

Keywords: Groundwater, Fluoride, Spatial distribution,

1.Introduction

 Groundwater is an essential resource for socioeconomic progress, providing approximately 50% of the world's drinking water and accounting for 98% of the unfrozen freshwater [1]. Despite its importance, its quality can be compromised by the presence of naturally occurring inorganic compounds, which, depending on the geomorphology of the region, can be potentially harmful for human consumption [2-3-4].

 Fluoride is one of the most common natural contaminants in drinking water. In low concentrations, this ion is frequently added to drinking water to prevent dental

caries, but in high concentrations, it can cause dental and skeletal fluorosis,

affecting public health [5-6-7].

- research aims to evaluate the fluoride concentrations in different groundwater
- samples of this region. In addition, we try to correlate fluoride concentrations with
- the presence of other ions such as calcium, magnesium, sodium, and potassium.

2. Methodology

- **2.1 Geographic location of the state of Paraguarí**
- The region studied is located in the southwest of the eastern region of Paraguay (Fig 1), limited to the state of Paraguarí. This state is geographically surrounded in the north by the states of Cordillera and Caaguazú, in the south by the state of Misiones, in the east by the states of Guairá and Caazapá, and in the west by the states of Central and Ñeembucú. Paraguarí has a total area of 8,705 km² and a population of 8,719 inhabitants. The region's climate is moderate-humid, with all-year-round rainfall and hot summers. The average annual temperature and rainfall are 22.2 °C and 1,384 mm, respectively. The rainiest periods are March-April and October-November.

115 **Fig 1. Location of the sampling points in the state of Paraguarí.**

116 **2.2 Sampling and parameters**

124 **Table 1. Sampling points for each district in the state of Paraguarí.**

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 All wells were deeper than 100m. Samples for fluoride determination were stored in 100 mL sterile polyethylene bottles, while those used for the analysis of the other ions were stored in 1L bottles. All bottles were previously washed with a 10% HNO3 (nitric acid) solution, following the laboratory's quality and biosafety protocols.

 The samples were sealed and properly stored before transport. All analyses were carried out at the Water Quality Laboratory of the Multidisciplinary Center for Technological Research.

 The fluoride concentration in the groundwater samples was determined potentiometrically utilizing an ion-selective electrode, as indicated in the Standard Methods for the Examination of Water and Wastewater (SM-4500-F-C). An OAKTON ION 6+ potentiometer, previously calibrated, was employed. For samples with significant fluoride content, the elements calcium (Ca2+) and magnesium (Mg2+) were determined by EDTA titration (SM-3500-Ca B y SM-3500-Mg B, respectively), while sodium (Na+) and potassium (K+) concentrations were quantified by atomic absorption spectroscopy using an air-acetylene flame (SM-3111 B). A Schimadzu, AA-7000 (APHA-AWWA-WEF, 2017) unit was used.

2.3 Statistical analysis

The obtained fluoride concentrations were compared with the maximum permitted

levels established by the Paraguayan Drinking Water Standard (NP 24 001 80). To

- evaluate a possible correlation between fluoride concentration and the
- concentrations of calcium, magnesium, sodium, and potassium, the Pearson
- correlation coefficient (r) was calculated using IBM SPSS Statistics software. Then,
- the spatial distribution of fluoride was determined using the Kriging geostatistical
- interpolation technique, implemented in ArcGIS 10.1. software.

3. Results and discussion

3.1 Evaluation of fluoride concentrations at different points

- 3.30 mg/L (Table 2). Most of the samples presented low fluoride concentrations,
- except Yere and Montiel Potrero, belonging to the Caapucú district. The pH values
- ranged between 5.26 and 7.29. García et al. (2023) [4] mention that an alkaline
- environment (7.6-8.6) with high bicarbonate concentration favors fluoride
- dissolution in groundwater. In contrast, Gutiérrez and Alarcón-Herrera (2021) [30]
- noted that at lower pH, fluoride speciation tends to show a higher proportion of F
- complex ions.
- The World Health Organization states that dental fluorosis occurs more likely when
- fluoride concentrations in drinking water exceed 1.5 mg/L, while skeletal fluorosis
- tends to manifest at concentrations higher than 3 mg/L. Both conditions result from
- chronic exposure to elevated levels of fluoride.

Nº	District	Code Well	Prof. (m)	$F \, mg/L-1$	pH	Cond ms/cm
$\mathbf{1}$	Acahay	AC114	160	0.01	6.14	42.3
$\overline{2}$	Acahay	AC166	120	0.00	5.26	51.1
3	Acahay	AC203	100	0.01	5.8	9.92
4	Acahay	AC222	150	0.01	6.39	78.4
5	Caapucu	CU121	102	3.20	6.74	331
6	Caapucu	CU143	126	3.30	7.29	594
7	Caapucu	CU144	121	2.50	6.03	43.7
8	Carapegua	CA085	132	0.00	6.18	30.3
9	Carapegua	CA110	126	0.02	5.67	41.7
10	Carapegua	CA133	150	0.01	5.97	34.7
11	Carapegua	CA187	122	0.01	5.79	47.7
12	Carapegua	CA191	150	0.01	7.28	436
13	Carapegua	CA221	120	0.14	6.9	183.9
14	Escobar	ES031	152	0.00	5.64	48.2
15	La Colmena	CO167	150	0.01	6.18	131.6
16	La Colmena	CO286	104	0.04	6.2	52.6
17	Mbuyapey	MB036	124	0.00	5.82	46.7
18	Mbuyapey	MB092	150	0.01	5.85	49.5
19	Paraguari	PA054	150	0.01	6	37.8

Table 2. Fluoride concentrations and recorded parameters.

 Considering the maximum allowable concentration of fluoride (1.5 mg/L) according to the Paraguayan Drinking Water Standard (NP 24 001 80), 93% of the sampled wells (38 samples) meet national and international standards. However, 7% of the samples (3 wells) exceed this limit, with concentrations higher than 2 mg/L. Figure 2 shows the fluoride concentrations obtained, where wells CU121, CU143 and CU144 stand out, which greatly exceeded the permitted limit. Well CU143 recorded the highest concentration, with 3.30 mg/L. These results are consistent with those obtained by the Ministry of

- Environment and Sustainable Development [6] (MADES, 2012) in the region
- "Cuenca Hídrica del arroyo San Lorenzo", where 95.38% of the samples presented
- concentrations between 0 and 0.5 mg/L. Similarly, Diez Pérez et al. (2019) [26]

Fluoride concentration (mg/L)

Fig 2. Fluoride concentrations registered according to the Paraguayan Standard NP 24 001 80.

3.2 Description of the spatial fluoride distribution

- Figure 3 shows the spatial distribution of fluoride in the state of Paraguarí estimated
- by the Kriging interpolation method. The areas with the lowest concentration are
- located in the northeast, while the highest concentrations are found in the
- southwest, suggesting a relatively uniform distribution over much of the area. The
- areas represented in light and dark blue tones correspond to areas with low fluoride
- concentrations, within the permitted limits. In contrast, the dark blue areas indicate
- concentrations that exceed the maximum allowable limit. These results are
- consistent with those reported by the Ministry of Environment and Sustainable
- Development (MADES, 2012) [6], which observed a uniform distribution of fluoride
- in the "Cuenca Hídrica del Arroyo San Lorenzo", without the presence of elevated
- concentrations. Similarly, Durán et al. (2017) [31] documented a heterogeneous
- geographic distribution of fluorides in the province of Tucumán, Argentina,
- differentiating between areas with deficit, excess, and concentrations within the
- recommended values.

Fig 3. Spatial distribution of fluoride Department of Paraguarí.

3.3 Correlation of fluoride with calcium, magnesium, sodium, and

potassium.

Figures 4 and 5 show graphically possible correlations between fluoride and other

compounds (Ca, Mg, K, Na) in the groundwater. Only samples with significant

fluoride concentration were considered (5 wells). Numerical values of the measured

- concentrations are given in Table 3.
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 Fig 4. Graphical detection of correlations between fluoride and sodium or fluoride and calcium. The red line is a linear fit of the sodium concentration versus fluoride concentration.

Fig 5. Graphical detection of correlations between fluoride and magnesium or

fluoride and potassium.

- 256 reported a positive correlation between F- and Na⁺, Ca²⁺, and Mg²⁺, while studies
- 257 by Liu et al. (2015) [34] documented negative correlations with Ca^{2+} , Mg²⁺, and K⁺.

258 **Table 3. Cation values in wells with high, medium and low fluoride concentrations.**

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260 **Table 4. Pearson correlation.**

261 *. The correlation is significant at the 0.05 level (two-sided)

262 **. The correlation is significant at the 0.01 level (two-sided)

263

264 **4. Conclusions**

265 This work emphasizes the importance of future studies to evaluate the dynamics of

266 other related elements. This work emphasizes the importance of future studies to

267 evaluate the dynamics of other related elements, such as calcium, magnesium, sodium, and

268 potassium, which could be influencing the distribution and concentration of fluoride in the

269 region.

270 This study on fluoride concentration in groundwater in the state of Paraguarí

271 reveals that most of the analyzed samples present fluoride levels within the limits

- allowed by Paraguayan and WHO regulations. However, a small percentage of wells,
- mainly in the district of Caapucú, exceed these limits, posing a potential risk to
- 274 public health, particularly concerning dental and skeletal fluorosis. Therefore, it is
- suggested that specific monitoring and treatment strategies, such as the application
- 276 of efficient technologies for fluoride reduction in affected water sources, should be
- 277 implemented to ensure the sustainability of drinking water sources and protect the
- health of local communities

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