

Fluoride Contamination in Water in the North East of Tunisia Ore Deposits

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ABSTRACT

The north east of Tunisia ore deposits (Hammam Zriba) contain a large amount of fluorides constituting a risk of environmental pollution as well as risks to human and animal health. The aim of our work was to assess the levels of fluorides in the water from the east of Tunisia region. This analysis study included 78 water samples taken during 3 days in the year 2019, at Hammam Zriba delegation. The determination of fluorine concentration in the samples was carried out by potentiometer with a selective electrode type ISE combined Fluoride

perfectION™. High Fluoride concentrations were found at a mean of 1.62 ± 1.18 , 1.45 ± 0.98 and 2.65 ± 1.61 mg/lit, respectively, in running, deep and stagnant waters.

Key Words: Fluorine, Tunisia, Water, Analysis

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INTRODUCTION

Fluoride is the 13th most abundant element in the earth's crust. It is essential for human and animal health. These latter are exposed to fluoride ions particularly by consuming water rich in fluorine. Ingesting small amounts of fluoride in water is generally beneficial for teeth and bones, especially in young animals [1].

The permissible limit for fluorides in drinking water is 1.5 mg/l. However, long-term ingestion of large amounts can cause serious dental and bone problems in animals.

Controlling the quality of drinking water is therefore essential to prevent animal fluorosis, which results in dental lesions (brown enamel stains+chalky appearance and irregularity of the molar table) and bone lesions (exostoses) affecting the mandible, ribs, metacarpus and metatarsus. Fluorosis is also responsible for a decline in zoo technical performance which explains the economic losses and even the difficulty to develop livestock farming in Tunisia [2].

Fluorides occur naturally in the environment. Because of its high reactivity, fluorine is never present in its elemental state in nature. It is always found in combined form with other organic or mineral elements that cause toxicity problems affecting fauna, flora and the environment.

Fluoride pollution comes from human activities such as agriculture, urbanization, industrialization, and mining. Indeed, the tailings of mining waste landfills coming from smelting and extraction procedures, including process fluids from factories, the remaining fluids after the extraction of minerals, metals, fuels, or coal contribute to the environmental contamination [3,4].

The impact of wind on atmospheric particles and dry or wet deposits are primary pathways for atmospheric dispersion and transport of this pollutant, which subsequently affects water, fauna and flora. Fluorides can also be transported by leaching from precipitation and contaminate streams and groundwater. Wind, by comparison, rapidly transports fluoridated airborne dust over long distances. Thus, the main risk of airborne fluoride dust emissions from abandoned mining areas is the presence of unconfined fluorite tailings ponds containing high fluoride loadings that are either wind-borne or transported by water runoff or leached to groundwater [5,4].

Few studies have evaluated the level of fluorides, emitted by the mining waste, in waters near the fluorite mine located in the east of Tunisia [6]. In a Mediterranean climate, with little rainfall and low ground cover, fluoride dust from mine tailings can specifically affect the environment surrounding the mine. The objective of our work was to study the level of fluoride contamination in the deposit region of Hammam zriba by determining the fluoride levels in the water in the study area.

METHODOLOGY

Collection of samples

Our work was carried out water samples. In the study area, sampling was performed over three points. A reference site was used in order to determine the difference in fluoride accumulation in the environment of the mines (Figure 1). All the samples were taken in November 2019 in order to assess the level of fluoride contamination in water. The concentration of fluoride ions in the different water samples was determined by potentiometry using a fluoride ion selective electrode of the ISE type combined Fluoride perfectION™. The water samples are divided into three groups according to the distance from the mine (E1 (Mine-400 m), E2 (400 m-1 Km), and E3 (>2 Km)).



Figure 1: Location of study area and sampling points. Note: Z1: Zone 1; Z2: Zone 2; Z3: Zone 3.

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Reagents and laboratory ware

The analysis method is developed and validated at the laboratory of Pharmacy and Toxicology at the National School of Veterinary Medicine-Tunisia. It is used to measure the concentration of fluorides in solutions where fluoride concentrations are higher than 0.02 mg/l (detection limit). Therefore, from a sodium fluoride main solution (100 mg/l), five standard solutions with concentrations ranging from 10–1 to 10–6 mg/l have been prepared.

The concentration of fluoride ions in the different water samples was determined by potentiometry using a fluoride ions selective electrode of the ISE type combined Perfection™.

The water sampling concerned surface water, groundwater, and drinking water in the ore deposit region of Hammam Zriba. These samples are distributed to cover most of the region and are selected locally based on the number of animals consuming the water. Samples are then stored in polyethylene sterile bottles to avoid contamination. Fluoride perfectION [7].

The determination of fluoride ions in the samples was done after the addition of an equal volume of Total Ionic Strength Adjustment Buffer with the following composition: Glacial acetic acid (57 ml); Sodium chloride (58 g); Sodium citrate (0.3 g) and bi-distilled water (500 ml). The solution is adjusted to pH 5–5.5 with 5 M Sodium hydroxide solution. This acidic solution is added to the buffer by successive additions with a graduated pipette. The pH control was done progressively with a calibrated pH meter. It is cooled and then made up to 1 liter with bi-distilled water.

In order to obtain the most significant results possible, we have procured the purest fluoride free reactants possible and used doubly distilled water for all handling. Each sample was tested twice. A coefficient of variation $\leq 2\%$ was used to validate the measurement.

Statistical analysis

The data were analyzed using SPSS (version 22.0). All data were expressed as mean \pm SD and the level of significance was determined at $p < 0.05$.

RESULTS

Variation of fluoride concentration in the water samples

In the 78 analyzed water samples, we noted a positive correlation between the mean of fluoride concentration (1.92 ± 1.38 mg/l) and the mean of pH water (9.39 ± 0.27) with a coefficient $r = 0.79$ and $p < 0.001$.

Each group consisted respectively of (32, 20 and 26 samples). The mean fluoride concentration was, respectively, 2.94 ± 1.55 mg/l in first group E1, 1.79 ± 0.96 mg/l in the second group E2, and 1.03 ± 0.83 mg/l in the third group E3. The difference between three groups was statistically significant and $p < 0.001$.

Comparison of the fluoride concentration according to the type of water demonstrated an average of fluoride concentration equal to: 1.62 ± 1.18 mg/l in the running water (32 samples), 1.45 ± 0.98 mg/l in the deep water (20 samples), and 2.65 ± 1.61 mg/l in the stagnant water (26 samples). The difference between this three groups was statistically significant ($p = 0.003$) (Figure 2).

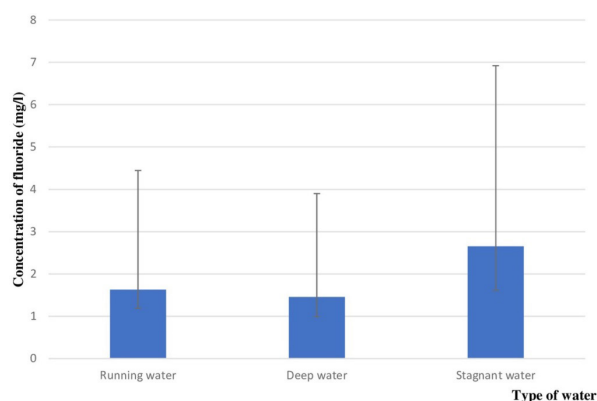


Figure 2: Fluoride concentration depending on the type of water.

DISCUSSION

In Tunisia, fluorosis is a real obstacle to the development of livestock farming in some regions of the country, particularly in southern Tunisia but also in some northern regions such as Hammam Zriba. The Hammam Zriba region is a mining area for the extraction of fluoride and other minerals where fluoride toxicity could affect flora and fauna. Sheep are the most affected by fluorosis in this area. The majority of the farms are traditional, free-range farms. The animals drink water from the wadis as well as from surface water located near the abandoned fluoride mine [8].

Our results show that the fluoride levels in water samples collected near the mine are higher than those collected from a greater distance. Our results match those found by Bengoumi and Kessabi, where the fluoride levels in water collected 200 m from a phosphate processing plant in southern Morocco are very high, in the order of 4.6 mg/l. This could be related to the weathering and erosion of the various mining discharges that seem to contribute to the contamination of the natural environment by fluoride [9,10].

Ambient fluorinated dust from abandoned mines and unconfined fluorite tailings containing a high fluoride load may be suspended by wind or transported by water runoff or leached to ground water [11,12].

High fluoride levels in ground water have been reported in other countries, particularly in England, France, Italy and USA. Fluoride concentrations range from 0.01 to 4 mg/l, but a predominance of values below 1 mg/l is still noted [7]. These high fluoride concentrations recorded in deep waters can be related to the prolonged contact of alkaline water with fluoride-rich rocks, which leads to their release and passage through the water. Sheep and cattle drinking from this water show dental and bone damage which represented a major signs of fluorosis [13].

As a consequence, they seem to be associated most often with ground water, with high pH values (>7) facilitating ion exchange between F-fluorides and OH-hydroxyl groups, and of the sodium bicarbonate type characterized by low concentrations of magnesium and calcium due to the low solubility of fluorine [6].

In our study, we noticed that high fluoride concentrations in water are related to the increase of its pH. Similarly, the experimental results carried out by other study show that an alkaline environment (with a pH ranging from 7.6 to 8.6) is favorable to the dissolution and release of

fluorine, which leads to high contents of this ore in the water analyzed [14].

Prevention consists to encourage farmers to use drinking water for livestock animals and to watering crops, to keep food at a safe level by conducting periodic checks of water and animal food rations and to ensure a balanced diet.

The contamination of water by fluorides remains a major problem for animals and humans health, which requires the implementation of

rigorous control measures. Several ways of fluoride decontamination should be used and are represented by the treatment of water at the source before distribution and consumption. Various techniques had been widely developed as precipitation, coagulation, and flocculation or by the new techniques of reverse osmosis which remain rather expensive. Annual testing program should be established regularly to monitor the physical and chemical quality especially fluoride content in the water used from these sources.

CONCLUSION

It seems to be important to encourage farmers to use drinking water for livestock animals and to watering crops, to keep food at a safe level by conducting periodic checks of water and animal food rations and to ensure a balanced diet. In this work we noted very high fluoride levels especially in the areas close to the mine. Therefore, the study area was highly contaminated by the fluoride for a 300 m radius from the mine (contaminated site) with a clear tendency to decrease while moving away from the study area.

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