










Water quality and sustainable solutions for drinking water supply in the Taquari-Antas watershed, RS, Brazil

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ABSTRACT

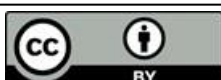
Access to safe drinking water is a fundamental human right and a critical component of sustainable development. This study is conducted in the context of the Taquari-Antas Hydrographic Basin, Rio Grande do Sul, Brazil, and assesses the quality of drinking water in 101 rural properties, focusing on identifying problems of potability, especially regarding excessive fluoride concentration, which is a known problem for the water in this region. The study involves the collection of water samples from rural properties, a survey to understand water use and quality perception by users, and water quality analysis using established analytical methodologies. Results show that 58.4% of the investigated rural properties have potability issues, with excessive fluoride being the most prevalent concern, affecting 39.6% of properties. High fluoride levels have significant health implications, including dental and skeletal fluorosis, with global relevance. To address this issue, activated bone charcoal filtration systems were installed in ten properties, effectively reducing fluoride concentrations to within acceptable limits for human consumption. These defluoridation systems are characterized as sustainable, cost-effective, and scalable, offering a practical solution for regions facing similar challenges.

Keywords: groundwater, rural properties, water stewardship.

Qualidade da água e soluções sustentáveis para o abastecimento de água potável na bacia do Taquari-Antas, RS, Brasil

RESUMO

O acesso à água potável segura é um direito humano fundamental e um componente crítico do desenvolvimento sustentável. Este estudo foi realizado no contexto da Bacia Hidrográfica



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Taquari-Antas, no Rio Grande do Sul, Brasil, e avalia a qualidade da água para consumo em 101 propriedades rurais, com foco na identificação de problemas em sua potabilidade, especialmente em relação à concentração excessiva de flúor, que é um problema conhecido na água desta região. O estudo envolve a coleta de amostras de água em propriedades rurais, uma pesquisa para compreender o uso da água e a percepção da qualidade pelos usuários, e análises da qualidade da água utilizando metodologias analíticas estabelecidas. Os resultados mostram que 58,4% das propriedades rurais investigadas apresentam problemas de potabilidade, sendo o excesso de flúor a preocupação mais prevalente, afetando 39,6% das propriedades. Altos níveis de flúor têm implicações significativas para a saúde, incluindo fluorose dentária e esquelética, com relevância global. Para enfrentar esse problema, sistemas de filtração com carvão ativado de osso foram instalados em dez propriedades, reduzindo eficazmente as concentrações de flúor para níveis aceitáveis para consumo humano. Esses sistemas de defluoretação são caracterizados como sustentáveis, economicamente viáveis e escaláveis, oferecendo uma solução prática para regiões que enfrentam desafios semelhantes.

Palavras-chave: água subterrânea, gestão da água, propriedades rurais.

1. INTRODUCTION

Drinking water quality is closely related with human health and the sustainable development of society (Li and Wu, 2019; Wu *et al.*, 2020), highlighting that access to water, sanitation and hygiene is a human right. Investments in infrastructure and sanitation facilities and hygiene education are among the measures necessary to ensure universal access to safe and affordable drinking water for all, with sanitation being one of the seventeen sustainable development goals of the United Nations 2030 Agenda (UN, 2020).

Access to piped water has been increasing considerably in urban areas of the developing world over the last two decades. In rural areas, however, it is still lagging, in that most of the rural population are still deprived of safe, convenient and cheap access to water. Access to piped water significantly reduces the risk of water-related diseases if compared to more basic solutions of access (Barde, 2017).

In remote rural regions where public or private water supply infrastructure is unavailable, the local population has no option but to depend on alternative, unsafe water sources. As a response to this lack of access to safe water, community-managed water supply (CMWS) has emerged as a viable alternative (Machado *et al.* 2022). Many smaller communities use alternative supply solutions, which can be classified into collective alternative solutions (CAS) and individual alternative solutions (IAS). These collective supply systems are managed by the communities themselves, in the form of cooperatives called “Hydric Societies”.

Despite being less of a priority when compared to microbiological aspects of water quality, chemical aspects are important to guarantee the health of the population in the face of chronic problems, according to the World Health Organization (WHO, 2022). As for the chemical aspect, the concentration of fluoride has gained prominence in several research groups. In Brazil, this problem has already been identified in different regions that use groundwater as a source of supply (Cangussu *et al.*, 2002; Catani *et al.*, 2007; Castilho *et al.*, 2010; Frazão *et al.*, 2011).

High concentrations of fluoride are most often associated with groundwaters, as fluoride accumulates from dissolving rocks. Chronic intake of high doses is linked to the development of dental fluorosis. As a result, large populations in developing countries suffer the effects of chronic endemic fluorosis. The most common symptom of dental fluorosis is a condition that involves interaction of fluoride with tooth enamel, which develops staining or weakening and eventual loss of teeth. Young children are at greater risk, as fluoride affects the development of

tooth and bone growth (Edmunds and Smedley, 2013).

Fluoride removal by water treatment is carried out in some countries, however, fluoride contamination is not easy to treat. Studies developed by UNISC (FUNASA, 2018) indicated that the construction of filtration systems with activated bone charcoal is the technically and economically most appropriate alternative to the reality of small communities. According to FUNASA (2018), bone activated carbon adsorption defluoridation systems made with 6 kg of charcoal were suitable for installation at the point of use, where water is used for direct consumption, producing 36 L of treated water per day, which is necessary to serve a family unit.

In this context, the objective of this research was to diagnose the quality of water supply in rural properties. In addition, alternative water treatment systems were installed, aiming to improve the quality of water for human consumption, especially with regard to excess fluoride, a classic problem in groundwater in this region.

2. MATERIAL AND METHODS

2.1. Study Area and Sampling

This study involved 101 rural properties contracted by Philip Morris Brazil (a multinational company in the tobacco industry). These properties are located in a coverage area approximately 30 km away in Taquari-Antas Hydrographic Basin, state of Rio Grande do Sul, Brazil. The rural properties were visited between June and December 2021 (Figure 1).

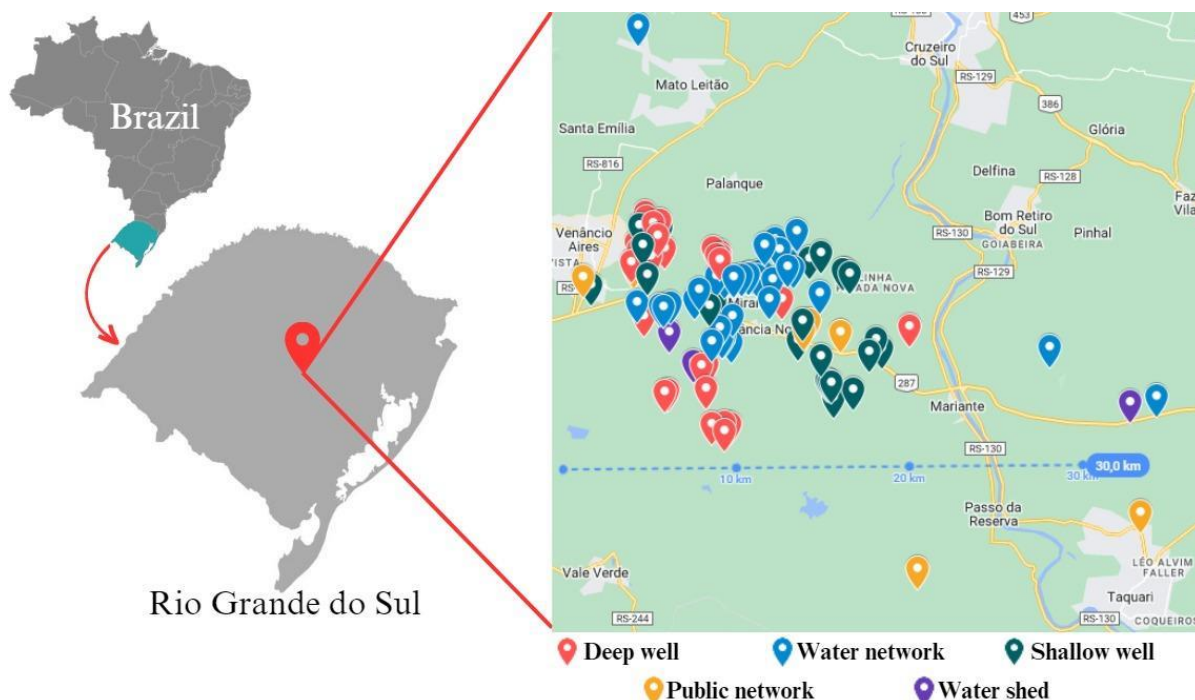


Figure 1. Location of rural properties included in this research, State of Rio Grande do Sul, Brazil.

All water samples were directly collected at the point of use following the residential deposit. To comprehend the conditions of drinking water use and users' perceptions of its quality, interviews were conducted with individuals responsible for rural properties. During these interviews, the satisfaction with water quality was assessed on a hedonic scale ranging from 0 (completely dissatisfied) to 5 (completely satisfied), considering the characteristics of water pressure, transparency, odor, and taste.

2.2. Analysis variables for water diagnosis

To diagnose water quality, analyses were carried out at the Limnology Laboratory of the University of Santa Cruz do Sul. All analytical and sample collection methodologies used followed APHA standards (APHA *et al.*, 2005). The following variables were determined in each of the samples (Table 1).

Table 1. Analytical methodologies used to determine water quality.

Parameters	Analytical Methodology
pH	Potentiometry with combined glass electrode
Temperature (T°)	Temperature sensors (thermistor)
Electrical Conductivity (EC) $\mu\text{s cm}^{-1}$	Direct conductometry
Turbidity (TUR) uT	Direct turbidimetry
Hardness mg L^{-1}	Calculated from the concentration of Ca and Mg
Total Solids Dissolved (TDS)	Calculated from the electrical conductivity
Alkalinity (CA) mg L^{-1}	Titration neutralization
Chloride (Cl) mg L^{-1}	Titration with mercuric nitrate
Sulfate (SO ₄) mg L^{-1}	Turbidimetry with barium íon
Nitrate (NO ₃) mg L^{-1}	Ultraviolet Spectroscopic (220 nm)
Fluoride (F) mg L^{-1}	Potentiometry with Ion-Selective Sensors
Iron (Fe) mg L^{-1}	Flame atomic absorption spectrometry
Magnesium (Mg), mg L^{-1}	Flame atomic absorption spectrometry
Manganese (Mn) mg L^{-1}	Flame atomic absorption spectrometry
Sodium (Na) mg L^{-1}	Flame atomic absorption spectrometry
Potassium (K) mg L^{-1}	Flame atomic absorption spectrometry
Zinc (Zn) mg L^{-1}	Flame atomic absorption spectrometry

In addition to assessing fluoride concentration, various analytical parameters are employed to comprehensively characterize water quality in the studied properties. This inclusive approach not only facilitates the identification of excessive fluoride but also enables the recognition of other potential water quality issues.

To interpret the results, the limit values established by Ordinance n° 888 (2021) of the Ministry of Health (Brasil, 2021) and, mainly with regard to fluoride concentration, Ordinance n° 10/1999 (Rio Grande do Sul, 1999) were used.

2.3. Alternative water treatment systems

To remove excess fluoride in the water, defluoridation systems were constructed by adsorption on bone activated carbon. This system was designed for water treatment at the point of consumption, with the filters assembled and installed by the team responsible for developing the project. The methodology used is described in the manual for removing excess fluoride in natural waters (Costa *et al.*, 2017). These systems were developed from 8"x17" fiberglass tanks (Structural® PolyGlass®) filled with 6 kg of bovine bone activated charcoal, 20x50 mesh (BONECHAR®), operated by a manual actuation valve (F56E), auxiliary filter (5 μm filter element). The remaining materials required for filter assembly are common hydraulic materials (as shown in Figure 2).

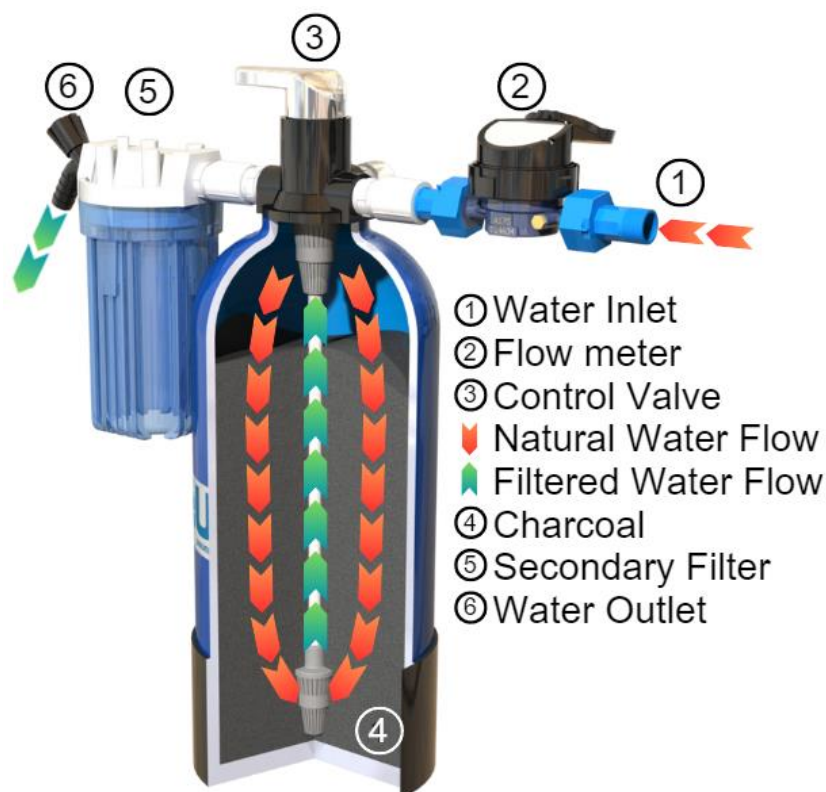


Figure 2. Schematic representation of the filtration system used in this project.

3. RESULTS AND DISCUSSION

3.1. Water quality diagnosis

Analytical results for determining pH, temperature (Temp.), turbidity (Turb.), hardness, electrical conductivity (EC), total dissolved solids (TDS), carbonate alkalinity (CA), bicarbonate alkalinity (BA), chloride (Cl), sulfate (SO₄), nitrate (NO₃), fluoride (F), iron (Fe), magnesium (Mg), manganese (Mn), sodium (Na), potassium (K), and zinc (Zn) are shown in [Annex 1](#).

Of the total of 101 rural properties investigated, 59 (58.4%) had potability problems in the water supply. The critical potability variables are manganese (2 properties), sodium (10 properties), pH (16 properties), fluoride (40 properties), nitrate (2 properties), and sulfate (2 properties).

In fact, excessive concentration of fluoride constitutes the main water potability problem, compromising 39.6% of the properties investigated (40), considering the limit established by Ordinance n° 10/1999 (Rio Grande do Sul, 1999) (Figure 3). It is important to highlight that the maximum value of fluoride in this set of samples was 5.7 mg L⁻¹, determined in property P27 (Linha Coronel Brito, Venâncio Aires, RS), exceeding by 6.3 times the maximum value allowed by the aforementioned Ordinance.

Of the 101 rural properties, only in 9 (8.9%) is the fluoride concentration in the ideal range for supply water (between 0.6 and 0.9 mg L⁻¹) and 52 (51.5%) have a concentration lower than 0.6 mg L⁻¹ (Rio Grande do Sul, 1999). Even considering the limit of 1.5 mg L⁻¹ for fluoride in the supply water, determined by Ordinance n° 888 of the Ministry of Health (Brasil, 2021), the number of properties with water unsuitable for consumption is still high, corresponding to 36 properties. In fact, the problem caused by the excessive concentration of fluoride in the supply water of this region is already known to the scientific community (Luiz *et al.*, 2019).

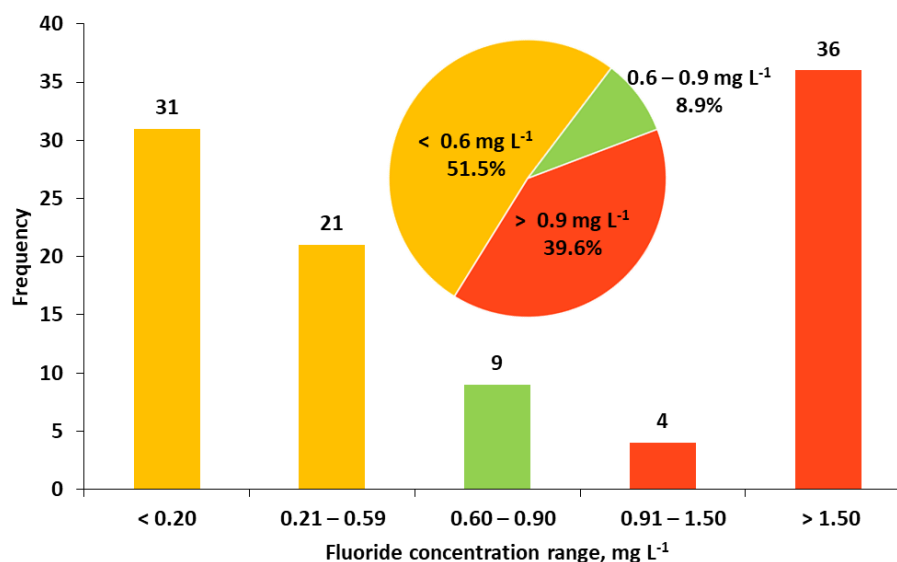


Figure 3. Histogram of the distribution of fluoride concentration in the water supply of the 101 rural properties investigated.

There are several types of health problems related to excessive fluoride consumption, with the most reported being the widespread occurrence of dental and skeletal fluorosis. Dental fluorosis is a condition that can primarily develop during childhood and adolescence when teeth are still in the development stage, potentially resulting in dental demineralization. Skeletal fluorosis, a bone-related disease, can occur with prolonged exposure, leading to joint damage and increased stiffness or decreased elasticity in bones, making fractures more common (Solanki *et al.*, 2022). The main route of human exposure to fluoride is through consumption of drinking water. Consequently, to prevent human exposure to fluoride and the development of fluorosis, it is essential to regulate the quality of drinking water. According to various reports (e.g., Kimambo *et al.*, 2019), more than 25 countries (including Brazil) around the world have water sources with high concentrations of fluoride, and approximately 200 million people rely on these sources that exceed recommended levels of fluoride, resulting in serious consequences for consumer health. A study conducted by Neeti and Singh (2023), using 13 groundwater samples in Jamui District (India), showed that all water samples exceeded the permissible limits for fluoride, indicating that the water was not suitable for consumption. In another study conducted in Gaya District (India), using 75 water samples from 15 different locations, 6 samples crossed the permissible limit of 1.5 mg/L, demonstrating variability in fluoride concentrations across different regions (Ahmad and Singh 2023a). In the same region, a health risk assessment was conducted using Chronic Daily Intake (CDI) and Hazard Quotient (HQ_{fluoride}). The results showed that the HQ_{fluoride} value in adult men ranged from 0.38 to 2.77, from 0.34 to 2.45 in adult women, and from 0.41 to 3.0 in children, exceeding the permissible limits in most of the sampled locations, indicating significantly higher health risks (Ahmad and Singh 2023b).

Regarding the origin of the water supply for this set of properties, it was observed that 36 properties were supplied by water networks (Hydric Societies), 30 by deep wells, 25 by shallow wells, 7 by public networks, and only 3 by springs watershed, it was found that of the total set of samples, 66 properties are supplied with water from deep sources, whether from private or community wells, through Hydric Societies. These are precisely the ones that present problems with fluoride concentration, since the presence of this material comes from deep waters. Therefore, if we consider only these samples for the percentage calculation, we have that 59.1% of the properties have levels above the limits allowed by state regulation, or 54.5% compared to the national limit.

Groundwater is the main source of freshwater on Earth, and a significant number of individuals depend on it for drinking. Fluoride is a widely distributed contaminant, found in both natural factors (soil, volcanic activity, rocks) and artificial sources (Solanki *et al.*, 2022). Fluoride is naturally introduced into groundwater and surface water through interactions with fluoride-rich rocks and soils. As water penetrates the earth, the deterioration or leaching of fluoride-containing rocks can lead to increased contamination of groundwater compared to surface water. The amount of fluoride added to groundwater is influenced by factors such as the rate of evaporation, the duration of water retention in aquifer zones, and the intensity and long-term use of irrigation (Ahmad *et al.*, 2022). Therefore, the concentration of fluoride varies daily from region to region.

Regarding the artificial sources of fluoride contamination, we can primarily highlight industries. Some industries, such as aluminum, ceramics, steel, pesticides, and fertilizers, release waste and emissions containing fluoride. These waste materials can seep into the soil and reach groundwater sources, contributing to contamination (Yadav *et al.*, 2018; Solanki *et al.*, 2022). It's important to adopt proper waste management practices and environmental regulations to control and reduce fluoride contamination from these artificial sources.

Several hypotheses have been raised regarding the origin of excessive fluoride ion concentrations in the groundwater in Rio Grande do Sul (Brazil), being that high fluoride concentrations are generally associated with underground sources Guarani Aquifer System (GAS) (Luiz *et al.*, 2019).

Figure 4 presents the information collected in interviews with rural property owners regarding their level of satisfaction. Despite 39.6% of the investigated properties showing an excess of fluoride in the drinking water, the level of consumer satisfaction in relation to variables such as taste, odor, transparency, and water pressure is high for more than 80% of the properties, indicating that fluoride is a silent issue that does not interfere with user satisfaction. However, 37% of the interviewees identified a salty taste in the water consumed. This user perception is consistent with analytical results found in natural water samples, especially due to high levels of chlorides, pH, alkalinity, and total dissolved solids. Furthermore, users have identified frequent problems of turbidity, clogging, scale and burnout of electric shower resistors, typical of groundwater with excess salts.

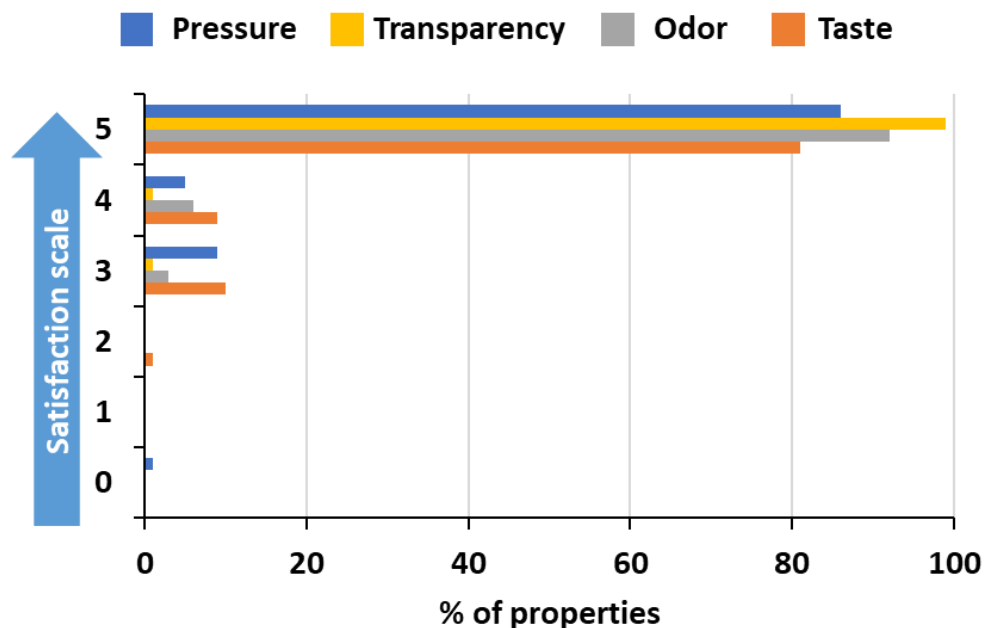


Figure 4. Results of the level of satisfaction in relation to the properties of drinking water. The interviews were carried out with those responsible for the 101 rural properties investigated.

3.2. Installation of alternative water treatment systems

Based on the results obtained in the diagnosis of water quality in the investigated properties, 10 were selected for the installation of activated bone charcoal filtration systems (Figure 5), built as described in FUNASA (2018). The selection criteria followed the guidelines of the Philip Morris Brasil technical team. Table 2 presents the physical-chemical characteristics of the water supply of selected rural properties. Results that are outside the potability standard are highlighted in red.



Figure 5. Filters installed at the point of use (near the kitchen sink) on two rural properties served by the project.

Table 2. Results of the water quality supply in rural properties selected for installation of a filtration system.

Variables	Unit	P4	P10	P11	P18	P19	P21	P26	P27	P30	P31
Hardness	mg L ⁻¹	31.3	20.9	20.3	36.4	38.3	26.7	29.8	27.7	31.4	37.2
Fe	mg L ⁻¹	0.16	0.02	0.02	0.16	0.16	0.16	0.15	0.16	0.16	0.16
Mg	mg L ⁻¹	1.17	0.49	0.48	0.70	0.70	0.27	0.33	0.30	0.32	0.38
Mn	mg L ⁻¹	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
K	mg L ⁻¹	245.7	0.1	0.1	0.1	200.9	227.6	0.1	242.8	0.1	297.3
Na	mg L ⁻¹	1.4	227.8	222.1	196.3	0.1	0.1	275.9	0.1	243.0	0.1
Zn	mg L ⁻¹	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02
pH	-	7.9	7.7	7.3	6.7	6.9	7.0	7.7	7.4	7.4	7.4
Temp.	°C	27.5	18.5	22.5	27.0	26.5	25.0	18.0	19.5	20.0	19.5
Turb.	uT	0.1	0.2	0.2	0.1	0.2	0.2	0.7	0.2	0.4	0.2
EC	mS cm ⁻¹	932	771	758	666	653	743	835	719	758	886
TDS	mg L ⁻¹	676	559	550	483	473	539	605	521	550	642
Fluoride	mg L ⁻¹	4.8	3.8	3.8	4.2	4.3	4.6	3.7	5.7	4.2	4.6
CA	mg L ⁻¹	25.6	9.9	23.6	0.0	0.0	8.9	0.0	0.0	0.0	0.0
BA	mg L ⁻¹	129.5	101.0	103.4	116.2	110.3	132.0	121.7	83.7	89.6	84.2
NO₃	mg L ⁻¹	1.38	0.10	0.10	0.27	0.27	0.10	0.10	0.10	0.10	0.10
Cl	mg L ⁻¹	209.0	113.5	119.2	72.8	77.6	116.3	148.5	63.4	103.1	134.3
SO₄	mg L ⁻¹	113.4	142.4	119.9	247.3	244.5	235.1	226.7	218.2	233.2	302.5

Results marked in red identify variables that are not within the standard threshold values. Temperature (Temp.), turbidity (Turb.), electrical conductivity (EC), total dissolved solids (TDS), carbonate alkalinity (CA), bicarbonate alkalinity (BA), chloride (Cl), nitrate (NO₃), fluoride (F), sulfate (SO₄), iron (Fe), magnesium (Mg), manganese (Mn), sodium (Na),

potassium (K), and zinc (Zn).

It is important to highlight that the treatment systems for properties P10 and P11 were installed in July 2021, as soon as the first properties with supply problems were identified. These two systems served as a model for the installation of the other 8 treatment systems, which took place in June 2022.

Figure 6 presents the results of monitoring the concentration of fluoride in the property's natural water, as well as the results obtained for the water filtered by the treatment system provided by the project. As can be seen, all results obtained for fluoride in natural water were above the standard established by Ordinance n° 10/1999 (Rio Grande do Sul, 1999), that is, above 0.9 mg L^{-1} . These results represented an average value of $4.3 \pm 1.0 \text{ mg L}^{-1}$, with property P27 having the highest fluoride concentration, being 6.2 mg L^{-1} .

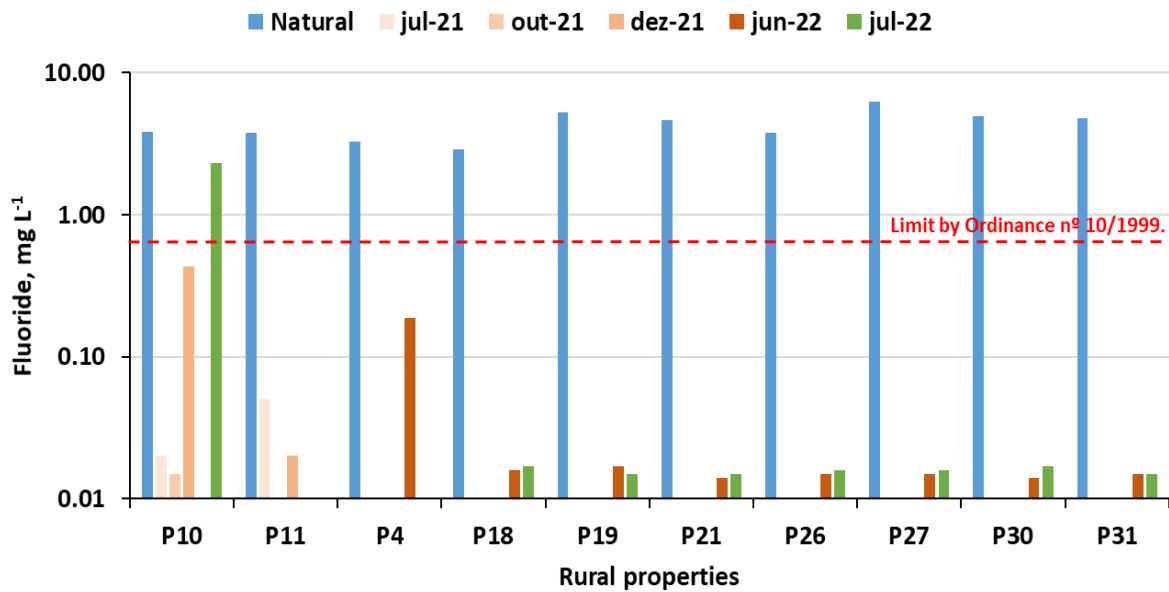


Figure 6. Results of monitoring the fluoride concentration in the water supply of the 10 rural properties served by treatment systems.

The results also demonstrate the efficiency of the proposed treatment systems, as they all reduced fluoride concentration, adjusting it to the standard limit established for human consumption. As can be seen in Figure 6, the results from July 2022 indicate that the system installed at property P10 is saturated and requires maintenance. For the other systems, the fluoride concentration remains below 0.9 mg L^{-1} . As described previously, properties P10 and P11 had their systems installed at the beginning of the project (July 2021), therefore the monitoring frequency is higher than the others. These systems have been in operation for 13 months.

The adsorption defluoridation process has significant potential for fluoride removal due to its cost-effectiveness, operational simplicity, high removal capacity and ability to reuse (regenerate) the adsorbent. In the adsorption process, there is a transfer of fluoride ions from water to the external surface of the adsorbent, followed by the adsorption of fluoride ions on the particle surfaces, and subsequently, the transfer of adsorbed fluoride ions to the internal surfaces of the adsorbent particles. Among the adsorbents used in defluoridation, those based on calcium are utilized due to their excellent affinity for fluoride and biocompatibility with the human body (Yadav *et al.*, 2018).

In our filters, we use activated bone charcoal, which consists of approximately 20% carbon and 80% hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$). This compound is the primary inorganic constituent of bovine bones. The structure of hydroxyapatite allows for cationic and anionic substitutions with great ease, such as the OH- groups that can be replaced by fluoride (Medellin-

Castillo *et al.*, 2014; Zúñiga-Muro *et al.*, 2017; Wei *et al.*, 2022).

The use of activated bone charcoal is a sustainable and efficient technology for drinking water defluoridation due to the human health issues related to fluoride exposure in developing countries. Many results showed that fluoride adsorption by bone char represents an eco-friendly, cost-efficient, and sustainable large-scale technology to enhance environmental and human health protection (González-Ponce *et al.*, 2023).

4. CONCLUSIONS

This study provides important information about the current status of drinking water quality in 101 rural properties in the Taquari-Antas Hydrographic Basin, RS, Brazil, and found that excessive fluoride concentration in drinking water is the main parameter that compromises the quality of this region's public water supply. The proposed treatment system improved the quality of drinking water.

It is crucial to emphasize the necessity of extending access to water treatment systems for rural properties in the region, ensuring that water quality is adapted for human consumption in a sustainable manner. To achieve this goal, it is imperative to establish an ongoing program to monitor the quality of water supplied to these communities. With the collaboration of public authorities and the private sector, it is essential to promote a comprehensive program aimed at expanding access to the treatment systems utilized in this study. It is also worth noting that the defluoridation systems installed in these properties were designed for six months of operation and require periodic maintenance to ensure a continuous water supply that meets potability standards.

5. ACKNOWLEDGEMENTS

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