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The hydrochemical characterization of the underground waters of the plain of Sidi Bel Abbès (northwestern Algeria).

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ABSTRACT/RESUME

Abstract:*The population of Sidi Bel Abbèshas become over the years moredependent on the neighboring cities of Tlemcen and Mascara to satisfy its growing needs of potable water. The absence of dams with big storage capacity combined with the semi-arid climate characterizing this region (irregular andlow to medium rainfall rates) is superposed tothe poor knowledge of the underground waters potential inthearea.The Plio-Quaternary aquiferof the Sidi Bel Abbèsplain can however be considered an exception.This unconfined aquifer, whichstretches over 800 km^{2}is by far the most important underground water reservoir in the region. The aquifer is mainly drained by the Mekerra River and is exploited by an impressive number of pumping wells (legal and illegal), destined for their majority to irrigation. The strategic importance of this water resource for the city of Sidi Bel Abbès is thus, immense and its characterization both qualitatively and quantitatively vital.Thehydrochemical study of the Plio-Quaternary aquifer waters shows that they vary from fresh (Total Dissolved Solid < 1 g/l) to extremely saline (Total Dissolved Solid >5 g/l) waters. The results demonstrate that the salinity of the Plio-Quaternary aquifer waters isderived from the combination of a multitude of processes. The anthropogenic activities materialize in the contamination of the aquifer's waters, both directly by the polluted waters (industrial and domestic water wastes) of the Mekerrariverandseptic fosses (absence/weak coverage of sanitization networks) and indirectly due to the extensive usage of fertilizers and pesticides in farming, which reach by soils leaching the aquifer, during the rainy and irrigation seasons. The hydrochemical results illustratethe important contribution of the evaporation in the salinization process of the Plio-Quaternary aquifer waters, especially East and North of the plain of Sidi Bel Abbes where the aquifer is shallow and its section and thickness small. They also emphasize the major role of the water/rock interaction (dissolution of carbonates, ion exchange processes andsilicates weathering) and its influence on the salinity, hardness and geochemical facies of the Plio-Quaternary aquifer waters.*

I. Introduction

Despite the efforts made by the country over the last years, Algeria will face a deficit of 1 billion m^3 by the Horizon of 2025; the city of Sidi Bel Abbès (SBA) (Fig. 1) is a perfect example to illustrate this alarming situation. The city's potential in terms of surface waters is derisory and the majority of its potable water supplies comes from the Dams of SidiAbdelli (Tlemcen) and Bouhanifia (Mascara), the sea water desalinization station of Tlemcenand the pumping wells exploiting the Plio-Quaternary aquifer (PQA) and those adjacent.The city of SBA rises on both sides of the Mekerra river; 430 km WSW of the capital Algiers. It shelters one of the most fertile plain of the country,whichoccupies a surface of about 1150 km^{2}at an altitude varying from 500 to 700 m. The plain has a semi-arid climate; humid and cold during the winter and dry and hot in the summer whereas the spring and autumnal periods are almost imperceptible.

***Figure 1:** General localization of the city of SBA, Algeria.*

The plain of SBA (Fig 2) is a large basin that rest on top of a Mio-Pliocene substratum formed by gray green clays and marls. The plain is surrounded by terrains with great disparity ; in the North, the Tessala Mountains are essentially made of Cretaceous formations, roofed by a thick Tertiary cover (Sourisseau, 1973 [1]);in the South, the Tlemcen-Saïda mountains are represented by materials of the Midddle/Superior Jurassic and the Inferior/Middle Cretaceous; on the Western Border, the Helvetian Marl hills separate the basins of the Isser and Mekerra rivers; to the East, the plain is limited by the Miocene Marl series of BouHenifia (city of Mascara).

As mentioned previously, the plain of SBA is hydro-geologically poorly documented. The only relatively complete survey found in the bibliography is the one conducted by Sourisseau in the early 70s. Currently, the plain only beneficiates of a non periodic follow up done by the ANRH of Oran (AgenceNationale des RessourcesHydrique, National Agency of water resources) on the water table and the salinity of the PQA. The SBA plain hosts five aquifers (Fig. 3):

The Limestones of Zigyne: A small aquifer East of the plain near CaïdBelarbi formed essentially of Limestones form the Aptian.

The Dolomite rocks and Llimestones ofSidi Ali Benyoub: due to the abundance of faults in the Jurassic Cretaceous formations (the Limestones of Remaïla and the Dolomitic Limestones of Tlemcen), they are considered a one sole aquifer horizon. The latter is mostly present in the South of the plain and communicates with the PQA either by lateral infiltration or through springs such as AïnSkhrouna and AïnMekarreg.

The Pliocene Sandstones of Ténira: this unit is comprised of Conglomerates from the continental Pliocene at the base, surmounted by sandy Sandstones, sometimes silty or clayey. The main importance of this formation resides in the fact that it contributes greatly to the recharge of the PQA.

The Plio-Quaternary alluviums: this aquifer is unconfined, formed of heterogeneous alluviums and Conglomerates along the rivers Tissaf and Mekerra and rests on top of a blue Marls substratum (sometimes sandy) of the marine Pliocene. Its recharge is done by precipitations, adjacent aquifers or infiltration by the rivers beds. The principle outlet of the PQA is located in the « Rocher » district; North of the city of SBA, where the Mekerra river drains most of the aquifer's waters.

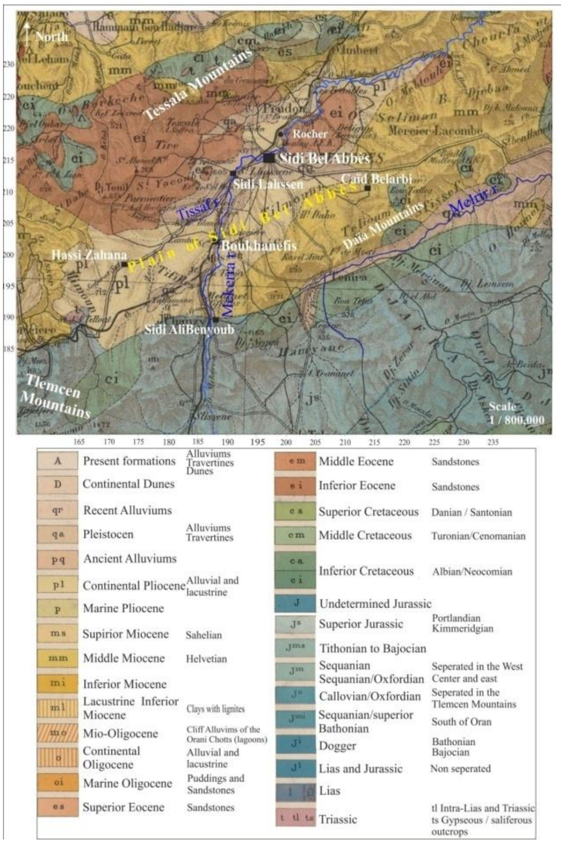

***Figure 2.** Geologic map of the plain of SBA. Extract of the geologic map of Algeria, third edition, Ministry of public works.*

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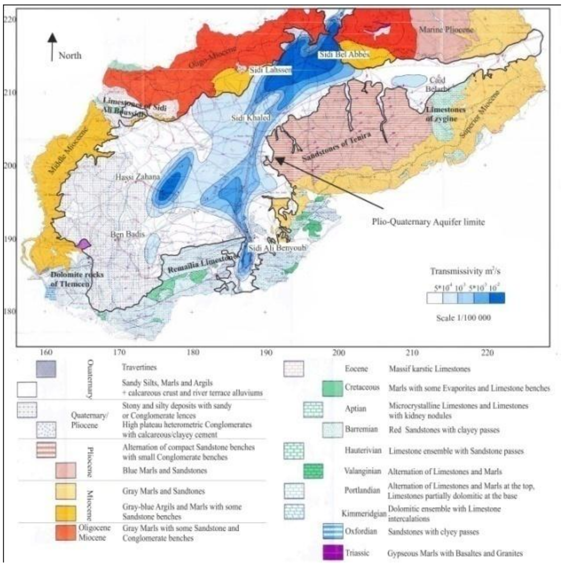

Figure 3.*Hydrogeologic map of the plain of SBA (K. Achi, A. Salem and F. Caquel&F.Zwahlen, 1974, based on the work of B. Sourisseau, P. Bonnet, S. Ramon with the collaboration of P. Combs and J. Leroux).*

II. Materials and methods

II.1. Sampling Locations

Due to the scarcity of recent data (less than 15 sampleswereanalyzedyearlyin the plain of SBA since 2008 and less than 10 are analyzed since 2010) compared to the aquifer extent (800 Km^2), samples utilized in this study are relative to the May/1989 campaignundertaken by the ANRH that concerned over 70 sites; all the samples were analyzed at the aforementioned agency's laboratory.50 samples whose percent charge balance errors were inferior to 5% were retained for the hydrochemical characterization of the PQA waters (Fig. 4).

II.2. Methods

The conventional methods based on the different diagrams, graphics and classifications, in addition to the statistical approach are utilized in the hydrochemical characterization of the PQA waters.

The study of the salinity is based on the different Total Dissolved Solid (TDS) and Electric Conductivity (EC) classifications,The Total Hardness (TH) of the PQA waters is calculated in $CaCO_3$ (mg/l) and converted to French degrees (F°).

The different geological facies are identified based on the Piper [2] and Chadha (1999) [3] Diagrams and the geochemical classifications of Durov's (1948) [4], Souline (1946-1948) [5, 6] and Schoeller (1951) [7].

The multivariate statistical analysis of the PQA waters is done by PCA (Principal Component Analysis); a method widely used in the chemical studies of underground waters.

The general mechanisms and processes controlling the salinity and affecting the chemical quality of the PQA waters are determined by the Gibbs diagram (1970) [8] and the study of the different chemical elements relations.

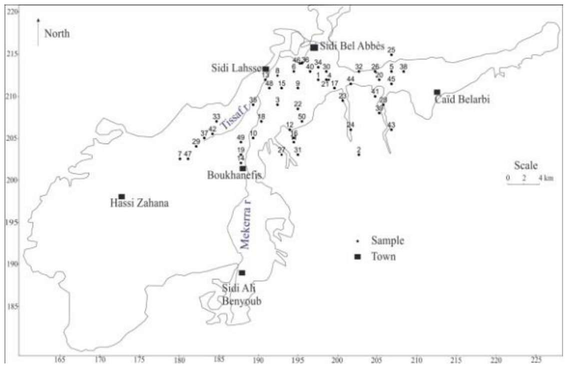

Figure 4. *Study area and sampling sites*

III. Results and discussion

III.1. Physical and chemical parameters

Appendix 1, shows that the majority of the samples have TDS values superior to 1g/l. According to the classifications of Robinove et al (1958) [9] and Heath (1983) [10], 30 samples are slightly saline and 20 moderately saline. According to Davis (1964) [11], however, they are all briny.

The salinity of the waters is clearly reflected by the high values of their Electric Conductivity (CE). In fact, based on the classifications of Potelon&Zysman (1993) [12] and Rodier (2005) [13], all the samples have an excessive salinity.

Fig. 5 represents the spatial distribution of the waters TDS means between 1970 and 2006. It shows that the augmentation of the waters salinity does not follow a defined preferential direction. However, it appears that the lowest salinityvalues (< 1g/l) are observedSouth of Ben Badis (zone scarsely populated with no industrial activity); the slightly saline waters (1 to 2 g/l) are represented by the samples North of HassiZahana (waters infiltrating the PQA from the Limestones of Sidi Ali boussidi), those between Lamtar and Ben Badis (presence of gravelly materials and some conglomerates along the Bedrabine affluent coupled with more important hydraulic gradients) and those along the Mekerra river (channel conglomerates up to 50 m thick near Sidi Khaled); the high TDS concentrations (> 3g/l) are on the other hand located in the NE, between

SBA (most populated and active area) and Belarbi (where the section, depth and thickness of the PQA are the least important).

The predominant ions in the PQA waters are the Chlorides for the anions and the Sodium for the cations. The chlorides (along with the EC) are a key element in any study relative to waters salinity. In the SBA plain, the elevated chlorides concentrations are responsible for the high TDS values. Most samples have Cl concentrations that oscillate between 1 and 2.5 g/l. These high concentrations in Cl are attributed mostly to pollution (sewage), the dissolution of Sodium chloride and to a lesser degree to the weather (aerosols).

The mean concentrations of nitrates from 1970 to 2006 in the study area are in their majority inferior to 50 mg/l (World Health Organization (WHO) norms); only 4 samples present nitrates concentrations superior to 100 mg/l. When the oxygen is depleted, microorganisms fall back on the nitrates and the milieu passes from an oxidant environment to a reducing one; a passage commonly known as the nitrate front (anoxic zone). During the nitrification process, the ammonium is firstly oxidized to nitrites, which in turn will be transformed to nitrates as the redox reactions progress.

$$2NH^{+}_{4(aq)} + 3O_{2(aq)} \rightarrow 2NO^{-}_{2(aq)} + 2H_2O_{(l)} + 4H^{+}_{(aq)}$$

$$2NO^{-}_{2(aq)} + O_{2(aq)} \rightarrow NO^{-}_{3(aq)}$$

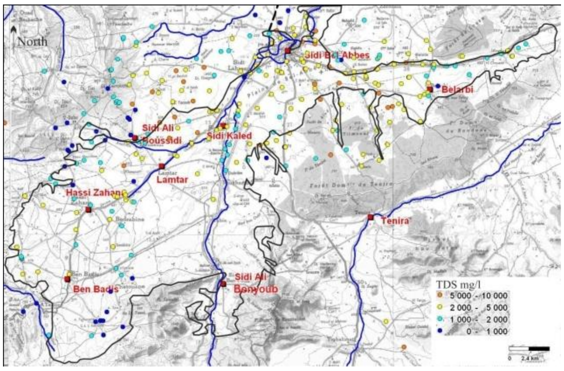

***Figure 5.** Spatial distribution of the mean TDS values of the PQA waters (ANRH, 1970 - 2006).*

***Tableau 1.** WHO normscompared to the concentrations of the PQA waters.*

	Concentrations (mg/l)			
Parameters	Desired	Number of samples	Max accepted	Number of samples
Ca	75	0	200	12
Mg	50	7	150	30
Na	200	10	200	10
Cl	200	1	600	8
SO_4	200	29	500	46
NO_3	45	14	50	19
TDS	500	0	1500	5
TH	100	-	500	-

It appears from Table 1, that theSO_4 concentrations are the ones respecting the most the WHO norms. This could be the result of their reduction or the low presence of SO_4 sources in the study area.Conversely, the Cl ions abundance clearly affects the PQA waters chemical quality for both domestic and agricultural uses.

III.2.Hardness

The total hardness of the PQA waters is calculated using the following equation (Todd, 1980 [14]; Hem, 1985 [15]; Ragunath, 1987 [16]):

$TH = 2.497\ Ca + 4.115\ Mg$, where all concentrations are expressed in meq/l.

***Tableau 2.**Total Hardness of the PQA waters.*

TH ($CaCO_3$in mg/l)	Water type	Number of samples
< 75	Soft	26
75 - 150	Moderately soft	20
150 - 300	Hard	4
> 300	Very hard	0

According to Sawyer &McCarty (1967) [17] and Vasanthavigare (2010) [18] (Table 2), only 26 out of the 50 samples are soft. Conversely, based on the classification of Berne and Cordonnier (1991) [19], the majority of the samples (46) are soft with TH values <15 °F.

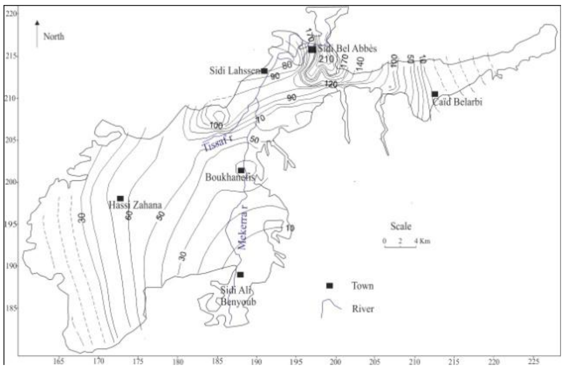

***Figure 6.**TH ($CaCO_3$en mg/l) spatial evolution of the PQA waters.*

From Fig. 6, it appears that the waters hardness increases as they flow towards the system outlet in the North. The low TH values in the center of the plain are the result of the quick circulation of the waters in the conglomerate channels present along the river Mekerra, which does not favor water/rock interactions sufficiently long enough to dissolve important quantities of Ca and Mg. The low TH values observed near the western and eastern limits

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of the Plio-Quaternary Alluviums correspond to the recharge zones of the aquifer; respectively, the Limestones of Zigyne and the Pliocene Sandstones of Ténira (see Fig. 3)

III.3.Geochemestry

The projection of the samples on the Piper Diagram [2] (Fig. 7), shows that the majority belongs to the Cl-SO_4-Ca-Mg type waters.

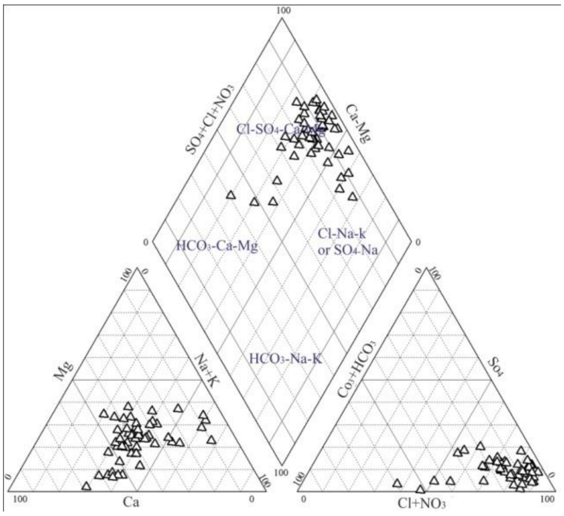

Figure 7.*Projection of the PQA waters on the Piper Diagram.*

From the Chadha diagram (1999) [3] (Fig. 8), the majority of the samples represent the Cl-Ca-Mg type waters in which, Alkaline earths and weak acidic anions exceed respectively Alkali metals and strong acidic anions. The Cl-Ca-Mg type waters have a permanent hardness and do not deposit residual sodium carbonate when used for irrigation (Chadha, 1999) [3].

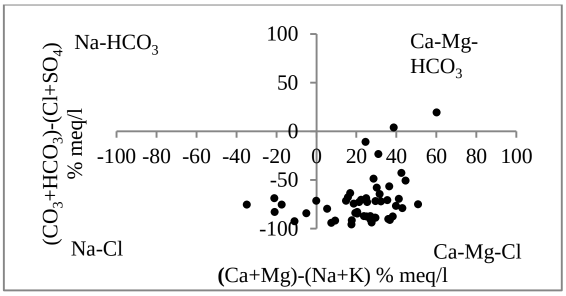

Figure 8. *Projection of the PQA waters on the Chadha Diagram.*

From the Ludwig-Langelierdiagram (1942) [20] (Fig. 9), all the samples are close to the Y axis; the majority (41 samples) plotted in the upper left corner of the diagram, with (Cl+SO_4) percentiles between 40 and 50 %. These characteristics are generally linked to recent (short transit period) waters, with an alkali (Na+K) alkaline (Ca+Mg) equilibrium (the mean (Na+K) / (Ca+Mg) ratio of the PQA waters is approximately equal to 0.7).

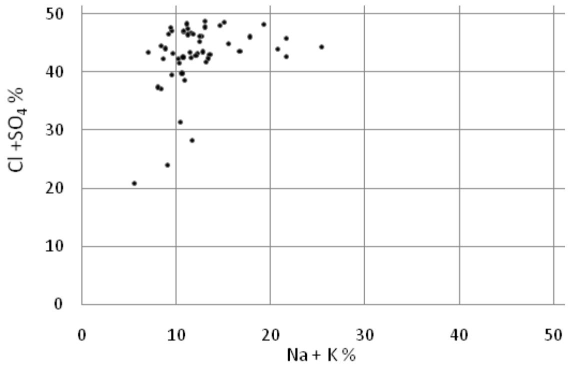

Figure 9.*Projection of the PQA samples on the Ludwig-Langelier diagram (1942).*

Based on Durov's (1948) [4], classification, 49 samples belong to the Cl waters class (the result of evaporation in closed basins), whereas the one sample left to the secondary waters class (TDS: 500 to 1000 mg/l and rMg / rCa : 0.3 to 0.7 meq/l).
According to Souline (1946, 1948) [5, 6] the 50 samples are subdivided between the Ca-Cl waters class (36 samples: rNa<rCl and rCl – rNa>rMg) and the Mg-Cl waters class (14 samples: rNa<rCl and rCl – rNa<rMg).

All waters in their concentration process, either due to evaporation or dissolution, tend to acquire a chemical composition converging towards the same water type. This results from the solubility differences existing between the mineral salts, which increases as follow:HCO_3,SO_4,Cl (only $NaHCO_3$and Na_2CO_3 have a solubility out this order). Thus, all waters generally converge towards the sequence: rCl> rSO_4> r$HCO_3$and rNa>rMg>rCa.

In the arid regions, this sequence will frequently be encountered in the highly concentrated waters (Schoeller, 1934) [21].Based on the chloro-alkaline indexes, Schoeller (1951) [7], distinguishes two types of waters: waters converging towards the rCl - rNa - rK< 0 type: waters characteristic of rivers, lakes, closed basins, underground waters flowing in crystalline rocks and aquifers in the arid regions.
Waters converging towards the rCl - rNa - rK> 0 type: waters similar to sea water: waters included in recent marine sedimentsand underground waters with very high concentrations; all 50 samples of the PQA converge towards this type.

The different classifications illustrate that PQA waters are mainly Cl-type, rich in sodium, calcium and magnesium, with a medium to strong salinity and low to high Hardness. These characteristics are generally the result ofion exchange processes and /or the mixture of fresh waters with others more saline (Adams et al, 2001) [22].

III.4.Statistics (PCA)

The biggest standard deviation values are relative to the Cl ions and the EC, whichillustrates their great dispersion and their inconsistent spatial evolution [23]. The best physical / chemical parameters correlations are noted between the EC and the Na-Cl ions, confirming the huge contribution of the two elements to the salinity of the aquifer's waters.
The good positive correlations (Table 3) of the EC with the Ca, Mg, SO_4, Na and Cl indicate that all these elements contribute to the salinity of the PQA waters. The relatively good correlation of the Ca and SO_4 (0.639) suggests the dissolution of gypsum. A dissolution, not very important in the study area as shown by the SO_4 concentrations (Log SO_4), all < 10 mmol/l. The weathering of silicates, the dissolution of carbonates and the ion exchange processes can commonly explain the good correlations of the Mg, Cl and Na in saline ground waters. The best positive correlations are noted between the Cl, Na and SO_4. They are the result of the dissolution of evaporites and intense anthropogenic activities (industrial and domestic water wastes, fertilizers and pesticides). The low correlation of the SO_4 with the NO_3 reveal the depletion of the two elements via redox reactions.

***Tableau 3.** Ccorrelation matrix of the PQA waters.*

Variables	Ca	Mg	Na	K	Cl	SO_4	NO_3	HCO_3	EC
Ca	**1**								
Mg	0.339	**1**							
Na	0.536	0.829	**1**						
K	0.365	0.525	0.479	**1**					
Cl	0.784	0.822	0.904	0.532	**1**				
SO_4	0.639	0.614	0.868	0.437	0.814	**1**			
NO_3	0.518	0.315	0.286	0.153	0.442	0.345	**1**		
HCO_3	-0.570	-0.150	-0.107	-0.144	-0.393	-0.159	-0.355	**1**	
EC	0.761	0.810	0.943	0.527	0.988	0.880	0.440	-0.293	**1**

Two factors (Table 4) explaining more than 75% ofthe total variance of the original data setare extracted. Factor 1 accounts for 61.64 % of the total variance with respective positivecorrelationswith the EC, Cl, Na, SO_4, Mg and Ca; strongly suggesting that these variables have common patterns. Thus, Factor 1 represents a salinization trend acquired probablyby the dissolution of carbonate rocks, evaporites, ions exchange processes and pollution. Factor 2 explains 15.2 % of the variance; 42% of which represented by the HCO_3. This factor is mainly attributed to the dissolution of carbonates (carbonates elements of the conglomerate channels), the redox reactions (reducing milieu) and the silicates weathering processes.

***Tableau 4.**Correlations factors/variables*

	F1	F2
Ca	0.778	-0.464
Mg	0.811	0.327
Na	0.909	0.325
K	0.594	0.227
Cl	0.984	0.003
SO_4	0.868	0.161
NO_3	0.509	-0.517
HCO_3	-0.383	0.767
EC	0.988	0.081

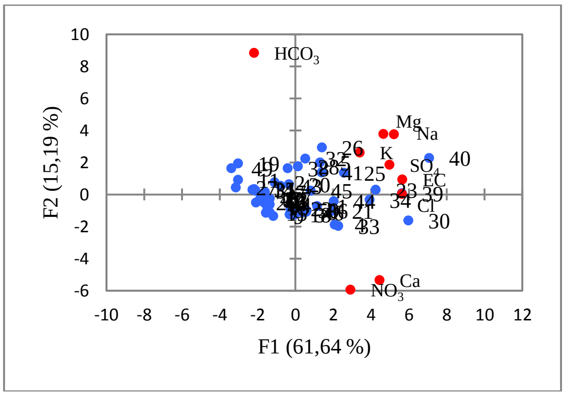

***Figure 10.** PCA biplot of the variables and the individuals of the PQA waters.*

Based on the PCA results (Fig. 10), we can classify the 50 samples in two big groups (Table 5). The first contains 27 samples and represents the fresh to moderately saline waters. These waters are mainly found near the recharge areas (the Sandstones of Tenira) and along the rivers Tissaf and Mekkera, where the circulation speeds are, considerable (conglomerates channels). The salinity of these waters is derived principally from the dissolution of carbonates; ions exchange processes and the weathering of silicates. The second group represents the saline to extremely saline waters, corresponding to the city of SBA and it vicinity (most populated and active area) and the region East of the plain (CaïdBelarbi), where the effects of the evapotranspiration are maximum due to the closeness of the water table to the surface and the smallness of the PQA section. The high concentrations characterizing these waters are mainly the result of anthropogenic activities (agriculture, industry and domestic wastes).

Tableau 5.*Classification of PQA waters based on the PCA results.*

	Group 1			Group 2	
	Relatively Fresh	Slightly saline	Moderately saline	Saline	Extremely saline
Number of samples	5	14	8	14	6
TDS mean (mg/l)	1159	1781	2279	3337	4693

The salinity of the samples 30, 39 and 40(TDS mean = 7259 mg/l) is considered an abnormality and could represent punctual pollution points.

III.5. Salinity origins of the Plio-Quaternary aquifer waters

The sources and mechanisms responsible for the salinization of waters are related to both, natural processes and to those triggeredby human activity. Often, a multitude of thesesources and mechanisms are found superposed, especially in complex situations.

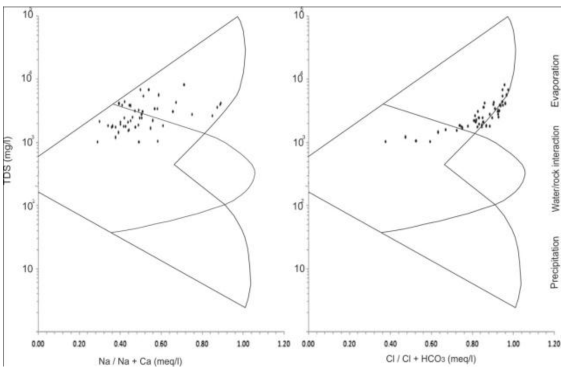

Figure 10. *PCA biplot of the variables and the individuals of the PQA waters.*

Fig. 11 depicts the projection of the PQA samples on the Gibbs diagram (1970) [8]. The latter is commonly utilized in the identification of the relationships existing between the underground waters and their aquifers lithology and consequently, the mechanisms controlling their chemistry (Feth and Gibbs, 1971 [24]; Wanty et al, 2009 [25]; Mamatha and Sudhakar, 2010 [26]; Bellaredj, 2013 [23]).

Out of the 50 samples, 30 have a ratio Na / (Na + Ca)< 0.5 and TDS values relatively low; suggesting that the water/rock interaction is the dominant mechanism controlling the chemistry of these waters (Wang and al). The 20 samples left have aratioNa / (Na + Ca)> 0.5 and high TDS values and owe their salinity to the evaporation process. The cationic exchange can also be considered an important factor to explain the predominance of the Na (Na / (Na + Ca) > 0.5) in relation to the other cations (Guo and Wang, 2004 [27]; Fisher and Mullican, 1997 [28]; Cirelli and Miretzky, 2004 [29]).

Thanks to their electric charge, ions in water are adsorbed on solid surfaces, especially those of iron oxides and clay minerals. Argils are particularly effective with cations, because they are always negatively charged.The major cations adsorption /desorption direction in natural waters is as follow: (highly adsorbed) Ca > Mg > K > Na (feebly adsorbed).

Na_2-(clay) + (Ca, Mg)-(water) ↔ (Ca, Mg)-(clay) +Na_2-(water)… (Hidalgo and Cruz-Sanjulian, 2001) [30].

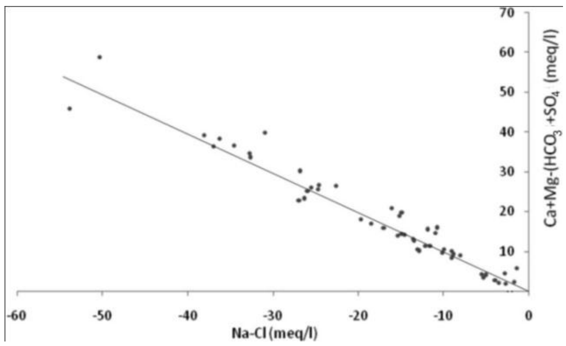

Figure 12. *(Ca + Mg) – (HCO_3+SO_4) vs (Na-Cl) plotfor sampled waters.*

All the samples on Fig. 12 are plotted along the line (-1:1), which confirms, that the ions exchange process plays a major role in the chemical composition of the PQA waters (Jankowski et al, 1997). Furthermore, all the samples have positives chloro-alkaline indexes (Schoeller, 1965) [31] CAI1 & CAI2, confirming that the PQA waters are in chloro-alkaline equilibrium.

The Cl / (Cl +HCO_3) ratio>0.8 of the majority of the samples (39), informs that the evaporation provides more Cl ions to the PQA waters compared to the water/rock interaction process.Generally underground waters coming in contact with sea water, brines or evaporites have ratios of Cl / Σ anions > 0.8, HCO_3 / Σ anions < 0.8 and low SO_4

concentrations (Hounslow, 1995) [32]; 38 % of the PQA samples meet these criteria.

The projection of fifteen or so samplesoutside of the Gibbsdiagram, is due to a Cl surplus in the waters. all the samples of the PQA have a ratio Na/Cl < 1, which is usually attributed to the ion exchange process, resulting in the softening of the waters (Hidalgo and Cruz-Sanjulian, 2001 [30]; Schwartz and Muehlenbachs, 1979 [33]; Phillips et al, 1986[34]). However, this, as mentioned previously, is not the case for the PQA waters, which in fact become harder as they transit towards the system outlet; a process referred to as base-exchange hardened water (Handa, 1979) [35].Thus and based on a Na / (Na + Cl) ratio < 0.5 for all the samples, it can be deduced that the high Cl concentrations are owed to an outside source of chlorides (Hounslow, 1995) [32]; essentially, a contamination by sewage.This is clearly shown by the Revelle Indexes (Revelle, 1946) [36]calculated (Cl / CO_3 + HCO_3 (meq/l))for the PQA waters, which are all > 1.

Despite the presence of an important sewage plant with a 300,000 eq/inha treatment capacity North East of the city, the water wastes still remain a major problem in SBA. Moreover, the plant, initially supposed to treat 28,000 m^3/day, receives only 6000 to 7000 m^3 /day (“Office Natinal de l’Assainissement” (ONA), 2007) [37].According to the « Direction de l’Hydraulique de la Wilaya (DHW) de SBA », the volume of all water wastes was estimated in 2006 at 98,000 m^3/day. Moreover, the Mekerra river which traverses the PQA South to North has become over time the main “receptacle” for the city’s wastes and receives throughout its length 47 pollutant effluents(Direction de l’Environnement de de la Wilaya (DEW) de SBAandtheONA, 2007) [38]. Furthermore, all the small localities with a population under 200 do not have sewage networks and still use septic fosses (DEW, 2005) [37].

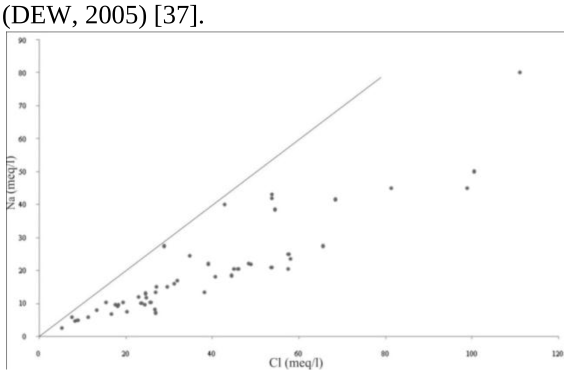

Figure 13.*Na vs Cl plotfor sampled waters.*

The Na, Cl relation is often utilized to identify the salinity mechanism in the semi-arid regions (Magaritz et al, 1981 [39]; Dixon and Chiswell, 1992 [40]; Sami, 1992 [41]; Singh et al, 2005 [42]; Bellaredj, 2013[23]). All the samples in Fig. 13 are plotted below the 1:1 line; indicating that the evaporation is not the only process controlling the chemistry of the PQA waters. Usually, when the evaporation is dominant and no mineral precipitates, the Na/Cl ratio stays constant (Jankowski and Acworth, 1997) [43]. furthermore, when the dissolution of Halite is the principal source of Na, the same ratio equals approximately 1; when it is inferior to 1 however, the Na originates rather from the weathering of the silicates (Meybeck, 1987) [44] ; a process generally accompanied with a predominance of the HCO_3 over the other anions.

When the pH falls under 6.7, the silicates minerals become unstable and convert to clay minerals and hydroxides. These reactions take longer and are more complexes than those relative to carbonates dissolution.

2NaAlSi3O8 + 2H2CO3+ 9H2O →
Al_2O2Si2O5 (OH)4+ 2Na+ 4H4SiO4+ 2HCO3 ;
or
NaAlSi3O8 + H2CO3+ 7H2O → Na + Al(OH)3 + 3H4SiO4 + HCO3.

From the (Ca + Mg) vs HCO_3 and (Ca + Mg) vs (HCO_3 + SO_4) plots (Fig. 14), a clear excess of the alkaline (Ca, Mg) over the (HCO_3, SO_4) is noted. This excess could be the result of inversed ions exchange phenomenon (Cerling et al, 1989 [45]; Fisher and Mullican, 1997 [28]; Ettazarini, 2005 [46]) and/or additional alternative sources of Ca and Mg other than the dissolution of carbonates; i.e., the dissolution of evaporites and the weathering of silicates (less acute) (Ettazarini, 2005 [46] ; Singh and al, 2005 [42]).

According to Datta&Tyagi (1996) [47], when Na + K = 0.5 Total cations, the cations input can be derived from the weathering of the silicates. In the study area (Fig. 15), the (Na + K) / TC ratio (0.2 to 0.67. mean ≈ 0.4), is inferior to (0.5). Therefore, the silicates are not the main alkali source for the PQA waters.

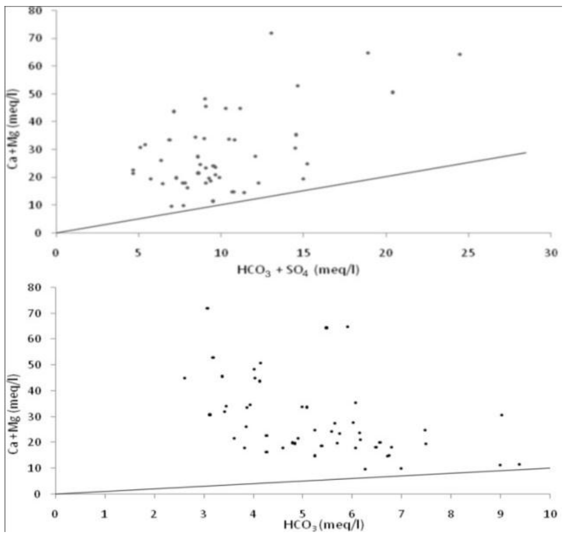

Figure 14.*Plots of (Ca + Mg) vs (HCO_3 + SO_4) (Datta&Tyagi diagram) and (Ca + Mg) vs $HCO_3$for sampled waters.*

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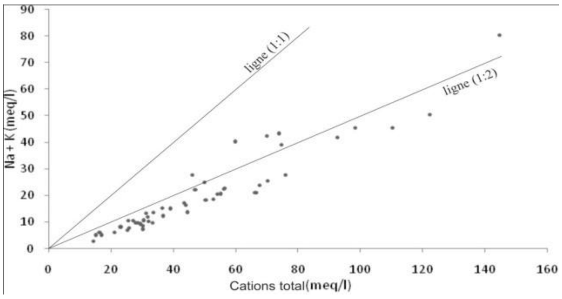

Figure 14. *Plots of (Ca + Mg) vs (HCO_3 + SO_4) (Datta&Tyagi diagram) and (Ca + Mg) vs $HCO_3$for sampled waters.*

The (Ca + Mg) vs cations total (CT) diagram (Fig. 16) indicates a growing contribution of the alkali (Na+K) in the salinity of the PQA waters. Nevertheless, the (Ca + Mg) / CT ratio (0.32 to 0.8, Mean = 0.61) reveals that the Ca and Mg remain predominant because of the evaporation and precipitation/dissolution processes (Ekwere, 2010) [48].

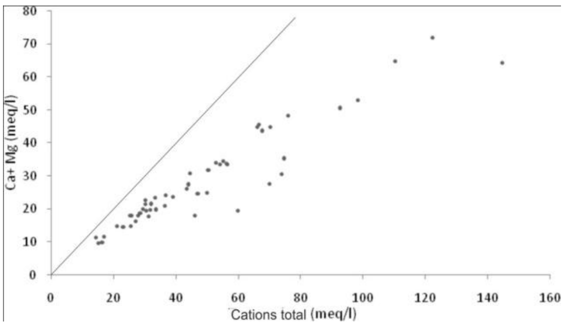

Figure 16. *(Ca + Mg) vs ∑Cations plot for sampled waters.*

Carbonates are presents in most sedimentary and even some igneous and metamorphic rocks. When the water infiltrates the soil, it is enriched with CO_2 and dissolves quit easily the carbonate rocks in its path, until either its saturation in carbonate minerals or the vanishing of the CO_2 present in the environment.

$CaCO_3 + CO_2 + H_2O \rightarrow Ca + 2HCO_3$

includes:

$CO_2 + H_2O \rightarrow H + 2HCO_3$ … (creation of acidic conditions (H^+) favoring the dissolution process)

And

$CaCO_3 + H \rightarrow Ca + 2HCO_3$.

The three reactions reveal that the calcite solubility is primarily controlled by the amount of carbon dioxide present in the milieu. When the pH declines, the CO_3 are converted into HCO_3 and the dissolution of the carbonates is intensified.overtime, this creates an acid front (pH = 7-8), below which the underground waters become aggressive.

Based on the Ryzenarindexes (RI) (Ryzenar, 1944) [49], the PQA samplescan be classified as follow: 42 represent waters in equilibrium, 2 (5 and 38): waters slightly corrosiveand 7 (7, 21, 34, 37, 39, 40 and 47): waters somewhat scaling.

Other processes such as the oxidation of sulphurouscompounds, can also produce hydrogen ions, thereby contributing in the carbonates dissolution process.The speed and direction of the redox reactions which control the nitrification/denitrification (ammonification), the oxidation of sulfides, the sulfates reduction and the methane formation depend on the oxidation state of the considered milieu. The oxygen and the organic matter are the major oxidant and reducing agents in nature.When nitrates are depleted, the oxidant agent for the underground waters becomes the sulfates. The latter, are reduced into hydrogen sulfur, part of which precipitates in the presence of iron into Pyrite. The remaining quantities have to be eliminated, because they not only give the waters an acrid taste, they also make them corrosive.

The SO_4 concentration in the PQA waters are relatively low; mainly resulting from the dissolution of gypsum (anhydrite) ($H_2O + CaSO_4.2H_2O \rightarrow Ca + SO_4 + 3H_2O$), irrigation waters (leaching of soils subjected to fertilizers and pesticides use) and sewage. The very law SO_4 / Cl ratio values (mean = 0.13, max = 0.35, min = 0.015) suggest that the sulfates are being reduced (Lavitt et al, 1997 [50]; Datta&Tyagi, 1996 [47]).The SO_4 reduction process can be explained by the following reactions.

$2CH_20 + S0_4 \rightarrow H2S + 2HC0_3$ … (Schwartz and Muehlenbachs, 1979 [33]; Phillips et al, 1986 [34]).

$15CH_20 + 2Fe_20_3 + 8S0_4 + H \rightarrow 4FeS2 + 15HC0_3 + 8H\ _20$... (Drever, 1988) [51]; this reaction necessitates the presence of bacteria.

IV. Conclusion

The hydrochemical study of the PQA waters demonstrated that they deteriorate as they travel from the recharge areas (adjacent aquifers) South and East of the SBA plain to the North towards the aquifer outlet (Rocher).The least saline waters (TDS < 1g/l) are found South of Ben Badis where the population density is weak and the industrial activity inexistent. North of HassiZahan and between Lamtar and Ben Badis and along the Mekerra river, the PQA waters are relatively of good quality (TDS: 1 to 2 g/l); in the area North of HassiZahana, most of the PQA waters with low salinity values come from the Eocene karstic Limestones of Sid Ali Boussidi; between Lamtarand Ben Badis, they are mainly observed along the Bedrabine river.This is due to the good hydrodynamic proprieties (permeability and hydraulic gradients)of the Eocene Limestones and the alluviums (gravels and conglomerates with abundant calcareous elements) along the Bedrabine and Mekerra rivers, which do not favor long periods of water/rock interactions in addition to the depth of the water table (relative protection) and the moderate agricultural and industrial (only Hassizahana)activity characterizing this zone in the study area.The saline to extremely saline waters (TDS>3 g/l) are present near the city of SBA, the most populated and active zone, through which a big part of the polluted Mekerra river waters transit and the locality of CaïdBelarbi, where the PQA is most exposed to the evapotranspiration (the aquifer is shallower, thinner and has a smaller section).

The PQA waters are in their majority relatively soft and can be utilized for industrial and agricultural purposes (if the Cl concentrations are reduced). They become harder, as they flow towards the Rocher outlet in the North,dissolving the carbonate rocks (The Limestones of Zigyne on the East, the Dolomite rocks and Limestones ofSidi Ali Benyoub on the South, the Eocene Limestones ofSidi Ali Boussidi and the carbonate elements present in the Conglomerate channels along the rivers Tissaf and Mekerra) on their path. Despite a slight (Ca+Mg) predominance over the (Na+K), most of the PQA waters are in chloro-alkaline equilibrium.

The ion exchange process plays a major role in the salinity of the PQA waters, especially with regards to the Na concentrations.The silicates weathering and the dissolution of evaporites contribute also in the increase of the concentrations of this element in the PQA waters. The relatively low sulfates and nitrates concentrations are the result of the redox reactions favored by the abundance of the organic matter (sewage) in the PQA waters. The high Cl concentrations characterizing the PQA waters, which arealong with the bacteriologic contamination, the main problem in the study area, are found to be in contrast with the weak presence of Evaporites and Chloride salts (except some Triassic, Cretaceous and Oligo-Miocene saliferousMarls and Argils in Aïntellout and mostly in the Tessala Mountains) in the region and are mostly attributed to sewage contamination. Due to the abundance of the Cl ions, most of the PQA waters are in their row state (untreated) improper for human consumption and harmful for most plants.

V. Recommendations

In order to protect and preserve the PQA waters, urgent steps have to be undertaken and the most pressing are cited bellow:

the gradual reduction of the water wastes volumes boththose directly rejected in the Mekerra river and those reaching the PQA due to the absence of sewage networks, until their complete elimination, either by constructing new sewage plants or restructuring the one already in place, which will allow the use of the treated waters both in irrigation and for the industry, reducing thereby, the volumes extracted from the PQA.

Conducting daily and monthly follow-ups on the chemical quality, respectively of the PQA and the rivers Tissaf and especially Mekerra,

the legislation and/or reinforcing of laws prohibiting the discharge of untreated industrial waters in the Mekerra river by obliging all the industrials operating in the region to treat their own waste waters before releasing them in the nature,

edify the farmers to produce the most appropriate plantations for the SBA plain (climate, soils, etc.) and generalize the use of modern irrigation techniques to avoid soils leaching and the over use of pesticides, fertilizers and water, catalogue all the users of the PQA resource to eliminate the illegal extraction points susceptible of deteriorating the quality or overexploiting the PQA waters.

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VII. Appendix

Appendix 1. Majorions and TDS concentrations in (mg/l) and EC values in (µS/cm) of the PQA waters

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Samples	X (km)	Y (km)	Ca	Mg	Na	K	Cl	SO_4	NO_3	HCO_3	TDS	EC µS/cm
1	198	212	580	180	541	11	2061	145	67	252	3837	4796
2	203	203	240	111	345	13	965	168	32	376	2250	2812
3	193	209	295	115	275	16	815	190	195	340	2241	2801
4	199	212	530	225	481	10	1905	300	196	246	3893	4866
5	207	213	109	270	965	13	1909	290	45	367	3968	4960
6	195	213	420	160	425	9	1578	265	85	210	3152	3940
7	181	202.5	455	9	220	7	870	160	90	350	2161	2701
8	193	212.5	305	78	232	8	839	178	26	299	1965	2456
9	195.5	211	270	55	171	12	721	191	96	233	1749	2186
10	190	205	175	75	240	6	550	264	71	320	1701	2126
11	195	204.5	85	71	135	9	270	35	19	426	1050	1312
12	194.5	206	221	105	240	10	916	43	54	295	1884	2355
13	191.5	212	350	30	310	7	957	120	54	292	2120	2650
14	188.5	202	185	70	135	7	405	190	55	411	1458	1822
15	193.5	211	235	56	240	6	691	178	86	260	1752	2190
16	195	205	255	122	165	9	955	20	42	260	1828	2285
17	200	211	170	115	300	10	876	90	19	280	1860	2325
18	191	207	350	105	390	12	1132	120	105	235	2449	3061
19	188.5	203	160	45	110	15	295	7	14	572	1218	1522
20	205.5	212	149	210	506	8	1386	168	51	320	2798	3497
21	199	212	761	125	631	14	2325	240	67	245	4408	5510
22	195.5	208.5	320	180	310	11	1357	95	60	190	2523	3153
23	201	209.5	640	255	1035	20	2885	551	52	194	5632	7040
24	202	206	235	120	191	12	951	51	39	220	1819	2273
25	207	215	380	200	885	27	1936	408	90	370	4296	5370
26	205	213	109	305	990	13	1909	264	87	550	4227	5283
27	193.5	203	105	55	115	6	320	35	16	382	1034	1292
28	206	209	260	145	565	16	1234	372	41	456	3089	3861
29	183	204	320	25	220	4	625	144	61	370	1769	2211
30	199	213	1020	255	1150	18	3561	480	162	187	6833	8541
31	195.5	203	174	115	155	8	594	58	63	395	1562	1952
32	203	213	119	165	920	13	1520	360	45	457	3599	4498
33	185.5	207	780	72	575	17	2045	410	98	159	4156	5195
34	198	213.5	801	130	955	16	2427	780	76	253	5438	6797
35	190	209	205	55	185	6	475	226	46	409	1607	2008
36	196	214	430	159	470	9	1632	216	95	240	3251	4063
37	184	205	420	35	345	5	1050	168	45	375	2443	3053
38	208.5	213	100	160	631	14	1025	264	47	414	2655	3318
39	205.5	208	780	315	1035	16	3507	624	169	360	6806	8507
40	197	213	660	382	1840	12	3937	912	62	334	8139	10173
41	205	210	320	215	505	29	1737	276	29	310	3421	4276
42	185	205.5	355	25	270	5	880	171	50	347	2103	2628
43	207	206	320	141	370	12	1109	142	25	344	2463	3078
44	202	211.5	600	190	471	24	2040	275	56	205	3861	4826
45	207	211.5	340	205	507	13	1716	264	70	304	3419	4273
46	196	214	400	165	470	8	1600	144	101	236	3124	3905
47	182	202.5	359	25	210	7	645	161	62	400	1869	2336
48	192	211	260	70	220	6	654	192	61	328	1791	2238
49	188.5	204.5	130	60	60	9	190	25	13	548	1035	1293
50	196	207	360	170	415	12	1443	96	81	208	2785	3481

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