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Flow Pattern and Residence Time of Groundwater within Volta River Basin in Benin (Northwestern Benin)

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Abstract

The knowledge about groundwater flow conditions within Volta river basin in Benin, has restricted information coming to piezometry, water storage time, water path, and water quality. A good groundwater resources assessment of this sudano-sahelian area, is a huge condition for the sustainable management of water resources, which since the part of the 20th century is facing a severe drought that leads to a greater aridity. This article provides a summary with the main elements of carbon isotope (^{13}C and ^{14}C) as well as tritium (^{3}H) coupled with hydrogeological and hydrochemical data. The goal is to improve the initial water recharging and the groundwater flow system within the aquifer. Two main results can be produced from the groundwater chemistry. First, the interactions between groundwater and clay minerals related to the residence time of groundwater are indicated by a slight evolution of Ca-HCO_3 and Ca-Mg-HCO_3 to Na-HCO_3. Beside that towards water types Cl-NO_3 indicates the anthropogenic influence on groundwater, related to agricultural activities and sanitation conditions. The carbon-14 activity measured on the TDIC is between 17.29 and 85.47 pmC. Therefore, it contains some samples covering a wide period of time from now to the Holocene implying a continuous system recharging over time. All the data confirm the assumption of a homogeneous, largely unified aquifer system with a multi-layer structure, but it also points out the low resource sustainability and a strong anthropogenic contamination of the most superficial horizons.

Keywords

Hydrochemistry, Radiocarbon, Recharging, Residence Time, Dating, Volta River Basin in Benin

1. Introduction

Groundwater is the main source of water for domestic and other uses in many rural and urban areas of the Volta river basin in Benin [1], because of the scarcity of available surface water resources in the region. In addition, surface waters that are often highly polluted were the root of Guinea worms, infestations and cholera [2].

Since then, most groundwater has been protected from surface activities; indeed it is often considered to be a higher-quality water that does not need treatment before use.

However, it is currently threatened by various sources of contamination. Over the past two decades, this basin has been experiencing a significant economic boom, with an increase of agricultural activity, coupled with a strong population growth. According to the fact that water is a huge part of this development it is necessary to acknowledge about the quality of this resource [3].

The knowledge of water flow conditions within the aquifers of this basin is relatively limited with very little information on piezometry, recharging processes, residence time and water quality.

So, a better assessment of groundwater resources in this area is a strategic point for the sustainable management of water resources, which since the mid-twentieth century is experiencing drought persistence leading to increase climate aridity [4] [5].

This problem mainly affects the surface but certainly also the recharging of groundwater. To be able to know about the evolution of water resources, recent research, under the aegis of the technical cooperation of the International Atomic Energy Agency (IAEA) has led to the application of isotopic technical, which helped acquire data relating to groundwater origin, its flow path and the residence time.

This article is a synthesis of results using isotopes of carbon (^{13}C and ^{14}C) and tritium (^{3}H) couple with hydrogeological and hydrochemical data.

2. Geological and Hydrogeological Setting

2.1. Study Area and Hydroclimatology

The Volta river basin in Benin, covers an surface area of 13,590 km^2, or 13% of the national territory (**Figure 1**) and 3.4% of the total area of the basin shared with Burkina Faso (43%), with Ghana (42%), (15%), with Togo, (2%) with Mali and Ivory Coast [4] [5] [6] [7] [8].

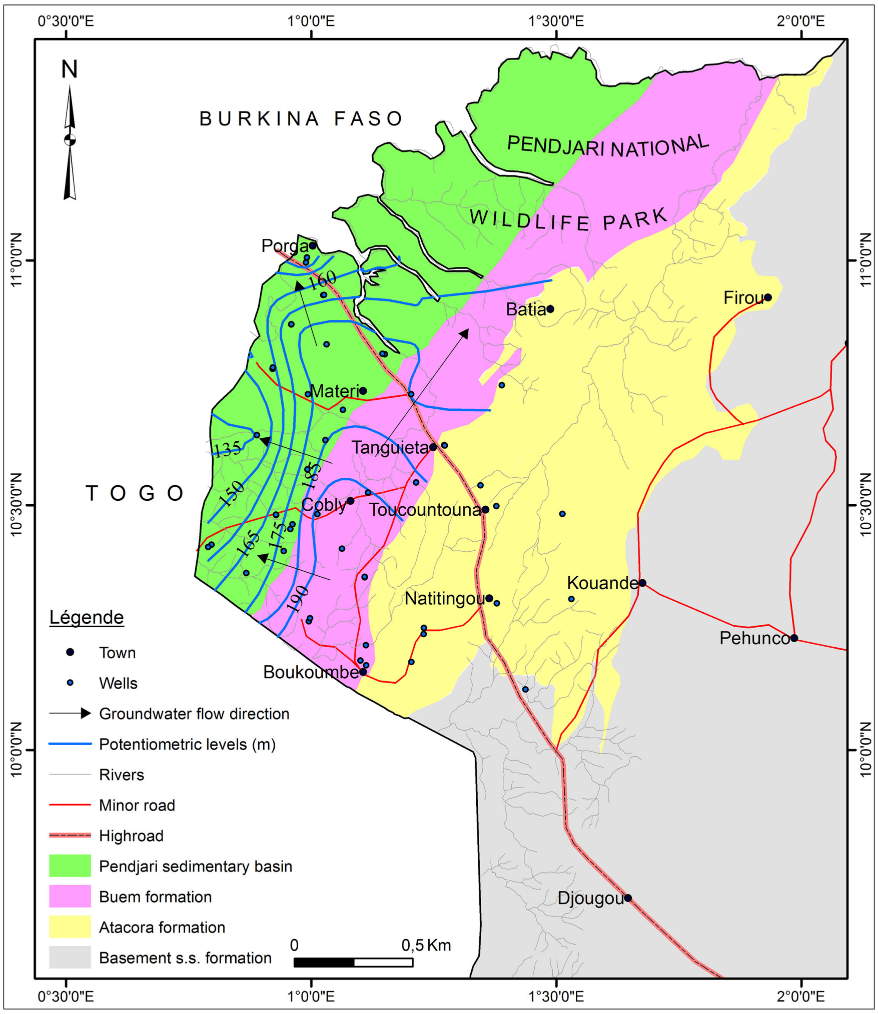

Figure 1. Map of the study area showing the location of the sampled boreholes and geologic and hydrologic information.

Located in the Sudano-Sahelian zone, this basin is between 9˚30' and a latitude of 11˚30' North and 0˚45' and a longitude of 2˚03' East (**Figure 1**).

It is characterized by a relatively contrasting geomorphology, made up of hill chains to the east and center, and a lowland to the west.

Its altitude gradually increases from 160 m on average in the Pendjari plain to the West, to a maximum of 650 m on the Atacora range to the East.

Half of the North area of the basin is occupied by the Pendjari National Park and the population's rate, in majority rural, is increasing around the park [9] [10].

The climate is characterized by a unique rainy season which lasts from May to October [11] [12]. The annual rainfall average recorded at the synoptic meteorological station of Natitingou for the period from 1979 to 2009 is 1173 mm, with an average temperature of 27.4˚C.

The annual evapotranspiration average of 1494 mm is much higher than the annual rainfall [12]. The Pendjari River is characterized by a steady flow, with a minimum flow of 1 m^3/s from March to April and a maximum flow of 300 m^3/s, in September [11].

They have decreased from 0 to 238 m^3/s in Porga and from 0 to 25 m^3/s in Tiélé, which confirms a flow deficit due to the rainfall recession and large losses of water per year through evaporation [4] [13].

2.2. Geology and Tectonics

The volta river basin in Benin is shrouded essentially in a geological set called of external units (**Figure 2**) [14]-[21]. It's an old Precambrian base cover (Proterozoic Terminal) s.s. (**Figure 2(a)**). It is folded with a tabular part that more or less changed by pan-African organ (**Figure 2(b)**). In the west, the sedimentary sequences are monoclinic and are the sedimentary basin of Pendjari. They become

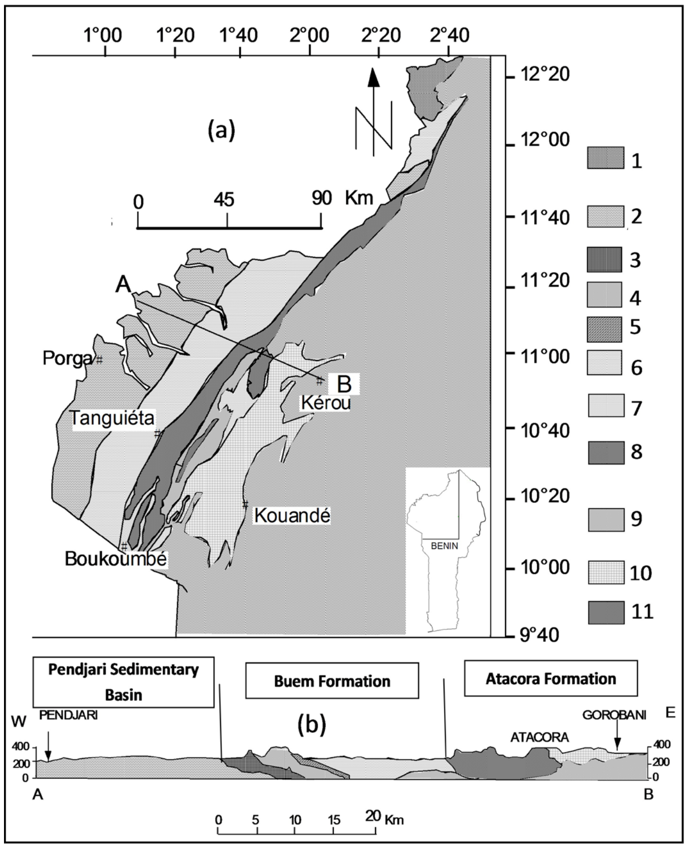

Figure 2. Regional geological map (a) of the Volta river basin in Benin, with the geological cross section AB; (b) (According to [15] [17] [18]): Paleozoic: 1—Volta sedimentary Basin (sandstones, argillites, quartzites); Upper Proterozoic: 2—Pendjari sedimentary Basin (argillites, fine sandstones); Upper Proterozoic (Panafrican orogeny) Buem Formation: 3—Buem serie (Jasper); 4—Buem serie (fine and medium quartzous sandstones); 5—Buem serie (basic rocks); 6—Buem serie (sandstone, quartzites); Atacora Formation: 7—Kandé serie (schists, quartzites); 8—Korontière serie (fine quartzites); 9—Kanson serie (schists, quartzites); 10—Kouandé serie (quartzites, schists); Middle Proterozoic (updated by panafrican orogeny): 11—Basement s.s. Formations (orthogneiss, gneiss and micaschists into the study area). AB line: position of the geological cross section AB.

increasingly folded and changed as we move on towards the east [15] [21] [22] [23]. Then they are gather together in two distinct parts according to the way they wrinkle and the way they change. We have: Buem formation, the less damaged one, and the Atacora formation the most affected. That one is overlapped by basement formations and overlapped also Buem formation which overlaps the sedimentary basin of Pendjari. The metamorphism that has affected Buem and Atacora is a lower degree than the one that affected the basement s.s.

The Atacora range is the most prominent range in the basin. It is oriented NNE-SSW [21] [24] in [25]. Buem formation is made up of argillites, siltites, quartzitic sandstones, hematic rocks and sericite schists, and also with a set of jasper, and basic magmatic rock [16] [26] [27] [28]. In addition, Atacora formation has a serie of schists and quartzites aquifers. In the West the tabular covers of terminal Proterozoic are free of any metamorphism and are composed by argillites, siltites and with highly indurated sandstones (**Figure 2**). Finally, the basement formations are constituted of orthogneiss, ordinary gneiss and micaschists in the study area.

So, the study area has four geological sub-units [15] [17] [18] namely, the sedimentary basin of Pendjari, Buem formation, Atacora formation and the basement s.s from West to East. Those four formations match respectively with four aquifers with the same names (**Figure 3**) that have been studied. The Buem formation is very similar to the aquifer of Pendjari which is generally considered to be unremitting and free-flowing at least in its affected surface area. The two

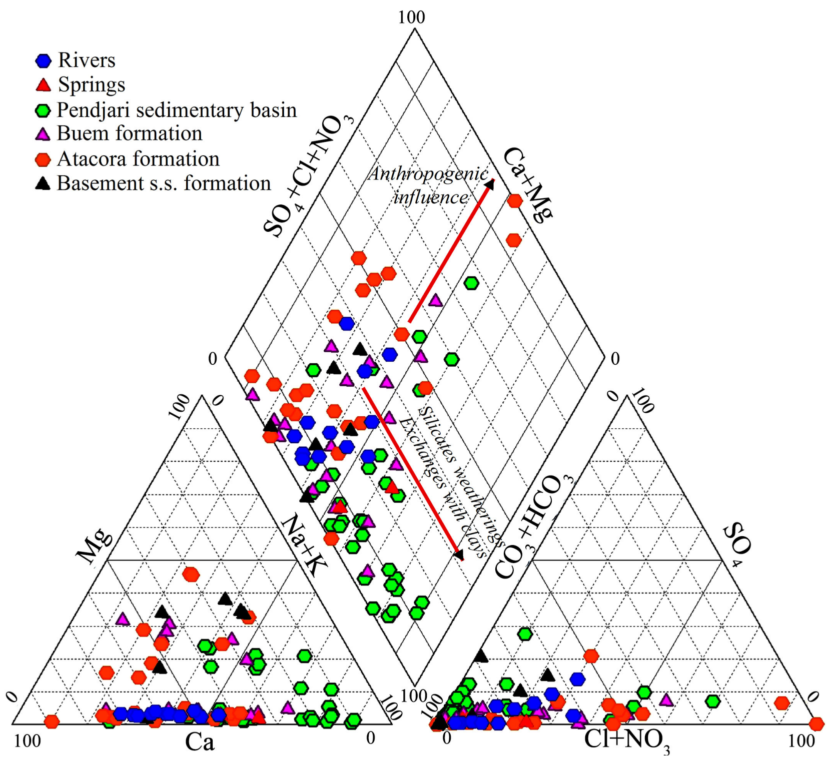

Figure 3. Volta river basin in Benin waters positions in the major ions (meq/L) Piper diagram.

one (Atacora and the basement s.s. formations) are so discontinuous with an aquifer of fractures crowned by an aquifer of alterites. The first porosity is destroyed in most aquifers by consolidation and case-hardening [29]. Nevertheless, due to the intensity of surface deterioration and brittle tectonics affecting all of these formations, the aquifers mentioned are likely to be in hydrodynamic (lateral hydraulic interconnection), and hence hydrochemical, interconnection through not only the superficial alterites, but also more or less deep and open fractures.

2.3. Hydrogeology

This region hydrogeology is not well known so that only few groundwater exploration projects have been carried on in this river. And the conditions are very complex as showed by the data providing from the existing drillings and the wells. The depth of the water changes throughout the basin, but is generally shallow, from 1.7 m to 84 m with the catchments depth from 31 m to 104 m [12]. The aquifer of the deteriorated region and the fracture zones are the major aquifers. As a unit, the altered zone extends about 4 m to 20 m thickness [29] [30] and in most of the village, it is built to supply water through wells digged by hand [31], but most of the wells dry up during the dry season. Fracture zones are developed below the soil surface in the bedrock with 20 m of depths or more [32]. They are mostly vertically close, narrow and linear. Groundwater is in the control of fractures [29] [30] [32] and generally occurs under semi-confined conditions, which may exist in places where static water level (SWL) diverse from 1 to 20 m below the earth surface [29]. The specific capacities (Q/s) of boreholes in the catchment range from 0.01 to 5.5 m^3/h/m and the transmissivity varies between 10^{-6} and 10^{-2} m^2/s [12].

3. Materials and Methods

A total of 93 water samples were taken from the whole Benin's Volta River, of which 30 were collected during the February-March 2012 campaign and 63 during the October-November 2013 season (**Figure 1**). Furthermore, monthly rainfall samples were obtained from the pluviograph of the ASECNA synoptic station at Natitingou. Since the results are almost the same we put them together, in this article for a better study. Going into this result, 34 samples come from the Pendjari Sedimentary Basin, 18 from Buem Formation, 21 from the Atacora Formation, 6 from the basement formation s.s, 2 from the springs and 12 from the rivers.

Before the measurements were taken, a pump was used to drill the wells till the pH stabilization, the electrical conductivity, and the Temperature is known. An HI 9828 multi-parameter was used for it. Then, the water samples were collected and stored in high-density, 1000 ml polyethylene bottles with poly-seal stoppers. The depths of the water table were measured in the wells using a WL500 piezometric probe. The Alkalinity was measured out by volumetric titration using chemical kits. To record all data and the sampling points altitudes the global positioning system (GPS) named Garmin GPSMAP 76 was used.

Each sample was tested at the Radio-Analysis and Environment Laboratory (Sfax, Tunisia) to determine the major components (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^-, CO_3^{2-} Nitrates (NO_3^-)) and stable isotopes (^2H and ^{18}O), but HCO_3^-, CO_3^{2-} was tested by Liquid-Phase Chromatography (ILC), equipped with IC-Pak TM CM/D columns for cations, using EDTA and nitric acid as eluent. For anions a Metrohm chromatograph, equipped with CI SUPER-SEP using phthalic acid and acetonitril acid as eluent was used for the test with an accuracy of 2%. The overall detection limit of the ions was 0.04 mg/l. HCO_3^- et CO_3^{2-} contents were analyzed by titration with 0.1 N HCl acid. All the results were tested for the ionic charge equilibrium according to [33]. The error margin between cations and anions is ±5%, meaning that all the results are valid for interpretation. Total dissolved solids (TDS) are measured by evaporating 100 ml of water sample for 24 h at 105˚C. The isotopic tracers (^{18}O and ^2H) were used to bring more light to the identified ions and other possible processes that control their concentration in the basin.

Those Stable isotopes (^2H and ^{18}O) were analyzed using an LGR DLT 100 laser absorption spectrometer [34] with the same measurements accuracy of ±1.5‰.

For the second campaign, 45 samples were selected for tritium analysis at Isodetect GmbH Laboratory. Those tritium samples were enriched by electrolytic enrichment and tested by the liquid scintillation counting method [35]. It is estimated by tritium unit (TU) matching with one atom for 10^{18} hydrogen atom.

Among these 45 samples, 11 were analysed by carbon isotopes at the Energy and Sustainability Research Institute in Groningen during the third campaign. While carbon-13 was tested with a mass spectrometer, Carbon 14 analysis was performed using the liquid scintillation counting method. They are estimated as percent of modern carbon (pmC) [36] with an average analytical error margin of 0.2 pmC. For carbon-13, the results are estimated in percentage (%) according to Pee Dee Belemnite's rule with an accuracy of ±0.2‰.

4. Results and Discussion

4.1. Water Chemistry

The results about groundwater chemistry and its stables isotopes, were related. The groundwaters within volta river basin in Benin are characterized by Ca^{2+} and Na^{+} and mainly HCO_3^- ions according to Piper diagram (**Figure 3**). These components are the same as those in the other volta's sub-basins by [29] [37] [38].

Two main conclusions can be draw from this diagram. Firstly, the evolution from Ca-HCO_3 or Ca-Mg-Na-HCO_3 to Na-K-HCO_3 show more interactions between groundwater and clay minerals due to isomorphic substitutions and exchange processes of cation and/or alteration of silicates [29] [37] [38] [39] [40]. This phenomenon is related to the mineralization of groundwater residence time in the aquifer as suggested by [40] in the Taoudeni sedimentary basin.

Therefore it could be considered as an indirect indicator to show how long water can last in rock. Indeed, petrographic analysis and X-ray diffraction of sample of rocks show that the mineralization of Pendjari's sedimentary basin is highly composed by plagioclase sodium and Quartz with low proportions of chlorite, muscovite, calcite, talc and zeolite. While the mineralization of the rocks of the Buem formation is dominated by plagioclases of sodium, calcite, titanium and iron oxide [16], the formations of Atacora, according to [19], are dominated by quartz, muscovite and chlorite. And the basement s.s formations are dominated by plagioclases, quartz and muscovite.

Secondly, HCO_3 evolution to Cl-NO_3 point out the anthropogenic influence on groundwater by the intensive use of chemical fertilizers in agriculture by [41].

4.2. Tritium Content in Groundwater

The Variations of tritium content provide an overview of the local recharging mechanism [29] [38]. The tritium values measured in the groundwater samples of the Volta river basin in Benin (**Table 1**) are between 0.7 and 3.9 TU with an average value of 1.6 TU. Those of surface water are between 2.7 and 3.4 TU for an average of 2.9 TU and they indicate very recent water or tritium content that has decayed over time because its half-life of radioactive lasts 12.32 years [42].

The tritium values obtained from most of groundwater samples are similar to current meteorological water values. Those higher than 1 UT indicate a recent recharging by modern rains, resulting in equilibrium between groundwater and the atmosphere contaminated by nuclear tests initiated around 1950 [33] [41].

However, some samples with tritium values less than 1TU may correspond to older groundwater, indicating a recharging before 1952 [38] [43] [44]. The corresponding wells located in the sedimentary part of Pendjari basin and characterized by low tritium values (<1 TU) and high TDS values (> 450 mg/L) (**Figure 4**) are interpreted as a residence time of groundwater more or less long. BV04-02, BV06-02, BV09-02, BV11-02, BV12-02, BV13-02, BV14-02, BV70-02 correspond respectively to the drilling waters of Nanagade, Datori, Tapoga, Porga, Materi, Namoutchaga and BV17-02 from the Atacora formation correspond to the Batia drilling water. All of these define the discharge area as shown by the piezometry (**Figure 1**). This seems to be in agreement with the hydrochemical results, which showed the first main conclusion of groundwater evolution.

4.3. Groundwater Age

4.3.1. Carbon Isotopes

The carbon isotopes are determined in the aquifer system in order to get more information on residence time of groundwater and to characterize the water mixing processes and the chemical reactions occurring there [45].

Table 1. Isotopic characteristic of analyzed samples of the Volta river basin in Benin.

Sample number	Aquifer (formation)	Z (m)	Depth (m)	TDS (mg/L)	$\delta\,^2H$ (‰ V-SMOW)	$\delta\,^{18}O$	^3H (TU)	^3H $\pm 2\sigma$	^{13}C (PDB)	^{14}C (pmC)	^{14}C $\pm 2\sigma$
BV04-02	Pendjari	183.6	35.37	525.5	−32.96	−5.17	0.70		−12.96	44.75	0.22
BV09-02	Pendjari	212.8	50.33	632.1	−28.35	−5.04	0.70		−11.19	85.47	0.31
BV12-02	Pendjari	159.2	51	881.1	−36.58	−5.81	0.70		−11.59	44.65	0.22
BV13-02	Pendjari	211.7	37.5	467.6	−28.51	−4.90	0.70		−14.43	17.29	0.14
BV11-02	Pendjari	198.8	33.77	746.8	−23.60	−3.94	0.80		−9.33	61.09	0.26
BV58-02	Pendjari	195	13	346.5	−23.81	−4.48	0.80		−11.94	33.68	0.19
BV70-02	Pendjari	202.3	47	867.4	−21.97	−3.56	0.80		−11.09	28.25	0.18
BV14-02	Pendjari	168.8	33.5	474.7	−24.30	−3.97	0.8		−11.2	66.96	0.27
BV06-02	Pendjari	166.9	39.5	533.9	−26.96	−4.70	0.90		−11.68	83.31	0.31
BV50-02	Pendjari	233.5	32.8	201.8	−23.40	−4.33	1.0	0.70			
BV07-02	Pendjari	200	41.66	514.5	−25.16	−4.72	1.00	0.70			
BV62-02	Pendjari	169.3	74	493.2	−19.31	−3.59	1.00	0.70			
BV18-02	Atacora	241.6	51	429.8	−21.37	−3.34	1.1	0.70			
BV54-02	Pendjari	176.2	26	302.2	−33.50	−5.14	1.1	0.70			
BV65-02	Pendjari	249.8	31.33	439.9	−24.16	−4.53	1.30	0.70			
BV71-02	Pendjari	216.8	14.97	75.1	−20.41	−3.43	3.1	0.70			
BV51-02	Pendjari	159	15.01	448.7	−27.65	−4.65	3.9	0.70			
BV04-01	Pendjari	187.4	35.37	239	−31.35	−5.11					
BV05-01	Pendjari	171.9	44.58	617	−25.20	−4.19					
BV06-01	Pendjari	180.2	39.5	648	−25.90	−4.16					
BV07-01	Pendjari	192.9	41.66	569	−24.67	−4.41					
BV08-01	Pendjari	215.3	23.93	915	−32.48	−4.98					
BV09-01	Pendjari	210.6	50.33	273	−26.41	−4.26					
BV11-01	Pendjari	197.9	33.77	782	−22.05	−3.26					
BV12-01	Pendjari	167.3	51	964	−35.46	−5.52					
BV13-01	Pendjari	192.9	37.5	676	−28.04	−4.19					
BV14-01	Pendjari	179	33.5	567	−24.28	−3.21					
BV49-02	Pendjari	199.8	9.05	466.8	−23.40	−4.14					
BV53-02	Pendjari	179.6	11.8	64.6	−24.47	−4.23					
BV55-02	Pendjari	180	8.89	412.8	−22.12	−4.31					
BV56-02	Pendjari	162.7	5.5	492.3	−25.14	−4.36					
BV57-02	Pendjari	198	9.65	269.6	−20.74	−4.07					
BV66-02	Pendjari	186.4	1.77	78.7	−23.74	−4.01					
BV67-02	Pendjari	179.2	3.08	320.0	−20.77	−4.04					
BV68-02	Pendjari	190.4	3.08	68.7	−21.90	−3.89					

Continued

BV23-02	Buem	225.2	50.73	361.4	−21.28	−4.02	0.70		−14.58	52.41	0.24
BV72-02	Buem	268	42.03	468.6	−17.36	−3.41	1.6	0.70			
BV10-02	Buem	189.9	30.83	416.4	−23.34	−4.29	1.69	0.70			
BV64-02	Buem	202.3	15.05	358.7	−23.53	−4.04	2.7	0.70			
BV22-02	Buem	296	27.67	110.7	−20.68	−3.48	2.8	0.70			
BV15-02	Buem	231	53.5	196.3	−19.55	−3.85	3.0	0.70			
BV01-01	Buem	240.9	24.1	717	−20.86	−3.49					
BV03-01	Buem	247.3	34.65	334	−23.95	−4.17					
BV10-01	Buem	190.1	30.83	716	−22.49	−4.28					
BV15-01	Buem	227.9	53.5	239	−18.79	−3.10					
BV22-01	Buem	233	27.67	130.9	−20.76	−3.50					
BV23-01	Buem	222.6	50.73	382	−22.66	−4.23					
BV61-02	Buem	225.8	5.89	130.7	−21.99	−4.03					
BV63-02	Buem	247	12.1	65.7	−21.62	−3.69					
BV73-02	Buem	221.6	13.3	175.1	−22.93	−3.61					
BV74-02	Buem	249.9	8.48	100.6	−19.79	−3.87					
BV76-02	Buem	210.8	1.77	149.0	−15.70	−3.14					
BV79-02	Buem	236	12.1	234.9	−22.67	−3.50					
BV17-02	Atacora	235.4	70.44	498	−22.36	−3.61	0.9	0.70	−13.37	37.51	0.2
BV44-02	Atacora	419.9	41.5	171.5	−19.41	−3.87	1.30	0.70			
BV46-02	Atacora	246.2	20.45	319	−22.33	−3.87	1.5	0.70			
BV29-02	Atacora	526	42.67	19.1	−21.53	−4.22	2.0	0.70			
BV21-02	Atacora	569.9	43.5	34.1	−23.10	−3.88	2.6	0.70			
BV20-02	Atacora	576.1	64.66	49.2	−21.83	−3.56	2.7	0.70			
BV38-02	Atacora	647.1	48.25	14	−23.00	−4.17	2.9	0.70			
BV25-02	Atacora	427.8	40	188.5	−20.48	−4.00	3.2	0.70			
BV17-01	Atacora	239.7	70.44	539	−21.77	−3.40					
BV18-01	Atacora	249	51	497	−20.62	−2.97					
BV19-01	Atacora	536.5	34.31	22	−23.10	−3.93					
BV20-01	Atacora	584.2	64.66	70.0	−20.94	−3.73					
BV21-01	Atacora	550	43.5	55.6	−21.44	−3.88					
BV25-01	Atacora	400	40	335	−19.79	−3.66					
BV29-01	Atacora	515.3	42.67	19	−21.24	−3.83					
BV30-01	Atacora	404.5	30.67	132.2	−21.37	−3.87					
BV32-01	Atacora	617.3	36.99	33	−21.26	−4.14					
BV42-02	Atacora	428.2	5.76	45.1	−25.24	−4.51					
BV47-02	Atacora	232.1	4.01	584.9	−19.84	−3.34					
BV77-02	Atacora	575.8	5.8	49.2	−22.74	−4.36					

Continued

BV26-02	Basement s.s	326.7	82.5	303.1	−19.14	−3.89	1.4	0.70
BV26-01	Basement s.s	348	82.5	385	−19.73	−3.37		
BV27-01	Basement s.s	405.9	23.6	92.7	−19.75	−3.45		
BV28-01	Basement s.s	387.1	41.39	144	−20.38	−3.67		
BV34-01	Basement s.s	462.6	32.68	153.8	−17.08	−3.31		
BV35-01	Basement s.s	403	36.11	167.6	−16.63	−3.23		
BV69-02	Spring	195		21.1	−21.14	−4.44	2.7	0.70
BV40-02	Spring	527.8		11.5	−22.27	−3.81	2.8	0.70
BV45-02	River	300.8		25.2	−17.48	−3.44	2.7	0.70
BV36-02	River	363		43.1	−21.89	−3.96	2.7	0.70
BV37-02	River	358		38.1	−21.26	−3.88	2.8	0.70
BV75-02	River	171.9		37.8	−18.68	−3.56	2.9	0.70
BV43-02	River	371.2		15.5	−13.40	−2.71	2.9	0.70
BV78-02	River	365		39.7	−20.19	−3.74	2.9	0.70
BV41-02	River	499		17.2	−19.44	−3.59	2.9	0.70
BV48-02	River	176.9		60.9	−22.51	−3.82	3.0	0.70
BV39-02	River	322.3		33.3	−18.37	−3.23	3.0	0.70
BV52-02	River	140		55	−15.41	−2.70	3.3	0.70
BV59-02	River	140		53.9	−16.11	−2.63	3.4	0.70
BV60-02	River	203.4		44.1	−13.64	−2.08		

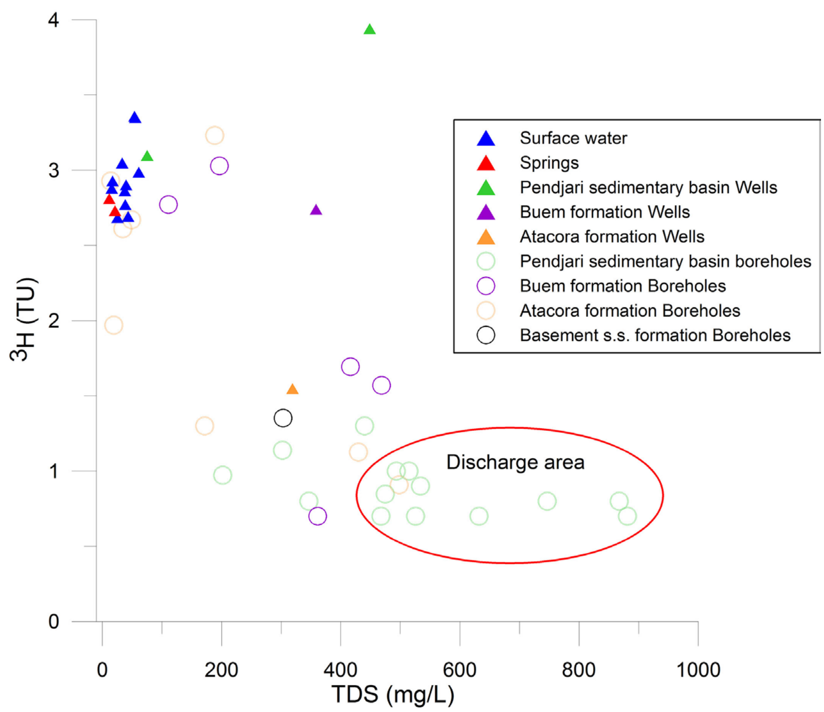

Figure 4. Relation ^{3}H/TDS in Volta river basin in Benin.

The values of $\delta^{13}C$, in ‰ vs PDB and ^{14}C activities, as a percentage of modern carbon (pmC) are given in **Table 1**. $\delta^{13}C$ contents are between −14.6 and −9.3 with an average of −12.1‰ vs PDB while ^{14}C activities is between 17.3 and 85.5 with an average of 50.5 pmC. The $\delta^{13}C$ isotopic fractionation of all samples was corrected to −25‰ vs PDB which is the average value between the vegetation cover and the marine carbonate (via CO_2) [36] [43].

The relationship between ^{14}C and $\delta^{13}C$ activity (**Figure 5(a)**) shows three groups of groundwater. Firstly, ^{14}C activity greater than 60% shows that waters are recent. Secondly, ^{14}C activity between 30% and 60% indicates old water or a mixture of old and new water. And a third group with a ^{14}C activity less than 20% testifies the presence of old water. These results are confirmed by the graph ^{3}H versus ^{14}C of **Figure 5(b)**.

Indeed, according to [43], when groundwater is very recent, its content in ^{14}C must be close to or greater than 100%, because the CO_2 in the soil likely contains thermonuclear ^{14}C. Thus, we refer to water that have infiltrated for some decades. The new groundwater can be any age counted in hundreds of years corresponding to the first group. The second group groundwater can be aged in several thousand years. The third group groundwater with more than ^{3}H is aged of several tens of thousands of years.

4.3.2. Groundwater Age Calculation

As explained by [46], the term "groundwater age", although practical, may be misleading. It really means the average of a residence time distribution. When a single recharging event occurs in sporadically reconstituted systems, groundwater age becomes definitely synonymous of recharging [40] [46].

Groundwater residence times have been estimated in this article from TDIC ^{14}C activity in 11 samples taken from the sedimentary part of the Benin basin of the Volta. Seven models based on chemical evolution and/or isotopic dilution of $^{13}C/^{12}C$ from soil CO_2 through interactions in the aquifer environment have been adopted. It is likely that the ages proposed by [47] [48] [49] [50] [51] are generally in agreement and provide similar solutions. The models of IAEA [52] and [53] tend to overestimate the residence times of groundwater.

In this article, the results of ^{14}C activities (**Table 2**) have been corrected using the [47] model. Indeed, this model provides an adequate estimate of age taking into account the conditions and the moment of the palaeorecharge [54]. The corrections used for the TDIC $\delta^{13}C$ and soil CO_2 and mineral phases are respectively −21‰ and 0‰. It is well adapted to the geochemical reactions occurring in the groundwater of the study area. The [47] model assumes a mixing of two poles: CO_2 and the aquifer matrix.

Table 2 summarizes the radiocarbon ages obtained for the 11 samples, using the seven kind of correction based on isotopic solutions and the estimate of the gross age. All those correction models suggest Holocene ages. The 1st group is of current age and round up water of the drillings of Dassari, Gouandé, Datori and Tapoga. The 2nd group is a post-Holocene age between 1216 and 8502 years BP.

It includes water of Namoutchaga, Nambouli, Batia, Porga, Nanagade and Korontiere. And finaly between 10,013 and 14,969 years BP we have the Holocene age, only with the drilling water of Materi.

In short, the data of chemistry (evolution of hydrochemical facies), piezometry and, above all, isotopic data show that the hydrogeological system of the Volta river basin in Benin is made up of sub-units more or less interconnected as indicated in this diagram (**Figure 6**). The formation of Atacora and the western sector of the Buem, with their reliefs, are the preferential recharging areas. The lowland areas, like the Pendjari sedimentary basin, are the areas of flow or groundwater transit.

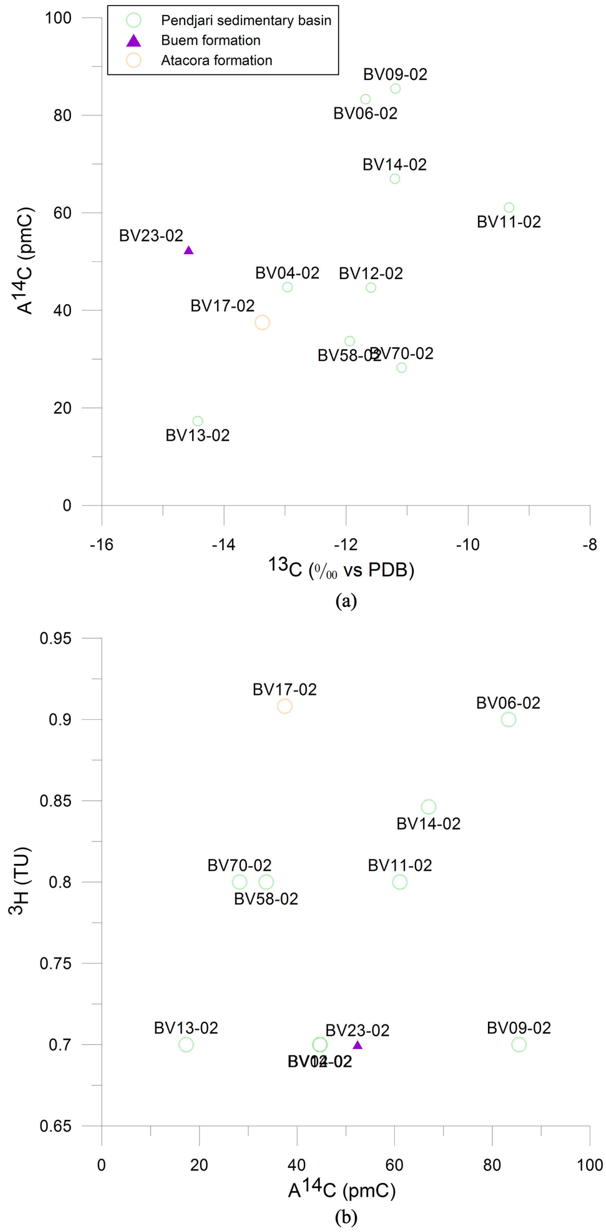

Figure 5. $A^{14}C/^{13}C$ (a) and $3H/A^{14}C$; (b) relations in Volta river basin in Benin.

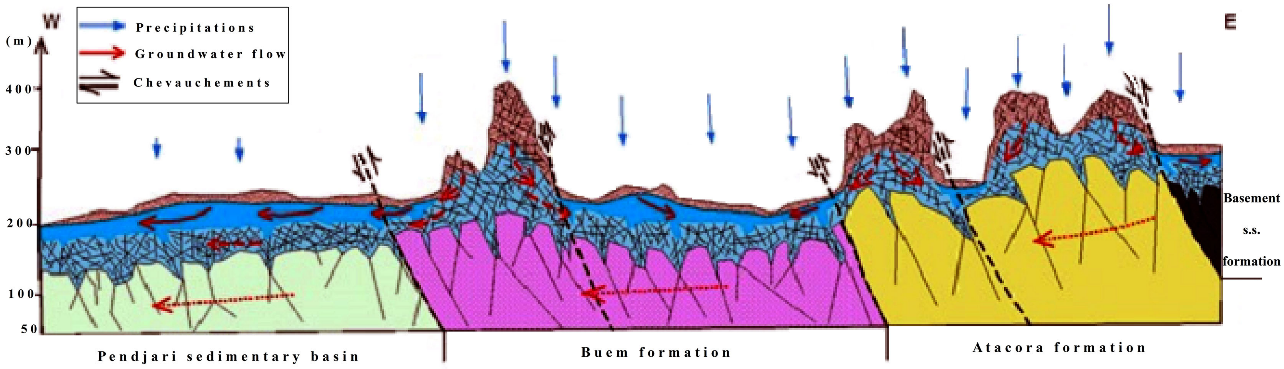

Figure 6. Conceptual diagram of the hydrogeological system within the Volta river basin in Benin.

Table 2. Groundwater age calculation (a) according to different correction models: [47] [48] [49] [50] [51] IAEA [52] and [53].

Sample number	Aquifer (formation)	Tamers	Pearson	Mook	F & G	AIEA	Evans	Eichinger	brut nc
BV13	Pendjari	10,013	11,407	14,314	12,070	14,969	11,184	11,233	14,509
BV70	Pendjari	5797	5172	8502	5132	8665	4708	4518	10,450
BV58	Pendjari	4249	4329	7600	4371	7835	3940	3859	8997
BV12	Pendjari	1976	1752	5041	1738	5264	1337	1207	6666
BV04	Pendjari	1219	2657	6219	3353	6281	2365	2395	6647
BV11	Pendjari	Actuel	Actuel	1266	Actuel	891	Actuel	Actuel	4074
BV14	Pendjari	Actuel	Actuel	1378	Actuel	1674	Actuel	Actuel	3316
BV06	Pendjari	Actuel	Actuel	Actuel	Actuel	196	Actuel	Actuel	1510
BV09	Pendjari	Actuel	Actuel	Actuel	Actuel	Actuel	Actuel	Actuel	1298
BV23	Buem	1657	2325	4768	2660	5861	2106	2014	5341
BV17	Atacora	3437	4374	7441	4831	7892	4085	4094	8106

5. Conclusions

The isotopes of radiocarbon, of tritium and stable isotopes of oxygen-18 and deuterium in the groundwater of the Volta river basin in Benin have been determined for a better understanding of the recharging source in the shallow aquifer system. Tritium concentrations, although generally low, are very close to current levels of precipitation and show that modern recharging occurs. Radiocarbon and tritium data led to the identification of groundwater with a long residence time of 10 ka.

The groundwater in this basin is characterized by Ca^{2+} and Na^{+} ions and mainly by HCO_3^-, which proves the interactions between groundwater and clay minerals and the processes of cation exchange and/or alteration of the silicates. The anthropogenic influence on groundwater through the intensive use of chemical fertilizers was also emphasized.

The groundwater system in the Volta river basin in Benin stands for the recharging in modern climatic conditions. Meteoric variations in stable isotope compositions show that groundwater is not strongly affected by kinetic evaporation and it is due to natural variations in local and regional climatic conditions.

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