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# **Determination of sources of fluoride contamination in groundwater in the Maradi region (central Niger) through a hydrochemical and geochemical approach**

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**ABSTRACT:** This work focuses on determining the sources of fluoride ion contamination in groundwater in the Maradi region. The waters of the study area capture different aquifer systems due to their locations. The methodology consisted in taking water samples spread over the seven (7) departments of the study area. The water samples taken relate to water from wells and boreholes and the physico-chemical parameters were determined for each sample. Also, the log-stratigraphic of certain works have been drawn. The hydrochemical data obtained show a strong mineralization of these waters; and fluoride ion concentrations exist at varying levels ranging from 0 to 2.84 mg/L. The results of correlation between the variables show that the minerals of biotite and hornblende constitute the main sources of fluoridation of the waters of the area on the one hand. And on the other hand, phosphate fertilizers, pesticides and soils also contribute to the contamination of water with fluoride ions in the study area.

**KEYWORDS :** fluoridation ; underground waters ; hydrochemistry ; geochemistry ; Maradi.

## **I. INTRODUCTION**

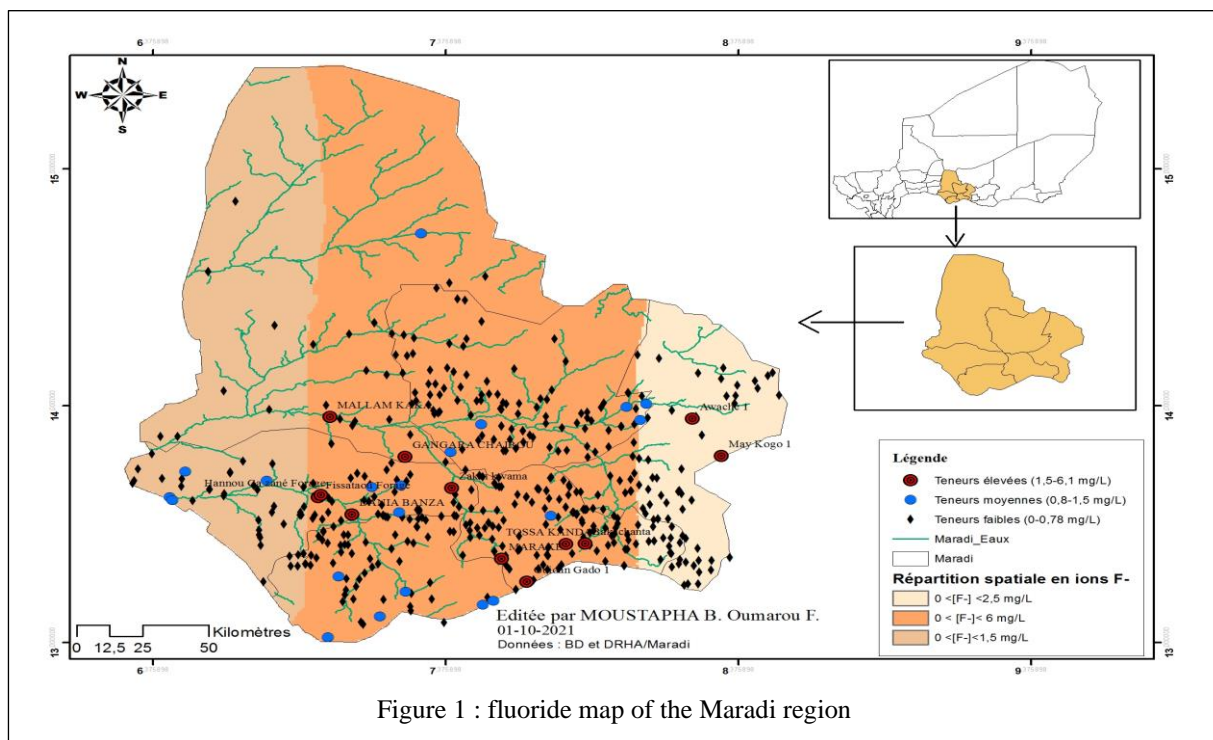
Water is an essential element for life [1, 2]. The water supply of several countries around the world depends on groundwater resources because of its good quality [2,3,4]. But some groundwater contains abnormal concentrations of fluoride ions (WHO, 1972). Fluoride is an element which, at low doses, is involved in the growth and maintenance of bone tissue and teeth [5, 6]. The Canadian government had carried out the fluoridation of drinking water with fluorinated substances [7, 8]. However, fluorine constitutes a considerable health risk if its level exceeds 1.5 mg/day [9]. Its excessive ingestion leads to inhibition of ameloblasts, change of absorption characteristics and surface properties of enamel crystals [10, 11, 12]. Studies have shown that the population is affected by fluorosis throughout the world [13, 14]. According to the report of [15, 16], 5000 children suffered from dental/ and or bone fluorosis in the department of Tibiri in Niger in the 1990s. Also, according to the results of physico-chemical analyzes obtained on the quality of the waters of the Maradi region, the [15], showed that there are other water structures whose concentrations exceed the relative standards. for human consumption. Therefore, it is imperative to identify the cause of this excess in fluoride ions. To our knowledge, no geochemical study has been conducted to describe the origin of fluoride ions in the waters of the study area and also in the entire region. According to others, this origin has several sources, namely: natural contamination due to hornblende in the departments of Guidan Roudji, Dakoro and Tibiri [17, 18]; or by depth effect [19]. This study aims to determine the origins of sources of fluoride ions contamination in groundwater in the Maradi region through a geochemical study coupled with hydrochemistry.

**II. MATERIAL AND METHODS****A Presentation of the study area**

The study area is the Maradi region. The Maradi region (Figure 1) is located in south-central Niger. It is located on the parallels 13°30' North and 7°06' East in the Sahelian zone. It is bounded: to the east by the region of Zinder, to the west by the region of Tahoua, to the north by the region of Agadez and to the south by the Federal Republic of Nigeria. It covers an area of 41,796 km<sup>2</sup>. It has a population which is estimated at more than 2 million [20]. Its annual rainfall varies between 700 mm in the south and 500 mm in the north. It has vegetation consisting of tree and shrub steppe [21]. The soils of the Maradi region are marked by a dune character. In the southern part, the basement only outcrops on a small strip of 75 Km<sup>2</sup> taken between the sedimentary formations of Jurassic-Lower Cretaceous age (Intercalary continental) with Nigeria [22].

**B Sampling**

To carry out this study, data on fluoride ions from water structures were first collected from the Regional Direction of Hydraulics of Maradi (DRH/A Maradi). With these data, a fluoride ion distribution map in the Maradi region was drawn (Figure 1). Thus, to better illustrate them, we have taken the average fluoride ion content of the various piezometers which are monitored by the DRH/A. And with regard to the other water structures, only recent fluoride data have been represented. These data were divided into three (3) categories: the red dots correspond to structures with high levels of F<sup>-</sup> ions ([F<sup>-</sup>] > 1.6 mg/L); the green dots are the works whose fluoride content varies between 0.8 – 1.5 mg/L; and finally the black spots are the works whose fluoride contents vary from 0 – 0.79 mg/L. These data have also made it possible to identify wells that have abnormal levels of fluoride ions. For this reason, these structures were also chosen as sampling points during our sampling campaign. Finally, a spatial distribution of fluoride ions was made according to the different locations in the study area (figure 1).



In November 2020, samples of water from wells and boreholes were taken in the different departments of the Maradi region. It should be noted that well water captures shallower aquifers than borehole water. Thus, to better distinguish them on the map, we have used triangles to represent the wells and stars to represent the boreholes (figure 2). The structures sampled and which relate to our study are located in the Center-East of the study area (Figure 2). The structures sampled mainly concern structures with high fluoride ion contents (DRH/A Maradi). A total of 27 water samples were taken from the thirty-three samples identified (figure 1); that is a probability of 81,81% of the representative set of structures having an abnormal fluoride ion content. Among the structures sampled, some do not appear in Figure 2 because of their proximity. It should be noted, however, that in the northern part the population is not dense. And as a result, works are rare in this part. Also, according to data collected at the level of (DRH/A Maradi), no structures with abnormal fluoride ion contents were observed in this area.

The water samples were taken in polyethylene (plastic) bottles. The bottles were first washed with water and then rinsed with water and then rinsed with distilled water before being filled with the water to be analyzed. The samples taken were transported to the laboratory in appropriate thermoses.

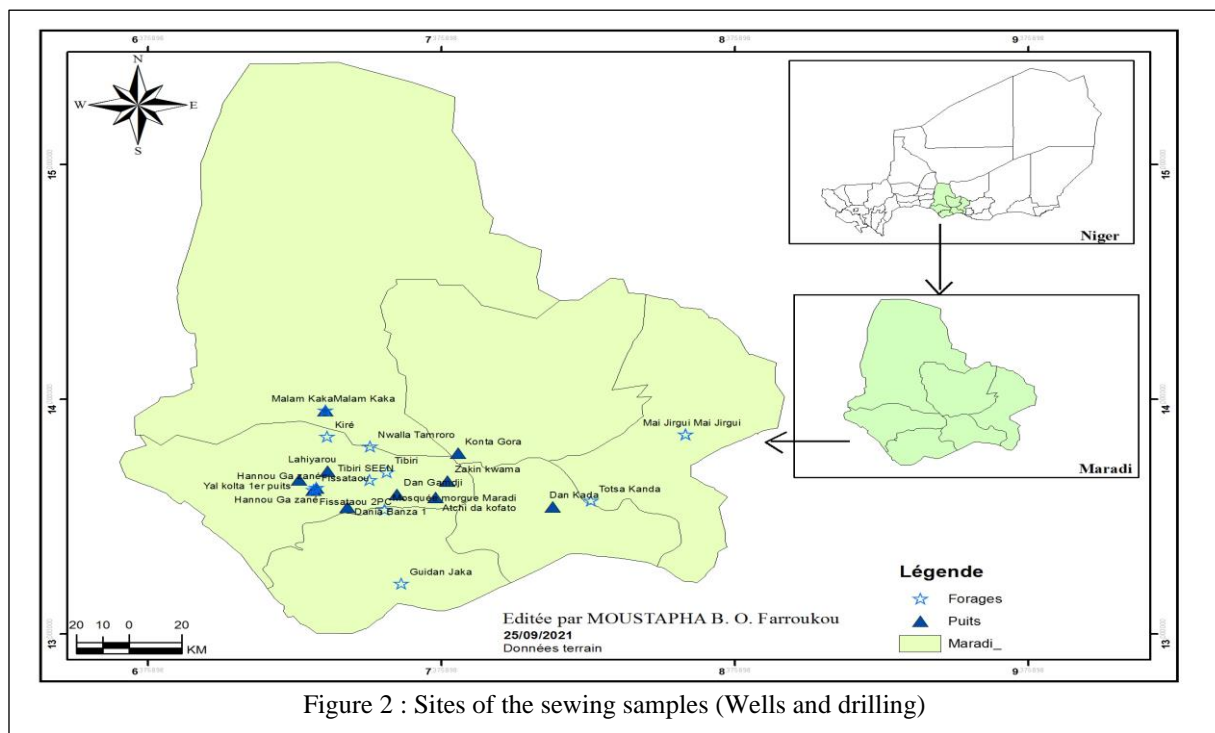


Figure 2 : Sites of the sewing samples (Wells and drilling)

### III. ANALYSE

Electrical conductivity (E.C.) was measured because it provides information on the degree of mineralization of water [23]. The pH, which is an indicator of the acidity or basicity of a medium, has also been measured [24]. Similarly, the temperature ( $T^{\circ}$ ) which is a factor capable of modifying the balance of an environment was measured. These three physical parameters (pH;  $T^{\circ}$ ; C.E) were measured in situ using a HANNA brand multivariate pH meter. Fluoride ion contents; sulfate ions; phosphate ions and iron ions were measured using a

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DR3900 type spectrophotometer (HACH). Sodium and potassium were assayed by flame photometry with a type photometer (JENWAY). Total hardness was determined by complexometry, with ethylenediaminetetraacetic acid (EDTA). The magnesium content was deduced from the following equation:  $[Mg^{2+}] = (TH - DC) \times 0,24$   
 TH : Hydrotimetric title. DC : Calcium hardness

### A. Simulation tool

The geochemical study was carried out by simulation using the chemical thermodynamic software, Phreeqci.v.2.12 [25]. The IS saturation index calculation of minerals dissolved in water was carried out using the law of [26] considering that the state of equilibrium is in the interval -0,5 to +0,5.

The log-stratigraphic of different groundwater structures were plotted using the GESFOR software.

## IV. RESULTS AND DISCUSSION

Tables 1 and 2 summarize the results of the physico-chemical parameters of well and borehole water respectively.

Table 1: Results of physico-chemical parameters of well water in the Maradi region

Villages	Ouvrages	pH	T°	CE	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	F <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Fe
Dania Banza 1	PC	6,45	27,5	940	37,6	10,08	70	20	1,47	3,438	280,6	43	33	0,29
Dania Banza 2	PC	6,89	28,1	800	29,6	8,64	59,08	7,02	1,56	1,535	207,4	45	23	0,23
Lahiyarou	PC	7,52	29,5	140	8	1,44	9,8	16	0,25	1,719	41,48	0	15	0,24
Fissataou 1	PC	7,62	29,8	530	32	13,44	21	10	0,74	19,218	123,22	22	16	0,15
Fissataou 2PC	PC	7,55	28,6	280	17,6	5,28	31,6	15	0,86	2,332	95,16	8	20	0,18
Hannou Ga zané	PC	7,54	30,9	930	38,4	12	54,54	15,84	0,97	3,561	207,4	45	27	0,38
Malam Kaka	PC	7,91	31	990	48	10,56	54,5	20,6	1,82	5,464	441,64	0	31	0,38
Atchi da kofato	PC	7,56	27,5	1690	208,8	11,52	11	24	1,05	8,81	695,4	0	15	0,53
Konta Gora	PC	6,97	30,6	530	64	3,36	13	20,6	0,59	11,352	48,8	0	10	1,12
Zakin kwama	PC	6,8	29,7	110	11,2	4,32	2,4	6,55	2,84	0,8596	42,7	0	15	0,22
Dan Kada	PC	6,06	30,9	90	16	1,44	15	13	1,25	9,762	43,92	0	23	0,35
Dan Gamdji	PC	6,5	29	190	11,2	1,44	6	9,8	0,01	1,811	208,62	0	7	0,12
Milli mada	PC	6,49	29	280	27,2	6,24	15,3	13,68	0,15	0	97,6	0	0,15	0
Yal kolta ler puits	PC	6,87	34,3	1540	10,4	5,28	9,6	12	0	0,89	73,21	1	7	0,08
Tibiri abattoir	PC	6,11	30,6	190	9,6	3,84	3	12	0	0,736	41,48	0	28	0,06

### PC : Cemented Wells

Table 1: Results of physico-chemical parameters of drilling water in the Maradi region

Villages	Ouvrages	pH	T°	CE	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	F <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Fe
Fissataou	F	7,24	30,9	690	4	3,84	38	15	2,05	16,086	136,64	40	22	0,37
Hannou Ga zané	F	7,64	32,1	390	6,4	0,96	31,81	6,39	1,8	1,473	86,62	21	18	0,17
Kiré	F	7,92	33,8	270	10,4	7,68	23,63	6,7	1,25	5,833	108,58	18	13	0,74
Nwalla Tamroro	F	8,23	32,7	390	28	10,56	17,76	9,67	0,89	2,732	35,38	0	12	0,37
Malam Kaka	F	7,85	32,9	480	8,8	1,44	42,72	2,9	2,53	10,99	168,36	25	20	0,35
Mai Jirgui	F	6,84	33,6	260	10,4	34,56	16,3	20,5	0,61	1,675	107,36	0	13	0
Guidan Jaka	F	6,77	32,9	670	61,6	27,8	31,81	6,7	0,91	11,359	362,34	1	0,15	0,15
Tibiri	F	9,01	28	150	10,4	5,76	15	12	0,42	4,08	31,72	0	8	0,02
Totsa Kanda	F	6,24	30	70	12	1,92	1,66	6,39	0,53	1,688	36,6	0	9	0,19
D.R.H Maradi	F	5,96	30,08	590	14,4	33,6	19,99	16,01	0,44	9,148	9,76	0	26	0,07
Garin kaka	F	8,36	30,4	130	11,2	4,8	8,5	14,5	0,39	0,982	25,62	0	9	0,04
Mai Jirgui	F	6,91	34,5	230	31,2	9,12	10,8	18,9	0,32	1,289	104,92	0	12	0
Tibiri SEEN	F	7,37	29	120	15,2	2,4	8,33	5,14	0,15	1,135	20,74	0	13	0,28
Mosquée morgue Maradi	F	7,96	29	230	22,4	1,44	12,21	13,18	0	1,596	19,52	0	16	0

**F : Drilling**

**A Hydrochemical characteristics and acquisition of fluoride ions in sampled waters**

**A.1 At the level of the wells**

The data in Table 1 show that the conductivity values of the water sampled vary from 90 to 1690  $\mu\text{S}/\text{cm}$ ; According to this result, 71.42% of the samples have a conductivity  $\geq 300 \mu\text{S}/\text{cm}$  (WHO standard). According to [4], these waters are highly mineralized and contain dissolved substances with a high ionization capacity. Also, these values indicate that these waters are favorable to water fluoridation in the study area. According to Saxena, 2001 [27], a specific conductivity ranging from 750-1750  $\mu\text{S}/\text{cm}$  could promote the dissolution of fluorinated minerals and enrich the waters with fluoride ions. The pH of the water sampled varies between 6.09 and 7.91 pH unit. The pH of the water sampled is slightly acidic in 42% of the samples. However, according to [28], acidic waters favor the transport of fluoride ions. Also according to [29], all samples whose pH exceeds 7 have properties capable of facilitating ion exchanges between hydroxyl and fluorine groups. Indeed, the  $\text{F}^-$  ions are released in the medium after their substitution by the  $\text{OH}^-$  ions. Well water temperatures vary between 27°C and 34°C. According to [30], temperature plays a very important role in increasing the chemical activity of water. These high, more or less



variable  $T^\circ$  could act on the physico-chemical properties and enrich the waters with fluoride ions. According to [27, 30], high  $T^\circ$  facilitate the release of fluoride ions.

Regarding the bicarbonate contents, they vary from 41.48 to 695.40 mg/L. These high, more or less variable levels could enrich the well water in the study area with fluoride ions. According to [27], a medium with a high concentration of bicarbonate ions (ranging from 350 – 450 mg/L) is favorable for the dissolution of fluorinated minerals. Its presence can mainly result from the dissolution of carbonate minerals in the soil, as well as from the  $CO_2$  content of the air and soil [31]. The results show that the  $Ca^{2+}$  ion contents vary from 8 to 208 mg/L. And with regard to the  $Mg^{2+}$  ions, their concentrations vary from 1.44 to 13.44 mg/L. The presence of these elements at low levels indicates that these waters are soft. Indeed, these low levels of calcium and magnesium ions could increase their affinities with fluoride ions and cause the water to be enriched with this trace element. According to [25, 29], the fluoride ion content increases with decreasing calcium ion content. According to [32], this decrease could result from the precipitation of calcite following a rise in temperature. The contents of  $Na^+$  ions vary from 2.40–70 mg/L and those of  $K^+$  ions vary from 6.55–24 mg/L. According to [24, 33], sodium ions come from salt leaching or percolation through salty soils. And according to [34], the presence of  $Na^+$ ,  $K^+$  ions could come from the leaching of fertilizers used in agriculture. The concentrations of phosphate ions ( $PO_4^{3-}$ ) vary from 0 to 19,21 mg/L. These high levels of phosphate ions indicate that these waters could contain considerable quantities of phosphate minerals. These are among others, the minerals of apatites, hydroxyapatites. In addition, it should be noted that the use of phosphate fertilizers could contribute considerably to the supply of fluoride ions in the waters of the study area (Figure 3). According to [35], phosphate fertilizers are a potential source of fluoride ion contamination. The sulfate ion contents vary from 0 to 45 mg/L. These more or less variable values indicate fluoride ion pollution in the waters of the study area. According to [36], the presence of sulfate ions at considerable levels could constitute an indicator of fluoride ion pollution.

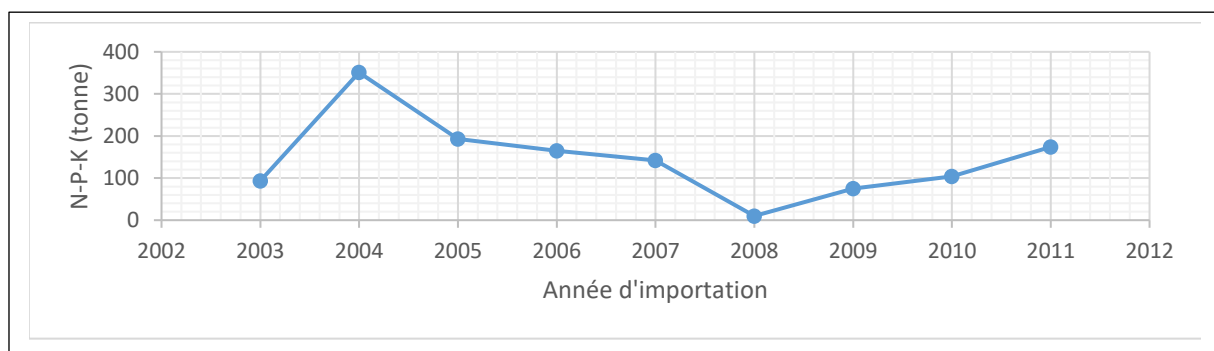
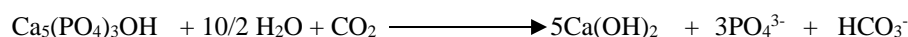


Figure 3 : Importation the phosphate fertilizers

## A.2 At the Boreholes

The results obtained show that the values of C.E vary from 70 to 690  $\mu S/cm$ . According to this result, 40% of the samples have a conductivity greater than or equal to 300  $\mu S/cm$  (WHO standard). According to [4], these waters with high conductivities are highly mineralized and contain dissolved substances with a high ionization capacity. It should be noted, however, that these values are favorable to water fluoridation in the study area. Because, according to [27], high conductivities favor the dissolution of fluorinated minerals and enrich the waters with fluoride ions. The pH of the water sampled varies between 5.96 and 9.01 pH unit. These pH values indicate that these waters are slightly acidic and tend towards alkalinity. The pH of water provides information on its acidity

and alkalinity; the nature of the land crossed by the water can be a natural cause of significant variations in pH [23]. However, according to [28], acidic waters favor the transport of fluoride ions. Also, the results obtained show that 60% of samples have a pH value greater than 7; these values are favorable to water fluoridation in the study area. According to [30], all samples whose pH exceeds 7 have properties capable of facilitating ion exchanges between hydroxyl groups and fluorine in order to enrich the waters with fluoride ions. It should be noted that phosphate minerals are among the fluorinated compounds that have this property capable of exchanging their fluorine with the hydroxyl group [31]. Groundwater temperatures in the study area vary between 27.5°C and 34.5°C. It should be noted, however, that temperature plays a role in the increase in the chemical activity of water. According to [30], water anomalies are controlled by geological structures that condition the geometry of aquifers and the type of underground water circulation. These high T° more or less variable, could act on the physico-chemical properties. Because high temperatures facilitate the release of fluoride ions, and thus enrich the waters with fluoride ions [27, 32]. The concentration of bicarbonate ions in the water sampled varies from 9.76 mg/L to 695.4 mg/L. 27.27% of the samples have bicarbonate contents which are beyond the WHO guideline value (200 mg/L). It should be noted, however, that these high values of bicarbonate ions are favorable to water fluoridation in the study area. According to [27], a medium with a high concentration of bicarbonate ions (ranging from 350 – 450 mg/L) is favorable for the dissolution of fluorinated minerals. According to [31], the presence of bicarbonate ions in water depends mainly on the dissolution of carbonate minerals in the soil, as well as the CO<sub>2</sub> content of the air and soil. And when the Ca<sup>2+</sup> ions are present with concentrations that vary between 4 mg/L and 61.60 mg/L. As regards the concentration of Mg<sup>2+</sup> ions, it varies between 0.96 mg/L and 34.56 mg/L. Indeed, this low mineralization in Ca<sup>2+</sup> and Mg<sup>2+</sup> ions indicates that these waters are soft. Also, these very low values of calcium and magnesium ions reflect an increase in the activity of fluoride ions in the borehole waters. And therefore, this environment will be favorable to the presence of fluoride ions. The presence of calcium and magnesium ions generally depends on the nature of the rocks crossed (limestone or gypsums rocks) [24]. The sodium ion is generally the dominant element ahead of potassium. The Na<sup>+</sup> ion contents vary from 1.66 mg/L to 42.72 mg/L and those of K<sup>+</sup> ions vary from 2.9 to 20 mg/L. The sodium ion contents come from the leaching of salts, or from percolation through saline soils or from the infiltration of brackish waters [24, 33]. In groundwater without contact with evaporates, the sodium content is between 1 and 20 mg/L [31]. The presence of these elements (Na<sup>+</sup>, K<sup>+</sup>) is essential to life and in particular to the growth of plants, because they are used as fertilizers in agriculture [34]. Still according to [33], the fertilizers used rich in potassium are, for example, potassium sulfate, potassium chloride, or even potassium nitrate. However, according to [34], fertilizers are a potential source of fluoride ion contamination. Phosphorus characterizes the concentration of PO<sub>4</sub><sup>3-</sup>, HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>2-</sup> ions. But in the soil, the phosphorus element is found mainly (98%) in the form of orthophosphate ions (PO<sub>4</sub><sup>3-</sup>). Its content in the medium depends on the pH of the solution and the temperature. The phosphate ion contents of the sampled waters are high and vary from 0.98 mg/L to 16.08 mg/L. According to [23], a content above 0.5 mg/L in water of phosphate ions must constitute pollution. The presence of phosphate ions is most often linked to anthropogenic contamination; through the phosphate fertilizers used or natural (fluoro-apatite, apatite, etc.). Consider the following apatite dissolution equation:

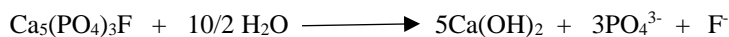


Could explain the origin of part of the phosphate ions in the waters of the study area. Indeed, when apatite minerals interact with groundwater and carbon dioxide, phosphate ions are released in sufficient quantities into the environment. In addition, it should be noted that the use of phosphate fertilizers in the study area (Figure 3) contributes considerably to the contribution of phosphate ions in these waters. Consequently, the leaching and then the infiltration of these substances could enrich the groundwater in fluoride ions. Also, the high concentrations of phosphate ions found testify to the considerable external contribution. Similarly, the presence of phosphate ions

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in these waters could result from the natural dissolution of fluoro-apatite by releasing a significant proportion of fluoride ions into the waters of the study area according to the equation:



## B Study of correlation and acquisition of fluoride ions

### B.1 At borehole level

The correlation results between the different ions contained in the borehole water are grouped together in Table 3.

Table 3: Correlation matrix between ions for borehole

Variables	CE	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	F <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Fe
<b>CE</b>	1	0,287	0,399	<b>0,815</b>	-0,011	<b>0,580</b>	<b>0,857</b>	<b>0,607</b>	<b>0,523</b>	0,346	0,200
<b>Ca<sup>2+</sup></b>		1	0,378	-0,001	-0,056	-0,273	0,095	<b>0,625</b>	-0,430	-0,613	-0,178
<b>Mg<sup>2+</sup></b>			1	0,047	<b>0,466</b>	-0,217	0,196	0,307	-0,350	-0,036	-0,274
<b>Na<sup>+</sup></b>				1	-0,284	<b>0,888</b>	<b>0,780</b>	<b>0,621</b>	<b>0,788</b>	0,351	<b>0,397</b>
<b>K<sup>+</sup></b>					1	-0,405	-0,115	-0,227	-0,237	0,163	-0,562
<b>F<sup>-</sup></b>						1	<b>0,629</b>	<b>0,441</b>	<b>0,887</b>	0,375	<b>0,539</b>
<b>PO<sub>4</sub><sup>3-</sup></b>							1	<b>0,574</b>	<b>0,649</b>	0,303	0,351
<b>HCO<sub>3</sub><sup>-</sup></b>								1	0,279	-0,380	0,160
<b>SO<sub>4</sub><sup>2-</sup></b>									1	<b>0,507</b>	<b>0,560</b>
<b>Cl<sup>-</sup></b>										1	0,136
<b>Fe</b>											1

The correlation results (Table 3) show that the C.E is very well correlated with the fluoride ions (r = 0.58). This value shows a relationship between these two variables. According to [34], a good correlation between C.E and F<sup>-</sup> indicates their common origin, which is related to the nature of the geological layer and could be the basis of the fluoridation of groundwater in the study area. Also, the correlation coefficient between fluoride ions and sodium ions with r = 0.88, shows that the dissolution of substratum containing compounds that contain both fluoride and sodium ions could be responsible for the fluoridation of groundwater in the study area. According to Revindra and Garg, 2007, the presence of fluoride in waters, would come in some cases, mainly from the dissolution of natural minerals containing both fluoride and sodium ions; such as, cryolite minerals (Na<sub>3</sub>AlF<sub>6</sub>) found in rocks and soils with which water reacts. Similarly, the correlation coefficient between fluoride ions and sulfate ions which is equal to r=0.88; then between fluorides and carbonates (r = 0.44), indicate fluoridation of groundwater in the study area by the dissolution of rocks containing both fluoride and carbonate ions on the one hand; then between fluoride and sulfate on the other hand [18]. Considering the correlation coefficients between magnesium-potassium ions (r = 0.46), then between sodium-iron ions (r = 0.39), and between fluoride-iron ions (r = 0.53) indicate a common origin between these on the one hand. According to the work of [35], cited by GOUROUZA M et al., 2019, the dissolution of hornblende could explain these relationships according to the equation:

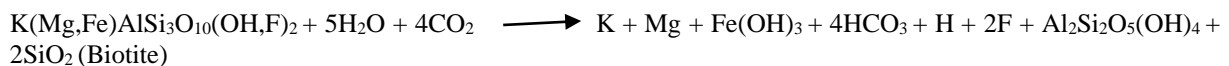




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On the other hand, the correlation between calcium and magnesium ions ( $r = 0.37$ ); between calcium and carbonate ions ( $r = 0.62$ ); between fluoride and chloride ions ( $r = 0.37$ ), between sodium and carbonate ions ( $r = 0.62$ ) also show a common origin between these ions. Considering the dissolution of the following biotite:



Could explain the common relationship of these ions. Indeed, according to [35], the dissolution of hornblende and biotite naturally enriches groundwater in fluoride ions.

### B.2 At the level of the Wells

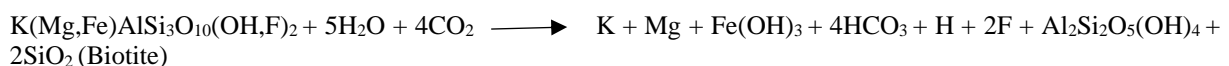
The correlation results between the different ions contained in the Well waters are grouped in Table 4.

Table 4: Correlation matrix between the ions for the waters of the wells

Variables	CE	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	F <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Fe
CE	1	<b>0,640</b>	<b>0,625</b>	0,336	<b>0,483</b>	0,037	0,103	<b>0,699</b>	0,248	0,101	0,198
Ca <sup>2+</sup>		1	<b>0,468</b>	0,008	<b>0,661</b>	0,116	0,346	<b>0,835</b>	-0,055	-0,014	0,472
Mg <sup>2+</sup>			1	<b>0,604</b>	0,279	0,295	0,380	<b>0,606</b>	<b>0,592</b>	0,368	0,026
Na <sup>+</sup>				1	0,235	<b>0,387</b>	-0,034	0,333	<b>0,810</b>	<b>0,667</b>	0,068
K <sup>+</sup>					1	-0,060	0,228	<b>0,597</b>	-0,092	0,216	<b>0,591</b>
F <sup>-</sup>						1	0,058	0,234	0,253	<b>0,452</b>	0,177
PO <sub>4</sub> <sup>3-</sup>							1	0,153	0,028	0,041	0,454
HCO <sub>3</sub> <sup>-</sup>								1	0,114	0,238	0,200
SO <sub>4</sub> <sup>2-</sup>									1	0,505	-0,038
Cl <sup>-</sup>										1	0,058
Fe											1

Analysis of Table 4 shows that:

The correlation coefficient between fluoride ions and chloride ions is  $r = 0.45$ . The correlation between these ions indicates that, these ions have a common origin. Consequently, the dissolution of the compound which contains both fluoride and chloride ions in contact with the water could contribute to the fluoridation of the water in the aquifers of the study area. Also, the correlation coefficient between sodium ions and fluoride ions with  $r = 0.38$ , shows that the dissolution of compounds containing both fluoride and sodium ions (cryolite for example of formula: Na<sub>3</sub>AlF<sub>6</sub>), could enrich the waters in the study area in fluoride ions. Considering the following correlation coefficients: calcium-potassium ( $r=0.66$ ); calcium-carbonate ( $r = 0.83$ ); calcium-iron ( $r = 0.47$ ); magnesium-sodium ( $r = 0.60$ ); potassium-iron,  $r=0.59$ ; fluoride-sodium,  $r = 0.38$  indicate a strong relationship between these ions. Consider the dissolution of biotite.



Could explain the relationship between these different ions. Indeed, according to [35], the dissolution of biotite naturally enriches groundwater in fluoride, bicarbonate, potassium and magnesium ions.

**V. Index of saturation and fluoridation of groundwater in the Maradi region**

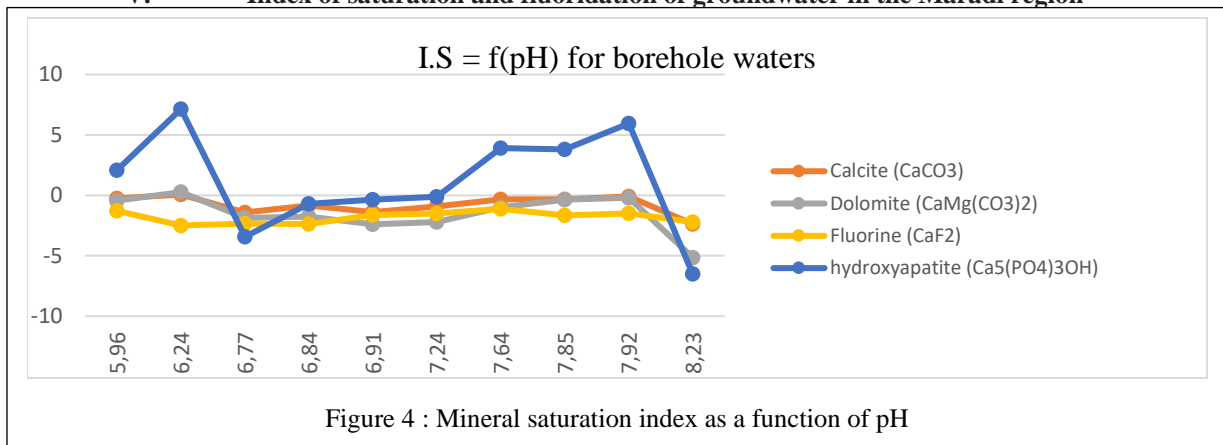


Figure 4 shows that fluorite is highly under saturated ( $-3 < IS < -1$ ) in all the borehole water samples taken. Indeed, in these water samples, where the I.S are negative vis-à-vis fluorite, this shows that this mineral does not contribute to the fluoridation of the waters of the study area. According to [24, 37], if the water is under saturated in fluorite, the fluorine content comes from the leaching of the quantity available within the other rocks except the fluorite.

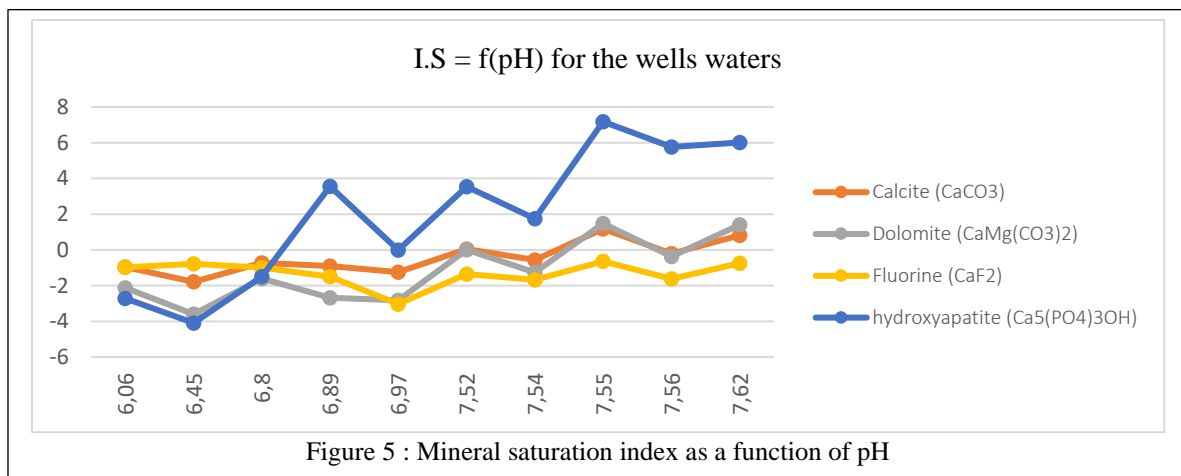


Figure 5 shows that fluorite is highly under saturated ( $IS < 0$ ) in all well water samples taken. Indeed, in these samples, fluorite does not contribute to the fluoridation of these waters. According to [24, 38], if the water is under saturated in fluorine, the fluorine content generally reflects the quantity available within the leached rock.



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It can be seen that, from  $\text{pH} = 7.54$ , the minerals: calcite, dolomite and hydroxyapatite are supersaturated. This state of oversaturation shows that these minerals strongly contribute to the mineralization of the waters of the study area. Also, this figure shows that the precipitation of carbonates and the dissolution of evaporates as well as fluorite increase with alkalinity (pH).

Similarly, Figures 3 and 4 show that the mineral hydroxyapatite is highly supersaturated ( $I.S > 0$ ) in almost all borehole and well water samples. This state of acute oversaturation with phosphate minerals could have a plausible relationship with the phosphate minerals/and or phosphate fertilizers used.

### VI. Geochemical approach and acquisition of fluoride ions in sampled waters

#### A Presence of fluorine in the sedimentary basins and basement formations of the study area

The log-stratigraphic of three boreholes belonging respectively to Quaternary, Continental Hamadien and Continental Intercalary formations have been plotted (figure 6). The fluoride ion concentrations in these structures are respectively: 2.84 mg/L; 2.05mg/L and 1.84mg/L. From the geological point of view, the sedimentary basins and the bases constitute the two main formations of the study area. This figure shows that (figure 6): Sandstones, sandy clays, limestone's, evaporates, conglomerates, quartz-clayey and silts are the detrital sets which constitute the lithological sequences of the aquifers of the sedimentary basins of the zone of 'study. According to [28], sedimentary rocks can contain 40 to 100 ppm of  $[\text{F}^-]$ ; sandstones (80-450 ppm); greywackes (40-80 ppm); loess (360 ppm); limestone (270 ppm); gypsums and anhydrites (800 to 900 ppm). Also, according to the works cited by [32, 39], sedimentary basins are among the lands whose waters could contain fluorine from a geological point of view. However, according to [40], the basement formations of the study area consist of a sequence of schists, quartz-schists, gneiss, and biotite porphyry granite (Figure 6). According to [27], sandstones contain up to 180 ppm of fluorides, limestone 220 ppm of fluorides and clays 800 ppm of fluorides in the bedrock formations.

Indeed, the dissolution of these rocks in the presence of water is favorable to the fluoridation of groundwater in the sedimentary and basement formations of the study area.

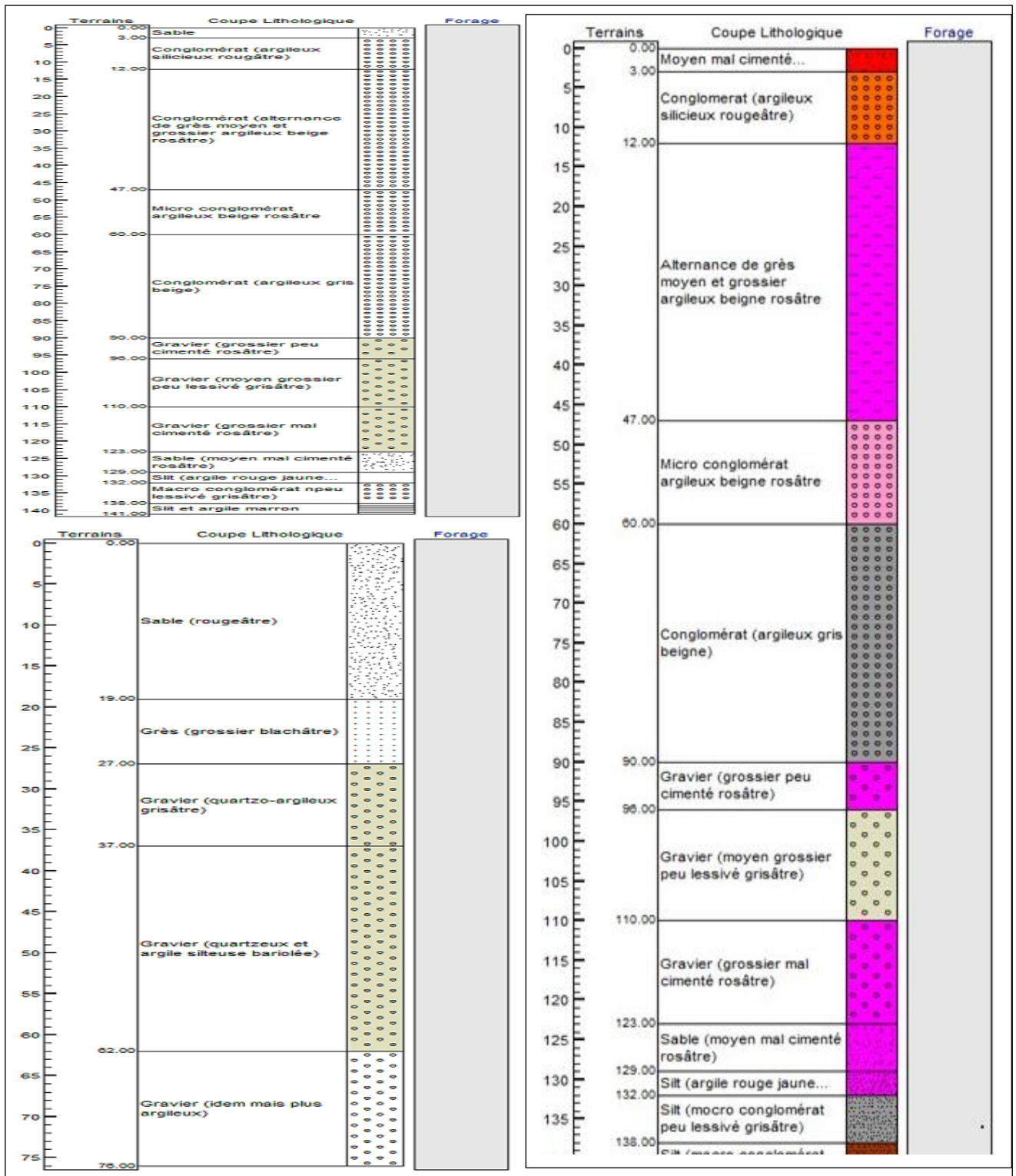


Figure 6 : logs stratigraphiques of some boreholes (F1 ; F2 ; F3) of the Maradi region [DRH/A]

## VII. CONCLUSION

The objective of this study is to determine the sources of fluoride ion contamination in the waters of the Maradi region. The results obtained show that the groundwater in the study area is highly mineralized. The fluoride ion contents vary from 0.24 to 2.84 mg/L. This study also shows that the fluoride ion contamination of the waters of the study area is partly of natural origin through the dissolution of fluorinated minerals. These minerals responsible for this contamination are biotite and hornblende. On the other hand, the external contribution is not also to be neglected coming from phosphate fertilizers and pesticides.

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