and lush vegetation of the study area could be a source of high organic content.

The brown colouration of some rivers and streams throughout the year in the study area may be a further indication of the presence of organic matter in the soil zone. Thus, reductive dissolution of iron minerals in the presence of organic matter and perhaps a reductant seems to be a more plausible process through which Fe^{2+} entered the groundwater particularly in the area where the major rock types are sandstone, quartz and limestone.

Additional source of iron could be leaching from ferromagnesian silicates and pyroxenes which may be in the rock types that underlain the study area.

Manganese (Mn)

Mn concentrations range between 941 and 21165µg/L except a groundwater at Asesewa which had extremely high Mn level of 338828µg/L. The groundwater at Asesewa is typically Mn-HCO_3 water type. The concentration of Mn in the area may be attributed to aquifer rocks and also the physicochemical conditions within the aquifer. There are insufficient rock chemistry data to be able to test this hypothesis robustly; however, the broad data distribution suggests that both the water chemistry conditions and Mn mineralogy are significant. Mn deposit is in western part of Ghana at Nsuta. According to Homoncik et al., 2010, the trace metal Mn is ubiquitous in the environment; it is a minor component of most rock types and is also present in soils from weathering and aerial deposition.

Redox and pH conditions may explain Mn distributions in groundwater. At the near neutral pH of all groundwater as in the study area, Mn^{2+} concentrations may be influenced by other factors such as complexation with bicarbonate ions at high concentration (Hem, 1972).

Excessive Mn concentrations can result in metallic tasting water, staining of clothes, dishes, and products such as paper or plastics, and reduced water pressure and flow in pipes from accumulation of Mn oxides (Sly et al., 1990).

Copper (Cu)

Cu concentrations range 10-363µgL^{-1}. The respective mean and median values are 110 and 84µgL^{-1}. The source may be lithology. Under acidic reducing condition, the stable phases of Cu are Cu$^+$ and metallic copper. Metallic Cu would adsorb onto host rock. This means chalcocite (Cu_2S) and cuprite (Cu_2O) are the probable sources of Cu in the water samples in the area.

Zinc (Zn)

Zn concentrations range 44-176µgL^{-1}. The mean value is 74.6µgL^{-}1. WHO (2004) permits 3000µg/L of Zn in drinking water.

Zinc is used as an anti corrosion agent where it is coated on iron pipelines to protect them against corrosion. During the construction of the boreholes galvanized pipelines were used. Corrosion of pump parts could also lead to Zn being released into the groundwater. The use of $CuSO_4$ as fungicide in agriculture provides that Cu could be more easily dispersed in the environment. Zinc may also be transported in organic-rich waters as acetate complexes or many other organic complexes (McPhail et al., 2003).

However, uniform distribution of Zn in the water samples indicates presence of Zn minerals in aquifer materials. The prevailing pH-redox conditions favour solubility and transportation of Zn in groundwater. Zn^{2+}, therefore, is likely the predominant aqueous species of zinc in the catchment.

Chromium (Cr)

Groundwater in the study area has undetectable concentration of Cr (<6µg/L). The host rocks of the groundwater may not contain Cr minerals or pH-redox conditions do not enhance dissolution of Cr species in the in the waters. Under moderately acidic reducing conditions as the case in the area, Cr may exist as insoluble Cr_2O_3 and may adsorb onto aquifer materials.

Cadmium (Cd)

Cd was also not detected in the groundwater samples i.e., <2µgL^{-1}. Cd^{2+} and Cd(OH)$^+$ are the stable species expected in the water samples under acidic reducing conditions but their absence means the minerals may also be absent or the aquifer materials may not be rich in Cd.

Groundwater acidification

The mobilization of some trace metals in groundwater system in the area prompted the authors to investigate acidification status of the resource. The pH of the groundwater in the study area as earlier stated varies from 5.20 to 6.92 and described as moderately acidic waters. According to Berner and Berner (1987), under normal atmospheric conditions, rainwater pH is approximately 5.7 units. Furthermore, Appelo and Postman (1999) stated that natural groundwater pH unaffected by anthropogenic processes is not expected to be less than 4.6. Thus, the moderately acidic nature of the groundwater in the Voltaian Basin accompanied by low concentrations of sulphate and TDS suggest that the acidity is apparently produced by natural processes possibly the production of carbonic acid from the atmospheric CO_2 during rainfall or dissolution of the soil-generated CO_2 and probably small quantities of dissolved organic acids. According to Langmuir (1997), in natural waters having pH range of 4.5–7.0, the acids are weak and usually include carbonic acid and smaller amount of organic acids such as fulvic acids. The CO_2 in the atmosphere is part of the atmospheric gases that occur through natural processes while the soil-zone CO_2 is produced as a result of roots respiration. Organic acids are produced mainly from the decay of organic matter. The lush vegetation and abundant rainfall in the area favours the decay of leaves and tree organic matter. The brown coloration of streams almost throughout the year in the area is an evidence of abundance of organic matter in the soil.

The hardness/alkalinity ratio, defined as

HAR = (Ca* + Mg*)/Alk

where * indicates non-marine or ‘excess’ concentration is a sensitive indicator of the influence of strong acids on natural waters (Jacks and Knutsson, 1981; Jacks et al., 1984; von Bromssen, 1989). Natural waters in equilibrium with atmospheric CO_2 have an HAR value of unity, whereas waters affected by strong, anthropogenic acids have values of two or greater (Jacks and Knutsson, 1981; Jacks et al., 1984). The HAR values along the Volta Lake have been consistently less than unity. This suggests an influence of weak acid probably of natural origin.

However, caution must be used in basing interpretation of natural water acidification on pH trends alone, because of influence by the amount of dissolved CO_2 (e.g. Gorham, 1957; Norton and Henriksen, 1983). Therefore, pH trends are interpreted only in the light of trends shown by other parameters. Henriksen (1979) suggested a method for quantifying acidification of natural waters, as defined by their alkalinity loss (‘acidification’ or Aci = Alk_0 - Alk), whereby the original (pre-acidification) alkalinity (Alk_0) could be estimated from the sum of non-marine calcium and magnesium (hardness). Data for original alkalinity (Alk_0) was not available for that computation. However, following Henriksen (1980), Henriksen and Kirkhusmo (1986) and Henriksen et al. (1989),

$Aci = 0.93(Ca^* + Mg^*) - 14 - Alk + Al$

is used here as a more reliable indicator of acidification than pH, because it avoids the problem of pH dependence upon pCO_2. The Aci value for groundwater along the Lake ranges between -23.7 to -10.7. The negative Aci computed show that groundwater in area were not acidified. The low values might be a result of dissolution of carbonate-rich rocks in the area.

Acid-neutralising capacity (ANC) of the groundwater, defined by

$ANC= (Ca^{2+}\ Mg^{2+}\ Na^{+} + K^{+})-(NO_3^{-}+ SO4^{2-}+Cl^{-}),$

where all concentrations are expressed in $meqL^{-1}$ (Stumm 1992; Caritat 1995) has varied for the sample between 0.16 to 23.10 $meqL^{-1}$. An ANC below 0 means the water is acidic and has no buffering capacity. If the ANC is above 0, the water has some buffering ability (Schmidt and Sharpe, 2002). The relationship between ANC and Aci are presented in Fig. 6. It is obvious from Fig. 6 that though ANC is low in most areas it remains positive for all samples while Aci remains negative. This gives positive acid-neutralizing capacity (NANC). The general trend is that of relatively low ANC (due to insufficiency of carbonate) in Kwahu plateau areas mainly sandstone terrain and bushy vegetation. The positive ANC values recorded throughout indicate a long-lasting superfluous in the acid-buffering capacity of the groundwater.

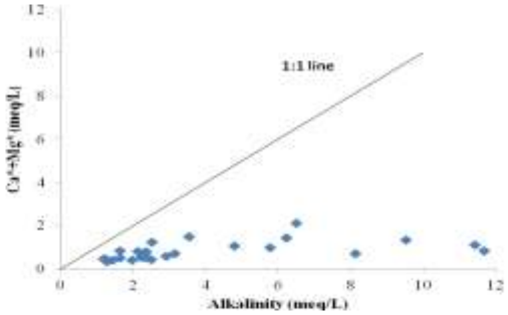

Fig. 5: Relationship between total hardness and alkalinity of Groundwater in the Manya Krobo area.

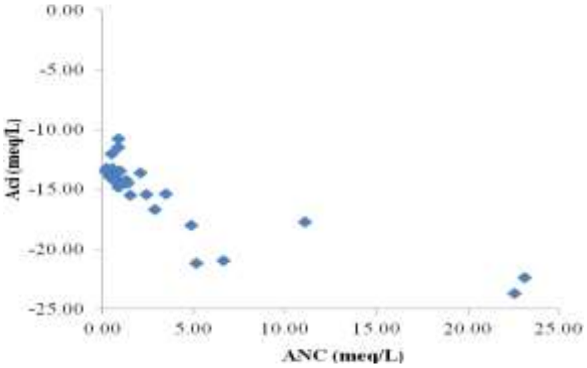

Fig. 6: A scatter plot of acid-neutralizing capacity (ANC) versus acidification (Aci) of groundwater in the Manya Krobo area.

Saturation Index (SI)

Saturation indices have been used copiously in literature to study the hydrochemistry of surface and groundwater bodies (e.g. Roubhia et al., 2009). Saturation indices express the extent of chemical equilibrium between water and mineral phases in the matrix of the aquifers and could be regarded as a measure of dissolution and/or precipitation processes relating to the water–rock interaction (Drever, 1997). The SI of a mineral therefore provides information on whether the mineral is thermodynamically likely to precipitate or dissolve.

The saturation index (SI) of a given mineral is defined as:

$SI = \log_{10}(IAP/Ksp)$

where IAP is the ion activity product, K_{sp} is the solubility product at a given temperature (the thermodynamic equilibrium constant adjusted to the temperature of the given sample). If the SI > 0, the mineral is supersaturated with respect to the system. This means that the precipitation or crystallization is thermodynamically favored. Minerals with SI < 0 are undersaturated with respect to the solution and are thermodynamically likely to dissolve if present in the system. Minerals with SI in the neighborhood of zero are saturated or are in equilibrium with the solution.

The summary statistics of saturated indices of some of the common mineral phases is presented in Table 3. It clearly shows that the groundwater is generally undersaturated with respect to most of carbonate phases. However, geology of the area indicates that limestone exists in sporadic beds, thus the undersaturation may be attributable to short residence time of the groundwater in the aquifer. Majority of the water samples have the Ca^{2+}/Mg^{2+} molal ratios greater than unity. This suggests conditions where calcite minerals appear to dominate.

In the current study, an attempt was made to determine the variation between the saturation indices of a major carbonate mineral (calcite) with the TDS. A strong linear relationship would suggest significant contribution of mineral weathering processes (particularly carbonate minerals and incongruent silicate mineral weathering) on the ionic composition of the water.

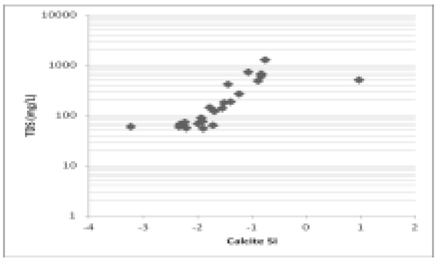

Fig.7: The relationship between TDS and SI of calcite.

Fig. 7 represents a plot of TDS (mg/l) against the SI of the groundwater samples. All the samples are undersaturated-supersaturated in calcite with respect to the solution. There is a generally strong correlation between calcite SI and TDS in the catchment.

The seemingly strong linear relation observed among the samples is probably due to mineral weathering processes. The relationships in Fig. 8 further suggest that there is evolution of fresh water which is undersaturated with respect to calcite into water supersaturated with respect to calcite contributing to salinity enhancement near the bank of the Volta Lake.

Calcite therefore has a propensity to precipitate in solution, under the right conditions. The supersaturation of a mineral may not necessarily lead to its precipitation. In the case of calcite, other factors such as the requisite nuclei for precipitation, the presence or absence of other minerals which might retard the processes of nucleation and precipitation, and the congenial thermodynamic conditions for precipitation. Precipitating minerals might seal pore openings and retard groundwater flow over time. However, hydrogeochemical and isotopic study of groundwater in the area (Kaka, 2010) showed that residence time of groundwater here is short.

In the stability diagram for the equilibrium relationship between calcite and gypsum in the study area (Fig. 8), all samples plot from the base of the gypsum and calcite supersaturation field, suggesting the relatively moderate content of calcium and high concentrations of bicarbonate ions in solution. This observed supersaturation of calcite is probably associated with massive enrichment of the groundwater with bicarbonate and calcium from the weathering of the carbonate minerals in the aquifers.

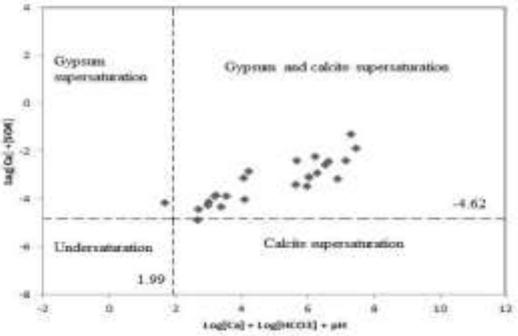

Fig. 8: The stability field for both gypsum and calcite

Conclusions

Aluminium, manganese, iron and vanadium concentrations in the boreholes at most areas groundwater are higher than originally anticipated (i.e in excess of the WHO recommended guideline values) of a non-mining area. While zinc and copper levels are within acceptable ranges, concentrations of cadmium and chromium were below detection limit. Dissolution of aquifer materials enhanced probably by moderately acidic waters is responsible for mobilization of trace elements in the groundwater in the area. The groundwater samples are generally undersaturated with respect to most of carbonate phases. Though pH showed slightly acidic waters, calculated groundwater acidification (Aci) was low (in fact, negative) and hardness alkalinity ratios (HAR) were consistently less than unity suggesting influence of weak acid probably of natural origin. The positive acid neutralizing capacity (ANC) values recorded throughout indicated a long-lasting superfluous in the acid-buffering capacity of the groundwater in the Manya Krobo area along the Volta Lake. Therefore, it is necessary to incorporate other trace metal removal techniques into borehole operations beyond removal of iron. High level of some metals, e.g. vanadium could be a precursor for presence of petroleum crude oil in sedimentary basin.

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Table 1: Statistical summary of physico-chemical and concentration of trace elements in the study area

Parameters	Minimum	Maximum	Mean	Median	Std. Deviation	WHO (2004)Guideline
Elevation(m)	87	342	194.44	197	80.76	
pH	5.24	6.92	6.6	6.69	0.34	
Eh (mV)	-33.5	70.8	-9.58	-13.7	20.06	
Temp (^{0}C)	25.3	29.4	27.16	27.1	1.09	
EC (µS/cm)	125.3	2970	614.96	286	708.63	
TDS (mg/L)	53.8	1274	261.67	122.7	300.75	
Salinity (‰)	0.1	1.5	0.32	0.1	0.41	
Cl^- (mg/L)	0.11	19.74	3.4	1.07	5.22	
HCO_3^- (mg/L)	1.2	11.87	4.08	2.53	3.23	
SO_4^{2-} (mg/L)	0.02	0.14	0.02	0.01	0.04	
NO_3^- (mg/L)	0	0.07	0.01	0.01	0.02	
PO_4^{3-} (mg/L)	0	0.29	0.03	0	0.07	
Na^+ (mg/L)	0.93	31.87	6.24	2.37	8.62	
K^+ (mg/L)	0.2	1.99	0.82	0.62	0.5	
Ca^{2+} (mg/L)	0.25	0.64	0.39	0.33	0.13	
Mg^{2+}(mg/L)	0.01	1.48	0.45	0.35	0.37	
Fe (µg/L)	260	2476	775	564	0.5	300
Cd(µg/L)	<2	<2	<2	<2	0	3
Zn(µg/L)	44	176	74.6	68	0.03	4000
Cr(µg/L)	<6	<6	<6	<6	0	50
Cu(µg/L)	10	363	110	84	0	2000
Mn(µg/L)	941	338.8	197.78	49.54	66.7	500
V(µg/L)	<2	155837	6987.7	551	31	10
Al(µg/L)	4714.9	36982	15686.2	122274	8.7	200

Table 2. Groundwater acidification data and acid neutralizing capacity of groundwater of the study area

Sample ID	pH	ANC(meq/L)	Aci(meq/L)	NANC=ANC-Aci (meq/L)
MKI	6.92	22.55	-23.72	46.27
MK2	6.62	23.10	-22.35	45.45
MK3	6.45	0.23	-13.22	13.45
MK4	5.24	0.39	-13.91	14.29
MK5	6.21	0.64	-13.71	14.35
MK6	6.82	0.17	-13.52	13.69
MK7	6.67	1.29	-14.20	15.49
MK8	6.65	1.37	-14.49	15.86
MK9	6.82	11.07	-17.73	28.80
MK10	6.8	5.13	-21.15	26.28
MK11	6.87	6.61	-20.94	27.56
MK12	6.81	1.51	-15.45	16.96
MK13	6.74	2.43	-15.41	17.84
MK14	6.48	0.87	-11.47	12.34
MK15	6.37	0.97	-13.45	14.42
MK16	6.39	0.75	-14.08	14.83
MK17	6.51	0.65	-14.26	14.91
MK18	6.76	2.87	-16.67	19.54
MK19	6.61	0.88	-10.74	11.62
MK20	6.51	0.56	-13.20	13.77
MK21	6.83	4.86	-17.98	22.84
MK22	6.85	3.47	-15.37	18.84
MK23	6.71	0.51	-12.02	12.53
MK24	6.69	2.09	-13.61	15.71
MK25	6.78	0.90	-14.80	15.69

Table 3: Saturated indices of some minerals in groundwater along the Volta Lake

ID	SI-Aragonite	SI-Calcite	SI-Dolomite	SI-Goethite	SI-Gypsum	SI-Halite	SI-Hematite	SI-Pyrite	SI-Siderite
MK1	-0.9	-0.8	-1.7	2.7	-4.4	-5.0	7.5	-33.7	-0.1
MK2	-1.2	-1.1	-2.0	2.4	-4.0	-4.9	6.8	-33.4	-0.1
MK3	-1.9	-1.8	-2.9	2.5	-4.5	-7.6	7.1	-33.1	-0.4
MK4	-3.4	-3.2	-6.0	-0.3	-4.6	-8.2	1.5	-31.0	-2.1
MK5	-2.5	-2.3	-4.2	1.7	-4.6	-7.9	5.3	-33.0	-1.2
MK6	-2.6	-1.9	-4.1	3.6	-4.7	-8.6	9.2	-34.0	-0.1
MK7	-2.1	-1.9	-4.2	2.7	-5.2	-7.3	7.5	-35.7	-0.8
MK8	-1.8	-1.7	-3.6	3.2	-4.4	-7.1	8.4	-33.8	-0.2
MK9	-1.4	-1.2	-2.1	3.2	-5.5	-5.6	8.3	-36.0	0.1
MK10	-1.0	-0.8	-1.4	2.7	-3.6	-5.9	7.3	-33.3	-0.2
MK11	-1.0	-0.8	-2.3	3.1	-3.7	-5.8	8.2	-33.7	0.1
MK12	-1.7	-1.6	-3.5	3.6	-4.8	-7.1	9.2	-34.6	0.2
MK13	-1.7	-1.5	-2.9	2.6	-4.8	-6.8	7.2	-34.8	-0.6
MK14	-2.4	-2.2	-4.6	2.3	-5.3	-7.8	6.5	-34.5	-1.0
MK15	-2.5	-2.3	-4.8	2.0	-5.5	-7.6	6.1	-34.9	-1.2
MK16	-2.4	-2.2	-4.4	1.8	-4.9	-7.8	5.5	-33.9	-1.3
MK17	-2.4	-2.2	-4.9	2.1	-5.6	-7.8	6.2	-35.2	-1.2
MK18	-1.6	-1.4	-2.3	2.9	-4.5	-6.4	7.9	-34.5	-0.2
MK19	-2.1	-2.0	-3.5	2.5	-5.6	-7.7	7.0	-36.7	-1.0
MK20	-2.1	-1.9	-3.9	2.6	-4.6	-7.5	7.1	-33.5	-0.5
MK21	-1.1	1.0	-1.6	3.1	-4.8	-6.0	8.2	-35.8	-0.1
MK22	-1.0	-0.9	-1.2	3.0	-4.7	-6.2	8.0	-35.4	-0.1
MK23	-1.9	-1.7	-2.8	3.0	-5.1	-7.9	7.9	-35.3	-0.4
MK24	-1.9	-1.7	-3.1	2.8	-4.4	-6.9	7.6	-34.0	-0.4
MK25	-1.5	-1.4	-3.2	3.0	-4.6	-7.5	8.0	-34.5	-0.3
Min.	-3.4	-3.2	-6.02	-0.26	-5.6	-8.6	1.5	-36.6	-2.1
Max.	-0.1	1	-1.2	3.6	-3.6	-4.9	9.2	-31.0	0.2
Median	-1.9	-1.7	-3.2	2.7	-4.7	-7.3	7.5	-34.5	-0.4
Mean	-1.8	1.6	-3.2	2.6	-4.7	-7	7.2	-34.3	-0.5
Std.dev	-0.6	0.8	1.2	0.8	0.4	1	1.5	1.2	0.6