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Determination of the Fluoride Ions in the Groundwater in the Region of Khouribga (Morocco)

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ABSTRACT

The objective of this work is to measure the fluoride ions in the groundwater in the region of Khouribga, The Great Basin phosphated in Morocco constitutes the basin of Ouled Abdoun and known of its effect on the groundwater table of Tadla which feeds the whole region.

All the samples have been extracted in an area where there is an activity of the Phosphate Plant, which extends from the city of Khouribga up to the city of Oued-Zem. Ninety samples have been collected from the different douars that exist in this area. These samples have been selected because of the activity of the OCP, and also as a function of the population that has been affected and show signs of fluorosis; the dental disease caused mainly by the excess of fluoride ion in the waters of drink. After the transport of samples to the laboratory of Hydrology within the National Institute of Hygiene of Rabat, the measurement of fluoride ions has been made by the specific electrical to ions F. The values found vary from 0.08 mg/L to 1.93 mg/L, and their standard deviation is 0.54 mg/L \pm 0.45 mg/L, which indicates that some samples are loaded with fluorine. Thus, we conclude the emergence of fluorosis among the population that uses the groundwater as a drinking water.

Keywords: Fluoride, Fluorosis, Groundwater, Phosphate region

INTRODUCTION

Fluorine is one of the elements that exist in abundance in nature. It comes under several forms: The fluorite (CaF₂), biotite ((Mg, Fe)₂Al₂(K,H)(SiO₄)₂), cryolite (Na₃(AlF₆)) and fluoro-apatite (Ca₁₀F₂(PO₄)₆). All these elements dissolve in water by some Physico-chemical parameters that help their dissolution like the temperature and the pH, which increases the concentration of fluoride ion in groundwater. This increase causes a severe intoxication for humans, animals and for the environment.

Fluorine as all trace elements, is beneficial to the human body but at low concentrations, and very toxic at high concentrations. It causes serious poisoning and its excess is the main cause of the disease of skeletal fluorosis. First to be affected with spots are teeth if the level is under (0.7 mg/l) but if the increases go beyond (0.7-1.5 mg/l) it will become a serious disease that may affect the bones and teeth (fluorosis). The Moroccan and the worldwide studies have concluded that whenever a phosphate activity is present there is a presence of the dental fluorosis disease [1-16].

The discovery of many areas affected by the dental and bone fluorosis have raised interests and researches since the beginning of the century with the presence of fluorine in natural waters. A reasonable rate of fluorine can reduce dental caries. Fluorine can quickly settle on bones that are the reason why it has been used to treat individuals suffering of osteoporosis (WHO).

But the excessive intake of fluoride in some regions has shown that this beneficial use may have a reverse effect to public health. In our case, dental fluorosis and more severely skeletal fluorosis [17]. In Algeria, the northern Sahara and the eastern zone are the most exposed regions to fluorite risk [3,4].

In nature, fluorine exists in several rocks and in groundwater. It is always associated with the meteoric process, especially in regions rich with shales and granite substrates. On the other hand, other artificial sources mainly the manufacturing of fertilizer having phosphate as main component, water in agricultural zones using fertilizers, and wastewater evacuation system treatment containing fluoride [5].

The region of Khouribga has the great phosphated basin in Morocco, the basin of Ouled Abdoun. The first Basin operated by the Cherifien office of phosphate in Morocco, the majority of its rural areas population use the water from wells as drinking water. Even with all the efforts made to limit its consumption.

Our main objective is to determine the concentration of fluoride ion in the waters originating from the wells of local douars surrounding the phosphate basin, and to figure out a serious solution to treat and minimize its effect.

The fluorine is measured by the potentiometric method through a specific electrode to the fluoride ions; this method is the mostly used in the studies concerning the determination of fluoride in groundwater [8].

MATERIALS AND METHODS

Study area

The region studied is part of the biggest phosphate basin in morocco. with 504000 citizens in 2010, limited to the north by the province of Khmisset, to the south by the province of Beni Mellal, to the east by the province of Khnifra and to the west by the province of Settat.

The region of khouribga is the mining capital with 60% of world reserves, estimated at 27 billion m³. It puts morocco as the number one exporter of phosphate. Deposits such as, Sidichennane, Daoui, and Meraelhrach constitute 66% of the national phosphate production.

Climate, geological, and water sources explain the scarcity of groundwater resources, in the form of aquifers exploited by the population of the region through wells.

The region of khouribga is formed by several douars, primarily those who are surrounded by the exploitation of phosphate and that constitute the base of our study because of the emergence of the fluorosis disease generally caused by the excess of fluorine in the groundwater of the region (Figure 1).



Figure 1: Location map of the study area and sampling sites

Sampling and analysis

Samples were picked out in the area of the phosphate exploitation, from douars located generally between the city of khouribga and that of Oued-zem. Those samples come from 90 wells where the activity of the cherifien office of phosphate is more focused. A minimum of 10 samples were taken in polyethylene bottles well washed with the same water collected from each douar with the same volume (1000 ml). The measurements are done on the spot taking in consideration various parameters such as "pH, temperature, and conductivity". Then the samples will be transported to the laboratory of hydrology of the national institute of hygiene in Rabat for the analyzed.

The analysis of fluorine in the groundwater in the region of Khouribga has been carried out by the specific electrode to ions F-, which is an electrode of crystalline membrane, that measures directly the content of fluoride ions dissolved in the waters of wells. After the mixture of 50 ml of analyzed water with 50 ml of the buffer solution made of leave of reagents sodium chloride, citric acid and sodium citrate. The values found are projected on the calibration curve track from standard solutions of 0.1, 1, 10, 100 and 1000 ppm, these standards are dilutions prepared from the parent solution of sodium fluoride NAF.

All measurements have been made by the specific electrode to ions F- of type Jenway France, in an ambient temperature 25°C. The values found included between 0.08 and 1.93 mg/l, with an average of 0.54 mg/l \pm 0.45 mg/l.

The measurement of fluoride ions are always coupled with the analyzes of the physico-chemical standard parameters in the drinking water 'pH, Temperature, and Conductivity'.

RESULTS AND DISCUSSION

Groundwater is generally loaded in F⁻ after Leaching of phosphate rocks by dissolution of fluorinated apatites. Including the presence of ions F⁻ in groundwater is always linked to some physic-chemical parameters which are the pH, temperature, and conductivity (Table 1 and Figures 2-4). These parameters are measured in situ during the levies, as healthy of the laboratory according to the standardized methods AFNOR French (AFNOR, T90-004) described by Rodier. The PH is measured using a pH meter as much as important factor for knowledge of the geological nature of the substrate and the watershed crossed, the temperature also integrated in the pH- meter, it usually plays an important role in the Speed dissolution of rocks contains fluoride, which influence on the quantity of ions F⁻ in the waters.

| Douars | рН | Temp. | Cond. | F ⁻ |
|--------------|-------|-------|--------|----------------|
| Ouled Brahim | 7,155 | 18,78 | 922,4 | 0,772 |
| Ouled Azouz | 7,347 | 16,96 | 1217,9 | 0,569 |
| Fassis | 7,169 | 20,09 | 612,4 | 0,126 |
| Elhamri | 7,434 | 16,74 | 621,1 | 0,843 |
| Ouled Abdoun | 7,254 | 16,47 | 996,6 | 0,893 |
| Lgufaf | 7,08 | 16,7 | 151,7 | 0,164 |
| Fokra | 7,556 | 19,42 | 602,1 | 0,924 |
| Bni Amir | 7,236 | 19,21 | 1008,9 | 0,311 |
| Bni Hassan | 7,208 | 18,85 | 577,9 | 0,264 |

| Table 1: The levels of the | parameters in situ | u and the ions F | in the groundwa | ater of Khouribga |
|----------------------------|--------------------|------------------|-----------------|-------------------|
| | | | | |



Figure 2: The concentration of the F'/pH



Figure 3: The concentration of the F⁻/Temperature

The results found indicates that the two parameters pH and temperature varies in a manner compatible with the ions f unlike the conductivity, which said that there is an influence on the presence of these ions in the groundwater in the region of Khouribga (Figure 5).

The region of khouribga is a phosphate region; it contains the great basin phosphated of Ouled Abdoun. In which the majority of its population suffers from the sulfur disease of the dental fluorosis especially those closest to the area of operation. The rural areas of the region of khouribga use the groundwater as drinking water. And according to the studies that have been made, the main source of the disease is the excess of the ions f- in these waters. This requires us to know and determine the concentration of these ions in the groundwater of the studied area. Ninety wells have been collected and analyzed, ten wells for each douar.

According to the results found the average values of the ions f- vary from a douar to another, 0.126 mg/l in minimum for Fassis and 0,924 mg/l in maximum for Fokra (Table 2).



Figure 4: The concentration of the F⁻/Conductivité



Figure 5: La concentration du F'/pH /Temperature/Conductivité

| Douars | Nbr/Wells | F ⁻ (mg/l) |
|-----------|-----------|---------------------------------------|
| O. Brahim | 10 | $0,772 \pm 0,55$ |
| O. Azouz | 10 | $0,569 \pm 0,56$ |
| Fassis | 10 | $0,126 \pm 0,13$ |
| Elhamri | 10 | $0,843 \pm 0,41$ |
| O. Abdoun | 10 | 0,893 ± 0,27 |
| Lgufaf | 10 | $0,164 \pm 0,04$ |
| Fokra | 10 | $0,924 \pm 0,42$ |
| Bniamir | 10 | 0,311 ± 0,17 |
| Bnihassan | 10 | $0,264 \pm 0,06$ |
| Total | 90 | $0,54 \pm 0,29$ |

Table 2: Average concentration of fluoride ion in the groundwater in the region

These average values are lower than the norms set by the WHO "1.5 mg/l" for all douars. But if we refer to the Moroccan norms" 0,7 mg/l", we conclude that the douars of Fokra, Ouled Abdoun, Elhamri, Ouled Brahim are way higher than the norm, and other douars "Bnihassan, Lgufaf, Ouled Azouz, Fassis, and Bniamir" are lower (Figure 1). from the comments and remarks on the degree of contamination by the dental fluorosis disease among the population, we deduce that the closest people to the area of phosphate operation are the most attacked "Fokra, Ouled Abdoun and Lhamri", these results are compatible with those who are found by the study of Mr. Haikel on "fluorine in the waters and the vegetation of the region of khouribga in 1986".

Dental fluorosis does not only affect the population of the region but also the animals under the name of "Daghmous" yellow spots on the teeth. This conclusion has been found also by Dr. Eljaoudi in his national studies on fluoride in the groundwater of morocco which indicates that the regions of khouribga and Bengurir are the most affected by this disease [17].

The concentration of fluoride ions for each well shows that some exceed the norms set by the WHO, but the majority is superior to that fixed by the Moroccan norms (Figures 6 and 7).



Figure 6: Average concentration of fluoride ion in the groundwater in the region of khouribga in mg/l as a function of the values national guides and international



Figure 7: Distribution of wells in function of the concentration of fluoride ions F in the wells in the area of khouribga in mg/l

In Morocco there are no studies concerning neither the problem of fluorosis nor the excess of the ions F^{-} in the drinkable water. Some work on fluoride in the waters done by: Dr. Eljaoudi and which shows that ion concentrations F^{-} varies from one region to another in the morocco 0.58 mg/l and 0.68 mg/l as the minimum values for the regions of Taza and tangier and 7.76 mg/l and 8.95 mg/l as the maximum value for the regions of khouribga and Bengrurir, these last two are the most infected by the disease of the dental fluorosis. Mr. Hakeil on the different component of the region of khouribga water, soil and vegetation," has shown us that the groundwater of the same region contain fluorine with a variation of a douar to another, 1.5 mg/l for Fokra and 0.43 mg/l for Bnikhlef. These results are compatible with our studies on the waters of the wells of the rural region of khouribga 0.92 mg/l for Fokra and 0.13 mg/l for Fassis. While this result confirms that the presence of the ions F- in the waters of beverage is linked with the presence of phosphate in the region [15,17].

In an international scale, several studies have been carried out in this direction, in Senegal a study shows that the concentration of f-varies between 0.1 mg/l and 7.4 mg/l, and that the prevalence of dental fluorosis affects only the regions that contain more than 4 mg/l of fluoride and the bone fluorosis disease among adults between 40 and 60 years who exceeds 7.4 mg/l [13]. Ethiopia and Tanzania are the most attacked by dental and skeletal fluorosis with content close to 10 mg/l and 21 mg/l [13,14].

The prevalence of dental and skeletal fluorosis depends not only on the presence of ions f- in the drinkable water but also in food and vegetation through the dust released by plants of phosphate.

For the region studied, the ONEP has tried to connect the douars with points of drinkable water, but due to the consumption of water in agriculture and breeding/farming, the rural population remains always linked to the wells.

CONCLUSION

Several countries in the world suffer from the problematic of excess use of the fluoride ions in the drinkable water, especially those who are known by phosphate exploitation.

Our study has allowed us to know the fluoride content is dissolved in the waters of wells in the area of Khouribga as a source of drinkable water in the rural population. The levels of fluoride are low for some douars and very high for some others. Especially those who are close to the basin phosphated of Khouribga Ouled Abdoun", the rural population in this region is affected by sulfur dental disease which requires a strict solution in order to minimize or eliminate XXC this problem.

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