

## Speciation and presence of fluorine in the groundwater in the Maradi region (central Niger)

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### Abstract

The present study aims to study the impact of seasonal variations on the different forms of fluoride in groundwater in the Maradi region. The methodology consisted in carrying out three (3) water sampling campaigns at different periods, rainy season, hot season and cold season; respectively in December 2019; May 2020 and November 2020. The results obtained show that the levels of fluoride ions exist at variable levels ranging from traces to 2.84 mg/L. These results also show that, in well water, fluorine is mainly present in the F<sup>-</sup>, NaF and HF forms whatever the season; whereas, in borehole waters, the F<sup>-</sup>, NaF and MgF<sup>+</sup> forms are those which predominate during all the seasons.

**Keywords:** Speciation; Tablecloths; Fluorine; Groundwater; Maradi

### 1. Introduction

In sub-Saharan Africa, groundwater is the main source of water supply [1, 2, 3]. The climatic changes observed in recent years, characterized by the increase in average temperature and the scarcity of rainfall, have resulted in the deterioration of water quality and availability [4]. In arid zones, the superficial and deep aquifers can be the seat of the evaporating action of the climate and of anthropogenic contamination (pollution of agricultural, domestic or industrial origins) [5]. As a result, this action could cause variation in the chemical composition of groundwater [3, 6, 7, 8]. In Niger, various studies have reported groundwater contamination [1,9]. In the 1990s, the Regional Directorate of Hydraulics and Sanitation of Maradi made the case of the fluoride ion pollution of groundwater in the Maradi region. And according to the Regional Directorate of Public Health of Maradi, this excess of fluoride ions has caused dental and/or bone malformations in several children's backgrounds. It is therefore imperative to know the different chemical forms of fluoride ions in groundwater in the Maradi region. According to [9], the fluoride ion content in water from wells and boreholes in the Maradi region varies in time and space. The objective of this study is to study the spatio-seasonal variations of the different forms of fluorine in the groundwater of the Maradi region.

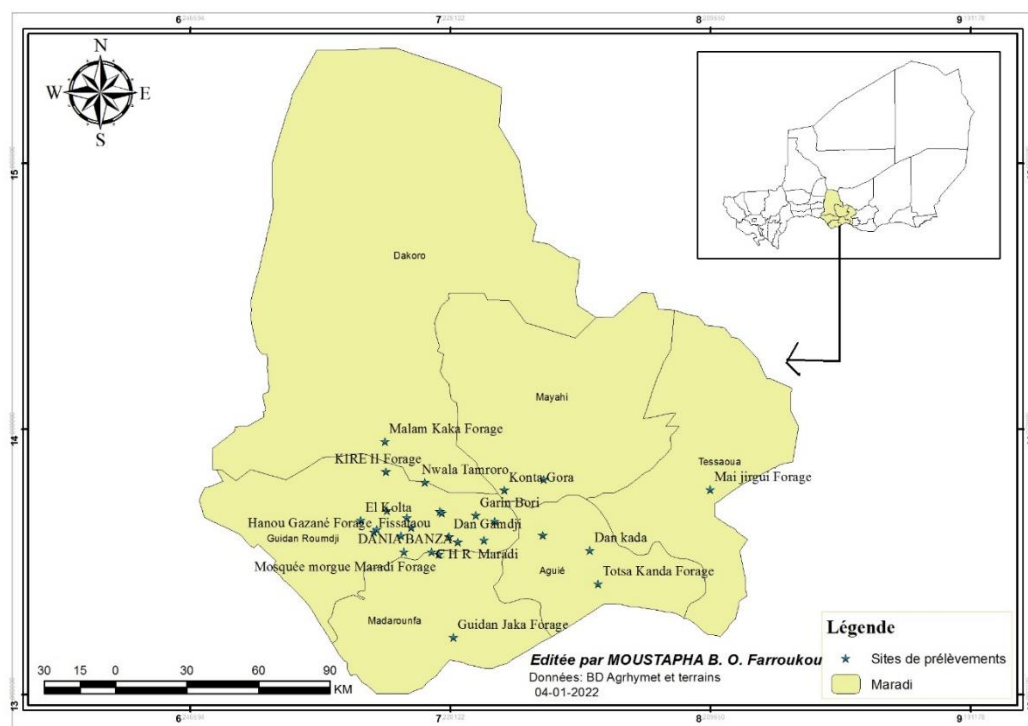
### 2. Material and methods

To carry out this study, three (3) water sampling campaigns were carried out. The first in December 2019, a period corresponding to a slight rise in the level of the aquifers. The second in May 2020, just before the first rains, when the groundwater level is as low as possible. The third, in November 2020, just after the last rains, when the water tables are at a higher level. During these three campaigns, a total of 60 water samples from wells and boreholes were taken (Figure 1). The works selected are those with high fluoride ion contents.

The water samples were taken in polyethylene bottles. The bottles were first washed with water and then rinsed with distilled water before being filled with the water to be analyzed. The samples thus taken were transported to the

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laboratory in an appropriate thermos. The fluoride ion content (wavelength 580 nm) was determined by spectrophotometry using a DR3900 type spectrophotometer (HACH).



**Figure 1** Location of the study area and sampling sites

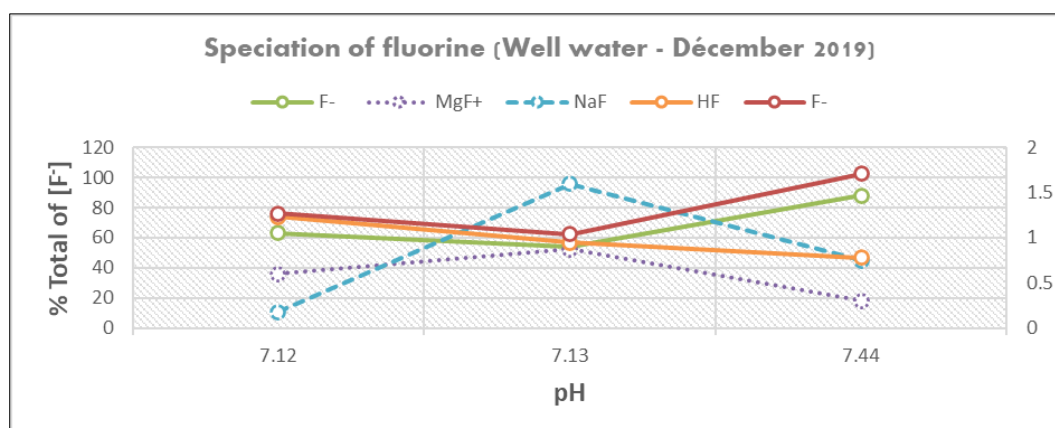
### 2.1. Simulation tool

Phreeqc.v.3 thermodynamic software was used to perform fluorine speciation calculations.

## 3. Results

### 3.1. Case of well water

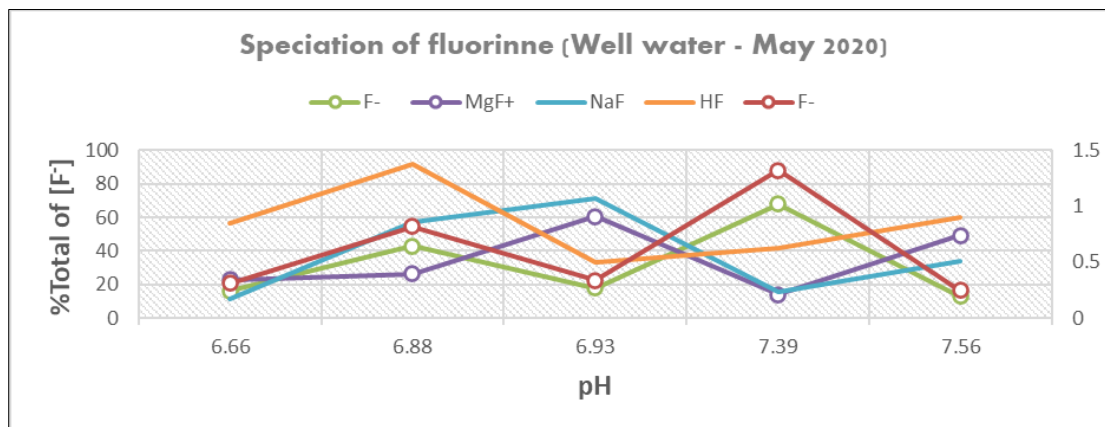
The chemical speciation of an element makes it possible to identify the different forms and compounds (free, complex, etc.) under which it is found in solution [10]. The results obtained according to the seasons are represented in the figs below.



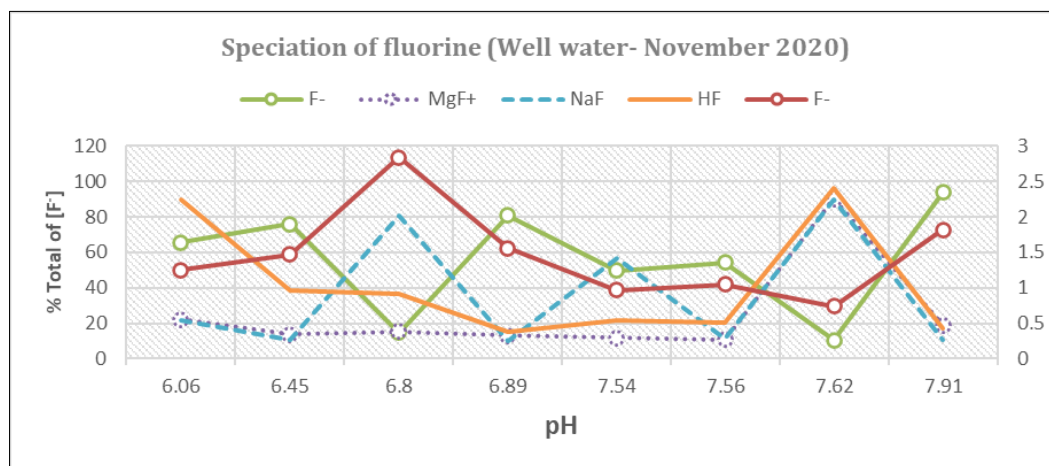
**Figure 2** Chemical speciation (in %total concentration) of fluorine in well water compared to all fluorinated species (December 2019)

Figure 2 shows that, in December 2019, the free ionic form  $F^-$  and the complex form  $NaF$  are the predominant forms in well waters. This figure also shows that the presence of the ionic form  $F^-$  is favorable with increasing pH.

Figure 3 shows a predominance of the complex form  $HF$  in the well waters of the study area during the month of May. This form is preceded by the  $NaF$  then  $MgF^+$  form. This figure also shows that the formation of these compounds in this medium are favored with increasing pH.



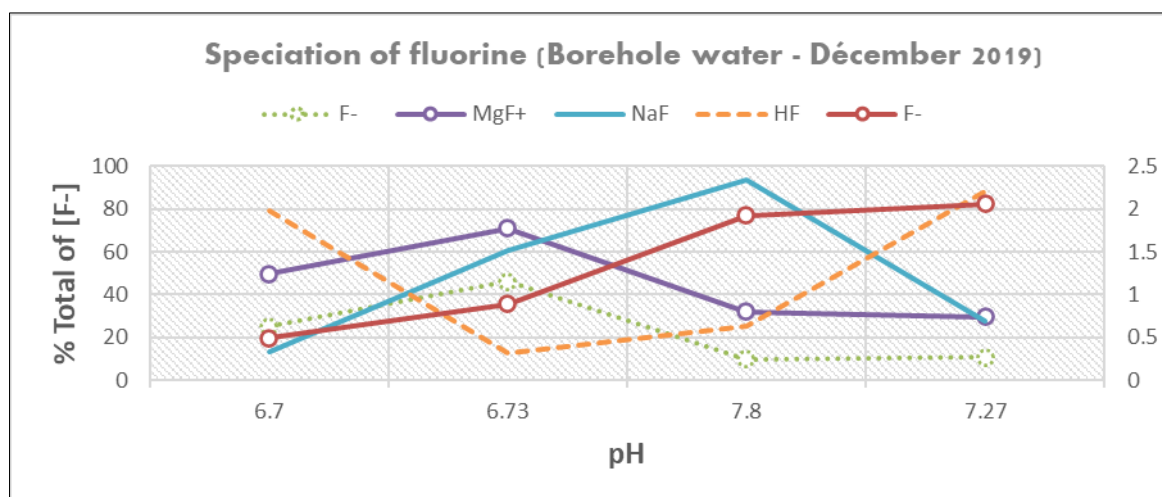
**Figure 3** Chemical speciation (in %total concentration) of fluorine in well water compared to all fluorinated species (May 2020)



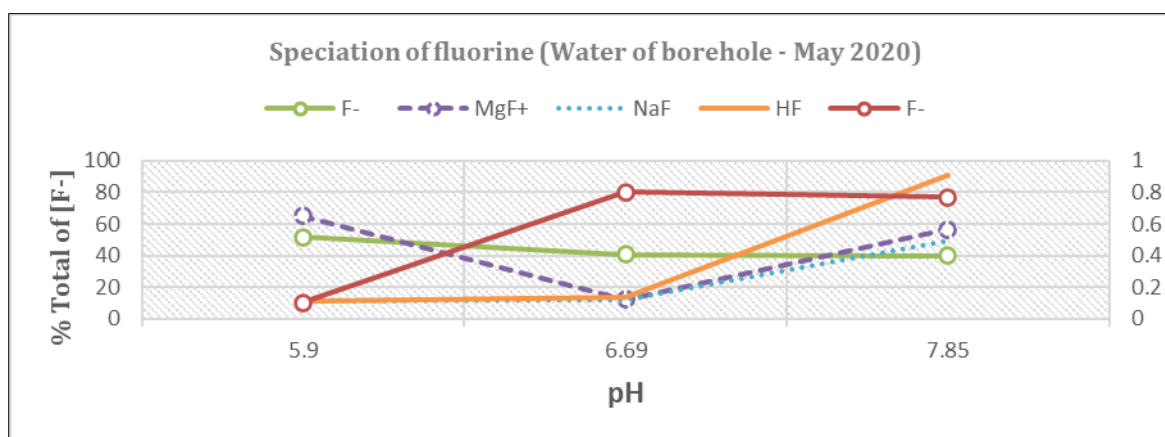
**Figure 4** Chemical speciation (in %total concentration) of fluorine in well water compared to all fluorinated species (November 2020)

Figure 4 shows a clear predominance of the dissolved free form  $F^-$  in well waters compared to other fluorinated species during the month of November 2020. It also shows an influence of pH in the formation of this compound. This figure also shows a predominance of the  $NaF$  complex form.

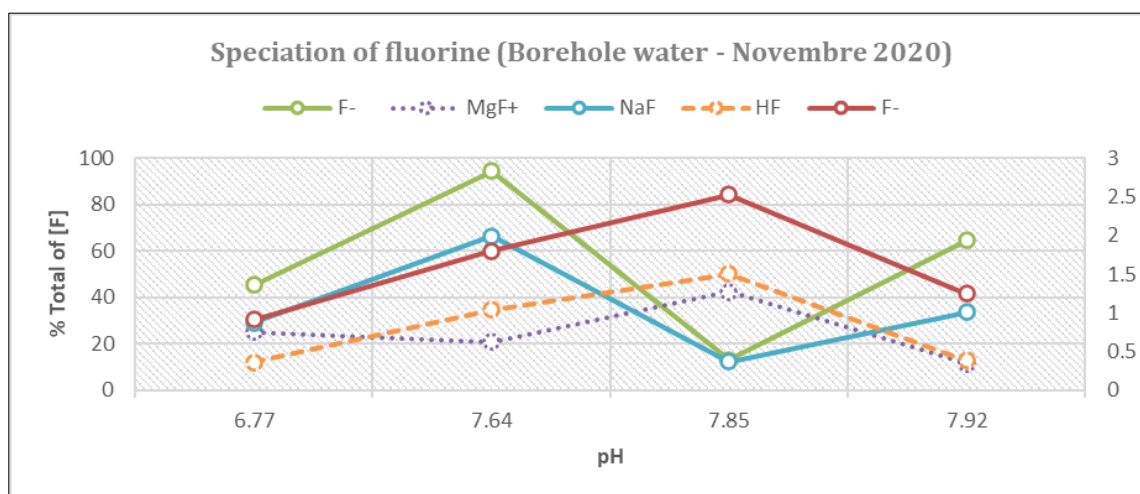
### 3.1.1. Case of borehole water



**Figure 5** Chemical speciation (in %total concentration) of fluorine in borehole water compared to all fluorinated species (December 2019)



**Figure 6** Chemical speciation (in %total concentration) of fluorine in well water compared to all fluorinated species (May 2020)



**Figure 7** Chemical speciation (in %total concentration) of fluorine in well water compared to all fluorinated species (rainy season – November 2020)

Figure 5 shows a predominance of the complex form  $\text{MgF}^+$  and  $\text{NaF}$  in borehole waters in December 2019. This figure also shows the influence of pH in the formation of these compounds.

Figure 6 shows a predominance of the  $\text{MgF}^+$  complex form and the  $\text{HF}$  form in the well waters during the month of May 2020. This figure also shows that the formation of these complexes is favored with the increase in pH. This shows that the fluorides present in borehole waters during the month of November are transported mainly in the free form.

## 4. Discussion

### 4.1. Discussion: Case of well water

The results obtained show that fluoride ions are mainly transported in well water in free  $\text{F}^-$  form during the months of December and November. Indeed, the content of fluoride ions in a medium could depend on the dissolved ionic form  $\text{F}^-$ . According to [11], the highest levels of fluoride ions in groundwater in the Maradi region are obtained during the month of November. According to [12], fluorides in free form ( $\text{F}^-$ ) could be adsorbed in significant quantities in clay minerals. Sandstones, sandy clays, limestones, evaporites, conglomerates, quartz-clayey and silts are the detrital sets that constitute the lithological sequences of the aquifers of sedimentary basins in the study area according to the DRH/M and cited by [11]. Thus, these soils are favorable for absorbing fluorine, then they could be released into the environment by hydrolysis. This could explain the high levels of fluoride ions obtained during the month of November; period during which the contact becomes more important between water and rocks. These figures also show a predominance of the complex form  $\text{HF}$  and  $\text{NaF}$  in these well waters. According to [13, 14], fluorine is found in abundance in the  $\text{HF}$  and  $\text{HF}_2^-$  forms at high temperatures. However, according to [11] and Meteorology-Niger 2009, the waters of the study area are marked by high temperatures. And according to the work of [15], hot and strongly alkaline springs are favorable to water fluoridation as indicated by these results obtained during the month of November 2020. However, the  $\text{HF}$  complex form is the predominant form during the month of May 2020. And according to [16], when the pH is below 5, the formation of  $\text{HF}$  in the medium reduces the activity of free  $\text{F}^-$ . According to [17], the quantity of fluorine capable of being transported in the  $\text{HF}$  and  $\text{NaF}$  form is around 1.7 mg/L. Therefore, the high levels of fluoride ions could depend on the presence of free fluoride ions in the medium. This could explain the low levels which vary between 0 and 1.32 mg/L obtained during the months of December and May in the well waters of the study area.

### 4.2. Discussion: Case of borehole water

The figures (5 and 6) obtained show a predominance of the  $\text{HF}$  and  $\text{MgF}^+$  complex form during the months of December and May at pH greater than 5. Indeed, according to [18], the formation of the  $\text{HF}$  complex could be favored at pH higher than 5. According to [17], the quantity of fluorine capable of being transported in the  $\text{HF}$  and  $\text{NaF}$  form is around 1.7 mg/L. According to [11], the highest levels of calcium ions and phosphate ions are obtained in November, a period during which the groundwater level is higher. However, according to [18], high levels of fluoride ions are favored in an environment rich in calcium ions and sulphate ions. Also, according to [19], when the  $\text{Ca}^{2+}$  activity is high, the environment then becomes favorable to the transport of fluoride ions. Indeed, calcium activity is related to pH and to the total activity of carbonate species. This relationship then shows that a low pH value leads to an increase in the limit value imposed on  $\text{Ca}^{2+}$  [16]. According to Vieillard, 1978, the dissociation of phosphate species (fluoro-phosphates, apatites, etc.) could become complete at very high pH (figure 7) in the medium and its compounds exert an influence on the  $\text{Ca}^{2+}$  ions; therefore, the activity of  $\text{F}^-$  becomes important. Similarly, according to [17], the  $\text{MgF}^+$  complex obtained during the months of May and December can exist in significant quantities in water, considering the balance below:



Also, according to [16], the activity of free fluoride ions in a medium becomes preponderant when the calcium ion contents are high and the pH becomes more alkaline.

## 5. Conclusion

The objective of this study is to assess the impact of seasonal variations on the different forms of fluoride in groundwater in the Maradi region. This study shows that fluorine could be transported in dissolved ionic form  $\text{F}^-$  and complex  $\text{HF}$  and  $\text{NaF}$  during the months of December, May and November in well water. However, the  $\text{F}^-$  forms;  $\text{HF}$ ,  $\text{NaF}$  and  $\text{MgF}^+$  are the dominant forms during the months of December, May and November in well water. The increase in fluoridation during the month of November could be due to the presence of the free dissolved ionic form and the complex form  $\text{HF}$ .

## Compliance with ethical standards

### Acknowledgments

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### Disclosure of conflict of interest

The authors declare that they have no competing interests.

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