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Hydrochemical study of some bottled water produced in the city of N'Djamena (Republic of Chad)

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Abstract

The study of bottled water collected from groundwater and their quality in different countries mostly in sub Saharan countries has become a matter of concern because of their important consumption. The physicochemical characterization of these water withdrawn from aquifers systems and bottled water is used to assess the natural process of acquiring their mineralization and also to identify the existence of anthropogenic pollution. The aim of this work is to study the physicochemicalcomposition ofseven (07) samples of bottled water found in N'Djamena, Chad. in terms of the major principal elements (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}; HCO_3^-, SO_4^{2-}, Cl^-), minor ions (NH_4^+ and NO_3^-), silica and some heavy metals. The results of analysis showed that the bottled water produced in N'Djamena had good physicochemical qualities despite a very slight excess of lead. These bottled water presented moderate mineralization and shown a diversified hydrochemical facies, HCO_3-Mg, HCO_3-Mg/Na, HCO_3/Cl-Na, Cl^-Ca/Mg.

1. Introduction

Although there's abundant water on the earth's surface, freshwater is scarce and resources are unevenly distributed over the world, with much of the water located far from human populations [1]. There are still more than 1 billion people without access to potable water, the vast majority located in 'developing' countries. About 2.3 billion of people suffer from infectious gastro enteritis each year [2]. In parallel, the bottled water industry has been increasingly criticized for its negative environmental and health impacts.It's one of the fastest-growing industries in the world [3].The capita consumption in the Western 'developed' countries is120 liters per person compared to 20 liters per person in Asia and 10 in Africa [4].

The Bottled water can be defined as any potable water that is bottled and distributed or offered for sale and specifically intended for human consumption [5].The Republic of Chad, is a country whose industrial base is still embryonic, thus it does not have enough bottled water production units. Almost, all of their production plants are located in the town of N'Djamena specifically in the first district, corresponding to an industrial area. Waters of the present study area are fed by the Chari and Logone rivers (two great rivers with waters confluence located inside N'Djamena city and which flow to the North towards the Lake Chad), which are subjected to a major pollution since the installation of food companies, industrial plants and oil refineries. The abundance of toxic chemicals, radionuclide, nitrites and nitrates in drinking water may cause adverse effects on the human health such as cancer, other human body malfunctions and chronic illnesses [6].

Shallow (rarely more than 3 m), Lake Chad provides water to nearly 30 million people in the four neighboring countries with high population growth: Chad, Cameroon, Niger and Nigeria. Its main water supplies come from the Chari River and its tributary Logone, which come from the hills of the Central African Republic.

The drying up of Lake Chad, from 25,000 km^2 in 1960 to 8,000 or 2,500 today, depending on the year, the season, and the modes of measurement, is certainly linked in part to the increase in the population, accentuated by the great drought of the years 1973-74, and the agricultural activity on its banks, but also to the companies of the riparian States, by their works of pumping and irrigation on the tributaries of the lake.[7]

N'Djamena, capital of The Republic of Chad is 12°8 north latitude and 15°2 east longitude.

The study carried out on the waters of the Chari River revealed that, the values of the physicochemical parameters retained for the characterization of pollution generally exceed the World Health Organization recommendations and international standards [8].

Several micro-pollutants (lead, cadmium, manganese, zinc, copper, chromium, nickel...) showed significant levels, and the presence of organic molecules (pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls...) were detected in the waters of Chari River [8].

Other studies have shown the presence of high level of nitrates, chlorides, potassium, mercury, barium, manganese, nickel concentrations in the Chari River, in the water withdrawn from N'Djamena groundwater aquifer (Fig. 1) [9, 10].

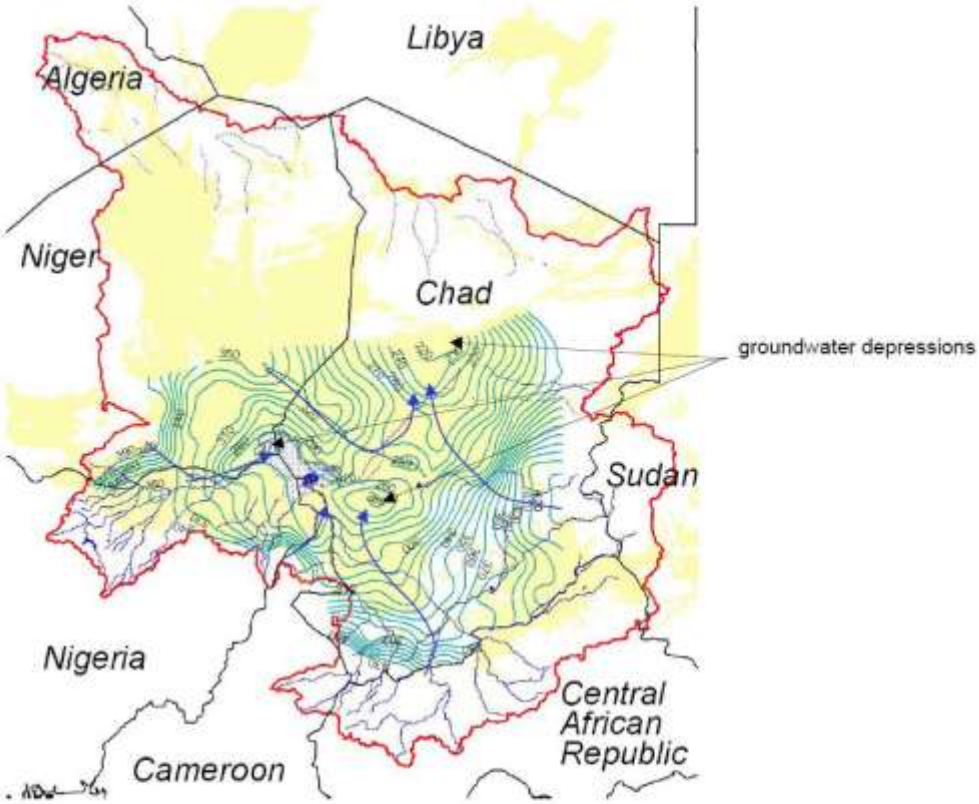

Figure 1: Lake Chad Bassin Quaternary aquifer [10]

The hydrogeology in this zone according [11] is complex (Fig. 2). The Lake Chad Basin is composed of a sequence of layers of different ages and thicknesses. The deepest known layer aquifer is the Continental Terminal (Oligocene/Miocene) composed ofsandstones of around 200 m in thickness and located at depths between 400 and 600 m belowthe surface. Overlying, the Lower Pliocene (aquifer) composed of fluvio-lacustrine sands isencountered. The Upper Pliocene, impermeable, follows as a massive layer of clays of 200-300 m ofthickness. The Quaternary (aquifer) composed the uppermost layer with a thickness from 75 to 100 m. Itis made in thenorthern part of the basin by prevails aeolian deposition with thepresence of dunes (Kanem region). Regionally, these Quaternary sands act as an unconfinedtransboundary aquifer.. Fluviatile, lacustrine and deltaic depositions that result inalternating sequences of thin layers of sand and clay and mainly clayey soils on the surfaceare typical in the south. In this zone,the Quaternary aquifers (among them N'Djamena area) vary between semi-confined and confined dependingon their relative position and the occurrence of clay layers.. South of the 14°N parallel this aquifer shows a low hydraulic conductivity,especially vertical, due to the sequences of sand and clay. In addition, because of its flatness and low gradient (average 0.5 ‰), the horizontal flow is very slow [10], sands with different sub-formations occur in the central basin of Chad [12].

The Quaternary aquifer groundwater flow map (Fig. 1) shows the presence of three important piezometric depressions: Chari-Baguirmi, Komadougou-Yobé and Pays-Bas. To the South ofthe basin, groundwater flow is

oriented from the South to the North in direction of Lake Chadand Chari-Baguirmi depression. To the North, the Pays-Bas depression acts as a finalcollector of groundwater flowing from the east (Chad) and west (Niger). Groundwater flowfor the Lower Pliocene and the Continental Terminal is less documented and sparseinformation is only available for the region around the Lake Chad [13].
For the Lower Pliocene aquifer, groundwater flow is also oriented globally from West to Eastand from South to North in the direction of Lake Chad. No piezometric information isavailable for the Eastern Chad region for this aquifer.
Groundwater flow in the Continental Terminal aquifer is organized from South to North inthe direction of Lake Chad and then to the North-East of the Lake. Very fewinformation is available up to now on this aquifer and this potentiometric map must beconsidered as schematic. Recent investigations based on ^{36}Cl [14] haveevaluated the residence time of the CT groundwater east of the Lake Chad to more than300,000 years.
The Pleistocene and contemporaneous sands are characterised by relatively good hydraulic conductivity and groundwater of drinking quality. TDS is generally low (<400 mg/l), in the absence ofanthropogenic influence. Few data regarding transmissivity of the aquifers in the area are available, they all show good aquifer potential with transmissivities ranging from 1.10^{-2} to 7.10^{-2} m^2/s [11], [15], [16]

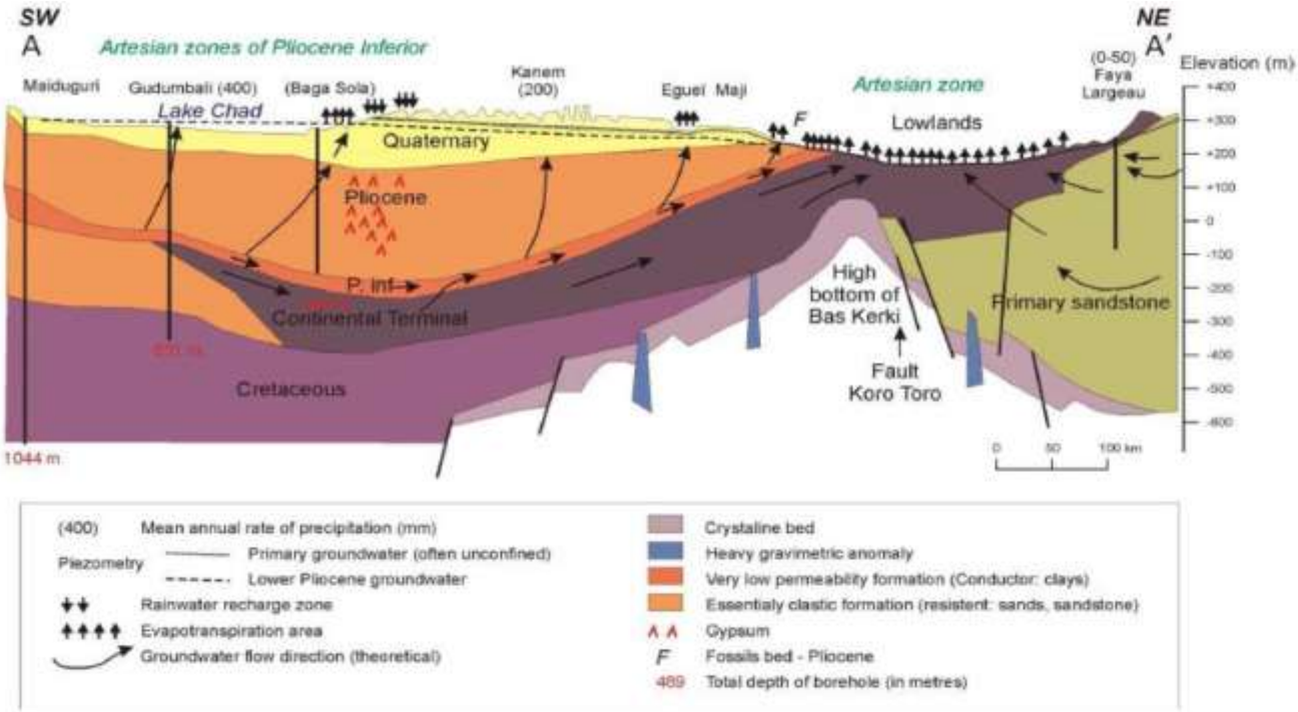

Figure 2: Lake Chad Bassin geology and hydrogeology cross section through the Chad lake Basin from Maiduguri (SW) to Faya Largeau (NE) from[11] in [17].

This situation is particularly worrying and it is linked to the multiple use of the Chari water by local inhabitants. The Republic of Chad is known to be one of the countries in the world where the major causes of death are linked to the water-borne diseases and poor hygiene. Due to this degradation of water quality, the population has rushed into the consumption of bottled waters. But the major interrogation is the following: Are the bottled waters consumed in the Chadian's markets are of good quality or do they respect the WHO recommendations and international standards?
Therefore, the present study analyzed the bottled waters found in N'Djamena and investigatedon the quality of the data reported on the labels of different bottles.
The validity of these results together with their interpretations are closely subordinated to the rigorous respect of the analysis protocol implemented.

2. Experimental details

2.1.*Sampling*

The four types of bottled waters used in The Republic of Chad are: Natural mineral water (Al-Djamal, La Rosée and Life), the table water (Al-Moussaffa, Cristal), spring water (Eau vive) and mineral water (Excel). The bottled waters consumed in N'Djamena are collected from the underlying confined Quaternary aquifer. According to the companies and sectors of bottled waters, the depths of the wells vary from 55.0 to 73.0 meters.

In order to complete this work, seven (07) types of bottled waters produced mainly in the town of N'Djamena have been collected and analyzed according to the quality criterias used at the Mineral Chemistry Laboratory of Solid and Analytical of the Faculty of Science of Oujda in Morocco, corresponding to the analytical methods of the French Association for Standardization, AFNOR [18, 19].

2.2.*Assay Methods*

a. Methods

The table 1 below summarizes the methods and equipment used to achieve our goal.

Table 1: Parameters studied, methods and equipments used

Parameters	Methods	Equipments
pH	Electrometric	pH-meter 150 thermo Russel pH Pl
Electrical conductivity	Conductimetry	Conductimetry H 19811 PH-EC-TDS
Density	Densimeter	Pyrex pycnometer calibrated
Ca^{2+},Mg^{2+}, HardnessTH	Complexometry EDTA dosage	-
HCO_3^-, Cl^-	Volumetric dosage	-
SO_4^{2-}, NO_3^-, NH_4^+,SiO_2	UV spectrophotometry	UV spectrophotometer Rayleigh - 9200
Na^+, K^+	Photometer Flame	Photometer Flame SHERWOOD 420 Model
Pb, Cu	AtomicAbsorption spectrophotometry flame	AA-6300 Shimadzu model and ASC-6100 auto sampler
TDS (Total dissolved solids)	Evaporating water sample in a 105 °C oven	Oven DAIHAN Labtech – LDO-080N

b. Analytical data quality indicated on labels

The indications pasted on the labels are reported in table 2.

Table 2: Physical and chemical characteristics of bottled water indicated on the labels

		Concentration in mg/L							
		Ca^{2+}	Mg^{2+}	K^+	Na^+	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^{2-}
EE1	Al-DJAMAL	8.0	4.0	0.0	2.0	8.0	35.0	0.0	
EE2	AL-MOUSSAFA	2.0	0.4	0.1	4.0	240	3.0	0.0	0.0
EE3	CRISTAL	18.0	5.0	3.9	17.2	108.0	6.0	8.4	Tr.
EE4	EAU VIVE	16.3	4.8	3.6	16.6	108.0	3.5	8.0	Tr..
EE5	EXCEL	9.05	2.05	0.9	4.13	7.3	8.45	0.5	Tr.
EE6	LA ROSEE	12.0	3.50	-	14.0	-	0.23	1.1	0.02
EE7	LIFE	5.6	0.5	0.2	0.8	0.8	2.0	-	-

The analytical data provided by the labels is incomplete (pH, EC, TDS) and reliable for the waters. The ionic balance (IB) showed that only two types of bottled waters (Crystal waters and Vive water with, IB <5%) have their analytical data well-regulated with ionic results and consequently the data mentioned on their labels may be used for hydrochemical study. The otherssampled waters, have an unbalanced ionic and therefore, cannot be used for hydrochemical study. Even though, the Excel water has acceptable values for the ionic balance, the TDS data is still underestimated. Tr. = traces

3. Results and Discussion

3.1.Presentation of results

The table 3 below shows the parameters analyzed and their values for different bottled waters analyzed in the Laboratory of the Faculty of Science of Oujda. These values are the averages of several measurements that have been done in an interval of eight (08) months. These results showed a good reproducibility.In some cases, the measured values are similar to those indicated on the labels, but in almost cases they are different.According to these results, it can be noticed that the water portability standard according to Guidelines for Drinking-Water Qualityof the World Health Organization,for most waters concerning the major elements. Whereas, for EE5 water, the value of pH is slightly lower than that required by the two standards (6.5-8.5). The water EE7 has a slight excess of Mg^{2+} which exceeds the 50 mg/L authorized. For the lead (Pb) concentration, it showed a very slight excess for all the waters, thus a potential industrial pollution of the aquifers.

Table 3: Mean values of the parameters analyzed

Bottled Water	EE1	EE2	EE3	EE4	EE5	EE6	EE7	WHO [20]	C. S. [21]
pH	7.10	6.70	6.95	7.22	5.40	7.32	6.30	6,5-8,5[a]	6,5-8,5
T (°C)	23.0	21.9	22.1	22.0	20.0	20.8	22.0	-	
EC (μs/cm)	12	75	242	240	6	203	640	1250[b]	2500
TDS (mg/L)	67	59	216	212	41	185	457	1000[4]	1500
TH (mg/L in $CaCO_3$)	45.5	32.3	91.9	82.9	26.5	80.5	316.1	-	
Ca^{2+} (mg/L)	10.00	7.08	7,45	6.99	5.00	4.84	39.61	c	100
Mg^{2+} (mg/L)	5.00	3.54	17,82	15.91	3.40	16.64	52.82	c	50
Na^{+} (mg/L)	2.4	12.3	19,6	18.7	1.4	20.8	4.3	200[a]	200
K^{+} (mg/L)	1.2	0.5	3,0	3.4	0.5	3.2	1.2	12	12
NH_4^{+} (mg/L)	0.01	0.05	0,02	0.05	0.01	0.01	0.02	0,5	-
Cl^{-} (mg/L)	24.85	19.52	5,32	5.32	12.42	5,32	70.11	250[a]	250
HCO_3^{-} (mg/L)	17.08	36.60	141.52	134.2	12.20	136.64	280.6	-	-
SO_4^{2-} (mg/)	5.30	4.95	14.07	14.83	5.07	10.01	7.66	250[a]	250
NO_3^{-}(mg/L)	0.28	0.32	0.89	0.86	0.6	0.47	0.43	50	50
Cu (mg/L)	0.02	0.01	ND	0.02	0.03	0.02	002	2[a]	2
Pb (mg/L)	0.02	0.03	0.04	0.06	0.09	0.12	0.15	0.01[a]	0.01
SiO_2 (mg/L)	2.14	2.09	46.95	45.66	0.23	46.33	47.21	-	-

WHO : World Health Organization Only the guideline value is fixed for nitrate (50 mg/L) in consumable water.
C. S. : Chadian Standard
[a]Indicative limit for taste.
[b]indicative limit issue from relationship between TDS and EC.
[c]Indicative limit for hardness (Ca þ Mg¼ 500 mg/L).

The amounts of nitrate and ammonium are very low (< 1 mg/L) with respect to WHO and CS standard. The agricultural activities practiced in this area are still traditional (low livestock, less use of fertilizers and pesticides). The impact of agricultural activities and livestock on the quality of groundwater is not yet extensive. The silica strongly varies with the conductivity, until it reaches to a state of saturation around 45 mg/L.
The quality of the analytical results is given in the table 4 below.

Table 4: The measured ionic balances

Sample	IB (%)	Observations
EE1	-2.33	Exploitable
EE2	-2.56	Exploitable
EE3	-0.16	Exploitable
EE4	-2.13	Exploitable
EE5	-4.51	Exploitable
EE6	-0.16	Exploitable
EE7	-1.51	Exploitable

According to the experimental values of ionic balances obtained, it implies that the analysis are of good quality and reliable (IB <5%).
The variousbottled waters sold in the republic of Chad showed different chemical facies (Fig. 3), the water (EE7) is bicarbonated magnesian, three of them (EE3, EE4 EE6) are bicarbonated sodico-magnesian (EE3, EE4, EE6), two(EE1 and EE2) chloride calco-magnesian (EE1 and EE5) and the last(EE2) bicarbonated sodic chloride.

3.2. Water Classification

3.2.1. Classification according to their hardness

The classification of the bottled waters consumed in Chad in respect to their hardness is reported in Table 5

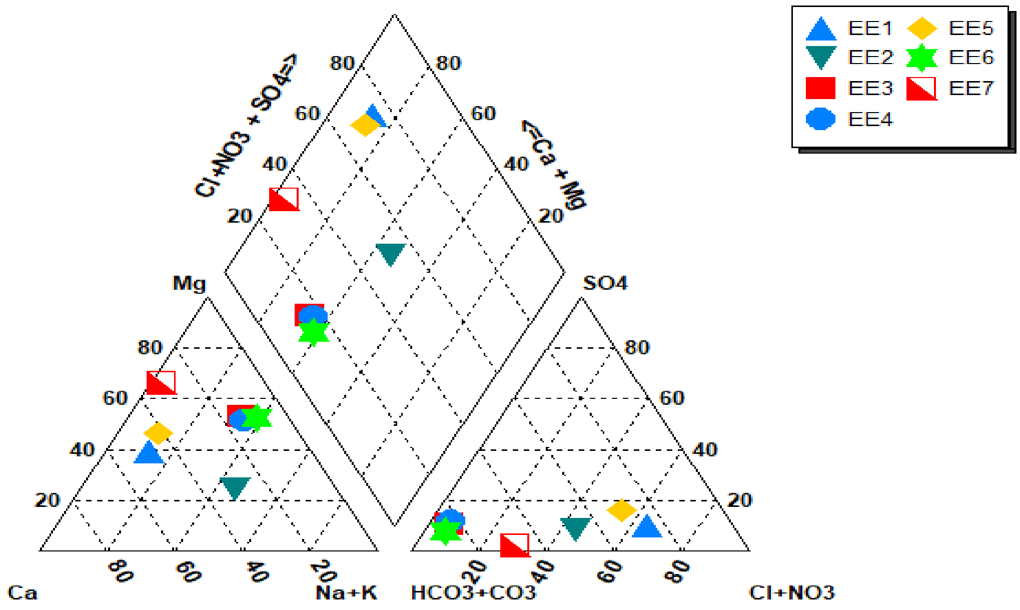

Figure 3: Diagram of Piper for the bottled waters produced in N'Djamena

Table 5: Classification of (07) bottled waters following their hardness

Water	Total Hardness (mg/L in $CaCO_3$)	water type[22, 23]:
EE1	45.5	soft (0-50)
EE2	32.3	soft (0-50)
EE3	91.9	Moderately hard (50-100)
EE4	82.9	Moderately hard (50-100)
EE5	26.5	soft (0-50)
EE6	80.5	Moderately hard (50 -100)
EE7	316.1	Very hard (>300)

The hardness variabilityof bottled waters produced in N'Dajamena (table 5) are presented in the (Fig. 4):

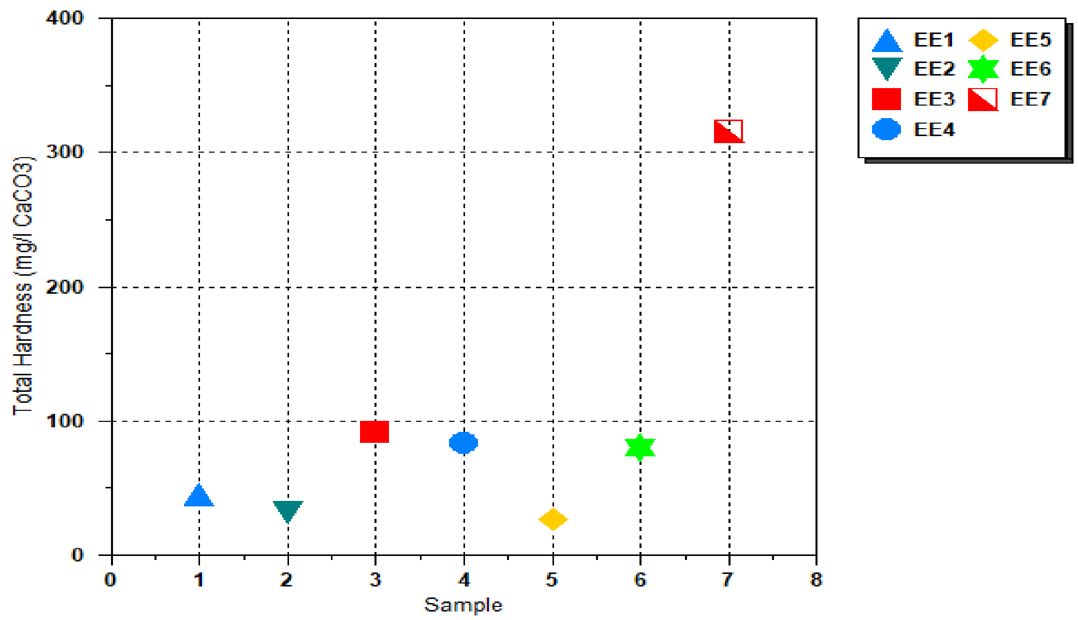

Figure 4: The hardness of bottled waters produced in N'Djamena

In this diagram, except for the EE7 sample which has a very high hardness, all the waters are lower mineralized and their hardness varies from the soft to the moderate ones. This is probably due to the geological nature of the soil. The groundwater is developed mainly in fluvio-lacustrine formation essentially sandy (alternating sand and clays) and in intermediate soils (sandy clay or sand clays). The thickness of the clay layers varies. A very long leaching of this soil can caused loss in minerals hence limiting recharge water mineralization in the unsaturated zone in the deep aquifers.

3.2.2. Classification based on total dissolved solid (TDS)

Considering the overall mineralization, the waters are classified from the lower to highly mineralized. The table 6 below summarizes the distribution according to the TDS obtained.

Table 6: Water mineralization

mineralization	TDS (mg /L	Water[24]
Very lightly mineralized	< 50	EE5
Lightly mineralized	50 < TDS < 500	EE1, EE2, EE3, EE4, EE6, EE7
Medium mineralized	500 < TDS < 1500	
High mineralized	>1500	

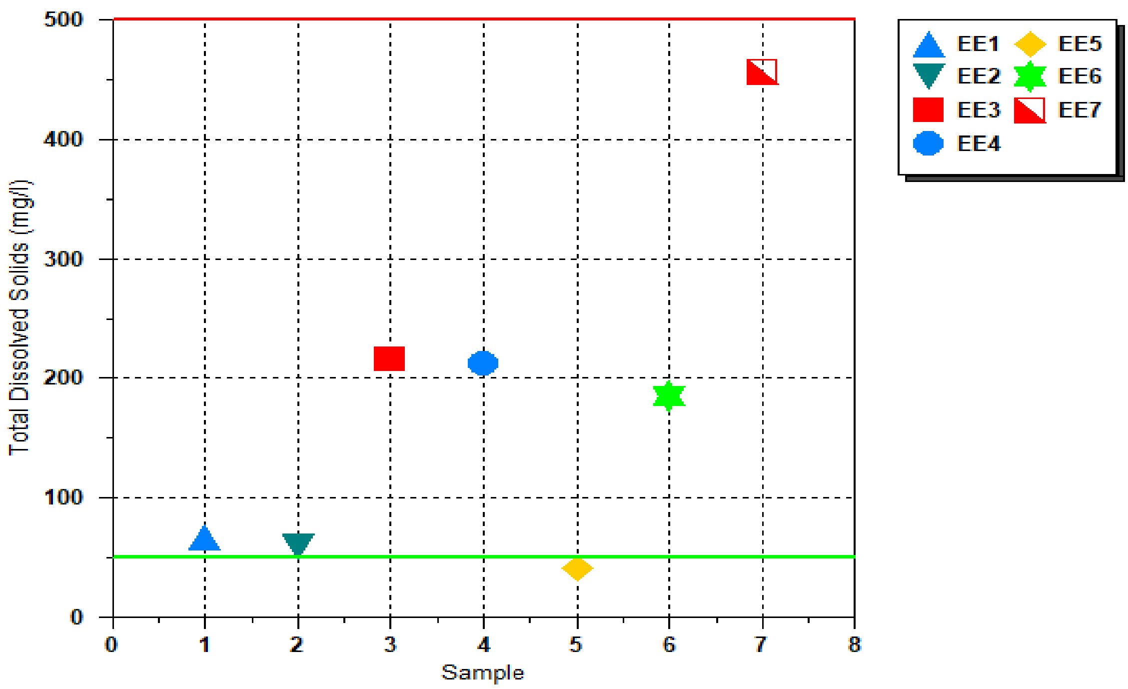

Figure5: Classification of waters according to the mineralization

The figure 5 shows, all the waters have low mineral content except for the EE5 water which has very low mineral content.

3.2.3. Classification of salinity

The salinity is expressed in terms of sodium salts (NaCl). Allowing assessing the risk of the water use for irrigation. Table 7 below shows the types of water according to their salinity.

Table 7: Classification of waters based on their salinity

Fresh-Salt class	[NaCl](mg/L)[25]
Unsalted water	< 1000
Lightly salted water	1000 – 3000
Moderately salty water	3000 – 10000
Salty water	10000 – 35000
High salty water	> 35000

The salinity level of the samples studied is showed in the Wilcox diagram [26] and the "Riverside" Richards diagram [27] allowing to deduce the risk of salinity and sodiof soils.

In order to complete the Wilcox and Richards's diagrams (Fig.6.a and 6.b), the electrical conductivities of different samples were measured.

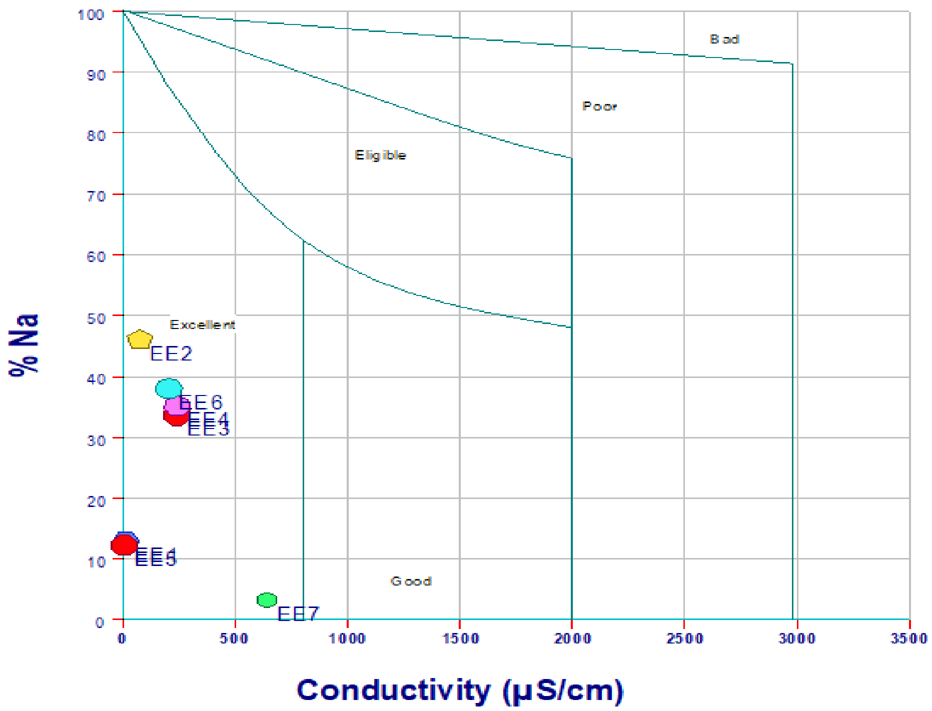

Figure 6.a: Diagram of Wilcox generated for bottled waterstudied

On the Wilcox diagram (Fig. 6.a), the percentage of Na with respect to Electric conductivity E.C. expresses an excellent quality of whole waters.

$$SAR = \frac{[Na^+]}{\sqrt{\frac{([Ca^2] + [Mg^2])}{2}}}$$

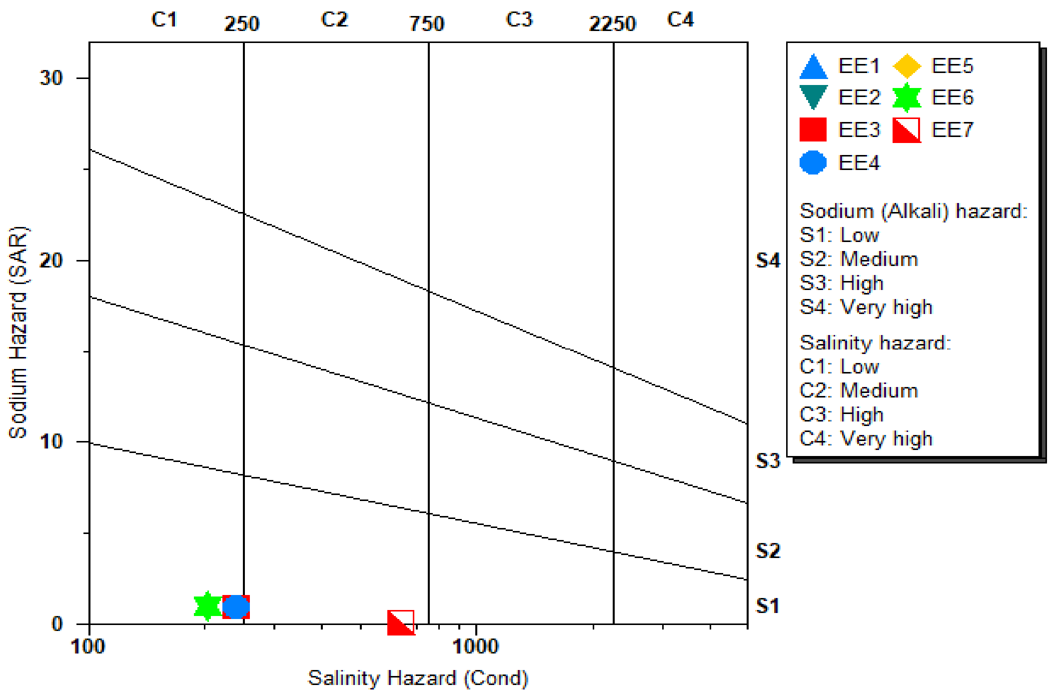

Figure 6.b: Richards' representation of the bottled water studied

In this diagram (Fig.6.b), all waters are classified as C1S1 quality (the Sodium adsorption ratio -SAR- is low), except EE7 classified as C2S, There arenot presenting a risk of sodization of the soils. Generally, the salinity levels in the various samples varied from low to moderated (EE7).

Conclusions

This work focuses on the hydrochemical study of bottled waters produced mainly in the city of N'Djamena from local groundwater to improve the knowledge about the mineralization process and the quality level of these waters at different depths in relationship with the Chari and Logone rivers contamination by agriculture, industrial and domestic wastewaters.

Information on the labels are not sufficient and reliable for all the bottles waters studied. The results of physicochemical analysis have shown low mineralization for all bottles waters studied.

The conductivities of EE1, EE2 and EE5 are very low and correspond to rain waters mineralization in a semi-arid context, while EE3, EE4, EE6 and EE7 which have shown significantly higher mineralization represent waters flowing in the soils. The pH of EE5 water is slightly lower than required value of the Chad republic standard. The amount of nitrates and ammonium remains low.

The hydrochemical facies of the waters are diversified in chlorinated, bicarbonated and magnesium with sodium.On the Wilcox diagram, the salinity of different waters is classified as of excellent quality. The Richards diagram also confirmed a low alkalizing power without risk of soil salinity.

Despite the anthropogenic aggression suffered by the Chari Baguirmi groundwater, the bottled waters withdrawn have good physical and chemical qualities, but still showed a slight lead content compared to the Chadian standard norms.

The agricultural activity or grazing over the area did not affect the portability of the waters taken at a depth exceeding 50 meters.

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