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Hydrogeochemical evolution and quality assessment of groundwater within the Atankwidi basin: the case of northeastern Ghana

M. Anim-Gyampo^{1,2} · G. K. Anornu² · E. K. Appiah-Adjei³ · S. K. Agodzo⁴

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Abstract

The hydrogeochemical evolution and quality assessment of groundwater within the transboundary Atankwidi basin have been carried out in Ghana. Various hydrochemical models and scenarios were employed to ascertain the possible sources, mechanism of mobilization, andthe processes controlling groundwater chemistry from points of recharge to areas of discharge. Analysis of twenty-six (26) groundwater samples showed that all parameters fell within acceptable limits for drinking water except fluoride, conductivity, and total hardness. The dominance of cations and anions was in the order Na > Ca > Mg > K and HCO₃ > SO₄ > Cl⁻ > F⁻ > PO₄⁻ > NO₃. Four groundwater types were identified—Ca-Na-Mg-HCO₃ > Na-Ca-Mg-HCO₃ > Na-Ca-HgO₃. The major source of chemical evolution in groundwater was water-rock interaction (silicate minerals) with infiltrating carbonic acid as the agent of weathering resulting in the release of Na, Ca, K, and HCO₃⁻. Cationic exchange between alkali metals and alkaline earth metals is the main chemical process altering groundwater chemistry, resulting in mobilization of Ca and the consumption of Na at favorable sites as groundwater approaches discharge points. There is possibly little or insignificant contribution from anthropogenic factors to the build-up of groundwater chemistry in the study area.

Keywords Atankwidi basin · Groundwater · Hydrogeochemistry · Cationic exchange · Water quality

Introduction

One of the major components of improving the socioeconomic well-being of a group of people is the provision of good quality water, defined by its chemistry. Several studies have revealed that poor water quality adversely affects human health in various forms and aspects of the ecosystem such as plant life, micro-organisms, and aquatic species (Hem 1991; Appelo and Postma, 2005; WHO 2008). The quality of groundwater even though superior to surface water in terms

M. Anim-Gyampo gyampom@gmail.com

- ¹ Department of Geological Science and Faculty of Earth and Environmental Science, University for Development Studies, Box 24, Navrongo, Ghana
- ² Civil Engineering Department, College of Engineering, KNUST, PMB, Kumasi, Ghana
- ³ Department of Geological Engineering, College of Engineering, KNUST, PMB, Kumasi, Ghana
- ⁴ Department of Agricultural Engineering, College of Engineering, KNUST, PMB, Kumasi, Ghana

of its quality is not sacrosant but may be subject to variations over time due to certain natural and anthropogenic processes. Natural processes include certain geochemical processes (soilwater interaction, water-rock-interaction, cation etc.), mixing waters, evapotranspiration, selective uptake by vegetation, and certain biological processes (Appelo and Postma 2005). Anthropogenic sources that may compromise groundwater quality include leachates from municipal and urban wastewater sources from landfills, domestic and petrochemical facilities; industrial wastes coming from manufacturing and pharmaceutical, mine effluents, as well as agricultural activities (i.e., application of fertilizers, weedicides, pesticides manures etc.). To ensure the sustainability of groundwater in terms of its quality so as to continuously remain reliable for the purposes of both domestic and agricultural usage, an in-depth knowledge of its hydrochemistry is fundamental. It determines the origin of chemical composition (evolution), geochemical alteration processes, quality status, and appropriate usability (Zaporozec 1972; Appelo and Postma 2005; Gupta et al. 2008; Kumar et al. 2009; Srinivasamoorthy et al. 2013; Kaka et al. 2011).

The Atankwidi basin is a transboundary sub-basin of the White Volta Basin of West Africa which is located between

the northeastern part of Ghana and southern part of Burkina Faso. The area, which used to be predominantly rural in nature about three decades ago, is fast becoming urbanized with several peri-urban centers. This has resulted in more than a quadrupled rise in water demand to meet both domestic and agricultural (GSS 2010; van der Berg 2008). The basin is located in a region (Upper East) considered to be among the poorest in Ghana and second-least with respect to food security, and these have been attributed to insufficient rain water to support local agricultural activities over longer periods as well as unreliable surficial water resources (rivers, streams, and small reservoirs) for irrigational farming in the long dry season (Barry et al. 2010). To improve the situation, several studies focused on improving food insecurity stature of the inhabitants (Ofosu et al. 2014; Barry et al. 2010; van der Berg 2008) had revealed the existence of large tracks of fertile lands within the Atankwidi basin, 80% of which remain uncultivated. The studies further revealed that the existence of insufficient surficial water resources to support irrigational farming is a major key setback and recommendation for the utilization of groundwater as a possible reliable alternative source has been made.

The identification of groundwater as key to the upscaling of irrigational farming on large scale had necessitated the need for comprehensive groundwater studies within Atankwidi basin of Ghana. So far, studies had focused on the effect of climate change on small-scale farmers, sustainable irrigation development and its socio-economic importance, potential upscaling of irrigational farming using groundwater, groundwater recharge, and others (Martin and van der Giessen 2005; van der Berg 2008; Barry et al. 2010; Namara 2011; Obuobie 2014; Ofosu et al. 2014). Martin (2006) estimated groundwater recharge within the Atankwidi basin and concluded that values ranged between 2.5 and 4%. Van der Berg (2008) studied on the use of dug-outs and hand-dug wells for dry-season irrigation within the basin and concluded they were unsustainable over a period beyond 2 months after cessation of rains and recommended studies on deeper well (boreholes). Obuobie (2014) estimated groundwater abstraction rate within the Atankwidi basin as at 2010 to be approximately 549,000 m³ for a population of 45,841, translating into approximately 11.976 m³ per person per year. Barry et al. (2010) studied the shallow aquifers within the basin and concluded that groundwater in storage within the basin was enough to support both domestic and upscaling of small-sized farming into large-scale irrigation over long periods. Outstanding studies of great significance but yet to be carried out include but not limited to groundwater aquifer risk assessment/ vulnerability to potential contamination, hydrogeochemical evolution, water quality appraisal for domestic and agricultural usage, aquifer definition, sustainability and evaluation of fate, contaminant transport, and modeling. The impending upscaling of irrigational farming means that much larger quantities of groundwater usage over time and the massive

expected usage of agro-chemicals in the up-scaled irrigational farming may potentially result in a possible alteration in the quality with the potential effects on human health and also the ecosystem. The current study is focused on assessing the hydrogeochemistry by employing various hydrochemical models and scenarios such as those developed by McKenzie (1983), Hem (1991), Hounslow (1995), Jankowski, Acworth (1997), etc. to identify the possible source(s) of groundwater chemical constitution, their mode of mobilization as well as the processes controlling groundwater chemistry from points of recharge to areas of discharge. This study seeks to provide a basis to fully understand the possible sources, processes controlling chemical mobilization and to evaluate its suitability for drinking, agricultural (irrigation), use in both Ghana and Burkina Faso. The knowledge espoused here will contribute to the improvement of knowledge on groundwater resources within the basin and areas of similar hydrogeological settings in Ghana, Burkina Faso and other parts of the West African sub-continent toward sustainable management of groundwater aquifer systems.

Materials and methods

Location, climate, and vegetation

The Atankwidi basin (Fig. 1) is a transboundary catchment located in the Upper East Region of Ghana, specifically in the Kasena-Nankana Municipality and West District and the south of Burkina Faso in the Nahouri Province. It has a total estimated area of about 275 km² and constitutes about 1% of the entire White Volta Basin of West Africa (Ofosu et al. 2014). The part of the basin found in Ghana is located within longitude 0°, 50′–1°, 10′W and latitude 10°, 45′–11°, 00′N with an estimated total area of about 156 km² (Martin 2006). It is bounded to the west by Kasena-Nankana Municipality, east by Kasena-Nankana West south by Bolgatanga Municipality and to the north by Burkina Faso.

The study area falls within the Sudan Savannah climatic zone with characteristic high temperatures and evapotranspiration and is among the driest places in Ghana. The average annual precipitation is about 990 mm while mean daily maximum and minimum temperatures are about 35 °C and minimum 23 °C respectively (Dickson and Benneh 1998). Two major air masses, the South-West Monsoon and the Northeast Trade Winds (Harmattan), generally influence the movement of the Inter-Tropical Convergence Zone (ITCZ). Rainfall period is mono-modal and occurring between May and September every year followed by a prolonged dry season with total estimated potential evapotranspiration exceeding the mean annual precipitation (Leibe 2002). Common vegetation types characterizing the area include the Shea, Neem, Acacia, Baobab, and grass (Pelig-Ba 2000).



Fig. 1 The study area

Geology, soil, and hydrogeology

The area is underlain by the paleoproterozoic Birimian supergroup and their associated belt and basin granitoids. The Birimian are metavolcanics and metasediments, which were intruded by belt-type and basin-type granitoids during the Eburnean orogeny (about 2250 ma on the average). The metasediments are mainly phyllites, schist, and quartzites which are found in small patches among the granitoids while the metavolcanic rocks are volcaniclastics interbedded with subordinate argillites and minor mafic flows with rocks being metamorphosed lavas, pyroclastic rocks, hypabyssal intrusive, phyllites, and greywackes (Castaing et al. 2003). Over 90% of the entire study area is underlain by the belt-type granitoids, which is made up of hornblende-biotite granodiorite, biotite granite, and biotite gneiss. The remaining (less than 10%) located on the south-eastern part of the basin is underlain by the younger potassium-rich Bongo granitoids, believed to be emplaced after the formation of the Tarkwaian (i.e., 1.97 billion years) age. They occur commonly as large blocky boulders which is evidence of their rather high resistance to weathering as a result of high quartz content. Bongo granitoids build the more prominent elevations in the otherwise rather smooth terrain (Griffis et al. 2002) in the study area (Fig. 2).

According to Martin (2006), three soil types (Leptosols, Lixisols, and Fluvisols) are found within the study area. Leptosols are predominantly found in the elevated northern and eastern border of the basin; Fluvisols are found in the flat terrain located on both sides of streams while the remaining of the area is covered by Lixisols. Leptosols are loamy sand and

sandy loam soils while lixisols consist of sandy-loam to sandy-clay loam with high clay contents in the upper part but the texture becomes coarser as depth increases.

Water sampling and analysis

Twenty-six (26) groundwater samples were collected from identified boreholes tapping shallow aquifers in well-labeled 0.5-1 polythene containers. Sampling was carried out in accordance with protocols described by Claasen (1982) and Barcelona et al. (1985). Sample bottles were first conditioned by washing with detergent and rinsed several times with acidified water containing 10% nitric acid to prevent contamination. Boreholes were purged for at least 5 min to obtain fresh samples which were subsequently filtered through 0.45-µm membranes. Two samples were collected at each site: one filtered and acidified with 2% v/v of HNO₃ to prevent ions getting stuck onto the walls of the bottles and keep ions in solution were used for heavy metal analysis, while unacidified samples were used for major cation and anion analysis. Unstable hydrochemical parameters such as electrical conductivity (EC), pH, and alkalinity were measured in situ (in the field) immediately after collection of samples, using a WTW field conductivity meter model LFT 91, WTW field pH meter model pH 95, and a HACH digital titrator, respectively, that had been calibrated before use. Major ions (sodium and potassium) were analyzed in the laboratory using the flame photometer. Calcium and magnesium were analyzed using the AA240FS the Fast Sequential Atomic Absorption Spectrometer. The ICS-90 Ion Chromatograph (DIONEX ICS-90) was employed in the analysis of chloride, fluoride,



Fig. 2 Geological map of the Atankwidi basin of Ghana

nitrate, and sulfate. Phosphate was determined by the ascorbic acid method using the ultraviolet spectrophotometer (UV-1201). A multipurpose electronic DR/890 Colorimeter was used to measure the color, turbidity, total dissolved solids. Five milliliters of each acidified water sample was measured, and 6 ml of nitric acid, 3 ml of HCl, and 5 drops of hydrogen peroxide (H₂O₂) were added for acid digestion and placed in a milestone microwave lab station ETHOS 900. The digestate was then assayed for the presence of zinc (Zn), lead (Pb), copper (Cu), chromium (Cr), and cobalt (Co) using VARIAN AAS240FS Atomic Absorption Spectrum in an acetylene-air flame. Arsenic (As) and mercury (Hg) were determined using argon-air flame.

Results and discussion

The statistically analyzed results on the chemical composition of the sampled groundwaters in the study area are presented in Table 1. The correlation between the measured parameters is presented in Table 2.

General properties of groundwater in the area

The pH of a solution gives an indication of its acidic or basic character, which when found to be less than 7 is generally said to be within the acidic medium, soft, corrosive, and usually enhances the dissolution and leaching of metals from natural salts and man-made materials such as pipes and other fixtures. According to Nishtha (2012), acidic waters (i.e., pH < 6.5) facilitate the dissolution of metals especially heavy metals beyond the permissible limits, which can affect the mucous membrane of cells of human. Hounslow (1995) characterized water according to pH as moderately acidic when pH value range is 4-6.5; neutral when the range is 6.5-7.8; moderately alkaline is 7.8-9 while water with pH greater than 9 is alkaline. In this study, groundwaters were observed to be generally neutral with values ranging 6.47 to 7.70 with a mean value of 7.08. Turbidity ranged from 0 to 2 NTU with a mean of 0.3 NTU while values of TDS were between 168 and 508 mg/L with a mean of 319.1 mg/L. The generally low TDS values are possible indication of the occurrence of young or recharging groundwaters since high values of TDS are mostly associated with old or discharging groundwaters. The possibility of the occurrence of adverse health implication to humans (i.e., gastro-intestinal irritation) is unexpected since according to Nishtha (2012), such situation may only arrive in groundwaters with TDS above the maximum allowable limit 1000. Freeze and Cherry (1979) categorized groundwater on the basis of TDS as being fresh when value range is 0-1000 mg/L, 1000-10,000 mg/L as brackish, 10,000-100,000 mg/L as saline, and greater than 100,000 mg/L as brine. Thus, groundwaters in the current study area are fresh. Conductivity values ranged from 280 to 835 μ S/cm with a mean of 531.84 μ S/cm. Twenty-one (21) samples representing approximately 81% were within acceptable limits of WHO (2008) while five (5) samples representing about 19% exceeded the maximum acceptable limit. The existence of predominantly lower conductivity

Table 1Summary results of thelaboratory analysis

Parameter	Unit	Minimum	Maximum	Mean	WHO (2008)
Temperature	°C	28.10	29.800	29.000	N/A
рН	pH units	6.470	7.700	7.080	6.5-8.5
Turbidity	NTU	0.000	2.000	0.300	5
TDS	mg/L	168.000	508.000	319.104	1000
Conductivity	uS/cm	280.000	835.000	531.84.000	500
Hardness	mg/L	164.000	364.000	238.600	150-300
Na ⁺	mg/L	34.700	72.500	53.600	200
Ca ²⁺	mg/L	11.220	80.160	45.700	200
Mg ²⁺	mg/L	0.979	8.630	4.800	150
K ⁺	mg/L	0.938	6.096	2.930	30
HCO ₃ ⁻	mg/L	200.080	588.040	394.100	N/A
$\mathrm{SO_4}^{2-}$	mg/L	0.840	33.360	17.100	400
Cl	mg/L	7.090	26.940	17.000	250
NO ₃ ⁻	mg/L	0.010	0.120	0.100	45
PO_4^{3-}	mg/L	0.002	2.873	1.400	30
F^{-}	mg/L	0.380	1.950	1.165	0.5-1.5
Pb	mg/L	0.005	0.021	0.128	0.006
As	mg/L	0.001	0.009	0.002	0.001
Fe	mg/L	0.0196	0.152	0.053	3
Zn	mg/L	0.005	0.033	0.013	0.01

All parameters below detection limit were not included in the table (Mn, Cd, Cr, and Cu)

values may indicate possible shorter residence time of the groundwater in the study area and this corresponds with the observation of relatively low TDS values the existence of fresh waters. The values of hardness in the current study varied from 164 to 364 mg/L with a mean of 238.6 mg/L. It was observed that with the exception of five (5) samples representing approximately 19% that exceeded acceptable limits, all water samples had values of hardness falling below the acceptable limit of 300 mg/L (WHO 2008) for potable water. According to McGowan (2000), encrustation and adverse effects on domestic use occur when the permissible threshold of 300 mg/L is exceeded. Saravanakumar and Ranjith Kumar (2011) categorized water based on its hardness as being soft when hardness values less than 75 mg/L, moderately soft when value range is 76-150 mg/L, hard when values are between 151 and 300 mg/L, and more than 300 mg/L water is described as very hard. In the current study, groundwaters can thus be described as being predominantly hard. The observed strong correlation ($r^2 = 0.73$ and 0.80) between total hardness (TH) and Ca^{2+} and HCO_3^{-} , respectively, gives indication that groundwaters in the study area possess carbonate hardness (temporal hardness).

Major ion chemistry

All major ions (cations and anions) measured were within acceptable or permissible limits for potable water when

compared to WHO (2008) guidelines with Na^+ and $HCO_3^$ being the major and anions, respectively. The orders of dominance for both categories of ions in analyzed groundwaters in terms of the estimated mean values are $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $HCO_3^- > SO_4^{2-} > Cl^- > F^- > NO_3^-$ with corresponding mean percentage distributions of 50.08, 42.70, 4.48, and 2.74% for cations and 91.76, 3.98, 3.96, 0.27, 0.02. Sodium appeared to be the most abundant cation with a percentage composition of 50.08%. Sodium is significant to human health in the area of human physiology and high concentrations may affect persons with cardiac difficulties (Srinivas and Nageswara 2011). Na-rich groundwaters may indicate the existence of young waters and/or recharging waters. The slight dominance of Na⁺ over Ca²⁺ may indicate fresh groundwaters undergoing mixing or in transition to Appelo and Postma (2005). There is an observed low correlations between sodium and salinity $(r^2 = 0.13)$; TDS (0.19) and EC (0.15) suggesting the possibility Na consumption through ion exchange. In Fig. 4, Na-rich groundwaters are generally located in the higher elevated eastern to northeastern parts (recharge areas) as compared to Ca-rich groundwaters, which exist in lowlying western-southwestern (discharge areas). Furthermore, There is an observed negative (though relatively weak) correlation ($r^2 = -0.21$) between Na⁺ and Cl⁻ while a significantly strong positive correlation ($r^2 = 0.62$) exists between Cl⁻ and Ca^{2+} . This more or less confirms a possible consumption of sodium from solution through cationic exchange between Na⁺

Table 2	The corre	elation mat	rix for wate	er quality p	arameters in	n the study	area												
	Sal	T (0C)	Ηd	TSS	TDS	Turb	EC	Alk	Hard	Ca	Mg	Na	K	HCO ₃	NO_3	PO_4	SO_4	CI	F
Sal	1.00					r.	r.												
T(0C)	0.14	1.00																	
μd	0.58	0.05	1.00																
TSS	0.27	-0.08	0.30	1.00															
TDS	0.93	0.15	0.64	0.36	1.00														
Turb	-0.03	0.11	-0.28	0.28	-0.05	1.00													
EC	0.93	0.17	0.62	0.33	0.99	-0.06	1.00												
Alk	0.83	0.23	0.68	0.25	0.87	-0.16	0.89	1.00											
Hard	0.77	0.14	0.57	-0.06	0.79	-0.12	0.80	0.79	1.00										
Ca	0.85	0.02	0.69	0.47	0.91	0.01	0.90	0.78	0.72	1.00									
Mg	0.10	0.04	0.07	-0.14	0.07	-0.03	0.08	0.31	0.16	0.00	1.00								
Na	0.13	0.23	0.12	0.39	0.19	0.47	0.15	0.16	0.04	0.20	-0.06	1.00							
K	0.25	0.06	0.04	-0.09	0.24	0.10	0.25	0.16	0.30	0.24	0.05	0.23	1.00						
HCO ₃	0.82	0.18	0.58	0.30	0.86	-0.09	0.87	0.92	0.80	0.78	0.35	0.07	0.05	1.00					
NO_3	-0.01	0.19	0.12	0.27	0.07	-0.04	0.08	0.12	-0.13	0.01	0.10	-0.08	-0.39	0.07	1.00				
PO_4	-0.03	-0.05	-0.12	0.08	-0.04	0.30	-0.02	-0.11	-0.03	0.01	0.01	-0.24	0.05	0.00	-0.10	1.00			
SO_4	0.58	-0.11	0.35	0.46	0.61	0.21	0.57	0.30	0.28	0.73	-0.20	0.06	0.06	0.37	0.00	0.09	1.00		
CI	0.62	0.07	0.28	-0.13	0.69	-0.17	0.71	0.45	0.62	0.62	-0.06	-0.21	0.27	0.51	-0.05	0.17	0.49	1.00	
ц	-0.04	0.03	-0.06	0.04	0.03	0.15	0.03	-0.17	-0.10	0.11	-0.13	0.04	0.57	-0.26	-0.17	0.02	0.31	0.22	1.00
Italicizec	l values inc	licate stron	g relationsl	ip $(r^2 > 0$.	5)														

and Ca²⁺ on clay surfaces resulting in the enrichment of Cl⁻ and Ca²⁺ as groundwater proceeds from recharge to discharge areas. Sodium may naturally originate from the weathering of plagioclase feldspar (albite), dissolution from halites and clay. Other sources may be from the oceans (during sea-water intrusion) in areas close to the sea as well as from agricultural and municipal wastes (Srinivasamoorthy et al. 2013). The current study area is quite further away from halites (> 500 km), municipal waste sites, the ocean (> 800 km), and is underlain by igneous rocks. Thus, the possible source of sodium could be from the weathering of silicate mineral (albite). The chemical reaction below reveals how sodium is generated from Albite weathering:

 $2NaAlSi_{3}O_{8} + 2H^{+} + 9H_{2}O \longrightarrow Al_{2}Si_{2}O_{5}(OH)_{4} + 2Na^{+} + 4H_{4}SiO_{4}$ (Albite)

(1)

(2)

Calcium is the second most dominant cation after sodium with a mean percentage composition of 43.9%. Calcium may be significantly beneficial to human health when in acceptable concentrations in water. It is able to block the absorption of heavy metals in the human body, increase bone mass, and also prevent certain types of cancer (Bohlke 2002). But in high concentrations, calcium may adversely affect human health by affecting negatively the absorption of other essential minerals in the body. Naturally, calcium may get into groundwaters through the dissolution of calcite, dolomite, gypsum, or weathering of silicate mineral anorthite. It is also possible to have calcium released directly or indirectly into groundwater system after prolonged agricultural activities in an area (Bohlke 2002). The area is underlain by igneous rocks quite further away from municipal waste sites > 500 km), and therefore calcium into groundwater may be from the weathering of the silicate mineral anorthite that are as shown below::

 $CaAl_2Si_2O_8 + 2H^+ + H_2O \longrightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 4H_4SiO_4$

(Anorthite)

As discussed elsewhere, the displacement of Ca^{2+} from clay surfaces into solution by Na⁺ in a continuous manner results in the increase of Ca²⁺ through the process of cationic exchange in solution (Deutsch and Siegel 1997). The continuous evolution of Ca in solution as resident time increases from clay surfaces may combine with the conservative anions (Cl⁻ and HCO₃⁻) and hence the observed strong positive correlation between these three ions. Thus, cationic exchange offers another avenue for Ca²⁺ mobilization in groundwaters in the study area. Magnesium is the least dominant among the major cations with a mean percentage of 4.8%. Magnesium in relatively high concentrations (above 100 mg/L) may impact undesirable taste to drinking water especially to very sensitive persons. However, at concentrations above 500 mg/L, ordinary persons may find the taste of drinking water undesirable. At concentration above 700 mg/L in drinking water, magnesium may have laxative effect, especially with magnesium sulfate (WHO 2008). Naturally, Mg may originate from the dissolution or weathering of dolomite (CaMgCO₃) and to a lesser extent from magnesite (MgCO₃), ocean (during seawater intrusion), and in rainwater. It can also be added to groundwater system during prolonged agricultural activities involving the application of fertilizers and cattle feed. The very low concentrations of Mg in groundwaters in the area, which is underlain by granitoids, show the possible nonexistence of calcareous rock formations.

Potassium concentration is the least among the major cations in all the sampled groundwaters with an estimated percentage mean value of 2.74%. Lower concentration of K⁺ is commonly recorded in groundwaters due to its relative greater resistance to weathering, and it is getting out of solution unto clay surfaces leading to its loss (Kolahchi and Jalali 2006). Low concentration of K and F- was recorded to occur in the study area but there exist a relatively strong positive correlation $(r^2 = 0.57)$ indicating a possible common source—the potassium-rich feldsparthic, well-jointed porphyritic Bongo granitoids found in the eastern-northeastern section of the study. All the four borewells containing fluoride concentration above recommended value of 1.5 mg/L are located between the elevated areas of Zokkor and Namoo that form the eastern flanges of the study area where the Bongo granitoids are well exposed as hills. The Bongo granitoids according to Smedley et al. (1995) and Apambire et al. (1997) contain the highest concentration fluoride. Natural sources may be from the weathering of K-feldspars, oceans (during sea-water intrusion) and prolonged agricultural activities involving the utilization of synthetic fertilizers. Potassium is an essential element in both plant and human nutrition and occurs in groundwaters as a result weathering of orthoclase (K-feldspar) and the mineral dissolution from decomposing plant material and also from agricultural run-off (Srinivas and Nageswara 2011).

Bicarbonate ion is the most dominant anion with an estimated percentage of mean concentration being about 91.76 with nitrate being the least with a corresponding value of 0.02%. It has strong positive correlations between Ca, salinity, TDS, and EC indicating that Ca and HCO₃⁻ are the two major ions controlling the overall dissolved salts in groundwaters in the study area. Natural sources of HCO₃⁻ are commonly from the action of infiltrating groundwater and calcareous rock formations (i.e., dissolution of, calcite and dolomite), decomposition of organic matter, and the metabolic activities of microorganisms in soils. Bicarbonate can also be sourced naturally from the dissolution or weathering of silicate minerals through the action of carbonic acid contained in infiltrating rain water, which has been formed from the dissolution of CO₂ in the atmosphere (Deutsch and Siegel 1997; Subba Rao 2002). The crystalline granitoids underlying the area contain aluminosilicate minerals such as feldspars and micas, and therefore, limestone and dolomite may be non-existent. Thus, carbonic acid formed from the dissolution of CO₂ in the atmosphere in infiltrating rain water reacts with feldspar minerals (e.g., albite, anorthite, and K-feldspar) resulting in the weathering of igneous rocks to form clay, leaving the relatively conservative HCO₃⁻ plus major cations (Na, Ca, and K) in solution (primary source of major ions in groundwaters in igneous environments). The continuous release of HCO_3^- in solution over geologic time as groundwater proceeds from recharge areas to discharge results in HCO3⁻ being the major anion in groundwaters in the study area. Thus, the natural source of the major anion (HCO_3) in groundwaters in the area from atmospheric CO2 and its interaction with silicate minerals with possible contribution from decomposition of organic matter and the metabolic activities of micro-organisms in soils.

Chloride concentration ranged from 7.09 to 26.94 mg/L with a mean values of 17 mg/L. In the form of sodium (NaCl), potassium (KCl), or calcium (CaCl₂), Cl is one of the major inorganic anions in groundwater. None of the samples in the study area exceeded 250 mg/L which has been recommended as the desirable limit for drinking water supplies (WHO 2008). There is low but positive correlation (0.21)between Cl and Na indicating that they likely not originating from a common source (halite), suggesting that Cl might possibly be originating from precipitation. Excessive chloride in potable water is particularly not harmful to human health even though studies had revealed that high Cl concentration could be injurious to people suffering heart and kidney diseases. High Cl may impart undesirable taste to potable water and could be very corrosive. It can adversely affect soil porosity and permeability. Fluoride, because of its effects on human health, especially the rural-poor in most developing countries, has gained universal attention in recent times as far as groundwater quality issues are concerned. Fluoride is known to have both beneficial and adverse effects on humans, depending on the total intake. Fluoride in suitable dose (i.e., 0.5-1.5 mg/L) has been found to promote the growth and strength of the human bone and the teeth (Apambire et al. 1997). Nevertheless, long-term use of groundwater with fluoride concentrations outside the WHO (2008) permissible limit of 1.5 mg/L for drinking can result in serious health implications, including dental caries, dental fluorosis, and skeletal fluorosis and crippling fluorosis. According to Pontius (1991), prolong drinking of water with fluoride concentrations below 0.5 mg/L may lead to the incidence of dental caries while Shike (2006) stated that consumption of waters with fluoride concentration below 0.5 mg/L may possibly lead to the occurrence of weakness in teeth and bones, dental cavities, and dental caries.

Waters with fluoride concentrations ranging 1.5-4 mg/L can result in the mottling of teeth (Shike 2006), dental fluorosis while the consumption of waters with fluoride concentrations ranging 4-10 mg/L may lead to the occurrence of skeletal fluorosis. Waters containing fluoride concentrations above 10 mg/L when consumed over a period can result in crippling fluorosis (Pontius 1991; Shike 2006; WHO 2008). In the present study, however, measured levels of fluoride ranged from 0.38 to 1.95 mg/L. It was observed that 4 borewells out of 26 had values exceeding recommended maximum limit of 1.5 mg/L of WHO (2008) guidelines. These elevated fluoride waters are found along the eastern to northeastern (Fig. 3) flanges of the study area between Zokkor and Namoo which are underlain by the potassium-rich Bongo granites (Fig. 2) known to contain the highest concentration of fluoride (Apambire et al. 1997).

The fluoride concentrations in groundwater are affected by many factors including availability and solubility of fluoride minerals, velocity of flowing water, temperature, pH, concentration of calcium, and bicarbonate ions in water, etc. (Khaiwal and Garg 2006), and according to Hounslow (1995), F^{-} in natural waters may originate from the solution of fluorite, apatite, or fluoride bearing micas and amphiboles. According to Edmunds and Smedley (1996), fluoride readily can be found in areas covered by rocks containing muscovite, hornblende, and fluorspar while anthropogenic source of fluoride may include phosphate fertilizers in agriculture, mine tailings, and landfilled with industrial and municipal wastes (EPA 1980). In Ghana, Apambire et al. (1997) concluded that the high incidence of fluoride in groundwaters was associated with water-rock interaction within the adjoining Bongo granitoids while elsewhere within the sedimentary formations of northern Ghana, high fluoride occurs in association with the mineral sericite. Trace element levels in groundwater in this study were generally below WHO (2008) limit with most (copper, chromium, cadmium, and manganese) having concentrations below detection limit. Concentrations of Zn, Pb, and As ranged from 0.005 to 0.033 mg/L, 0.005 to 0.021 mg/ L, and < 0.001 to 0.009 mg/L, respectively, with means of 0.0126, 0.0127, and 0.00195 mg/L.

Groundwater types or hydrogeochemical facies in the study area

Facies are recognizable parts of different characters, belonging to any genetically related system. The concept of hydrochemical facies or the determination of water types was developed in order to understand and identify the water compositional classes based on the dominant ions present in a groundwater system. This is usually achieved by plotting measured values of major cations (Ca, Mg, and Na + K) and anions (HCO₃, Cl, and SO₄), obtained from sampled groundwaters on the Piper (1944) tri-linear **Fig. 3** Distribution of fluoride concentration in the study area



diagram. This is a graphical representation of chemical data of representative samples from a study area that reveals the analogies, dissimilarities, and different types (Kaka et al. 2011). Thus, the Piper tri-linear diagram is useful in bringing out chemical relationships among samples of groundwater in a more definite terms compared to the other possible plotting methods by Stiff (1951), Chadha (1999) etc. According to Back and Hanshaw (1965), subdividing the trilinear diagram to define composition class to interpret distinct facies from the 0 to 10 and 90 to 100% domains on the diamond-shaped cation to anion graph is more helpful than using equal 25% increments. In the current study, the plot of major cations and anions from groundwater within the study area is shown Fig. 4. The plots reveal no clear dominant cation but a predominantly mix of Na and Ca (50.08 and 42.7%) that constitute about 92% with minimal concentrations Mg and K (4.48 and 2.74%) constituting about 7%. However, HCO₃⁻ clearly dominates the major anions with over 90%. Thus, the water in the study area could be



Fig. 4 Piper plot showing the major ions

Fig. 5 Spatial distribution of water types



considered to be mixed water involving of Na, Ca, and HCO₃. Four main water types or classes identified from the plot were Ca-Na-Mg-HCO₃, Na-Ca-Mg-HCO₃, Na-Ca-HCO₃, and Ca-Na-HCO₃ with corresponding percentages of distribution in the study area being 34.61, 26.92, 23.07, and 15.38% as shown in Fig. 5. Analysis of the water types from the Piper plot (Fig. 4) show that no particular cation dominates while the dominant anion is HCO₃. According to Garrels and Mackenzie (1967) and McKenzie (1983), the breakdown of Ca and Na-bearing silicate minerals such as plagioclase (albite) and anorthite to release Ca and Na ions into the groundwater system and the subsequent chemical interactions (such as cationic exchange, revers ionic exchange) between Na and Ca ions as the groundwater travels from the recharging areas

towards discharging areas may be responsible for the occurrence of mixed waters.

Source(s) of major ion chemistry in groundwaters in the study area

To establish the likely source(s) of ions that influence groundwater chemistry, Gibbs (1974) plot of

TDS against the ratio of (Na + K)/(Na + K + Ca) (Fig. 6) was used. The Gibbs plot reveals that about twenty-five (25) samples with exception of one representing a little above 96% plotted within the rock dominance zone indicating that the interaction of rocks with water is the major source of major cations in groundwaters in the basin.





Fig. 7 Plot of Cl against Na



Mechanism controlling groundwater chemistry

According to Srinivasamoorthy et al. (2013), the salinity of a groundwater system may originate from different sources such as the dissolution of halite, saline intrusion or weathering of silicate mineral, and to determine the geochemical process(es) serving as the possible source(s) of salinity in groundwater the plot of Cl⁻ against Na⁺ (Fig. 7). According to Meybeck (1987), if data points plot along the 1:1 equiline means salinity is due to halite or sea-water intrusion, if they plot below or above the equiline, it means that salinity is due to the weathering of silicate minerals/ cationic exchange or reverse ion exchange, respectively. In the current study, all data point plotted below the 1:1 equiline, which indicates that salinity in the groundwater system may originate from sources other than NaCl (halite or sea-water intrusion), and which could be from the weathering of silicate mineral or cationic exchange.

The molar ratio Na/Cl is a well-known criterion to determine the source of salinity in groundwater system. In this study, the estimated ratio Na/Cl for all groundwater samples was greater than 1, which according to Meybeck (1987) indicates the release of Na+ into groundwater as a result of the occurrence of cationic exchange or weathering of silicate minerals, typically albite as illustrated by the dissolution reaction below:

$$2NaAl_{3}SiO_{8} + 2CO_{2} + 11H_{2}O - Al_{2}Si_{2}O_{5}(OH)_{4}$$
$$+ 2Na + 2HCO_{3}^{-} + 4H_{4}SiO_{4}$$
(3)

The plot revealed that alkali metals (Na and K) dominate alkaline earth metals (Ca and Mg) as shown by plots of data points above the equiline. According to Sarin et al. (1989), this observation indicates the involvement of silicate weathering in the geochemical processes which contributes mainly Na⁺ and K⁺ ions to the groundwater.

Determination of type of ion exchange

To determine or verify the type of ion exchange process taking place between groundwater and the medium through it resides or travel through in the study area, the chloro-alkaline indices (CAI) developed by Schoeller (1965) are utilized.

The plot of chloro-alkaline indices CAI-2 and CAI-1 as suggested by Schoeller (1965) for the current study is as shown in Fig. 8. According to Schoeller (1965), if CAI-1 and CAI-2 have both positive values, it implies that there is equilibrium between the two chloro-alkaline indices and the ion exchange process occurring between Mg^{2+} and Ca^{2+} in the host rock and Na⁺ and K⁺ in water cationic exchange. But if both indices are negative, then there is disequilibrium between the indices and the ion exchange process is a reverse ion exchange. The formula that was used in the evaluation of the chloro-alkaline indices in this study is as follows:

$$CAI \ 1 = \frac{Cl - (Na + K)}{Cl}$$
(4)

$$CAI 2 = \frac{Cl - (Na + K)}{SO4 + HCO3 + NO3}$$
(5)

In the current study, the estimated indices were which suggests that cationic ion exchange occurred between the alkali metal in water and the alkaline earth metals in the host environment.

To ascertain the degree of influence of cation exchange with respect to the weathering of silicate mineral in the mobilization of major cations in the groundwater system in the study area, $(Ca^{2+} + Mg^{2+})-(HCO_3^- + SO_4^{2-})$ (meq/L) was plotted against Na⁺ + K⁺ - Cl⁻ (meq/L). According to Jankowski and Acworth (1997), water undergoing ion exchange will plot along a line with a slope of -1, and this according to Appelo and Postma (2005) commonly occurs



Fig. 8 A plot of CAI-2 against CAI-1

in areas of sea water intrusion. In this study (Fig. 9), about five (5) data points representing approximately 19% plotted along the line with a slope of -0.4 and revealing poor correlation ($r^2 = 0.17$). This implies that cationic exchange reaction even though occurs, it was not significant chemical process.

Conclusion

The hydrochemistry and its suitability for drinking purposes of groundwaters within the Atankwidi sub-catchment located within the White Volta basin of northeastern Ghana have been found to be generally good except in few cases. Temperature, pH, EC, alkalinity, total hardness, color, salinity, TDS, and turbidity of most groundwater samples (> 80%) fell within the acceptable limits for potable water. Communities such as Kandiga, Mirigu Nabaago, Kandiga Bembisi, and Mirigu Gurwonko had EC values above the acceptable limit of 500 mg/L. The presence of high EC concentration in two communities indicates potentially aggressive waters.

Zokkor Kodoroko and Akamo had total hardness values exceeding the permissible limit of 300 mg/L while fluoride concentration in four communities namely, Pubea, Namoo Sikabisi, Namoo Bokobisi, and Zokkor Kodoroko were above permissible limit of 1.5 mg/L while in Agusi, fluoride was



below 0.5 mg/L. The inhabitants of the above communities therefore are vulnerable to possible incidences of dental caries, mottling of teeth, and dental fluorosis over a long period of consuming such waters.

All major ions (cations and anions) were within the acceptable limit while the concentration heavy metals (Mn, Cu, Cr, and Cd) below detection limit. Na⁺ and HCO₃⁻ were the dominant cation and anion, respectively. The order (decreasing) of major cations and anions was, respectively, $Na^+ > Ca^{2+} >$ $Mg^{2+} > K^+$ and $HCO_3^- > SO_4^{2-} > Cl^- > F^- > PO_4^{2-} > NO_3^-$. Groundwaters in the area were fresh and possessed carbonate hardness (i.e., temporal hardness). Cl is likely originating from precipitation and chemical fertilizers while HCO₃ is from the dissolution of calcite. The weak correlation between NO_3^- , PO4⁻, and SO_4^{2-} suggests that these anions may not be emanating from similar source. The low concentration of potassium in groundwaters could be due to higher resistance of K-feldspar to weathering. Potassium appeared to have a similar source with fluoride as indicated by their strong positive correlation, which could be geogenically linked to the Bongo granitoids. Trace element concentrations were within the permissible limits for potable water.

Groundwater was mixed with respect to major cations but bicarbonate-rich as depicted by the four different water types (hydrochemical facies), which in decreasing order of dominance was Ca-Na-Mg-HCO₃ > Na-Ca-Mg-HCO₃ > Na-Ca-HCO₃ > Ca-Na-HCO₃.

The main source of major cations (Na, Ca, and K) in groundwaters in the area is from water-rock interaction arising from the weathering of silicate mineral by carbonic acid contained in infiltrating water within the subsurface and the saturated zones with very little or no insignificant influence from anthropogenic factors. The major source of Ca was from weathering of the silicate mineral anorthite while that of Na is from the weathering of the silicate mineral (albite). K could be coming from the weathering of orthoclase (K-feldspar) from the surrounding much resistant Bongo granitoids. Cationic exchange is the minor source Ca while Na gets consumed as groundwater residence time increases along the flow paths towards discharge points.



The main source of the extremely dominant anion (HCO₃[¬]) from the atmospheric CO₂, which forms the weak carbonic acid in rain water and upon reaction releases the relatively conservative HCO₃[¬] into solution. The continuous repetition of this process (the major geochemical process in the area) over geologic time has resulted in the accumulation of very high concentration HCO₃[¬] in the study area.

The findings of this study by extension will reflect the chemistry of groundwaters in the southern parts of Burkina Faso since the climate, vegetation, soil types, geology, and the socio-cultural settings are the same.

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