

Presence and Origin of Fluoride in the Complex Terminal Water of Ouargla Basin (Northern Sahara of Algeria)

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Abstract: Problem statement: The underground waters in the oriental regions of the Algerian Sahara, present real chemical quality problems. Their content in fluorides always exceeds the limit of the recommended levels. That is 0.8 mg L^{-1} , according to the maximum temperature in the region. Combined to a high salinity, it affects the health of the population living around the region. The present work, deals with the presence of fluoride and the geochemical origin in the Complex Terminal aquifer of Ouargla, rarely examined in the Algerian Sahara. **Approach:** Is based on the following aspects: Sampling and physico-chemicals analysis of water, statistical treatment of the physico-chemical water parameters and simulation to natural and isotherm 25°C evaporation of water parameters. **Results:** The results show the presence of fluoride in the studied water. The rates vary between 1 and 2 mg L^{-1} . The calculation of water saturation index in relation with the preponderant minerals, using the thermodynamic model «phreeqci» reveals a sensitivity of carbonate minerals towards precipitation and dissolution of evaporitic minerals and clayey fluorides as well. **Conclusions/Recommendations:** The increasing alkalinity of water in contact with the aquifer during long periods of stay decreases the chemical activity of calcium and helps with alteration of clayey minerals and fluoride as a necessary condition for a possible fluorite mineralization. Knowing the origin of that fluoridation leads to possible solutions, through the optimization of a water treatment meets the standards.

Key words: Ouargla, complex terminal, geochemistry, fluoride, saturation index.

INTRODUCTION

The underground water resources in the basin of Ouargla, are represented, as everywhere in the Sahara regions of northern Algeria and Tunisia by two major aquifer systems superimposed: The Continental Intercalaire (CI) and the Complex Terminal (CT), which contain large reserves estimated at $31000 \times 10^9 \text{ m}^3$. The current levies are around 1.4 billion m^3 a year, resulting in practical terms, by continuing drawdown of CT aquifer^[7]. The groundwater is highly mineralized (over 5000 mg L^{-1})^[7].

The concentrations of fluoride in the water of CT often exceed the recommended levels by the World Health Organization (WHO). It is between 0.6 and 0.8 mg L^{-1} , according to the maximum diurnal temperature in the region. The problem was raised throughout the region, by various studies on water quality in the Algerian Sahara^[3].

The Complex Terminal aquifer is heterogeneous and made of sand, sandstone, clay, lime and evaporates, containing, theoretically, in their aquifer matrix significant and variable proportions of fluoride. However, the lack of detailed knowledge about the mineralogy of these formations in the northern Sahara is an obstacle to understand the hydro-geochemical process of fluoride mineralization in the waters of the Complex Terminal. To face this failure, this study attempts highlight the relationship between fluoride mineralization in water and the geology of different aquifers. The approach is based on the following aspects:

- Water sampling and physico-chemical analysis
- Statistical treatment of the physico-chemical parameters of water to get a global approach of the water's chemical composition process of acquisition

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- Simulation to natural and isotherm 25°C evaporation of the water parameters to clarify the mechanisms of acquisition of water fluoridation

MATERIALS AND METHODS

The Valley of Ouargla (Fig. 1), corresponding to a major depression, which covers an area of 750 km² around the quaternary bed of lower fossil valley in of oued M'ya. The climate of Ouargla is Saharan hyper arid, with temperate winters and a permanent drought. Precipitation is about 43.20 mm year⁻¹ and still below the double temperatures whose maximum average is about 42.69°C. The total Potential of Evapo-Transpiration (PET) is about 2758.80 mm year⁻¹, almost 60 times that of rainfall.

The underground of Ouargla basin contains four aquifers used in urban and agricultural activities:

Sandstones and sandy clays of the Continental Intercalaire (CI), containing the so-called Albian water, whoses thickness is about 600 m, located at a depth of 1500 m:

- Limestone, with containing water of Senono-Eocene carbonate whose thickness is about 300 m, located at a depth of 200 m
- All detritics of the continental formation (sand, clay and evaporites) with the water of the Mio-Pliocène, located at a depth of 20m to 100 m and thick of approximately 100 m
- Quaternary sands with groundwater table, located at a depth of less than 2 m

All the permeable formations contained in the series from the Cenomanian to Mio-Pliocene, are grouped, by Conrad Kilian (1931), under the name «Complex Terminal Water». The geological age of water determined by radiocarbon, is estimated between 10,000 and 20,000 years BP^[4]. Therefore, the water is ancient, having taken place in the reservoir of sedimentary formations of the Complex Terminal water during long periods.

Nineteen (19) samples of water (Fig. 1) are collected (February 2002) from ten (10) wells in Mio-Pliocene (MP1,...MP10) and nine (09) wells in Senono-Eocene (SE1,...SE9) using in plastic bottles. Before to be used, the bottles were treated with nitric acid, then washed with distilled water and dripped before being washed three times with the water to be analyzed.

The analyses are conducted in the laboratory of the National Agency of Hydraulics Resources (ANRH) of Ouargla according to the technical standard^[9].

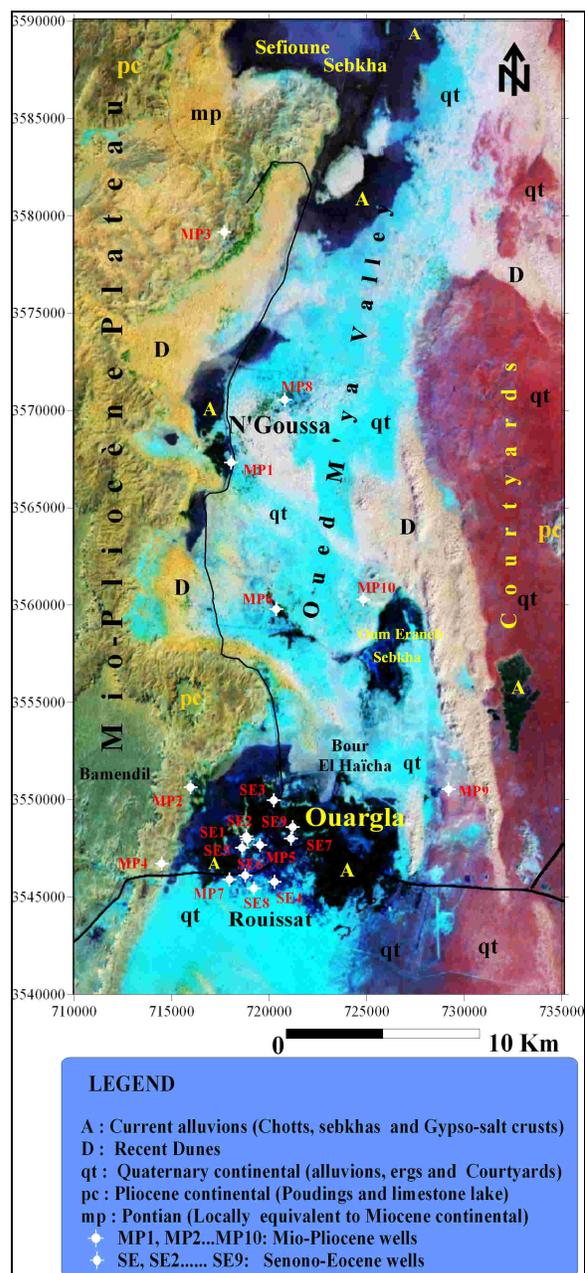


Fig. 1: Location of the studied area and the individual sampled wells

The fluoride, phosphorus, nitrates, sulphates and chlorides were measured using the spectrophotometer type DR2000 (HACH). Calcium, sodium and potassium were measured using flame spectro-photometry (410 CORNING). Magnesium measured by complexometry, with Ethylene-diaminetetracetic titration (EDTA) ($Mg^{2+} = TH-Ca^{2+}$). The pH and

bicarbonates measured using a pH-meter type E632 (METLOOHM) with the data we conducted a simulation to natural evaporation.

Data of four wells (MP4, MP7, SE4 and SE6), is used, where analysis are conducted in laboratory of water chemistry of Ouargla University. The data are not limited to major elements and fluoride, but are extended to others, such as temperature (in-situ measured) and phosphorus.

The software «Statistica.v6.1»^[11] was used for the statistical treatment basing on the Ascending Hierarchical Classification (AHC) method.

The method consists to classify "p" variables and "n" observations constructing a matrix of distances between variables and observations. Then a rule for calculating the distances between separated groups of variables or observations is defined. Groups whose distance is the lowest meet together in a couple (according to this criterion) and the process is repeated until a complete regrouping of classes^[10]. A dendrogram or classification tree can represent the Ascending Hierarchical Classification (AHC).

The geochemical survey was carried out by simulating the natural evaporation (temperature of the sample) or isothermal (25°C), using the software chemical thermodynamics «phreeqi.v.2.12»^[8]. The calculation of the saturation index (SI = log (Q)/log (K_{ps})) of dissolved minerals in water was conducted using the law of Debye-Hückel^[8], considering that the state of equilibrium done in the interval -0.5+0.5.

The chemical monitoring of the fluoride concentration in water depends mainly on the state of saturation towards the fluorite (CaF₂). If water is under-saturated, the fluoride concentration reflects, generally, the available amount within the washed rock. However, if water is saturated, the fluoride concentration is limited by the solubility constant value (K_{ps}) of fluorite dissolution reaction:



Fluoride in the waters of sedimentary rocks: The solid forms of fluorides, which can be likely found in natural waters, are: fluorite CaF₂ and sellaïte MgF₂. The fluorapatite (Ca₅(PO₄)₃F) may be found in the environment when phosphorus is present. The fluoride is the most abundant halogen in sedimentary rocks^[12]. The fluorite and fluorapatite of the phosphatic basins' rocks are the main fluoride minerals^[6]. If there are not phosphates, the origin should be checked in the clayey roof of the aquifers.

RESULTS

The hydro-chemical characteristics of water results, show high values of conductivity ranging from 1840-4090 μ S cm⁻¹ and beyond fluoridation of drinking water standards, or 0.6-0.8 mg L⁻¹, associated with pH, tending towards alkalinity, between 7.34 and 8.7. Three chemical elements show dominant concentrations SO₄²⁻, Cl⁻ and Na⁺ varying between 200 and 942 mg L⁻¹, followed by Ca²⁺, Mg²⁺ and HCO₃⁻ with variable concentrations from 86-238 mg L⁻¹.

The concentrations of fluoride observed in the CT water table (Mio-Pliocene and Senono-Eocene) vary between 0.90 and 1.42 mg L⁻¹.

The concentrations recorded in their entirety exceed 1 mg L⁻¹ (74% of samples) and remain beyond the optimum dose (0.7 mg L⁻¹) estimated using the formula of Galagan^[5] for the people of the studied region. The highest concentrations come mainly from waters of Mio-Pliocene, where we recorded: 1.27, 1.30, 1.31, 1.33 and 1.42 mg L⁻¹, respectively, in wells MP8, MP9, MP6, MP10 and MP3, located in the north area of Ouargla city.

Phosphorus levels recorded in the waters MP4, MP7, SE4 and SE6 vary between 0003 and 0028 mg L⁻¹. The natural temperature of water measured in four wells mentioned above varies between 20 and 23°C.

Three chemical facies were observed (Fig. 2), two of which two remain characteristic: The first one is sodium chloride Cl-Na whose conductivity is more than 2600 μ S cm⁻¹ in the Mio-Pliocene water. The second one is SO₄-Mg whose conductivity is less than 2000 μ S cm⁻¹ and is the mainly observed facies in the water of Senono-Eocene.

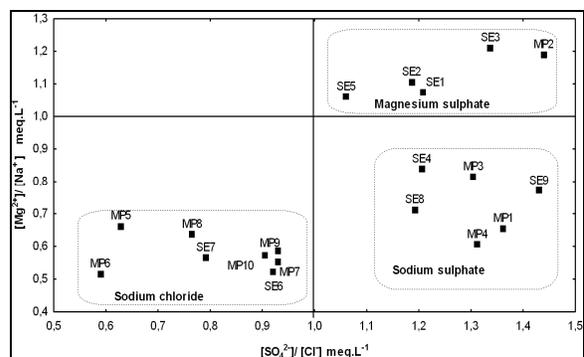


Fig. 2: Spatial distribution of chemical facies in the CT aquifer (February 2002)

The third facies is SO_4 -Na whose conductivity is more than $2000 \mu S cm^{-1}$. It is found in the water of both aquifers of CT.

DISCUSSION

Origins of fluoride in water:

Statistical analysis: The dendrograms of variables and observations (Fig. 3 and 4) show that four (04) well-correlated families can be distinguished:

- The first-family characterizes the exclusivity of the parameter (EC), highly high in the Mio-Pliocene drill (MP5) located in Ouargla city
- The second-family containing the evaporitic pole (Na^+ , Cl^- and SO_4^{2-}), characterized by high salinity, whose facies is Cl -Na or SO_4 -Na and includes wells drilled primarily in the in the Mio-Pliocene water table. It shows high concentrations of chlorides, sulphates and sodium, corresponding to gypsum ($CaSO_4 \cdot 2H_2O$) and the halite ($NaCl$), of geochemical structure of the aquifer formations
- The Third family, characterized by the presence of carbonated pole (Ca^{2+} , Mg^{2+} and HCO_3^-) rich in calcium, magnesium and bicarbonate, corresponding to the limestone ($CaCO_3$) and dolomites ($CaMg (CO_3)_2$) of the Senono-Eocene water, represented by the wells SE1, SE2, SE3, SE4 and SE8. The facies of this family is SO_4 -Mg
- The Fourth-family is relatively heterogeneous. Its facies is SO_4 -Na, containing wells in the Mio-Pliocene: MP1, MP3 and MP8 and Senono-Eocene: SE5, SE7 and SE9, with alkaline pH ($7.6 < pH < 8.7$), which includes nitrate, potassium and fluoride parameters

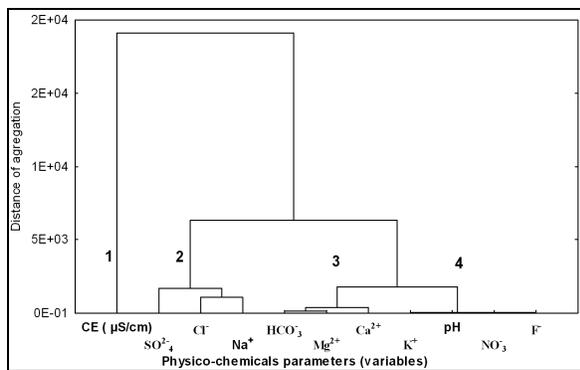


Fig. 3: Dendrograms of physico-chemical parameters in water of the CT aquifer

Such family could therefore represent water pollution under the effect of a partial increasing pressure of CO_2 , or any possible alteration of clays, under the effect of a relatively high alkalinity of water (Fig. 3), especially in the case of fluoride and potassium.

The richness of water elements Na^+ , Cl^- and SO_4^{2-} is due to the dissolution of evaporitic formations. However, the elements Ca^{2+} and Mg^{2+} , generated from two sources: gypseous formations (evaporites) and limestone in the case of carbonates.

Thermodynamics simulation:

Geochemical monitoring of fluorite: The balance compared to the fluorite (CaF_2), in water of the complex terminal, resulting in a straight line of slope 1 in the diagram (Fig. 5), which is related to $\log (Ca^{2+})$ versus $2\log (F^-)$, in terms of activities Ca^{2+} and F^- .

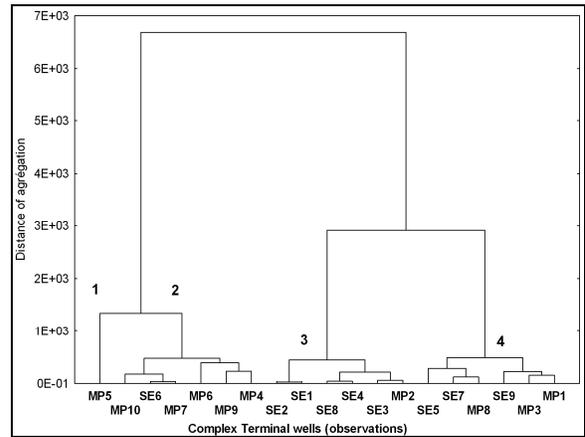


Fig. 4: Dendrograms of samples in the waters of the CT aquifer

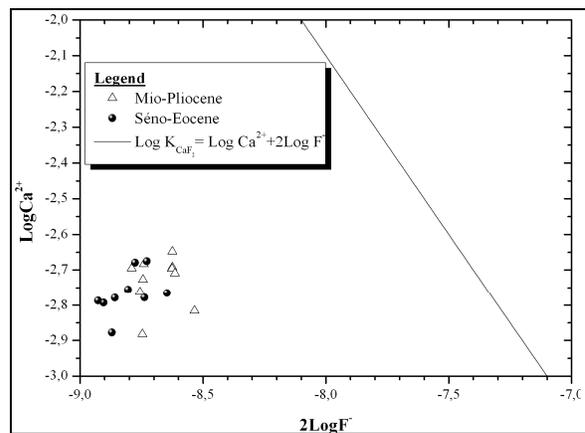


Fig. 5: Balance diagram by fluorite in waters of the CT aquifer

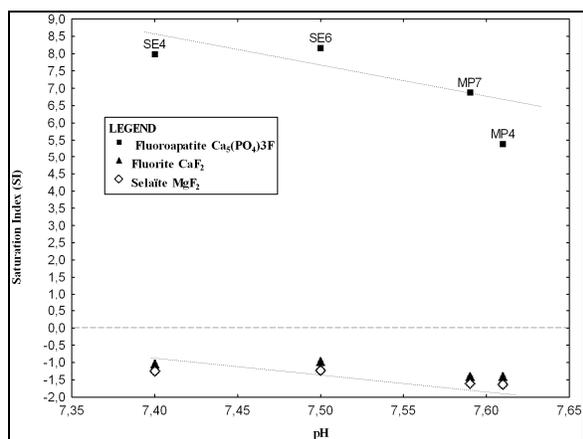


Fig. 6: Evolution of the saturation index of fluoride minerals depending on water alkalinity (simulation to natural evaporation)

The diagram shows an under-saturation of water towards fluorite. The analysis of the cloud of points on the diagram reveals an evolution toward a branch of calcium, indicating that there might be other minerals, which control the area of calcium and/or minerals, which control the area of fluoride, other than fluorite. While the correlation between concentrations of calcium and fluoride in water provides additional information. The correlation is of an average quality ($r = 0.45$). However, this is contradictory for the under-saturated waters in fluorite. Hence, there may be other calcium fluoride minerals, which could control this element in water.

Saturation index and fluoridation of water: The calculation of water saturation index by fluoride minerals (Fig. 6) reveals an over-saturation (precipitation) by the fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) and an under-saturation by the couple fluorite (CaF_2) and sellaite (MgF_2) in all samples (simulation to natural evaporation). The saturation index had highlighted a plausible relationship between fluoride and phosphate minerals, which may participate in the aquifer matrix. The relation pH-IS, shows saturation index towards the fluoroapatite ($\text{IS} \gg 0.5$), the fluorite and the sellaite decrease as the pH increases (Fig. 6).

The pre-acquired statistics, showing the relationship pH-potassium-fluoride, which undoubtedly contributes to any alteration of clay, under the effect of the alkalinity of water increasing, which leads to more solubility of chemical elements such as fluoride and potassium. Indeed, the saturation index of dissolved minerals (simulation to isotherm (25°C) evaporation) in water shows the sensitivity of carbonated minerals: dolomite, calcite, aragonite, towards precipitation and evaporitic minerals, especially gypsum and anhydrite (Fig. 7).

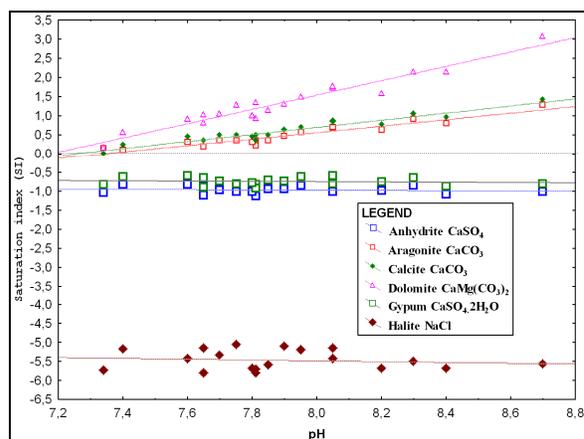


Fig. 7: Evolution of the saturation index minerals depending on water alkalinity (simulation to isotherm (25°C) evaporation)

The carbonates precipitation and dissolution of evaporates (Fig. 7) and fluorite (Fig. 6) increase proportionally with alkalinity (pH) of water, reflecting the character of the common ion which is calcium. It shows that the alkali ($7.6 < \text{pH} < 8.7$) (Fig. 7) of water helps with ionic exchanges between fluorinated minerals and hydroxide group (OH^-), which induces the solubility of fluoride, according to the studies^[1,2,6].

CONCLUSION

The study highlights the hydro-geochemical origin of fluoride, rarely examined in the Algerian Sahara, to valorise the relation «geology» and hydro-chemical characteristics” of the studied aquifer. The water is characterized by a high salinity, combined with a fluoridation that can harm the health of population. The concentrations of fluoride found vary between 1 mg L^{-1} and 2.03 mg L^{-1} , exceeding 1 mg L^{-1} in 74% of sampled wells. The method of Ascending Hierarchical Classification allowed us to individualize two levels of aquifers in the Complex Terminal. According to their lithological nature in two distinct poles, namely the carbonate pole (Ca^{2+} , Mg^{2+} and HCO_3^-) on the ground of Senono-Eocene and the evaporite pole (Na^+ , Cl^- and SO_4^{2-}) on the Mio-Pliocene. The thermodynamics simulation shows that the increasing alkalinity of water in contact with the aquifer during long periods of stay, decreases the chemical activity of calcium and helps with alteration of clayey minerals and fluoride as a necessary condition for a possible fluorite mineralization.

Knowing the origin of that fluoridation leads to possible solutions, through the optimization of a water treatment meets the standards.

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