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QUANTITATIVE EVALUATION AND HYDROGEOCHEMICAL PROPERTIES OF GROUNDWATERS FROM PRECAMBRIAN ROCKS OF SAN PEDRO AREA (SOUTHWESTERN CÔTE D'IVOIRE)

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ABSTRACT

San Pedro area covers 6,912 km^2 at southwestern Côte d'Ivoire. Its rural population returns to use surface waters for domestic and agricultural needs because of many drillings previously established were damaged. This study aims to contribute best knowledge of quantity and quality groundwater from basement aquifers of this area. Database includes monthly temperatures, rainfalls, outflows and groundwater samples. The calculation of pluviometrical indexes through reduced centered data led to identify climate variability. Recharge of aquifers was calculated by hydrological balance following Thornthwaithe and GR2M methods. Hydrogeochemical properties were determined through the calculation of ions exchange indexes and chemical classification with Korjinski and Riverside diagrams.
During last three decades (1977-2007), climate variability presented consecutively humid, dry and humid periods. Aquifers recharge was evaluated to 701 m^3/ hectare and 1008 m^3/ hectare respectively through Thornthwaite and GR2M methods. Surface and groundwater levels are influenced by climate variability. Groundwaters are healthy for drinking water and agricultural

irrigation. Hydrolysis of primary silicate minerals is the major process of groundwater mineralization. Groundwaters develop stability with kaolinite. During interaction between groundwater and surrounding-rocks, waters exchange their ions Mg^{2+} and Ca^{2+}.

Keywords: Climate variability, chemical, groundwater, recharge, San Pedro.

RESUME

La région de San Pedro couvre une superficie de 6 912 km^2 au Sud-ouest de la Côte d'Ivoire. La population rurale de cette région se dirige de plus en plus vers les eaux de surface pour satisfaire leurs besoins domestiques et agricoles en eau car plusieurs forages précédemment implantés sont endommagés. Cette étude envisage de contribuer à une meilleure connaissance de la quantité et la qualité de l'eau souterraine des aquifères de socle de cette région. La base de données est constituée par les températures, les précipitations, les débits de cours d'eau et les échantillons d'eaux souterraines.
Le calcul des indices pluviométriques a permis d'identifier la variabilité climatique traduite par la succession de période humide, sèche et humide. La recharge est évaluée à 701 m^3/ hectare et 1008 m^3/ hectare respectivement selon les approximations de Thornthwaite et du modèle GR2M. Le calcul des indices d'échanges de base a révélé que les eaux échangent leurs ions Mg^{2+} et Ca^{2+}. La classification hydrochimique a montré que les eaux souterraines sont saines pour la consommation et l'irrigation agricole. La minéralisation des eaux est majoritairement due à l'hydrolyse des silicates primaires. Les eaux souterraines sont principalement en équilibre avec est la kaolinite.

Mots clés: variabilité climatique, chimique, eau souterraine, recharge, San Pedro

INTRODUCTION

During last decades, according with one of the millenium goals of development, government of Côte d'Ivoire built many drillings at San Pedro in sight to reduce the need of drinking water in rural areas. However, a great number of these drillings becomes more and more abandonned by population because of many reasons such as pump failures, bad quality, or undesirable color of groundwaters.Consequently, population returns to use rivers and rainwaters for drinking in spite of their uncertain quality and quantity respectively due to pollution and climate variability. This study aims to contribute best knowledge of quantity and quality of groundwater from San Pedro area.

PRESENTATION OF STUDY AREA

San Pedro area is located between latitudes 4°and 5°30 northern and the western longitudes 6°15 and 7°20 at southwestern of Côte d'Ivoire (Figure 1). This area covers 6,912 km^2 dominated by much peneplain (0-100 m) and few down-tableland (< 500 m). One meets many rivers whose hydrological behavior follows closely the variation of rains. Vegetation is dominated by humid dense forest. Study area abundantly receives rain such as many southwestern areas of the country. The population registered at 1998 was 442 204 inhabitants (Géohive, 2012). At 2015, their number approximates 639 000 following annual population growth rate estimated to 2.2% (INS, 2014). They mainly settle near natural water points because of their regular practices of farming and fishing. The basement of San Pedro area is dominated by the crystalline and metamorphic rocks: gneiss, granite, migmatite, micaschist and granodiorite (figure 1).

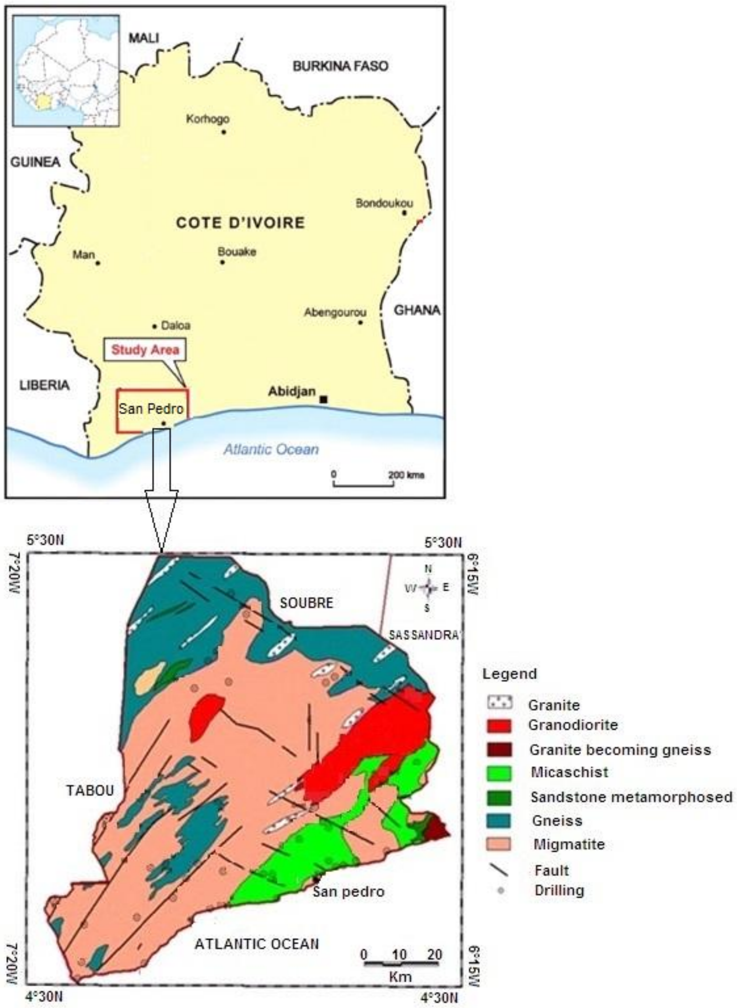

Figure 1: Location of study area and rock formations

Several faults affected these rocks due to tectonic events occurred in this area (Papon and Lemarchand, 1973; Yacé, 2002). The fracture networks reached advanced development stage with two principals directions: N90-100 and N00-10 (De Lasme, 2013; Lasm et al., 2014). On hydrological view, 4 rivers (Nero, Brimay, San Pedro and Dodo) flow out. The main river is San Pedro which annual runoff and catchment area respectively equal to 336 mm and 3,300 km^2 (MINEF, 2003). Previous hydrogeological studies on Precambrian basement indicated that groundwaters are met in 3 aquifers: weathered material, fissured horizons and deep opened fractures (Lachassagne et al., 2011; De Lasme et al., 2012; De Lasme, 2013; Lasm et al., 2014).

DATA AND METHODOLOGY

Database is constituted on one hand by monthly hydroclimatic: temperatures from 1995 to 2009, rainfalls from 1977 to 2009 and outflows measured at measurement station from 1969 to 2004. On the other hand, 45 and 10 groundwater samples are respectively collected during dry seasons of 1999 and 2010. These groundwater samples were analyzed 2 weeks after the sampling at the laboratory.
Rainfall data came from Tabou and San Pedro measurement stations. Indeed, two localities are separated by few kilometers and belonged to the same climate. Rainfalls data of Tabou were measured from 1970 to 2004. Hydrologic balance was determined by applying empirical climate method (Thornthwaite, 1948) and GR2M model (Mouehli, 2003). Thornthwaite method was applied by many authors in Côte d'Ivoire (Biémi, 1992; Savané, 1997; Kouamé 1999; Jourda, 2005). GR2M model uses monthly rainfall, potential evapotranspiration, and outflows at outlet of catchment. Model approach detailed by Mouehli (2003) and Mouehli *et al.* (2006). Its flow chart is presented on figure 2.

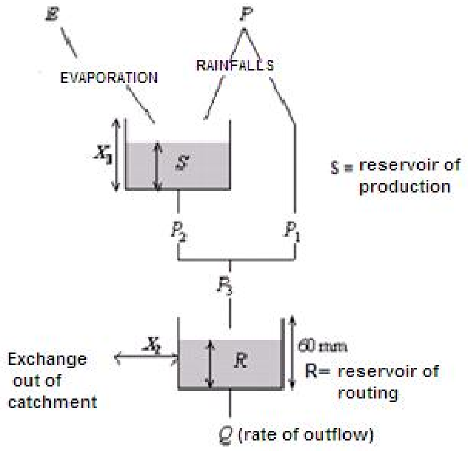

Figure 2: GR2M model flow chart

According to this model, infiltration-water goes through two reservoirs (S and R) before getting groundwater outlet with rate flow (Q). The capacity of first reservoir (S) depends of effective rainfalls and potential evapotranspiration but the second reservoir (R) is fixed to 60 mm. Model optimization is made by the two parameters X_1 and X_2: X_1 is a coefficient of production capacity of reservoir S and X_2 is a coefficient of underground exchanges between R and out of the watershed. Modeling is satisfied when simulated rate flows are similar with observed ones. So, modeling performance is appreciated by the behavior of graphs of rate flows and the value of optimization criteria below (equation 1) proposed by Nash and Sutcliffe (1970):

$$Nash = 1 - \left[\frac{\sum_{t=1}^{N}\left(Q_{obs,t} - Q_{sim,t}\right)^2}{\sum_{t=1}^{N}\left(Q_{obs,t} - \overline{Q_{sim,t}}\right)^2}\right] \quad (1)$$

Nash ≥ 90%, corresponds to excellent fitting; 80%≤ Nash ≤ 90%, corresponds to high satisfactory fitting; 60%≤ Nash ≤ 80%, corresponds to satisfactory fitting, and Nash ≤ 60% corresponds to bad fitting.
After a best fitting, the effective monthly evapotranspiration (ETR) is determined by using equation 2:

$$ETR = S_1 - S_2 \quad (2)$$

S_1: water infiltration inside the reservoir S at the beginning of the month;
S_2: water infiltration inside the reservoir S at the ending of the month.
During the period that GR2M fitting is satisfied, the depth of infiltration water (recharge of aquifers) is calculated by using water balance equation (equation 3):

$$I = P - (ETR + R) \quad (3)$$

With I: depth of water infiltration;
P: rainfalls;
ETR: effective evapotranspiration;
R: depth of outflows.

The climate variability occurred in the studied area was identified by calculation of centered reduced data and applying of Hanning filter low-pass at step 2 (Assani, 1999). The centered reduced data equation is given by equation 4:

$$X_i = \frac{R_i - R_m}{\sigma} \quad (4)$$

With X_i: rainfall index for year i;
R_i: rainfall for year i;
Rm: rainfall average of considered period;
σ: standard deviation of annual rainfall.

Low- pass filter of Hanning is constituted by arithmetical equations written with annual rainfalls indexes [x(t)] early determined. These equations (5 to 9) are:

$x(1) = 0.54\,x(1) + 0.46\,x(2)$; (5)

$x(2) = 0.25\,x(1) + 0.50\,x(2) + 0.25\,x(3)$; (6)

$x(t) = 0.06x(t-2) + 0.25x(t-1) + 0.38x(t) + 0.25(t+1) + 0.06x(t+2)$ (7)
for $3 \le t \le (n-2)$;

$x(n-1)=0.25x(n-2)+0.50x(n-1)+0.25x(n)$; (8)

$x(n)=0.54x(n)+0.46x(n-1)$. (9)

Hydrochemical properties of groundwaters were determined by using chemical classification with diagrams of Riverside and Korjinski included in software

Diagram 4.0. This software was developped at laboratory of hydrogeology of University of Avignon-France (Smiler, 2007). Riverside diagram is based on water conductivity and Sodium Adsorption Ratio (SAR). This ratio is determined by equation 10:

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}} \tag{10}$$

Using of Riverside diagram leads to know ability of groundwater for agricultural irrigation. Korjinski diagrams are 3 logarithm graphics those identify mineral stability of groundwater according its temperature and chemical components. These graphics are followings:
log $((Na^+)/(H^+))$ *vs* log (H_4SiO_4);
log $((K^+)/(H^+))$ *vs* log (H_4SiO_4);
log $((Ca_2^+)$ /(H+)) *vs* log (H_4SiO_4).

Ten samples were used to study mineral stability of groundwaters from study area.
To determine the different exchanges during the interaction of groundwater and surroundings rocks, ions exchange index (IEB) is calculated with equation 11:

$$IEB = \frac{rCl - (rNa + rK)}{rCl} \tag{11}$$

According Schoeller (1954):
I.E.B = 0, there is no exchange between surrounding rocks and groundwater;
I.E.B > 0, groundwater exchanges ions Na^+ and K^+ against Mg^{2+} and Ca^{2+} ions from surroundings rocks.
I.E.B < 0, groundwater exchanges ions Mg^{2+} and Ca^{2+} against Na^+ and K^+ ions from surroundings rocks.

RESULTS

Hydrological balance

Main results through Thorntwaithe approach indicate that from 1995 to 2009, averages of annual rainfalls and effective-evapotranspiration (ETR) are respectively 1489 and 1206 mm. Annual water surplus equals to 283 mm. Sum of runoff reached 213 mm per year. This value corresponds to 15% of annual rainfalls. Consequently, recharge is evaluated to 70 mm per year. Quantity of water infiltrated under the ground can be estimated to 231 330 km^3 per year or 701 m^3/hectare/year.
Principal result obtained through GR2M model is illustrated on figure 3.
Setting of model is realized on 1995 and satisfactory fitting is obtained from 1996 to 2000 where observed and simulated outflows are the same evolution

with Nash coefficient reached 66%. From 1996 to 2000, average of annual effective-evapotranspiration evaluated to 947 mm. Then, calculation of hydrological balance for San Pedro catchment led to determine recharge (the depth of water infiltrated) reaching to 100.8 mm/year or 1 008 m^3/hectare /year.

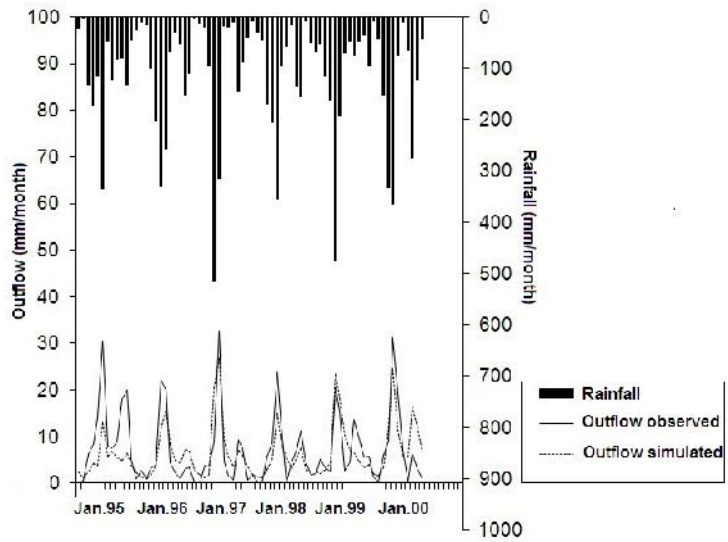

Figure 3: Adjustment of rainfall and outflow of San Pedro with GR2M

Climate variability

Pluviometrical indexes values spread into interval -2 to 2. Principal climatic periods distinguished after applying of filters of Hanning are 3 (figure 4): the first humid period from 1977 to 1984, dry-period from 1985 to 1998 and second humid-period from 1999 to 2007. Average of rainfalls of second humid period is higher than the first one. During last three decades, 1990 was the driest year.

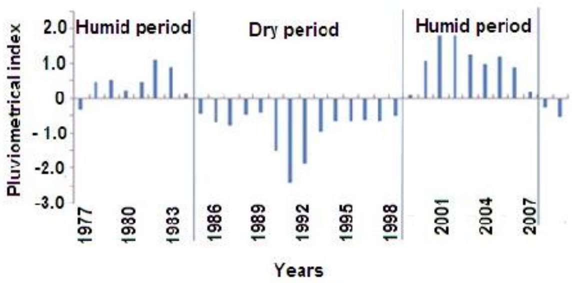

Figure 4: Evolution of filtred pluviometrical indexes from 1977 to 2009

Impact of climate variability on water resources

Evolution of rainfalls and outflows of San Pedro River is presented on figure 5. On this graphic, it can be identified two types of evolution for those two parameters: similar and opposite evolution. Generally, outflows follow rainfalls.

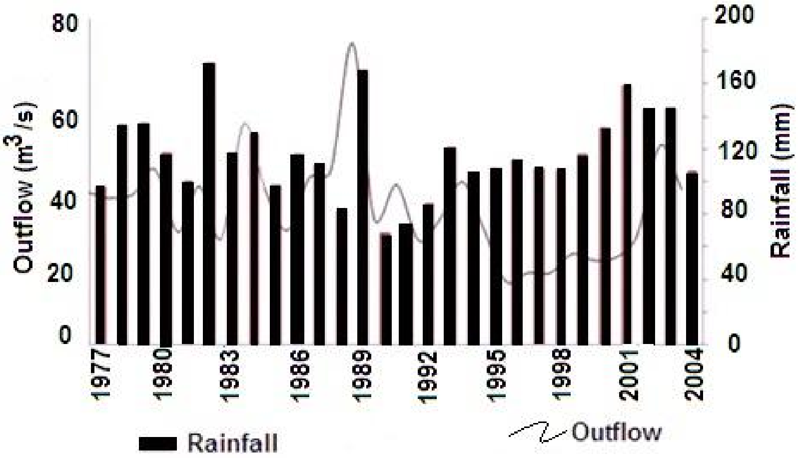

Figure 5: Evolution of rainfalls and outflows of River at San Pedro

However, from 1986 to 1988 and from 2001 to 2003 rainfalls dropped when outflows increased. From1990 to 2000, rainfalls increased when outflows turned down. Evolution of groundwater and rainfall from 1996 to 2000 is illustrated on figure 6.

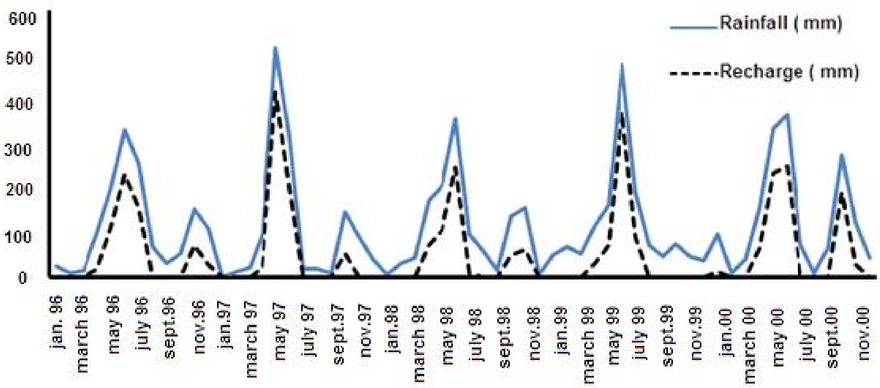

Figure 6: Evolution of rainfall and recharge at San Pedro from 1996 to 2000

According these graphics, groundwater and rainfall have the same behavior from 1996 to 2000. This interval of time corresponds to transition period where dry period is achieving and the humid period is starting. At this transition-period, outflows decreased when rainfalls and groundwater increased. Probably, it is due to effective exchanges between surface water and groundwater at connexion points. In spite of rainfalls increasing, outflows of river are decreasing because of soil-plants needs and/or great part of infiltrated water through fractures. When there is a climatic transition from humid to dry period, such as 1986 to 1988, rainfall decreased and outflows increased. It can be due to drainage phenomena.

Groundwater habilities for human drinking and agricultural irrigation

According standards of drinking water potability from United Nations Organization of Health, about 95% of groundwater from Precambrian rocks of San Pedro area is not bad for human drinking.
Distribution of groundwater samples following their Sodium absorption ratio (SAR) and conductivity is presented by Riverside diagram at figure 7.

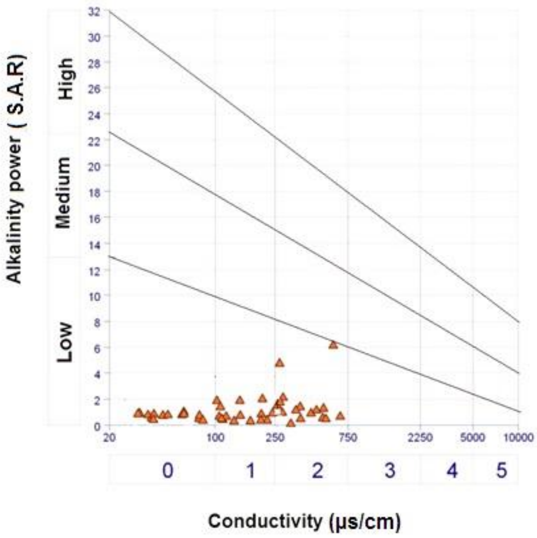

Figure 7: Distribution of San Pedro groundwater samples in Riverside diagram

This distribution reveals that all groundwater samples have a poor alkanity power (SAR < 14) 65% of them have also a poor salinity (Cond. < 250 µs/cm) when leftover have medium salinity (250< Cond. < 750 µs/cm). Then, SAR values are so weak and cannot lead to bad reaction of soil, such as reduction of soil permeability. Conductivity values indicate that groundwater have not great salinity power. That is convenient for best growing of many plants with a light allowance to salinity such as rice and tomato.

Mineral stability of groundwater

Diagrams of mineral stability with groundwater from Precambrian rocks of San Pedro area are displayed at figures 8 to 10. All the diagrams revealed that principal mineral which is stable with groundwater is the kaolinite (clay mineral). Some of these groundwaters are stable with microcline. However, none of groundwater samples is stable with anorthite, gibbsite, montmorillonite, albite and muscovite. In tropical areas, hydrolysis of primary silicate minerals such as anorthite leads to the formation of hydrogenocarbonate mineral and kaolinite according to chemical reaction below (equation 12):

$$\underset{\text{(Anorthite)}}{CaAl_2Si_2O_8} + 3H_2O + 2CO_2 \longrightarrow \underset{\text{(Kaolinite)(hydrogenocarbonate)}}{Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^-} \quad (12)$$

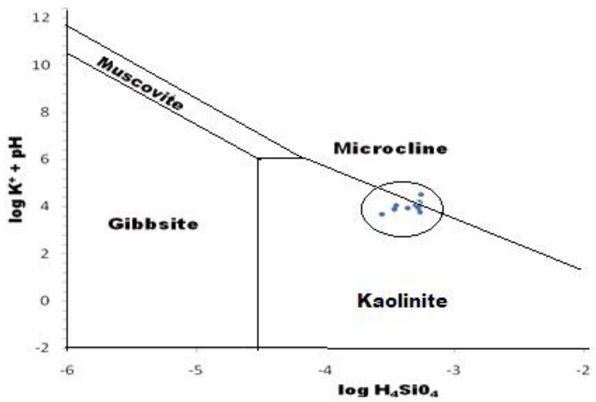

Figure 8: Diagram (log K^++ pH *vs* logH_4SiO_4) for groundwater of San Pedro.

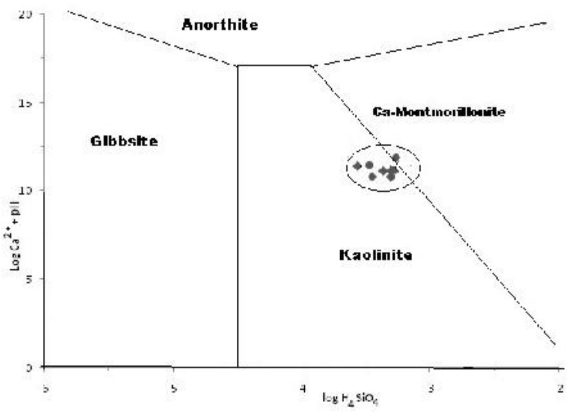

Figure 9: Diagram (logCa^{2+}+ pH *vs* logH_4SiO_4) for groundwater of San Pedro

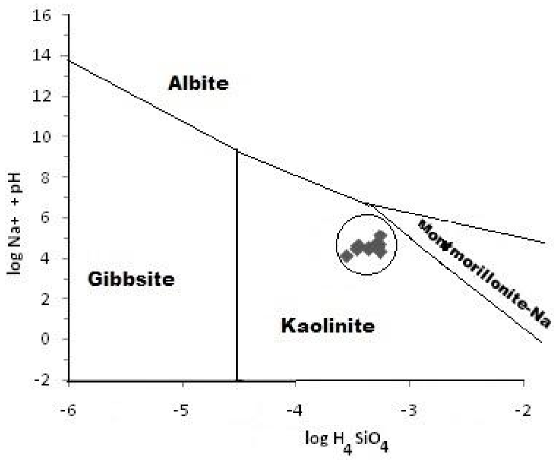

Figure 10: Diagram (log Na^{+}+ pH *vs* logH_4SiO_4) for groundwater of San Pedro

Interaction groundwater and surrounding rocks

Values of exchanges base index spread from -12 to 0.81 with average value of -4.15. IEB values mainly are negative. These values mean that groundwater exchanges their ions (Ca^{2+} and Mg^{2+}) against the alkaline ones (Na^{+} and K^{+}) from surroundings rocks. Distribution of groundwater samples in arithmetic diagram of (Na^{+} + K^{+}) according to (Ca^{2+} + Mg^{2+}) is presented on figure 11. Groundwaters with ratio (Na^{+} + K^{+})/ (Ca^{2+} + Mg^{2+}) inferior to 1 represent 65% of all samples. This result indicates that ions Ca^{2+} and Mg^{2+} are numerous than ions Na^{+} and K^{+}.

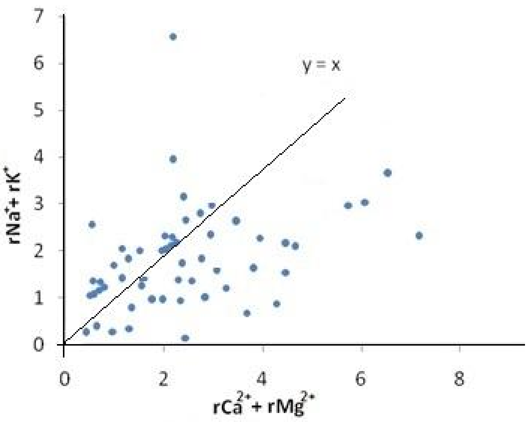

Figure 11: Diagram (rNa^{+}+ rK) *vs* (rCa+ rMg) for groundwater of San Pedro.

DISCUSSION

Value of annual recharge of aquifers

Annual recharge of aquifers was estimated to 70 and 100 mm respectively through Thornthwaite and GR2M methods. These values can be register among previous values of recharge of catchment from Precambrian basement of Côte d'Ivoire (Soro, 1987; Biémi, 1992; Savané, 1997; Kouamé, 1999). The value determined at San Pedro through GR2M method, is similar to value (105.61 mm) obtained at N'zi-Comoe area by Kouassi *et al.* (2012a) even if these authors used Coutagne and Tixéront (1964) methods to calculate respectively effective-evapotranspiration and runoff.
Analysis of previous values of recharge assessment through Thornthwaithe and GR2M methods revealed that values from second approach are superior to those obtained from first. At Marahoue catchment (center area of Côte d'Ivoire), Biémi (1992) used Thorntwaithe method and obtained 46 mm/year while Kouassi (2007) obtained 350 mm/year with GR2M method. At sedimentary catchment such as Aboisso area (southeastern Côte d'Ivoire), Dibi (2008) estimated annual recharge of aquifers to 18 mm and 386 mm respectively through Thornthwaithe and GR2M methods. Concerning Thornthwaite method, the value of recharge determined at San Pedro is closely to the value (74 mm) calculated at Man area by Kouamé (1999). This proximity of values can be explained by similarity of geomorphological and climate characteristics (Kouamé, 1999). Indeed, evidence of groundwater is determined by abundant rainfalls on areas and intensity of tectonic events occurred and led to favorable hydrodynamic properties (high permeability and great porosity) of rock formations. Man and San Pedro areas are characterized by the same climate periods and, according to Lasm et al. (2014), their fracture networks reached advanced development stage.

Climate variability

Climate variability identified at San Pedro area during last three decades (1977 to 2007) is characterized by a lack of normal climatic period where pluviometrical index value is nearly zero. This result is similar to Fadika (2012) even if this author used other method. However, normal climatic period was identified elsewhere in Côte d'Ivoire by many authors such as Dibi (2008) at Aboisso (southeastern Côte d'Ivoire), Kanohin et al. (2009) at Daoukro (center of Côte d'Ivoire), Soro et al. (2011) at Grand-Lahou (southwestern Côte d'Ivoire) and Fossou et al. (2015) at Dimbokro (east-central Côte d'Ivoire). At Sassandra area located eastern of San Pedro, Soro et al. (2011) highlighted a drought occurred during 1974, a normal period from 1941 to 1947, a humid period from 1948 to 1975 and dry period from 1976 to 2001. We can note that limits of climatic periods are not the same in these two neighboring areas (San Pedro and Sassandra). It can be explained by intensity of upwelling phenomena developped there. Indeed, Cissoko (1995) revealed that interannual pluviometric changes of countries near the gulf of Guinea are strictly guided by the ocean Atlantic surface temperatures. Direct influence of climate variability on groundwater levels inside aquifers corroborate several studies (Hughes, 2004; Vissin, 2007; Dibi, 2008; Kanohin et al., 2009; Soro et al., 2011; Fadika, 2012).

Hydrogeochemical properties of groundwater

Mineralization process of groundwater such as hydrolysis of primary minerals and ion basis exchanges, during interaction water and surroundings rocks, occurred in others fissured aquifers from precambrian basement of Côte d'Ivoire. According to Biémi (1992) and Kouassi et al. (2012b) it developped these two processes respectively at Marahoué area (center of Côte d'Ivoire) and Guiglo-Duékoué area (western Côte d'Ivoire). At Eastern Senegal, Diouf (1999) showed that groundwaters from fissured granite aquifers contained more chlorides, and those from schist aquifers and basic rocks are rich in calcium and magnesium. He explains relation between groundwater chemistry and surrounding-rocks by mobility and alterability of many elements from primary minerals. The quantity of completely dissolved matters inside groundwater depends on the intensity of the interaction water-rock and residence time of water in the aquifer (Adiaffi et al., 2009). At San Pedro, interaction between groundwater and surrounding rocks were dominated by hydrolysis of silicate minerals where Ca^{2+} and Mg^{2+} ions are abundant such as anorthite, labrador and hornblende.
Stability with clay mineral "kaolinite" of groundwater from precambrian basement" corroborates results of Ligban *et al.* (2009) in Côte d'Ivoire, Edet and Okereke (2005) in Nigeria and Sandow *et al.* (2008) in Ghana. Nevertheless Soro and Goula (1997) highlighted a stability with montmorillonite, anorthite and albite for groundwater from crystalline basement at south of Côte d'Ivoire. According Derron (1999), groundwater mineral stability can be explained by the velocity of primary minerals dissolution. According Appelo and Postma (1999), mineral stability of groundwater can be due to climatic and geomorphological conditions. Indeed, the work undertaken by Edet and Okereke (2005) and Sandow et al. (2008) revealed that the weathering of the primary silicate minerals which leads to the formation of kaolinite, occurs typically in tropical areas characterized by abundant rainfalls and good conditions of drainage. On the other hand, the groundwater stability with montmorillonite occurs at zones where there is dry climate and the erosion of soil carried out slowly (Appelo and Postma, 1999). Concerning San Pedro area

where rainy season is longer than dry season, stability of groundwater with kaolinite is due to weathering of primary silicate minerals.

CONCLUSION

This study contributes to best knowledge of quantity and quality of groundwaters from aquifers of Precambrian basement of San Pedro area. Groundwaters evaluated to 701 m^3 and 1008 m^3/hectare through respectively Thornthwaite method and ETR estimation by GR2M calibration. During last three decades (1977-2007), climate variability presented consecutively humid period, dry period and humid period. Surface and groundwater levels are influenced by climate variability. The chemical properties of groundwater allow to use them for drinking water and agricultural irrigation. On hydrogeochemical view, the major groundwater mineral acquisition process is the hydrolysis of primary silicate minerals. Kaolinite is the principal stable mineral with groundwater inside the aquifers. During interaction between groundwater and surrounding-rocks, there is an important exchange of ions where groundwaters exchange their ions Mg^{2+} and Ca^{2+} against ions Na^+ and K^+ from surroundings rocks.

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