Chapter

Fluoride Levels in the Groundwater and Prevalence of Dental Fluorosis in the Municipality of Santana, in Region Karstic of West Bahia, Brazil

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Abstract

This chapter was aimed to investigate the relationship between the consumption of water of Bambuí Aquifer with natural fluoride levels and the prevalence of dental fluorosis in the municipality of Santana, Bahia, Brazil. Hydrochemistry and cluster analysis indicated that there were two groups differentiable in relation to TDS, pH, F-, rNa^{+}/rCa^{2+}, and saturation indexes of minerals. The fluoride concentration varied from 0.05 to 9.16 $mg.L^{-1}$ in the samples and the prevalence of dental fluorosis was 53%, 17% moderate, or severe, which was associated of the consumption of groundwater. The toxic levels of fluoride reached 47% of the samples, where the risk of skeletal fluorosis (20%) and incapacitating fluorosis (20%) was estimated. The water supply service should include the monitoring of fluoride in groundwater, the implementation of sanitary and environmental health surveillance of endemic fluorosis, and the continuing training of professionals for health in this municipality.

Keywords: medical geology, fluoride-health, drinking water, bambuí aquifer

1. Introduction

The care with water quality should be universal because human dignity and health public depends on the access to drinking water. The quality of natural waters can naturally be modified by the enrichment of dissolved ions, such as fluoride, which may reach adverse amounts to human health [1]. The fluoride-health relationship has a worldwide relevance because the main route of exposure is the ingestion of water with toxic levels of fluorine [2].

Dental fluorosis is the first sign of chronic fluoride poisoning; it is related to discoloration and the appearance of blemishes on the enamel of homologous teeth [3]. It is a chronic intoxication from exposure to toxic doses of fluoride, a hypomineralization of the enamel, which has esthetic and morphofunctional repercussions [4].

The severity of dental fluorosis is dependent on both the dose and time of exposure to fluoride levels [5]. It refers to the chronic intake of toxic doses of fluoride during enamel formation, whose critical period extends until 6 years of age, although it depends on individual differences in amelogenesis [6].

The continuous consumption of water with optimal fluoride content represents a protection factor against caries or dental fluorosis, whereas the excess represents a risk factor for fluorosis and the deficiency is a risk factor for dental caries [5]. The changes in the constitution of the enamel, which cause staining or loss of its structure, can provide esthetic, functional, and psychological problems [7]. Due to the epidemiological relevance of fluorosis, consumption with toxic levels of fluoride, the World Health Organization [8] recommended a maximum limit of 1.5 $mg.L^{-1}$ of fluoride in drinking water. Other factors may aggravate the distribution and severity of fluorosis, such as metabolic disorders [9], nutritional status that accompanies the socioeconomic context [10], and temperature [11].

Fluorine, very electronegative, reacts easily with cations, for example, calcium ion. This behavior explains why most of the fluorine in the matrix of bones and teeth is associated with fluorapatite crystals, $Ca_5 (PO_4)_3 F$, combined as a solid solution with hydroxyapatite, $Ca_5 (PO_4)_3 OH$ [12]. The dental enamel is composed of a prismatic mineral, which in the absence of fluoride (F^-) is known as hydroxyapatite [$Ca_{10} (PO_4)_6 (OH)_2$]. Fluoride in the diet during odontogenesis favors the conversion of part of the hydroxyapatite into fluorapatite [$Ca_{10} (PO_4)_6 F_2$] by replacing the OH^- group. Fluorapatite, less soluble in oral acids than hydroxyapatite, gives teeth a protection against the erosional action of caries.

Chronic ingestion of natural waters containing fluoride levels greater than 3.0 $mg.L^{-1}$ correlates with the prevalence of dental fluorosis or skeletal fluorosis and represents a risk of deformities in the hips and incapacitating fluorosis [13, 14]. In this way, the importance of the epidemiological and environmental health surveillance of the contents of fluoride in the waters of human consumption as a preventive measure of endemic fluorosis is evidenced.

Fluoride occurs in natural waters mainly in the form of fluoride (F^-), who's levels vary from residual amounts up to 2800 $mg.L^{-1}$ [15]. In the rocks, fluorine is release mainly from the fluorite mineral phase, occurring also in amphiboles, micas, fluorapatite, topaz, cryolite, certain clays, and villiaumite [16]. The chemical weathering of rocks bearing fluorine minerals releases this halogen to the atmosphere, biota, soils, dust, and water [17]. The weathering of the fluorine-containing minerals promotes the leaching of this halogen, which has high mobility, through the water-rock interaction [18]. Fluoride levels are high in groundwater where the source minerals abound in the geological substrate [19].

In this context, the application of hydrochemical methods and techniques can help the management of water quality. The knowledge about the origin and behavior of major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}) in groundwater allows the elucidation of the hydrogeochemical composition [20]. This varies depending on the solubility of the chemical elements from the dissolution of the mineral constituent of the rocks that host the aquifer.

Fluorite deposits and sulfide levels have a widespread occurrence in the carbonate rocks of the Bambuí Group, in the western Bahia, Brazil [21]. These carbonate rocks shelter the Bambuí Aquifer, whose waters complement the public supply of several municipalities, including Santana (**Figure 1**). In turn, information on hydrochemistry could guide water and health planners.

The chemical composition of the waters of the Bambuí Aquifer varies as a function of the mineral composition of the rocks of the Bambuí Group [23]. The hydrochemical of karstic environments varies according to the climate, water circulation, residence time, and mineralogy of the rocks of the aquifer [24]. In this perspective,

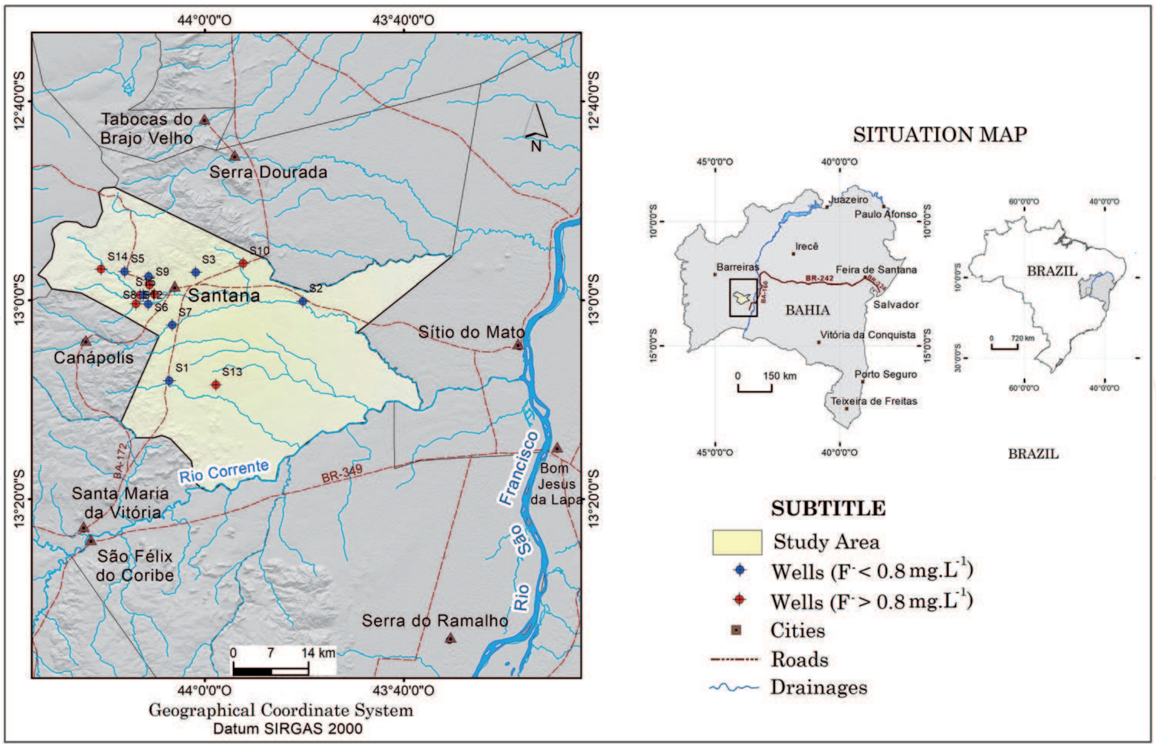

Figure 1.
Map of location of the municipality of Santana, based on the data of IBGE/SEI (2008) [22].

it is expected that the integration of geochemical and statistical techniques helps elucidate the basic aspects of water-rock interaction, groundwater flow, and hydrochemical evolution [25].

In the municipality of Santana, in the karst province of western Bahia (**Figure 1**), the prevalence of dental fluorosis could relate to the consumption of groundwater with toxic levels of fluoride, which complemented the public supply [26]. This research aimed to investigate the relationship between the consumption of water of Bambuí Aquifer with natural fluoride levels and the prevalence of dental fluorosis in the municipality of Santana, Bahia, Brazil.

2. Area of study, climate, and hydrogeology

The Santana municipality is situated in the western Bahia (**Figure 1**) and has an area of 1909,352 km^2, gross domestic product (GDP) of R$130,550, and a population of about 24,750 inhabitants [27]. In 2010, this municipality had a Human Development Index of the Municipality (HDI-M) of 0.608 [28] ranking 125th in relation to the other 417 municipalities of Bahia. This municipality occupies 133rd position in relation to income (economic aspect) and 151rd position in relation education (socio-cultural aspect), which represent the fundamental conditions to dealing with health as an individual responsibility. The individual and public power revealed a municipal profile with inequalities of conditions of human development.

The region presents a subhumid to semiarid climate, with average temperature of 24.3°C and precipitation between 800 and 1000 mm/year (1961–1990), concentrated between November to April and the dry season from May to September (IMNET, 2016) [29]. It is important to note that from 2011 to 2012, the precipitations fell from 498 to 821 mm/year (**Figure 2**).

The geology includes pelitic, calcareous, and dolomitic rocks of Neoproterozoic age belonging to the Bambuí Group [30]. In addition, there are pelitic rocks (siltstones, shales, argillites, and slates) with subordinate limestones. This sedimentary

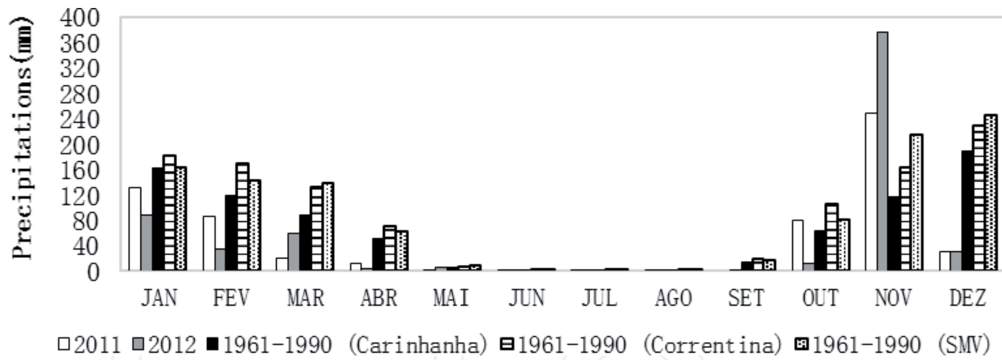

Figure 2.
Distribution of monthly precipitation averages in the stations Carinhanha, Correntina, and Santa Maria da Vitória (SM) (2011–2012 and 1961–1990), based on the data available by INMET [29].

set was deposit in the gneiss-migmatite complex Arqueano. The Urucuia Group sandstones and alluvial and detrital coverings were deposit on the Bambuí Aquifer. The wells drilled in the municipality of Santana cross the rocks of the Bambuí Group, which hosts the Bambuí Aquifer. The Urucuia Aquifer contributes to the recharge of the Bambuí Aquifer, in consortium with the infiltration of rains [31]. The main direction of the displacement of the groundwater follows from west to east, in the direction of the San Francisco River.

3. Materials and methods

3.1 Hydrogeochemical and (geo)statistical

Epidemiological data on dental fluorosis in the municipality of Santana have been compiled from Coutinho's master dissertation [32]. The hydrochemical data have been obtained from of the thesis of Gonçalves [33] and the study of Coutinho [32]. Data collection included the methodological procedures described below.

Water samples were collected from 41 tubular wells in the years 2011 (rainy season) and 2012 and 2014 (dry) in the municipality of Santana. In the 2014 sample campaign, only the fluoride levels have been measured in the locality where epidemiological information have been obtained. The hydrogenation potential (pH) and total dissolved solids (STD) were determined in situ, using a multiparameter probe (*Horiba U-50*), and aliquots have been taken for laboratory analyses. The aliquots were stored in polyethylene (0.5 and 1 L), according to APHA [34].

The cation (Na^+, K^+, Ca^{2+}, and Mg^{2+}) reading was performed by inductively coupled plasma optical emission spectrometry (ICP OES *700 Agilent Technologies*), performed in duplicate, counting with 20% in triplicates to improve the analytical quality. Anion analyzes were performed by titrimetric (HCO_3^-, Cl^-), UV-Vis spectrophotometric (*Varian*) ($N–NO_3^-$, SO_4^{-2}), and colorimetric (SPANSD) (F^-) methods using a fluorometer (LS 4000), in the Plasma Laboratory, Institute of Geosciences, of the Federal University of Bahia.

The use of the PHREEQC software allowed saturation index (SI) calculations [35]. These were grouped as subsaturated (IS <−0.5), in chemical equilibrium (SI: −0.5 and 0.5), and supersaturated (SI > −0.5). Merkel and Planer-Friedrich [36] recommend the admission of SI values of the interval 0 ± 0.5, due to the uncertainties inherent in the calculation of this or the equilibrium constant of the dissolved mineral and of the chemical analyses.

The statistic includes a descriptive and using test of normality (Shapiro–Wilk), with significance of 95%, and cluster analysis, which uses the similarity between individuals to classify the samples hierarchically into groups [37]. The Euclidean distance was chosen as a measure of similarity between the sample points, along with the Ward method, for the connection between the groups. The geostatistical was estimated by ordinary kriging by the application of ArcGIS 9.0 program. In addition, it included selected data from the well data from the Groundwater Water Information System (SIAGAS) of the Geological Survey of Brazil (CPRM).

3.2 Health research and statistical analysis

The prevalence and severity of dental fluorosis were obtained by cross-sectional study, whose research had a descriptive design, starting from an epidemiological survey that included 159 schoolchildren, of both genders, with age of 12, of the municipal schools of the Santana. Children 12 years old are chosen because they have the majority of permanent teeth erupted [38]. The schoolchildren were examined in 2014 by dental surgeon Dr. Carlos Alberto M. Coutinho, who registered the study by the research ethics committee through the website of Brazil Platform (Ministry of Health). All the steps for clinical analysis to assess the prevalence and severity of fluorosis were previously informed those involved in the study by free informed term of consent (FITC).

The schoolchildren were examined in public or private schools, according to the criteria of inclusion of sample selection: (i) born and resided in the municipality of Santana until the date of the tests according to the Department of Education; (ii) the presence of the person responsible at the time of examination and interview; and (iii) the sample included only the children whose parents signed the IC, according to Resolution 196/96 of the National Health Council [39].

Oral examinations in schools followed recommendations from the Dean index, advocated by the WHO [40] (**Table 1**). The oral examinations were performed by dentist previously calibrate and trained, using images available through the national oral health research of SB Brazil 2010 [42], in the school environment with natural light, aided by spatula and wooden gauze. In the calibration, the agreement of the results was evaluated by the Kappa statistic [43], until a suitable inter-examiner agreement was reached (Kappa = 0.85). A sample of 118 individuals was estimated by simple finite random sample, without repetitions, with proportion estimator (prevalence

Rating	Value	Diagnostic criteria
Normal	0	Enamel presents usual translucency with semi-vitric structure. The surface is smooth and polished and has bright cream color
Questionable	1	Enamel reveals little difference from the normal translucency, with occasional white spots. Use this code when the “normal” classification is not justified
Very light	2	Areas are whitish and opaque; small spots scattered irregularly by the tooth but involving no more than 25% of the surface. It includes clear opacities with 1 mm to 2 mm at the tip of the cusps of molars (snowy peaks)
Light	3	The opacity is more extensive but involves no more than 50% of the surface
Moderate	4	All tooth enamel is affected and the areas subject to attrition show up worn. There may be brown spots or yellowish often disfiguring
Severe	5	Hypoplasia is widespread and the very shape of the tooth may be affected. The most obvious sign is the presence of depressions in the enamel, which seems eroded. Generalized brown spots

Table 1.
Criteria and values for fluorotic teeth classification according to Dean index [41], adapted from SB Brazil Project [42].

or incidence) and a 95% confidence level and prevalence of 0.815, extracted from Velásquez et al. [44] at the age of 12. The sample was obtained from a population of ±423 adolescents at 12 years of age, according to information of IBGE [27].

4. Results and discussion

4.1 Hydrochemistry, source the fluoride, and cluster analysis

The analysis of **Figure 3** revealed that calcium bicarbonated (40%), mixed calcium (20%), sodium bicarbonated (27%), and sodium chlorinated (13%) hydrochemical facies were representative. The uncertainty of ionic balance was at most 20%, based on practical error [46]. For the calcium bicarbonated or calcium mixed facies, the content of the ions was in decreasing order: $rCa^{2+} > rNa^{+} > rMg^{2+} > rK^{+}$ and rCO_3^{2-} - $rHCO_3^{-} > rCl^{-} > rSO_4^{2-} > rF^{-} > rN{-}NO_3^{-}$. While in the sodium facies, the cation contents followed in the order $rNa^{+} > rCa^{2+} > rMg^{2+} > rK^{+}$. There is a clear relationship between the sodium hydrochemical facies and the fluoride levels above the optimum limit (0.8 $mg.L^{-1}$) of the groundwater sample.

Table 2 presents the statistical summary of the hydrochemical variables, whose calcium levels exceeded the limit recommended by the WHO [47], for 40% of the wells. These calcium contents have been derived from the interaction between the water and the rocks of the Bambuí Group. The hydrochemistry of karstic aquifers reflects the dissolution of the minerals calcite and dolomite, residence time, and water circulation in the aquifer [48].

The cluster analysis was used to classify the samples into groups (G1 and G2), with the aid of visual observation of the dendrogram, inserting the hydrochemical facies (**Figure 4**). The cut line was marked on the dendrogram at a distance of 80, whose samples that showed lower bond distance belonged to the same category. In the samples, the increase of mineralization accompanies the evolution of bicarbonate calcium facies to the bicarbonate or sodium chlorate facies.

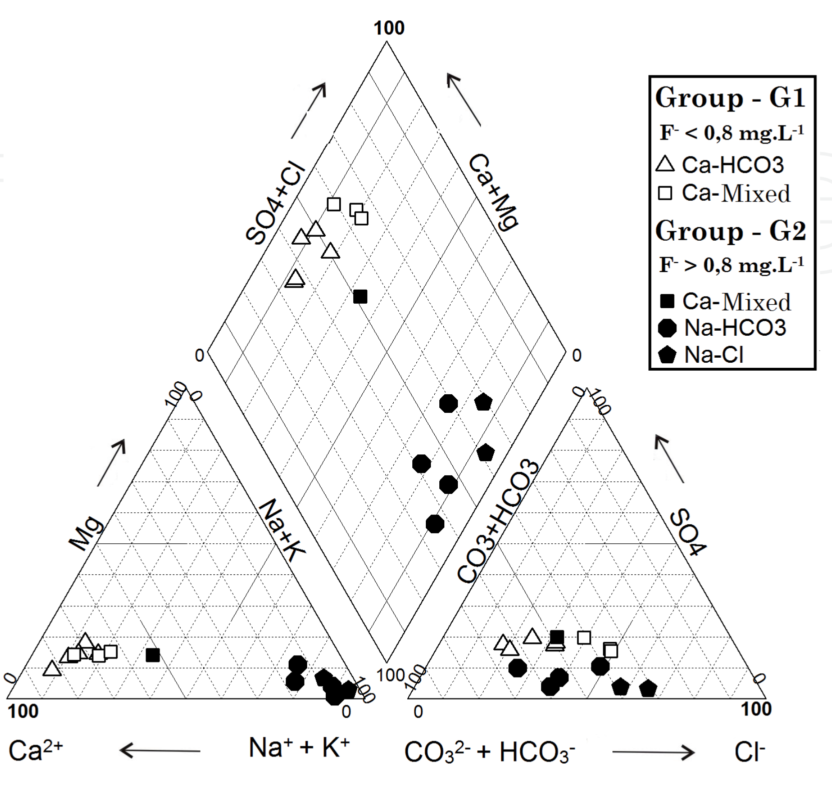

Figure 3.
Diagram of Piper [45] for groundwater classification and indication of hydrochemical groups and fluoride contents.

Parameters	VMP*	Min.	Max.	Mean	Median	EP	CV (%)	p-valor**
pH	6.5–9.5	7.26	8.93	7.92	7.65	0.15	7.32	0.04**
STD ($mg.L^{-1}$)	1000.00	440.00	1110.00	625.00	597.00	43.73	27.09	0.001**
Na^+ ($mg.L^{-1}$)	200.00	18.80	238.30	58.05	35.96	19.92	90.71	0.001**
K^+ ($mg.L^{-1}$)	—	1.30	5.21	2.69	2.70	0.27	39.20	0.15*
Ca^{2+} ($mg.L^{-1}$)	75.00	5.45	197.27	77.65	93.21	15.23	75.96	0.13*
Mg^{2+} ($mg.L^{-1}$)	50.00	1.22	16.86	10.74	13.50	1.33	47.82	0.01**
Cl^- ($mg.L^{-1}$)	250.00	40.39	300.50	113.74	95.69	16.46	56.05	0.01**
HCO_3^- ($mg.L^{-1}$)	—	178.00	366.00	234.92	232.50	11.60	19.13	0.01**
SO_4^{2-} ($mg.L^{-1}$)	250.00	10.57	85.53	50.09	53.74	6.06	46.84	0.44*
N-$NO3^-$ ($mg.L^{-1}$)	10.00	0.04	5.40	1.05	0.56	0.36	133.71	0.01**

*Non-Gaussian distribution.
**Gaussian distribution.*

Table 2.
Statistical summary of the hydrochemical and isotopic variables.

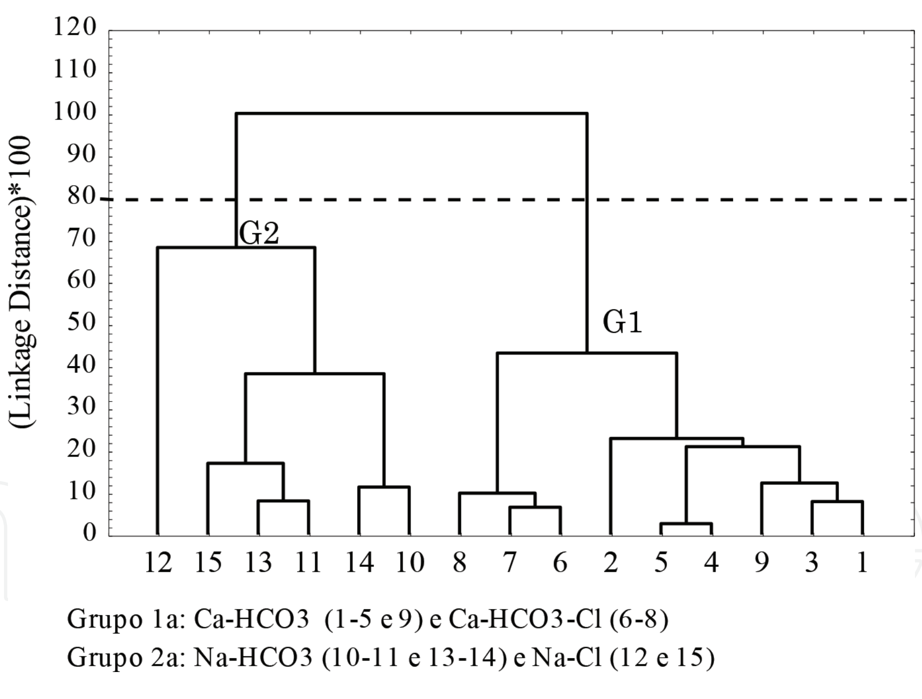

Figure 4.
Dendrogram and hydrochemical classification of the groundwater of Santana.

The formed hydrochemical groups showed differences in TDS values, pH, and calcite and dolomite saturation indexes (**Table 3**). This trend was also indicated by the geochemical reasons rNa^+/rCa^{2+} and $rHCO_3^-/rCa^{2+}$, which modeled that the base-exchange processes and the chemical weathering of pellets could add lithogenic Na^+ and $rHCO_3^-$ to the groundwater and remove Ca^{2+} from them.

The values of the $rHCO_3^-/rCa^{2+}$ ratio were lower than 1.5 for the G1 group, reflecting the importance of the water-rock interaction. The values of this ratio less than 1.5 result from the dissolution of the calcite and solutions subsaturated in calcite [49]. The values of the $rHCO_3^-/rCa^{2+}$ ratio were greater than 1.5 in the G2 group, corroborating the relevance of the water-rock interaction, whose chemical

Well	Facies	SI $_{Calcite}$	SI $_{Dolomite}$	SI $_{Gypsum}$	SI $_{Fluorite}$	$[rCl^- - (rNa^+ + rK^+)]/rCl^-$	rNa^+/rCa^{2+}	$rCl^-/(rCl^- + HCO_3^-)$
Group 1 (G1): the hydrochemical facies presented fluorine contents lower than 0.8 mg.L^{-1}								
P1	Ca-HCO$_3$	0.71	0.96	−1.75	−1.5	0.39	0.13	0.39
P3	Ca-HCO$_3$	0.39	0.25	−1.7	−1.79	0.39	0.26	0.39
P9	Ca-HCO$_3$	0.19	−0.06	−2.02	−0.91	0.39	0.63	0.39
P4	Ca-HCO$_3$	0.67	0.89	−1.83	−2.23	0.22	0.18	0.22
P5	Ca-HCO$_3$	0.91	1.4	−1.6	−1.92	0.24	0.17	0.24
P2	Ca-HCO$_3$	0.57	0.37	−1.44	−1.82	0.31	0.09	0.31
P6	Ca-HCO$_3$-Cl	1.01	1.47	−1.79	−1.46	0.49	0.15	0.49
P7	Ca-HCO$_3$-Cl	0.43	0.35	−1.65	−1.42	0.57	0.26	0.57
P8	Ca-HCO$_3$-Cl	0.33	0.1	−1.9	−2.06	0.58	0.32	0.58
Mean		0.35	0.58	−1.74	−1.68	0.40	0.24	0.40
Median		0.40	0.57	−1.75	−1.79	0.39	0.18	0.39
Group 2 (G2): the hydrochemical facies presented fluorine content higher than 0.8 mg.L^{-1}								
P10	Na-HCO$_3$	0.73	1.54	−3.48	−0.5	0.54	5.53	0.54
P11	Na-HCO$_3$	0.15	0.19	−2.83	−0.91	0.42	11.96	0.42
P13	Na-HCO$_3$	0.3	−0.16	−2.72	−0.26	0.29	11.27	0.29
P14	Na-HCO$_3$	0.37	0.3	−3.06	−0.46	0.39	4.59	0.39
P12	Na-Cl	1.02	2.12	−2.94	−0.06	0.68	10.04	0.68
P15	Na-Cl	0.07	0.18	−3.48	−0.75	0.60	28.36	0.60
Mean		0.54	0.44	−3.09	−0.49	0.49	11.96	0.49
Median		0.60	0.34	−3.00	−0.48	0.48	10.66	0.48

Table 3.
Values of the saturation indexes (SI) and the geochemical ratios of the samples.

weathering of the minerals of the pelitic lithophytes would supply bicarbonate and sodium ions to the solution.

The analysis of **Table 3** allows the proposition that part of the samples of G1 group are located under the influence areas of the meteoric recharge zones of the aquifer, presenting a shorter transit time. The higher ionic contents and values of the geochemical ratios rNa^+/rCa^{2+} and $rHCO_3^-/rCa^{2+}$ related to the G2 group were verified, which were attributed to the influence of the water-rock interaction processes and the action of the base-exchange reactions. The hydrogeochemistry of karstic aquifers reflects the dissolution of calcite and dolomite minerals, the transit time, and the water circulation in the aquifer [50].

In the G2 group, related to the fluorine content higher than 0.8 mg.L^{-1}, most alkaline and sodium geochemical conditions favor the addition of alkalinity and the dissolution of fluorite, a hypothesis corroborated by the saturation conditions of fluorite, calcite, and dolomite revealed in **Figure 5**. These hydrochemical conditions explain the relationship between sodium waters and fluoride levels above 0.8 mg. L^{-1} as was as shown in Piper's diagram in **Figure 3**.

In the natural waters, the saturation of the solution in calcite controls the solubility and the precipitation of the fluorite [51]. In the karstic province of western Bahia, Brazil, the fluorite is the main source of fluorine for groundwater. Gonçalves et al. [33] have shown that the Handa [41] model can be adapted for geochemical investigation of the Bambuí Aquifer. This model elucidates the relationship between F^-, Ca^{2+}, and HCO_3^- ions relatively constant for pH conditions.

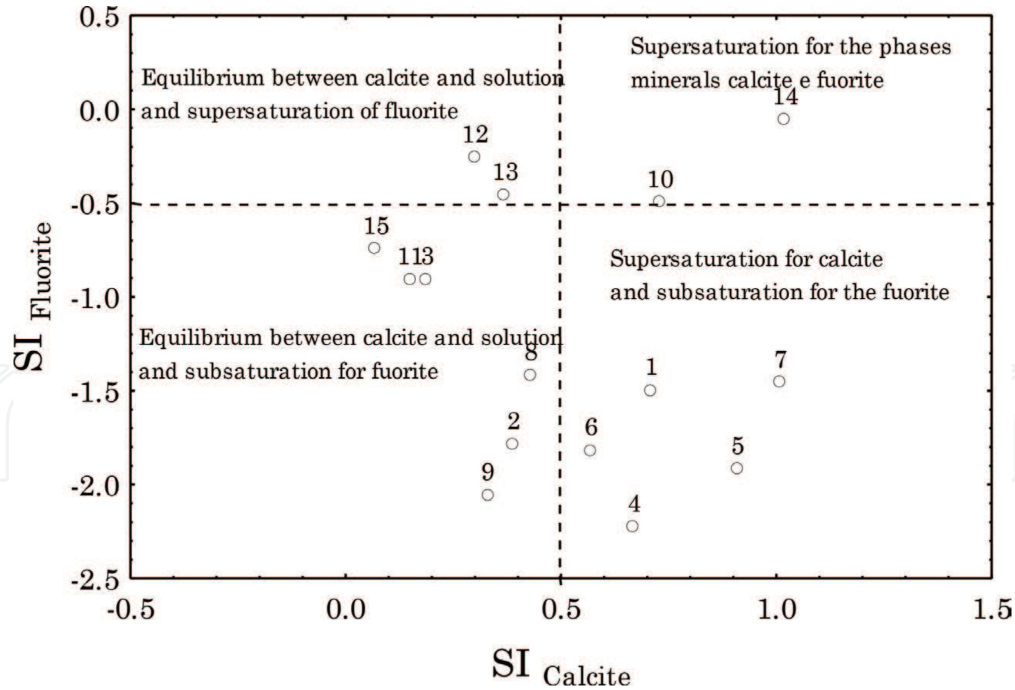

Figure 5.
Dispersion of saturation indices (SI) of calcite and fluorite minerals.

Handa [52] proposed a model for the hydrogeochemistry of fluorine, synthesized in Eq. (1), which covers the solubility constant (**K**) and ionic activity (α). It predicts that the precipitation of the calcite in consortium with the base-exchange reactions adds Na^+ and HCO_3^- to the solution, a condition that favors the solubility of the fluorite. This model has been applied to the hydrogeochemical investigation of crystalline aquifers [52]:

$$KCaF_2 \leftrightarrow CaCO_3 = \left[\alpha\left(HCO_3^-\right)\right] / \left[\alpha\ (H^+).(F^-)_2\right] \quad (1)$$

Costa [53] proposed that the plagioclase mineral phases would provide lithogenic Na^+ to the waters of the Bambuí Aquifer in the north of Minas Gerais. The interaction of the waters with the clay minerals (M), due to the weathering of impure carbonates and pelitos, removes Ca^{2+} and provides Na^+ to the solution by the base-exchange reactions (Eqs. (2)–(5)). The ionic activity of sodium interferes with the alkalinity, saturation, and calcification conditions of the precipitation and the solubility of the fluorite [15]:

$$(M)\ SiO_3 + CO_2 + H_2O \leftrightarrow M^{2+} + SiO_2 + 2HCO_3^- \quad (2)$$

$$Na\ (M)(S) + Ca^{+2} \leftrightarrow Ca(M)(S) + 2Na^+ \quad (3)$$

$$CaF_2 + Na2\,CO_3 \leftrightarrow CaCO_3 + 2F^- + 2Na^+ \quad (4)$$

$$CaF_2 + 2NaHCO_3 \leftrightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2 \quad (5)$$

Figure 6 shows the Gibbs diagram and indicates basic processes for hydrogeochemical evolution. The samples reported the influence of the water-rock interaction. The increase in the ratio $rCl^-/(rCl^- + rHCO_3^-)$ accompanies the hydrochemical composition

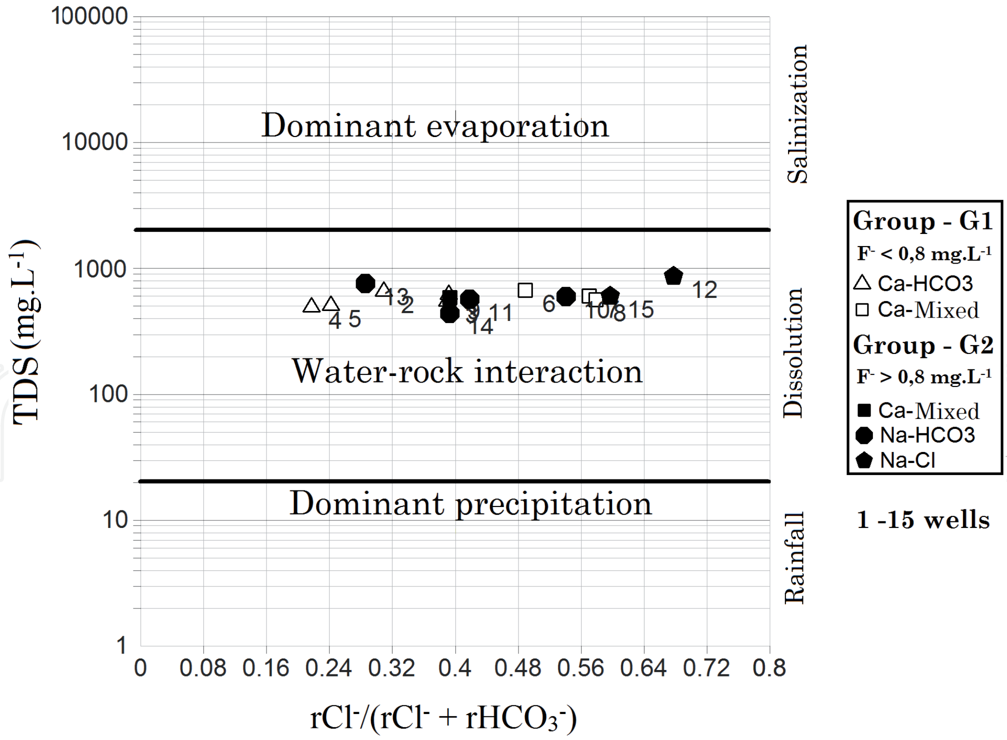

Figure 6.
Diagram of Gibbs [54] indicating the controls the hydrochemistry.

of the local flow to the regional (Ca–HCO_3 → Ca–Cl–HCO_3 → Na–HCO_3 → Na–Cl). The transition from calcium to sodium facies also reflects the action of base exchange and weathering of the pellets. These processes add lithogenic sodium and bicarbonate to groundwater while removing calcium.

Miranda et al. [55] and Conceição Filho et al. [56] studied the fluorite in the carbonates of the Bambuí Group, in Bahia (BR). Conceição Filho et al. [57] conducted a statistical analysis of the physical-chemical data of current sediments of the Bambuí Geochemical Projects (PGB) [58] and São Francisco Basin (PBSF) [56]. Fluoride contents were 25–6500 mg.L^{-1}, with geometric means of 235.78 (PGB) and 303.85 mg.L^{-1} (PBSF), whose pH values were predominantly alkaline. The anomalous content ranged from 900 to 1600 mg.L^{-1} (PGB). In these sediments, the pH values were predominantly alkaline.

Costa [54] analyzed fluoride in rocks of the Bambuí Group in northern Minas Gerais (BR). The mean values of fluoride in pelitic rocks ranged from 120 to 620 mg.L^{-1} and in carbonate rocks ranged from 320 to 508 mg.L^{-1}. The fluoride values of the rocks of the Bambuí Group were higher than the average level of this element in carbonate rocks (300 mg.L^{-1}) [59]. The rocks of the Bambuí Group may represent relevant geogenic sources of fluorine for groundwater.

4.2 Fluoride levels, epidemiology, and medical geology

The optimum content of fluoride (C) in solution for public water supply in the region was obtained according to Galagan and Vermilion [60] (Eqs. (6) and (7)), as a function of the regional average air temperature (T). This optimum limit was recommended by Ordinances n°. 2,914/11 [61] and WHO. [47]. From this premise, fluoride content of 0.78 mg.L^{-1} as optimum limit for water of human consumption of Santana and of the neighboring municipalities can be proposed:

$$€(T) = 10.3 + 0.725T \tag{6}$$

$$C = 22.2/€ \tag{7}$$

Table 4 presented a statistical summary for the fluoride values obtained in the current research in the municipality of Santana and the SIAGAS data. The fluoride contents varied between 0.05 and 9.16 mg.L^{-1}, which could be compared to the levels of the groundwater of the Canápolis, Serra Dourada, and Sítio do Mato. Gonçalves et al. [62] found fluorine levels of 0.11–2.15 mg.L^{-1} in the groundwater of the Bambuí Aquifer in municipality of Serra do Ramalho, Bahia.

Velásquez et al. [44] analyzed the contents of fluorine in waters of 78 wells drilled in the Bambuí Aquifer, in the municipality of São Francisco, northern Minas Gerais, Brazil. Fluoride contents ranged from 0 to 3.9 mg.L^{-1}, with 13 wells (17%) exceeding the local optimum limit (0.8 mg.L^{-1}). The municipalities of Santana (Bahia) and São Francisco (Minas Gerais) have similar geological, climatic, and precipitation index. The municipalities of Santana and São Francisco represent endemic areas of dental fluorosis, which require the identification of sources and understanding of hydrogeochemistry.

The samples were classified according to fluoride levels and risk for oral health and with the SIAGAS well data for a regional perspective (**Figure 7**). The groundwater classified in the protection factor category may assist in the promotion of oral health, which included only 20% of the samples in Santana. The municipalities of Canápolis, Santa Maria da Vitória, and Serra Dourada have a higher percentage of groundwater samples with optimal natural fluorine content, which may represent a viable alternative to public water supply.

The risk category of dental fluorosis comprised 47% of the groundwater samples of the municipality of Santana, being equable only to the percentages found in the municipalities of Serra Dourada and Sítio do Mato (**Figure 7**). The chronic exposure of children up to 6 years of age at high fluoride levels during tooth germ formation has epidemiological relevance and health surveillance [63].

A portion of the samples (40%) had fluoride contents higher than 3.0 mg.L^{-1}, whose prolonged consumption represents a risk of bone fluorosis or deformities in the hips and incapacitating fluorosis (**Table 5**). This risk also includes the municipalities of Canápolis, Serra Dourada, and Sítio do Mato. The chronic ingestion of natural waters containing fluoride levels greater than 3 mg.L^{-1} correlates with the prevalence of dental fluorosis or skeletal fluorosis [14].

The fluoride levels in the groundwater of the municipality of Santana presented epidemiological relevance. Rouquayrol [64] defined epidemiology as the science that studies the health-disease process, population distribution, and determinants of diseases and damage to health and events associated with public health, proposing specific measures to prevent, control, or eradicate diseases and provide indicators that support the planning, administration, and evaluation of health actions. This observational science is based on the concept of risk (incidence and prevalence), defined as the probability of members of a given population developing a specific disease or

Municipality	Size (n)	Minimum	Maximum	Mean	Median	CV (%)
Santana (current)	41	0.05	9.16	1.41	0.54	135
Canápolis (SIAGAS)	21	0.15	7.0	1.02	0.66	141
Santa Maria da Vitória (SIAGAS)	39	0.02	3.5	0.73	0.53	89
Serra do Dourada (SIAGAS)	28	0.17	5.20	1.43	0.95	87
Serra do Ramalho (SIAGAS)	08	0.11	1.95	0.52	0.13	127
Sítio do Mato (SIAGAS)	10	0.16	6.12	2.39	1.46	96

Table 4.
Statistical summary of fluorine levels in the groundwater of Santana (current) and neighboring municipalities (SIAGAS).

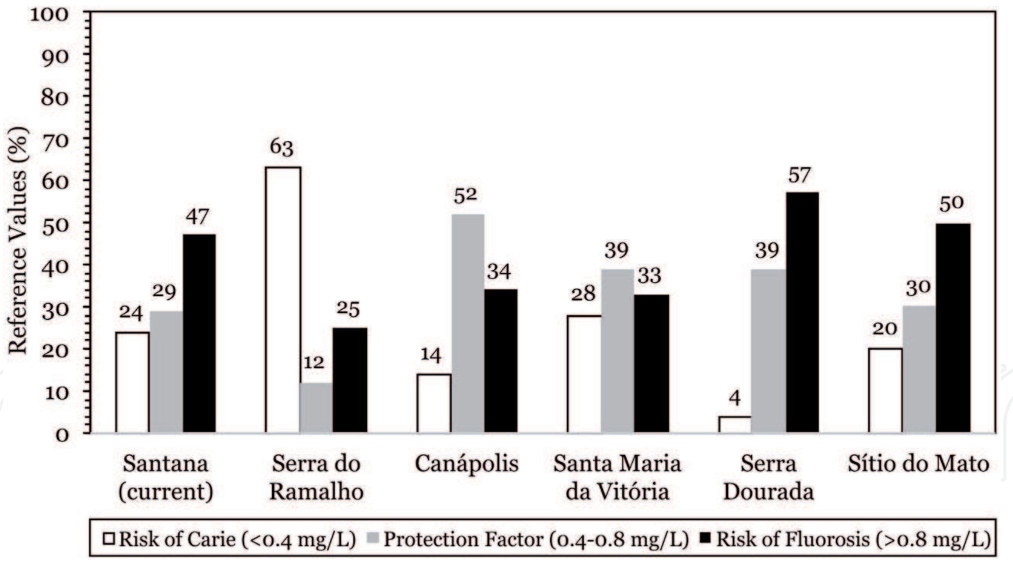

Figure 7.
Classification of samples according to fluoride values and health risk.

health-related event at a time interval. The prevalence of fluorosis is an epidemiological indicator that represents the number of cumulative cases over a period (new and old), and the incidence quantifies the number of people who lost health over a period [65].

Table 6 presents the descriptive analysis of the fluorosis condition in 159 12-year-old schoolchildren (87% resided in rural); 53% had dental fluorosis (Dean index) and 17% in moderate to severe forms. It obtained 60% of the examined in the female gender and was observed (interviews or clinical examination) that the male students were less likely to be examined, which configured a bias to obtain the sample. The prevalence and severity of dental fluorosis in this study are in disagreement with the national oral health survey of the SB Brazil Project [42]. This national survey found a prevalence of dental fluorosis at 12 years of age of 17% (Dean index), with 15% very light or light and 1.5% moderate or severe.

Clinical examination revealed that moderate to severe forms of dental fluorosis were the most relevant, with clinical aspects presented in **Figure 8D**. The clinical aspect of the dental fluorosis includes emergence opaque spots on the enamel, teeth counterparts, to yellowish or brown areas in cases of severe changes [38]. In the most severe forms, the detachment of the enamel portions can occur, after eruption. This leads to the appearance of dental surface depressions observed in

Meenakshi and Maheshwari [12]	WHO [8]	Risk to health	%				
			Santana (current)	A*	B*	C*	D*
<0.40	<0.50	Caries risk	24	14	28	3.5	20
0.4–0.8	0.5–1.5	Local optimal limit	29	52	39	39	30
0.8–3.0	1.5–3.0	Risk of dental fluorosis	10	29	31	47	0
3.0–4.0	>3.0	Bone and joint Problems	17	0	2	3.5	10
4.0–6.0 (or >6.0)	—	Deformities in the knees and hips and disabling fluorosis	20	5	0	7	40

**Hydrochemical data of the Bambuí Aquifer, Bahia (BR), from SIAGAS wells: (A) Canápolis; (B) Santa Maria da Vitória; (C) Serra Dourada; and (D) Sítio do Mato.*

Table 5.
Fluoride (F^-) ($mg.L^{-1}$) levels in drinking water and risks related to human health.

Fluorosis	Male		Female		Total	
	N	%	N	%	N	%
Absent (0)	35	22	38	24	79	46
Contestable (1)	4	2.5	5	3	9	5.5
Very light (2)	11	7	17	11	28	18
Light (3)	5	3	17	11	22	14
Moderate (4)	5	3	10	6	15	9
Severe (5)	4	2.5	8	5	12	7.5
Total	64	40	95	60	159	100

Table 6.
Absolute and relative frequency of the gender and categories indicated by the Dean index in a sample of 12-year-old schoolchildren from the municipality of Santana.

severe forms (**Figure 8D**). The several degrees of fluorosis can be related to whitish, yellow, and brownish spots (severe) [4]. Severe fluorosis often produces painful hypersensitivity to the teeth and esthetic disharmony, compromising the individual's quality of life [26], [66–67].

Figure 9 showed a correlation between the prevalence and severity of dental fluorosis in schoolchildren at 12 years of age examined and the consumption of groundwater with toxic levels of fluoride from the Bambuí Aquifer, in the municipality of Santana. The proportions of the prevalence and severity of dental fluorosis

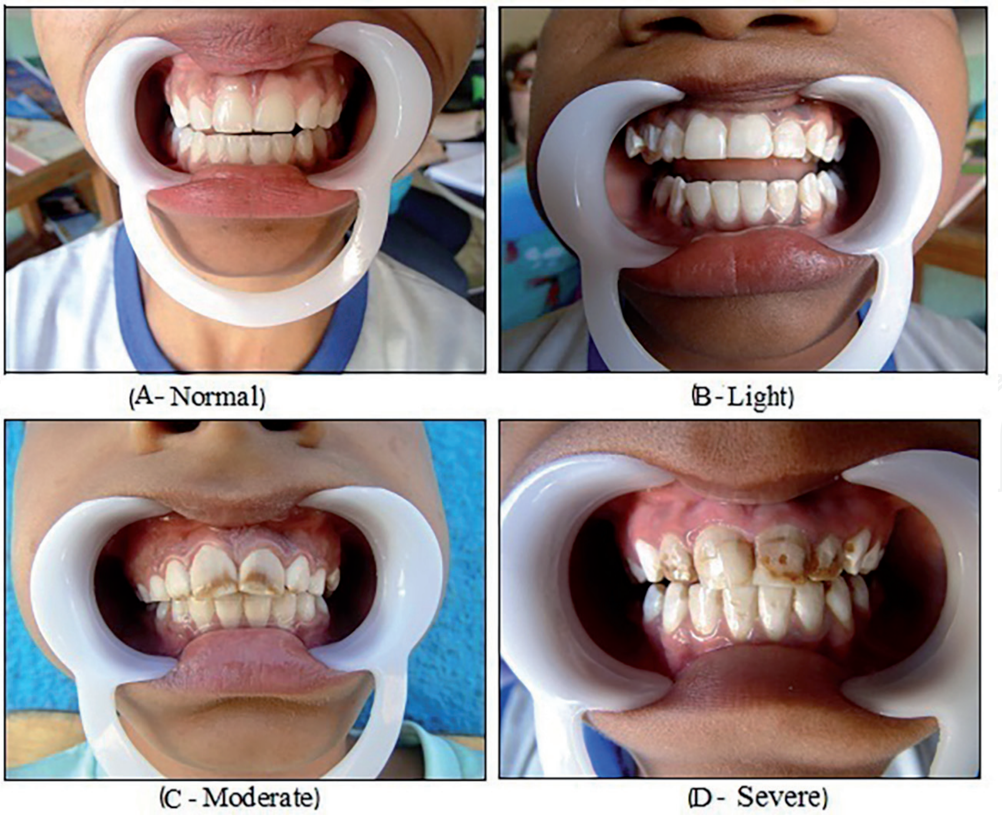

Figure 8.
*Clinical aspects of dental fluorosis, obtained in the municipality of Santana by Coutinho, 2014, according to Dean's classification [44]. **A**: Enamel presents usual translucency with semi-vitric structure, with surface is smooth, polished and has bright cream color. **B**: The opacity is more extensive but involves no more than 50% of the surface. **C**: All tooth enamel is affected and the areas subject to attrition show up worn, with may be associate the brown spots or yellowish often disfiguring. **D**: Hypoplasia and brown spots are widespread, the shape of the tooth may be affected and the most obvious sign is the presence of depressions in the enamel.*

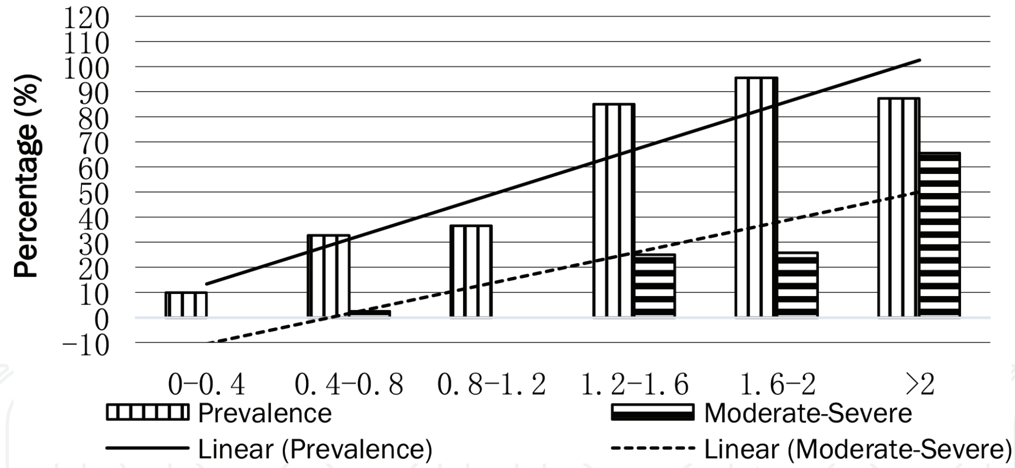

Figure 9.
Prevalence and severity of dental fluorosis versus fluoride contents.

increase significantly from fluoride values in the range of 1.2–1.6 mg.L^{-1}. The propagation of severe fluorosis, grade 5 (**Figure 10D**), increases sharply from the range of fluoride values greater than 2 mg.L^{-1} (>2).

Figure 10 shows the map of spatial distribution of fluoride levels in groundwater of the municipality of Santana, based on data from the field survey or selected from the SIAGAS registry. This figure also spatializes the risk categories of fluorosis and indicates the locations where the epidemiological information was obtained. The fluoride contents of the groundwater collected in tubular wells drilled in the localities of Areão, Cachoeira, Canabrava, Caracol, Olhos d'Água, Pedra Preta, Sossego, and Várzea do Mourão presented epidemiological relevance for children up to 6 years of age, since they ingest these waters for a chronic exposure.

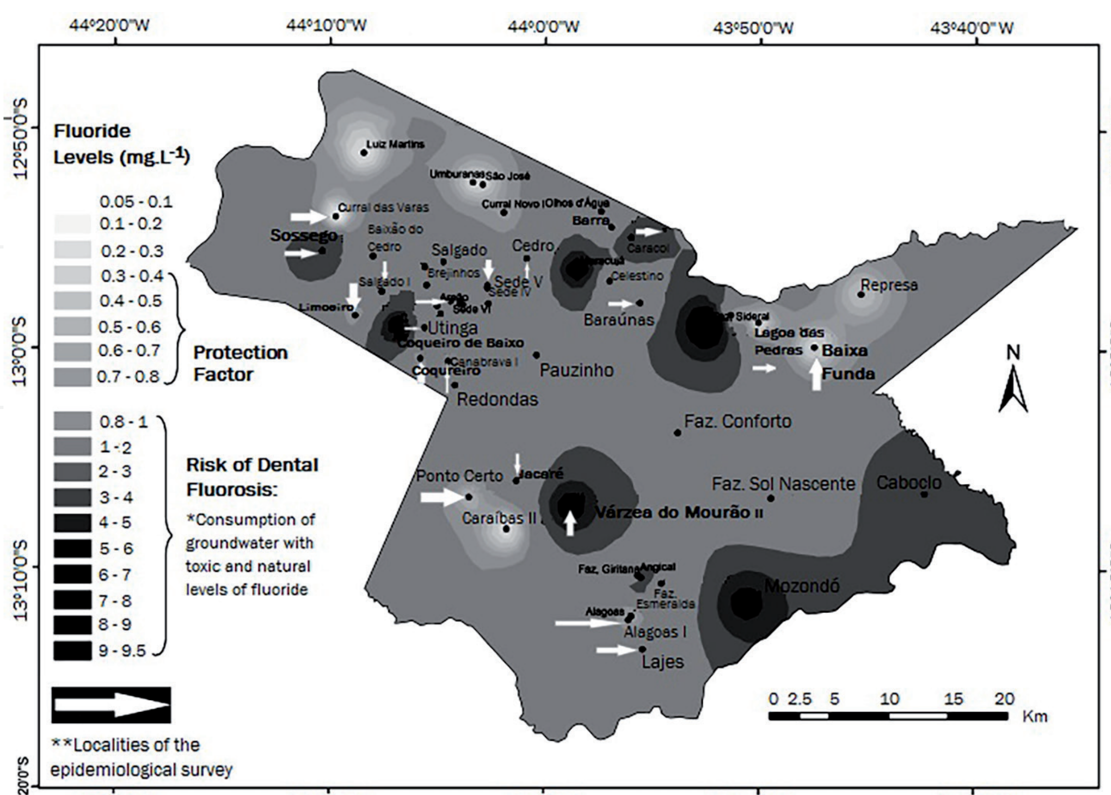

Figure 10.
Map of distribution of fluoride levels in groundwater and indication the spatial information of the dental fluorosis. The categories of epidemiological risk were protection factor (0.4-0.8 mg.L^{-1}) and risk of fluorosis dental (> 0.8 mg.L^{-1}).

The spatial analysis of fluoride isoteores revealed epidemiological relevance and allowed the indication of Santana as an endemic area of dental fluorosis, whose consumption of water with toxic and natural levels of fluoride is the main risk factor. It is expected that water resource managers in city of Santana could apply viable cost-benefit technologies for defluoroating in groundwater with toxic levels of fluoride used in public water supply. The technical-scientific literature offers several technologies for the natural deflowering of water [68–78], which cover the use of activated alumina, activated carbon, ion exchange resins, reverse osmosis systems, electrodialysis and nanotechnology.

Table 7 presents the prevalence and severity of dental fluorosis and fluoride levels of groundwater used in the public supply of endemic areas. Churchill [85], in a study conducted in the United States, observed a direct correlation between permanent tooth enamel patches or dental fluorosis and the presence of high levels of fluoride in the water supply. Dean et al. [86] discussed the correlation between the prevalence of dental caries or fluorosis and fluoride values in the water supply of four cities in the United States. The proportions of dental fluorosis in the moderate or severe forms are higher in the endemic areas, attributed to the consumption of natural waters with toxic levels of fluoride [87].

In this context, it is imperative to emphasize that the presence of dental fluorosis and its influence on the self-esteem of the people may not affect equally the population of the municipality, because the access to drinking water and the socioeconomic conditions to individually deal with the dental fluorosis impacts in esthetics and self-esteem are unequal. Funtowicz et al. [88] call attention to the complexity dimension in epidemiology and other health sciences, as well as to the technical, methodological, and epistemological uncertainties that accompany the risk assessments.

Author/year	Study area	Prevalence (%)	Severity	F^- (mg.L^{-1})
Costa et al. [75]	São Francisco, Minas Gerais, Brazil	56–67	35% moderate/severe[B]	0–3.9
Cruz et al. [26]	Santana, Bahia, Brazil	53	18% moderate/severe[B]	0.1–6.20
Azcurra et al. [3]	Sampacho, Córdoba, Argentina	78	25% moderate/severe[A]	9.0
Loyola-Rodríguez et al. [76]	San Luis Potosí, Mexico	78	46% moderate/severe[A]	0.7–3.1
Dozal et al. [77]	Chihuahua, Mexico	82	41% moderate/severe[A]	0.7–8.6
Yadav et al. [78]	Distrito de Haryana, India	45–60	22–39% moderate/severe[A]	1.52–4.0
Vazquez-Alvarado et al. [79]	San Miguel Vindhó, Mexico	85	41% moderate/severe[A]	0.7–2.0
Ding et al. [80]	Inner Mongolia, China	42.6	20% moderate[A]	0.24–2.84
Gallará et al. [5]	Córdoba, Argentina	76–87	17–22% moderate/severe[A]	1.4–7.0
Jarquín-Yañez et al. [81]	Hidalgo, Mexico	100	95% severe[A]	4.1
Larquin et al. [82]	Camagüey (Cuba)	51	47% moderate/severe[A]	1.7–2.0
Haritash et al. [83]	Haryana, India	23–32	29–44 moderate/severe[A]	0.5–2.40
Chaudhry et al. [84]	Uttar Pradesh, India	14–24	30% moderate/severe [A]	0.20–25.0

[A]*Dean index.*
[B]*Index of Thylstrup and index of Fejerskov.*

Table 7.
Epidemiology of dental fluorosis and fluoride contents in waters of endemic areas.

The collective health paradigm expands the health-environment relationship and contemplates the biomedical and sanitation paradigms, as well as the political, cultural, economic and ecological dimensions of health [89].

The integrated analysis of the hydrochemical research and multivariate and epidemiological statistics indicated that the chemical weathering of the rocks of the Bambuí Group and the leaching of its constituent mineral phases provide fluorine to the groundwater in the municipality of Santana. In this way, the minerals that make up the rocks provide fluorine and other chemicals for the biogeochemical cycles, which if conducted by natural waters can influence human health. This perspective, according to Selinus [90], defines medical geology, an interdisciplinary science that gathers professionals of geosciences, health, and biosciences around the understanding of the interaction between environmental geological factors and the geographical distribution of diseases, such as fluorosis.

An environmental health and education program would provide information for the population and for municipal accountability regarding the identification and reception of those affected by endemic fluorosis. Future research would help promote health in this municipality and encourage collaboration between geoscientists, ecologists, and health professionals to develop studies that relate geological processes to the ecosystem and human health. In addition, it would guide water quality managers, public health planners, and educators.

5. Conclusions

The groundwater samples were predominantly alkaline. The hydrochemical characterization indicated that there were two aquifers, with different levels of sodium, calcium, and fluoride. The most representative aquifer covered the bicarbonated calcium and mixed calcium waters (66%) and the lower levels of fluoride. The pelito-carbonático aquifer contemplated the sodium bicarbonated and sodium chlorinated waters, whose fluoride levels exceeded the local optimum limit. Analysis of clusters also indicated that there were two hydrochemical groups (G1 and G2) that differed in STD, pH, F^-, rNa^+/rCa^{2+} ratio, and saturation indexes of the mineral phases calcite, dolomite, and fluorite minerals.

The risk category for dental fluorosis comprised 47% of the samples. A portion of the samples presented fluoride levels representative of the category of risk of skeletal fluorosis (20%) or associated with the risk of incapacitating fluorosis (20%). The descriptive analysis of the dental fluorosis condition in the sample universe revealed a prevalence of dental fluorosis of 53%, with a 17% prevalence of moderate to severe forms. These proportions were associated to the consumption of groundwater with high toxic levels of fluoride.

The monitoring of fluoride levels in groundwater, application of defluoridation techniques, and environmental health surveillance and sensitization programs for endemic fluorosis in the municipalities of Santana and neighboring (Canápolis, Serra Dourada and Sítio do Mato) are recommended. Future research in medical geology would help encourage studies that link geological processes to the ecosystem and human health. They would also guide the management of water quality and the decisions of municipal public health managers.

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