Fervença River water quality evaluation – Water Quality Index (WQI)

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DEDICATION

I dedicate this work to my mother Eliana,

my father Wagner and my brother Caio,

the loves of my life.

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To my family, for providing me all the love and good education that a human being can possibly have.

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To everyone, who somehow crossed my path and left their mark, always making me a better person than yesterday in this beautiful life.

ABSTRACT

Water is fundamental for the survival of every specie on planet Earth and is a crucial element of the environment. Water bodies, however, have degraded over time due to various natural and mainly human-polluting activities. As a result, water quality control is required to monitor and reduce polluting agents while maintaining river health. The adoption of a Water Quality Index is one of the most extensively utilized ways of water quality control (WQI). The WQI developed by the National Sanitation Foundation determines the water quality of a river in a single value ranging from 0 to 100 by analyzing many physical, chemical, and biological parameters and employing mathematical methods. The water quality of the Fervença River in Bragança, Portugal, was assessed to use the WQI by monthly collections between January 2022 and June 2022. Samples were taken at five distinct locations along the river within the city so that the results could be compared over time and at different locations. In general, points 1 to 4 showed good water quality indexes and similar results. Point 5 on the other hand, had the lowest water quality indexes of all campaigns, which could be attributed to the neighboring city wastewater treatment plant. The winter (the region's wettest period) was characterized by a severe drought, hence no effect of rain on the analytical data could be found, as was predicted primarily for the months of January to March. From the comparison of the results obtained, it is possible to conclude that as the Fervença River flows through the city of Bragança, the quality indexes decrease in most of the campaigns, especially after point 5, demonstrating the city's negative influence on the river water quality.

KEY WORDS: Fervença river; water analysis; water pollution; Water Quality Index.

RESUMO

A água é fundamental para a sobrevivência de todos os seres vivos e é um elemento crucial do meio ambiente. Entretanto, devido a diversas atividades naturais e sobretudo humanas de poluição ao longo dos anos, corpos d'água vêm se degradando. Com isso, o controle de qualidade da água se torna necessário para monitorar e minimizar agentes poluidores, mantendo a saúde dos rios. Um dos métodos mais utilizados de controle de qualidade da água é a utilização de um Índice de Qualidade da Água (IQA). O IQA desenvolvido pela National Sanitation Foundation permite, através da análise de diversos parâmetros físicos, quimcos e biológicos, e do emprego de modelos matemáticos, avaliar a qualidade da água de um rio em apenas um simples número, de 0 a 100. Através de amostragens mensais entre Janeiro/2022 a Junho/2022, foi avaliada por meio do IQA a qualidade da água do Rio Fervença, em Bragança, Portugal. A recolha das amostras foi feita em cinco pontos diferentes do rio, na zona envolvente da cidade, assim os resultados ao longo do tempo e em localidades distintas puderam ser comparados. De uma maneira geral, os pontos 1 a 4 mostraram bons índices de qualidade de água e resultados similares. Para o local 5 foram obtidos valores reduzidos para o índice de qualidade de água em todas as campanhas, com provável relação com a descarga da estação de tratamento de efluentes, próxima do local. O inverno (período mais chuvoso da região) foi marcado por uma forte estiagem, assim não pôde ser avaliada a influência da chuva nos parâmetros do IQA, o que era esperado principalmente para os meses de Janeiro a Março. A partir da comparação dos resultados obtidos, é possível concluir que à medida que o Rio Fervença atravessa a cidade de Bragança, os índices de qualidade diminuem na maioria das campanhas, principalmente após o ponto 5, demonstrando a influência negativa da cidade na qualidade da água do rio.

PALAVRAS CHAVE: Análise de água; Índice de Qualidade da Água; poluição da água; rio Fervença.

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INDEX OF ACRONYMS

BOD_5 – Biochemical Oxygen Demand (5 days)

CCMEWQI – Canadian Council of Ministers of the Environment Water Quality Index

CETESB - Environmental Company of the State of São Paulo

DO – Dissolved Oxygen

NSF - National Sanitation Foundation

NSFWQI – National Sanitation Foundation Water Quality Index

OWQI – Oregon Water Quality Index

pH – Hydrogen Potential

SDGs – Sustainable Development Goals

TS – Total Solids

UN – United Nations

WQI – Water Quality Index

WWTP - Wastewater Treatment Plant

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1 INTRODUCTION

Water is fundamental for the survival of every specie on planet Earth and is a crucial component of the environment. For centuries, it was considered a compound of infinity quantity and public domain. However, due to natural and principally human activities, surface water and groundwater have long been deteriorating. According to the World Health Organization (2019), by 2025, half of the world's population will be living in water-stressed areas. Urbanization and population growth, city development, and the expansion of industrial and farming activities are the main reasons for that (Gloria et al., 2017).

Therefore, water quality control has become essential and in order to minimize surface water pollution and monitor the pollution-caused agents, and it can be assessed by a variety of chemical, physical and microbiological parameters (Rao & Nageswararao, 2013; Paca et al., 2019). These parameters values, if they exceed the defined limits, can represent public health issues for the local society (Tyagi et al., 2013).

The management of these parameters requires the collection and analysis of a large amount of data, and it can be difficult to evaluate and understand if done independently (Uddin et al., 2021). To make this easier to understand, mathematic tools that allow the aggregation of various data have been developed, allowing the general state of the water to be represented by a single number (Bollmann & Edwiges, 2008; Uddin et al., 2021). One of these tools is the Water Quality Index (WQI).

WQI is a simple and effective approach for assessing water quality in bodies of water. It provides a single number (like a grade) to the overall water quality based on several parameters (Rao & Nageswararao, 2013; Noori, 2019). It is one of the most effective ways to characterize water quality and it appeals to water agencies since it is easy to use and to understand (Tyagi et al., 2013; Uddin et al., 2021).

One of the most widely applied indexes in the world is the National Sanitation Foundation Water Quality Index, which is composed by the analysis of nine water quality parameters (Gloria et al., 2017). The application of this index allows the obtaining and comparison of results to understand and evaluate variations in quality of water at different points of the river and over time.

2 OBJECTIVES

The main objective of the present work is to apply the Water Quality Index method (developed by the National Sanitation Foundation) to evaluate the water quality of the Fervença River, in a section in the neighborhood of Bragança, Portugal.

The specific objectives are:

- Identify critical points along the Fervença River where water should be collected and examined due to its relevance;
- Evaluate the water quality and analyze the situation at different river locations and their temporal evolution using the WQI and quality classes;
- Compare the results and understand the possible cause of their variations, taking into account different river locations and temporal evolution.

3 STATE OF THE ART

The classic definition of water contamination, and its evaluation, involves the determination of potentially harmful substances and their respective concentrations (Bollmann & Edwiges, 2008). In the past decades, with the increase of industrial and farming activities, and consequently wastes production and its bad disposal, water contamination has achieved the worst moment so far. According to the World Health Organization (2019), globally, at least 2 billion people use a drinking water source contaminated with faeces and, by 2025, half of world's population will be living in water-stressed areas.

In this scenario, it is totally necessary the implementation of effective measures to secure better water conditions for the present and future. In many countries, water for different uses must follow certain standards, required by law (Neto, 2021). In the Portuguese Legislation, the Decree-Law n.^{0} 236/98 (Ministério do Ambiente, 1998) establishes quality standards, criteria and objectives in order to protect the aquatic environment and improve the quality of water according to its main uses. It also defines the requirements to be observed in the use of water for the following purposes: water for human consumption, water for support of aquaculture life, bathing water and irrigation water; as well as standards for discharging wastewater into water and soil (Diário da República, 1998).

Also, in 2015 the United Nations (UN) defined 17 Sustainable Development Goals (SDGs), part of the 2030 agenda for sustainable development, as an urgent call for action by all countries in a global partnership. These goals are related to a variety of thematic issues including water, energy, climate, oceans, urbanization, science and technology, gender equality and end of poverty (United Nations). The goal number 6 "Clean Water and Sanitation" represents the importance of monitoring groundwater and surface water quality, as one of the steps to achieve this goal (Figure 1).

Figure 1. UN Sustainable Development Goal 6 (United Nations).

Thus, water quality control turns out to be necessary in order to monitor pollution-caused agents, prepare action plans and minimize water pollution, and it can be assessed by a variety of chemical, physical and microbiological parameters (Rao & Nagesward, 2013; Paca et al., 2019).

Any surface water quality control program, made among time and in different spots, generates a lot of results and database that needs to be aggregate and transformed in a more comprehensive, accessible and simple information. The calculation of a Water Quality Index (WQI) is one of the most effective and popular ways to do it nowadays (Tyagi et al., 2013; Paca, 2015; Uddin et al., 2021).

3.1 WATER QUALITY INDEX (WQI)

Horton (1965) was the first to come up with the concept of expressing surface water quality as a single number. Since then, many other WQIs have been developed, like the Canadian Council of Ministers of the Environment Water Quality Index (CCMEWQI), the Oregon Water Quality Index (OWQI) and the National Sanitation Foundation Water Quality Index (NSFWQI).

The aim of a WQI is to provide a single value (like a grade) that express the overall waterbody quality based on several water quality parameters. It is a simple and powerful tool calculated by an aggregation function and allows the changes in water quality over time and space to be evaluated (Rao & Nageswararao, 2013; Noori et al., 2019; Uddin et al., 2021). They are very attractive to water management agencies, as they are easy to use and to understand.

3.2 NATIONAL SANITATION FOUNDATION WATER QUALITY INDEX

Created in 1970 by the National Sanitation Foundation, the National Sanitation Foundation Water Quality Index (NSFWQI) is a comprehensive and generally applicable index for classification of surface water based on their quality (Noori et al., 2019). It is considered the most popular and utilized index by researchers in the world (Gloria et al., 2017).

Since introduced, many studies have been conducted with this method. Bollmann & Edwiges (2008) evaluated the Belem River water quality in Curitiba, Brazil. Hoseinzadeh et al. (2014) applied the NSFWQI in the evaluation of the Aydughmush River, Iran. Jiang et al.

(2019) based his studies in the NSFWQI to assess the water quality of the Luanhe River, China. In addition, an adapted version of the NSFWQI is the official method utilized by the Environmental Company of the State of São Paulo, Brazil (CETESB) (Gloria et al., 2017).

The index consists in the analysis of nine parameters, including Dissolved Oxygen (DO), pH, Total Solids (TS), Biochemical Oxygen Demand (BOD_5), Turbidity, Total Phosphate, Nitrates, Temperature and Fecal Coliforms (Brown et al., 1970; Lobo et al., 2012; Tyagi et al., 2013; Noori et al., 2019). For each of these parameters, the results and concentrations are converted to single-value dimensionless sub-indexes, and the weighting factors are determined. Finally, a single value water quality index is calculated by an aggregation function (Uddin et al., 2021).

3.3 NATIONAL SANITATION FOUNDATION WATER QUALITY INDEX CALCULATION

The aggregation function that defines the NSFWQI is expressed in the equation (1) (Brown et al., 1970; Tyagi et al., 2013; Noori et al., 2019).

$$WQI = \sum_{i=1}^{n} qiwi \qquad \text{(equation 1)}$$

where:

WQI: Water Quality Index (range from 0 to 100).

q_i: sub-index assessed for each parameter, obtained from its quality variation slope (variates from 0 to 100).

w_i: weight defined for each parameter, based on its importance for the final WQI (variates from 0 to 1).

n: number of parameters.

The graphics below (Figures 2-6) represent quality variables for each parameter, necessary to obtain the sub-indexes. The value of q_i, in the abscissa's axis, can be identified from its correspondent value in the ordinate axis, obtained from experimental analysis (Lima, 2018).

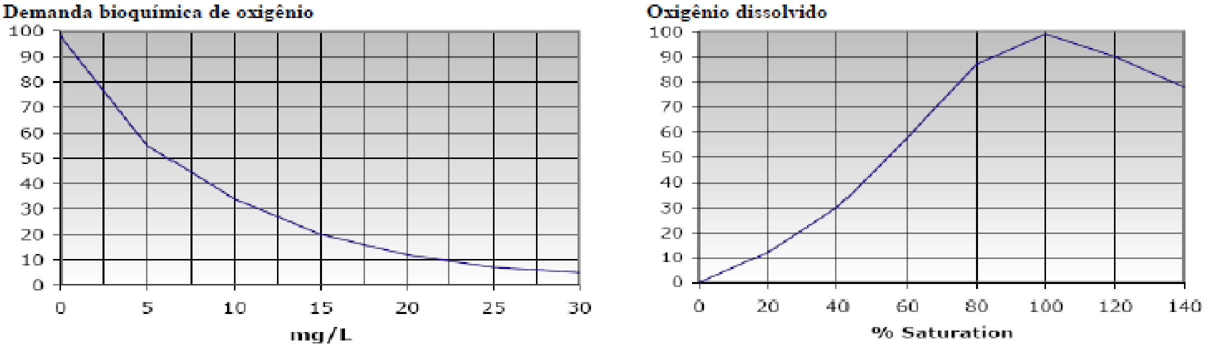

Figure 2. Quality variables for BOD_5 and Dissolved Oxygen (Lobo et al., 2012).

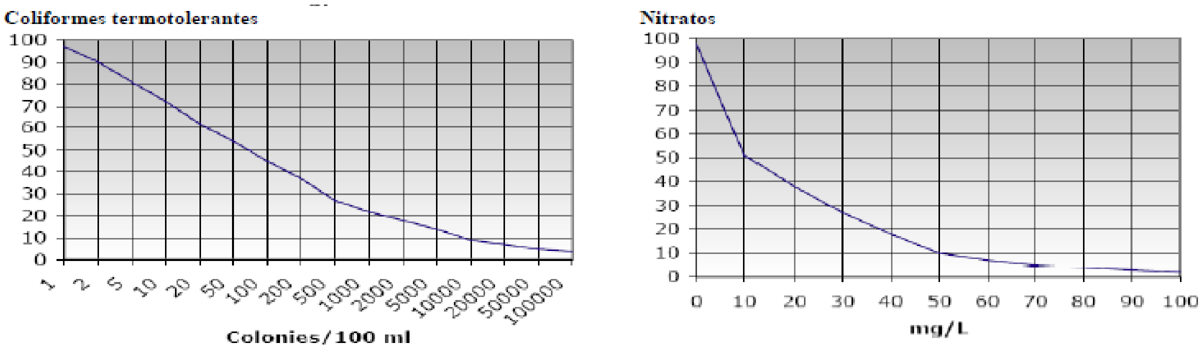

Figure 3. Quality variables for Fecal Coliforms and Nitrates (Lobo et al., 2012).

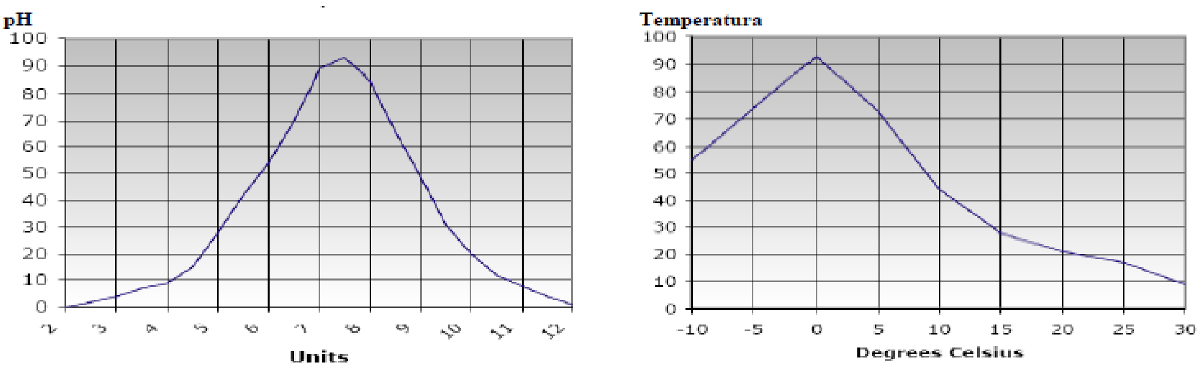

Figure 4. Quality variables for pH and Temperature (Lobo et al., 2012).

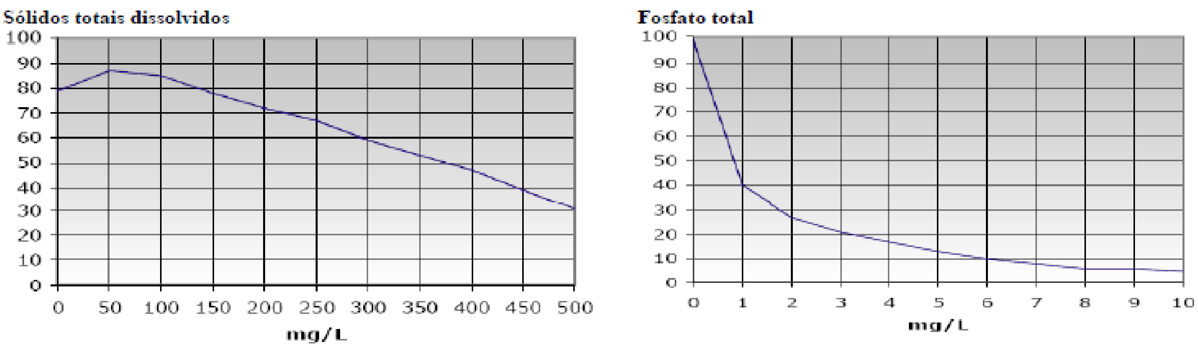

Figure 5. Quality variables for Total Solids and Total Phosphorus (Lobo et al., 2012).

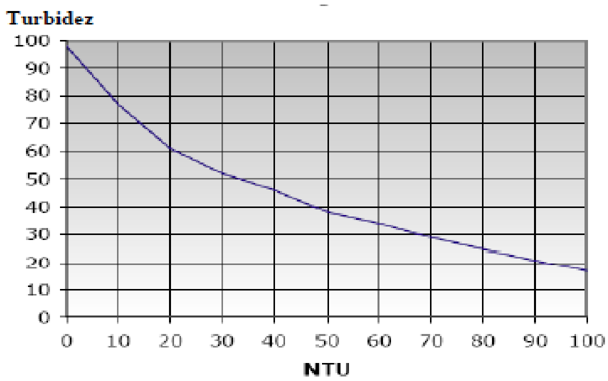

Figure 6. Quality variable for Turbidity (Lobo et al., 2012).

Additionally, the graphics above can be represented in terms of their equations, in order to obtain a more accurate q_i value (Table 1).

Table 1. Representative NSF quality equations adaptable from CETESB (Paca, 2015; Silva, 2016).

Parameter	Minimum Limit	Maximum Limit	q_i Equation
Fecal coliforms (UFC/100 mL)	0	10^5	98.24034-34.7145*(log(FC))+2.614267*(log(FC))^2+0.107821*(log(FC))^3
	10^5		3
pH	0	2	2
	2	4	13.6-10.6*pH+2.4364*pH^2
	4	6.2	155.5-76.36*pH+10.2481*pH^2
	6.2	7	-657.2+197.38*pH-12.9167*pH^2
	7	8	-427.8+142*pH-9.695*pH^2
	8	8.5	216-16*pH
	8.5	9	1415823*10(-1.1507*pH)
	9	10	50-32*(pH-9)
	10	12	633-106.5*pH+4.5*pH^2
	12	14	3
BOD_5 (mg/L)	0	30	100.9571-10.7121*BOD5+0.49544*(BOD5)^2-0.011167*(BOD5)^3+0.0001*(BOD5)^4
	30		2
Nitrates (mg/L)	0	10	-5.1*(N)+100.17
	10	60	-22.853*ln(N)+101.18
	60	90	-10000000000*(N)$^{-5.1161}$
	90		1
Total Phosphorus (mg/L)	0	10	79.7*(PO_4+0.821)$^{-1.15}$
	10		5
Temperature difference			93 (in general, the variation of temperature is close to 0)

Table 1. Representative NSF quality equations adaptable from CETESB (Paca, 2015; Silva, 2016) (cont.)

Parameter	Minimum Limit	Maximum Limit	q_i Equation
Turbidity (NTU)	0 150	150	100.17-2.67*Turb+0.03775*Turb2 5
Total Solids (mg/L)	0 500	500	133.17*e$^{(-0.0027*ST)}$-53.17*e$^{(-0.0141*ST)}$+[(-6.2*e$^{(-0.00462*ST)}$*sen(0.0146*ST)] 32
Dissolved oxygen (%)	0 50 85 100 140	50 85 100 140	3+0.34*(%sat)+0.008095*(%sat)2+1.35252*0.00001*(%sat)3 3-1.166*(%sat)+0.058*(%sat)2-3.803435*0.0001*(%sat)3 3+3.7745*(%sat)0.704889 3+2.9*(%sat)-0.02496*(%sat)2+5.60919*0.00001*(%sat)3 3+47

For the w_i term in equation 1, the weight for each parameter is defined based on its importance for the final water quality status, and the sum of factors is equal to one. The Brazillian National Water Agency, the Environmental Company of São Paulo (CETESB) and many other authors, all use the same weight distribution, as represented in Table 2 (Paca, 2015; Gloria et al., 2017; Neto, 2021).

Table 2. Weight of water quality parameters in the calculation of the WQI.

Parameter	Weight (w_i)
Dissolved oxygen	0.17
Fecal coliforms	0.15
pH	0.12
BOD_5	0.10
Nitrates	0.10
Total Phosphorus	0.10
Temperature	0.10
Turbidity	0.08
Total Solids	0.08

Finally, with all sub-indexes (q_i) and weights(w_i) determined, it is possible to obtain the final Water Quality Index, from equation 1. The results can range from 0 to 100, and differentiated into five water quality categories (Table 3) (Lobo et al., 2012; Tyagi et al., 2013; Noori et al., 2019).

Table 3. Water Quality Index categories classification.

Category	Water quality Index
Excellent	91-100
Good	71-90
Regular	51-70
Bad	26-50
Very bad	0-25

3.4 NATIONAL SANITATION FOUNDATION WATER QUALITY INDEX PARAMETERS

Most of the parameters used in the WQI determination are indicators of contamination by domestic sewage release (Agência Nacional de Águas, 2017) and they will be discussed below.

3.4.1 pH

The pH represents the hydrogen ion activity in water, which results from the dissociation of water molecule and other contaminants such as sulfuric acid, hydrochloric acid, nitric acid and more, prevenient from industrial wastewater (Paca, 2015). Exaggerate acidity can be a contamination indicative, while excess of salts solubility can make water inappropriate due to its elevate hardness (Baird & Michael, 2014).

3.4.2 Temperature

The importance of temperature as a water quality parameter is related to its variation. Temperature elevation increases chemical and biological reactions indexes, decrease gases solubility and increase their transfer rate, what can generate bad smells in case of bad smelling gases release (Von Sperling, 2007).

Temperature also determines many chemical, biological and physical processes that happens in an aquatic system, such as organic matter degradation and organism's metabolism (Silva, 2016).

3.4.3 Dissolved Oxygen (DO)

Dissolved Oxygen is essential for aerobic organisms. During organic matter stabilization, bacteria consume oxygen on their respiratory process, which can decrease its concentration in the water environment. Depending on the severity of this fact, many aquatic animals can die (Von Sperling, 2007).

Basically, Dissolved Oxygen is a pollution indicator caused by organic matter. Thus, a non-polluted water must be saturated with oxygen. On the other hand, low DO rates might indicate intense bacteria activity decomposing organic matter thrown into water (Mota, 2012).

3.4.4 Turbidity

Turbidity represents the decrease of intensity of a light beam that passes thru water. It happens due the light absorption and dissolution generated by suspended solids (sand, seaweed, debris, etc.). Natural activities, like erosion on the riverbanks on rainy stations, and human activities, like wastewater disposal, are the main reasons for turbidity increase (Lima, 2018).

The main consequence of the turbidity increase in a waterbody is the reduction of the penetration of sunlight and consequently decrease on photosynthesis indexes, harming the dissolved oxygen concentration on the river environment (Branco, 1986).

3.4.5 Biochemical Oxygen Demand (BOD_5)

The expression "BOD_5" indicates the amount of oxygen that bacteria and other microorganisms consume in a water sample, during a five-day period, to stabilize organic matter. It indicates how much dissolved oxygen (mg/L) is needed for the biological degradation of the organic constituents (Costa & Ferreira, 2015).

It is one of the most important parameters to show the degree of pollution in a waterbody, as it indicates the potential dissolved oxygen consumption and consequently the organic matter content (Von Sperling, 2007).

3.4.6 Total Phosphorus

Total Phosphorus analysis provides the eutrophication level in aquatic ecosystems (Borges et al., 2003), and it can be added from natural and artificial sources to a waterbody. Among natural sources, rocks from the drainage basin provides the basic supply of phosphates for aquatic ecosystems. Among artificial sources, small amounts thru water treatment, and bigger amounts thru water drainage in farming areas (present in fertilizers) and bad disposal of wastewaters (very present on dish soaps and many other commercial cleaning preparations), are the ones that happen the most. (Dellagiustina, 2000; Costa & Ferreira, 2015).

3.4.7 Nitrates

High nitrogen concentrations in a waterbody can also increase eutrophication levels. As a crucial element for the seaweed growth, it can promote an exaggerated development of these organisms, causing problems with smell and flavor, decrease of dissolved oxygen and the death of aquatic organisms. The bad disposal of domestic and industrial wastewater is the main source of nitrogen in a waterbody (Von Sperling, 2007).

In aquatic systems, nitrogen can be found under many ways: nitrite, nitrate, ammonium ion, nitrogen, nitrous and organic oxide. The most oxidized and stable form is the nitrate ion (NO_3^-). Nitrates naturally occurs in trace quantities in surface water, but it can significantly increase when nitrates sources are loaded, prevenient from fertilizers, farming activities or wastewater (APHA, 1998; Dellagiustina, 2000). In excessive amounts, it contributes to an infant's illness known as Methemoglobinemia (APHA, 1998).

3.4.8 Fecal Coliforms

Bacteria from the coliform group are considered the main indicator of fecal contamination. These organisms indicate when the water is contaminated with human or other animal's feces, and, consequently, it's potential to transmit diseases (Von Sperling, 2007).

Its high concentration indicates the possibility of existence of pathogenic microorganisms, responsible for the spread of hydric diseases, such as cholera, bacillary dysentery, and typhoid fever (Agência Nacional de Águas, 2017).

3.4.9 Total Solids

Total solids are all substances that remain after the processes of drying, evaporation or calcination of the water, after a certain time and temperature. Water with high total solids concentration is not convenient for any use (Mota, 2012).

3.5 SEASONAL FACTORS INFLUENCE ON WATER QUALITY

Recent studies have noted that some seasonal factors play an important role in relation to water quality (Carroll, 2013). Pluviosity, temperature and riparian forest growth are discussed next.

3.5.1 Pluviosity

Many authors have related the conclusion of their water quality index results to rainfall indexes. Some of them believe that more runoff in rainy seasons increase the quantity of eroded material and cause more serious water pollution (Jiang et al., 2019). Paca et al. (2019) concluded that in the dry season, water quality was enough to be submitted to a treatment for the production of drinking water, and, on the other hand, was unsuitable to any treatment in the rainy season. Paca (2015) appointed precipitation as the main degradation factor in the water quality assessment of the Kuanza, Bengo and Dande rivers, in Angola, especially because the higher concentrations of organic matter and fecal coliforms.

However, there is a general rule that when sampling within 24h after a rainfall event, results show poor water quality due to the short-term increase in the pollutant concentration cause by surface runoff. And, when sampling is performed 48h after a rainfall event, the concentration of pollutants would dilute due to the high flow rates, and water quality would be better (Carroll et al., 2013; Jiang et al., 2019).

On the other hand, water quality can also be affected by drought periods. Zwolsman & van Vliet (2008) analyzed the impact of summer droughts on the water quality of the Meuse River, and based on their results, concluded a general deterioration on water quality, mainly caused by favorable conditions for the development of algae blooms and a reduction of the dilution capacity of point source effluents.

3.5.2 Temperature

External temperature is naturally related to groundwater temperatures, due to the transfer of heat by radiation and conduction of atmosphere and soil (Silva, 2016). High water temperatures increase phytoplankton and the dissolution of many chemical compounds, and decrease the dissolved oxygen indexes (Lima, 2018).

3.5.3 Riparian forest growth

The riparian forest growth is considered a seasonal factor because it is more intense during the spring. Souza (2013), analyzing the influence of the riparian forest on the Jacarecica River water quality, concluded that without any doubts, the riparian forest has an important role in sediments retention (total solids), especially on rainfall runoffs. The increase on organic matter can influence on worst results for parameters like BOD_5, Dissolved Oxygen, Total Solids and others.

3.6 LAND USE INFLUENCE ON WATER QUALITY

Land use has direct influence on water quality, as it results in inputs of different species to surface water (Carroll, 2013). Runoff from different types of land use may be enriched with different kinds of contaminants. It is expected for example, that close to high developed urban areas, runoffs may be enriched with rubber fragments, heavy metals, sodium and sulfate, and runoffs from agricultural lands may carry nutrients and sediments to surface water (Tong & Chen, 2002).

Tong & Chen (2002) and Fisher et al. (2002) concluded that runoffs from agricultural and impervious urban lands had much more nitrogen, phosphorus and fecal coliforms, especially after rainstorms.

3.7 FERVENÇA RIVER

The drainage basin of the Fervença River is located in the district of Bragança, northeast Portugal. The source of the river is located at 1300 meters of altitude, in the Nogueira Mountain Range, and the river flows to its mouth at 400 meters of altitude, the Sabor River. The river crosses the district capital Bragança, a city with 35 341 habitants (Instituto Nacional de Estatística, 2011). This region, called “Trás-os-Montes”, has a temperate climate, with influences from the Continent and the Atlantic Ocean. The summer is typically hot and dry, and it is in the winter the rainiest months (Fernandes, 2002).

The Fervença River basin is 202.9 km^2 large and is calculated that half of it is available for agriculture, with cereals, orchards (olives, vines, chestnut) and irrigation (potatoes, vegetables, corn, hop, strawberry) as the most common productions. The city of Bragança urban areas represents 3.2% of the river basin total area, 20.3% is occupied by groove and 20.1% by dense bush (Fernandes, 2002).

In addition to the economic importance, the Fervença River has a social impact in the city of Bragança as hundreds of people circulate nearby. The river crosses the Instituto Politécnico de Bragança (local university) and the city center area with several local stores, parks and squares. It is also the final destination of the treated effluent from the Bragança's wastewater treatment plant (WWTP).

During 2006 and 2007, Teixeira et al. (2009) evaluated the Fervença River water quality through chemical, physical and microbiological parameters, in five different sampling points along the river, in the Bragança urban area. An increase in the dissolved salts and nutrients, especially phosphates and nitrates, could be observed as the river flows inside the city.

From January to December of 2012, Rodrigues et al. (2013) collected monthly samples, in nine different spots, to evaluate the Fervença River water quality. By the obtained results, it was concluded that the Fervença River presented significant levels of disturbance that decisively affects the quality and the ecological integrity of this aquatic ecosystem, and the need to establish different measures aimed at improving the water quality was shown.

4 METHODOLOGY

This study was carried out at the Chemical Process Laboratory (D-002), at the Instituto Politécnico de Bragança, from January 2022 to June 2022.

The samples were collected from the Fervença River once a month, during six months, at five different river points, so the results could be compared over time and spatially.

4.1 STUDY AREA

The five sampling places were strategically chosen to check the influence of Bragança city and some agricultural activities in the Fervença river water quality. The first place (1) is in the rural part and before the most populated area, and the last place (5) is located after the river crosses the Bragança center area and the discharge point of the WWTP, involving the whole city area from one side to the other.

As middle points, point 2 is already inside the city and right next to one of the biggest Bragança's avenues, the Avenue Sá Carneiro, and point 3 is inside the Campus of Instituto Politécnico de Bragança. Point 4 is located in the center area, close to cafeterias, stores and a large crowd of people.

The sampling points are represented in the Figure 7, numerically ordered from 1 to 5, following the river's flow direction.

Figure 7. Fervença River sampling locations (Google Maps).

The points and their respective Cartesian coordinates are presented in Table 4.

Table 4. Sampling points along the Fervença River, Cartesian coordinates (Google Maps).

Point	Cartesian Coordinates
Point 1	41º47’37.6’’N, 6º47’15.3’’W
Point 2	41º47’54.9’’N, 6º46’16.7”W
Point 3	41º47’54.6’’N, 6º45’54.0’’W
Point 4	41º48’17.0’’N, 6º45’26.6’’W
Point 5	41º48’04.5’’N, 6º44’38.4’’W

Point 1: following the river’s flow direction, point 1 is located before the most populated area of the city, passing through different local farmer’s lands (Figure 8).

Figure 8. Point 1 sampling place (no polluted area).

Point 2: located right next to a gas station and to one of the Bragança’s biggest avenues, the avenue Sá Carneiro (Figure 9).

Figure 9. Point 2 sampling place.

Point 3: located inside the Campus of Instituto Politécnico de Bragança, where hundreds of students and employees circulate nearby (Figure 10).

Figure 10. Point 3 sampling place.

Point 4: located in the city's center area, close cafeterias, local businesses and a large movement of people (Figure 11).

Figure 11. Point 4 sampling place.

Point 5: the last sampling place following the river's flow direction, located right after (around 200 m) Bragança's WWTP discharge point, where the treated effluents are thrown back to the river (Figure 12).

Figure 12. Point 5 sampling place.

4.2 SAMPLING CAMPAIGNS

The chosen strategy was to the collect the samples once a month, during six months, from January 2022 to June 2022, so the results could be compared over time and at different places. Each sampling campaign was made in the same day, with an average time of 1h – 1h 30 min to collect the samples in all five places. The samples were collected in pre-sterilized glass bottles (for microbiological analysis) and plastic bottles (for chemical analysis), and were transported in a thermal box.

The day and time of each sampling campaign is shown in Table 5.

Table 5. Date of each sampling campaign.

Sampling Campaign	Date	Hour
Date 1	11/01/2022	09:00 – 10:20
Date 2	16/02/2022	09:10 – 10:20
Date 3	15/03/2022	09:00 – 10:15
Date 4	20/04/2022	09:00 – 10:10
Date 5	24/05/2022	09:15 – 10:30
Date 6	22/06/2022	09:10 – 10:15

4.3 ANALYTICAL METHODS

The samples were analyzed, all in triplicate, following the analytical methods described in the manual *Standard Methods for the Examination of Water & Wastewater* (APHA, 1998).

4.3.1 pH

The pH was measured with a pH *meter* device HANNA model Edge, which provides instant results (4500 H^+ B Method). The instrument was first calibrated with pH 4, 7 and 10 buffers.

4.3.2 Temperature

Temperature was measured in field immediately following sample collection with a temperature-measuring device, Winys TP – 101 (2550 B Method).

4.3.3 Dissolved Oxygen

The InoLab WTW Oxi Level 2 pre-calibrated measuring instrument was utilized for the Dissolved Oxygen (4500-O G Method). The values were obtained in mg/L and then turned to percentage (%) of DO saturation for the calculation of the NSFWQI, following the procedure described in the *Standard Operating Procedure Lakes-4 for Dissolved Oxygen* (Massachusetts Water Watch Patnership), where:

$$\frac{DO\ measurement}{Max.DO\ concentration\ at\ measured\ Temperature} x\ 100 = \%DO\ saturation \qquad \text{(equation 2)}$$

4.3.4 Turbidity

The turbidity was measured with the VWR Portable Turbiditymeter TIR 200 device, already pre-calibrated (2130 B Method).

4.3.5 BOD_5

The Biochemical Oxygen Demand was defined using the WTW OxiTop System, via plezoresistive electronic pressure sensors (5210-D Method), in a 5-day test. Detailed description of this method of analysis is presented in Annex 1.

4.3.6 Total Phosphorus

The Acid Ascorbic method (4500-P E Method) was used to determine Total Phosphorus, using a UV/VIS Spectrophotometer Jasco V-530 screening at a wavelength of 880 nm (Annex 1).

4.3.7 Nitrates

For Nitrates, the Ultraviolet Spectrophotometric screening method was used (4500-NO_3^- Method), at a wavelength of 220nm (Annex 1).

4.3.8 Fecal Coliforms

In the quantification of fecal coliforms bacteria, the membrane filtration method with m-FC agar base and incubation at 44ºC was used (ISO 9308) (Annex 1).

4.3.9 Total Solids

For the determination of Total Solids, the 2540 B Method was followed, with total solids dried at 103-105ºC (Annex 1).

4.4 CALCULATION

For the calculation and definition of the final NSFWQI, the mathematic procedure described in the item 3.3 of the present work was followed, with the q_i terms calculated thought the equations on Table 1. For the w_i terms, the values defined on Table 2 were used.

5 RESULTS AND DISCUSSION

5.1 SAMPLING CAMPAIGNS

The results from the water analysis campaigns collected in the five sampling places are shown in Tables 6-11, organized by collection date.

5.1.1 First campaign

In Table 6 are presented the results from the analysis performed in the first sampling campaign.

Table 6. Parameters analysis results for the first sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	7.84	8.37	8.25	8.26	8.12
DO (% sat)	93.7	95.0	81.1	79.7	76.9
Turbidity (NTU)	0.61	4.80	0.69	0.87	14.67
Temperature (ºC)	8.6	12.4	9.8	10.1	10.5
Total Solids (mg/L)	144	242	144	134	173
FC (CFU/100 mL)	1,117	1,707	667	7,067	20,367
BOD_5 (mg/L)	2.00	3.93	1.45	3.00	26.2
Nitrates (mg/L)	0.70	3.32	1.00	1.30	1.54
Total P (mg/L)	0.07	0.11	0.11	0.09	1.73

This sampling campaign was performed on a sunny day, with a registered temperature of 8 ºC. The river flow was low due to the lack of rain in the previous days.

According to the attachment I in the Decree-Law n.^{0} 236/98 (Ministério do Meio Ambiente, 1998), and considering only the studied parameters, points 1 to 3 would fit in the class A2 (physical, chemical and disinfection treatment) for drinking water production, as the values of pH, dissolved oxygen, temperature, fecal coliforms, BOD_5, nitrates and total phosphorus are all within the accepted range. Point 4 could be considered a drinking water production option only after physical, chemical, disinfection and refining treatments (class A3). Point 5 would not be recommended for drinking water production due to the high values of fecal coliforms and BOD_5.

For turbidity and total solids, any limit was fixed in the attachment I of the Decree-Law n.^{0} 236/98.

5.1.2 Second campaign

In Table 7 are presented the results from the analysis performed in the second sampling campaign.

Table 7. Parameters analysis results for the second sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	7.73	8.08	7.97	8.19	8.20
DO (% sat)	80.7	81.9	81.7	79.7	81.5
Turbidity (NTU)	0.54	0.43	0.39	0.76	5.46
Temperature (ºC)	8.0	9.1	8.7	8.7	10.2
Total Solids (mg/L)	98	194	229	179	192
FC (CFU/100 mL)	1,370	89	370	263	1,763
BOD_5 (mg/L)	0.20	4.93	1.33	3.87	12.13
Nitrates (mg/L)	0.43	0.74	0.60	1.03	1.46
Total P (mg/L)	0.01	0.03	0.03	0.05	0.58

This sampling campaign was performed on a cloudy day, with a registered temperature of 10 ºC. Low pluviometry indexes were recorded in the previous days, which did not affect the low flow of the river.

Points 1 to 4 were considered acceptable for drinking water production after class A2 treatment in the attachment I of the Decree-Law n.^{0} 236/98 (considering only analyzed parameters). With a high BOD_5 measured value, Point 5 was not an option for drinking water production after any treatment class.

5.1.3 Third campaign

The third sampling campaign was performed under very unusual weather conditions. On March 15th, 2022, a dust storm coming from the Sahara desert hit Portugal. No rain was recorded that day, which could help carry detritus to the Fervença River. The registered temperature was 12 ºC during sampling hours. Also, this campaign marks the last one held during wintertime. The results from the analysis performed in the third sampling campaign are presented in Table 8.

Table 8. Parameters analysis results for the third sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	7.17	7.32	7.37	7.31	7.50
DO (% sat)	79.1	78.1	80.4	77.4	79.0
Turbidity (NTU)	1.13	1.19	1.43	2.31	39.53
Temperature (ºC)	9.6	10.1	10.3	10.2	11.9
Total Solids (mg/L)	124	137	148	159	274
FC (CFU/100 mL)	1,243	1,820	2,280	1,340	87,000
BOD_5 (mg/L)	0.00	0.27	0.00	0.00	30.83
Nitrates (mg/L)	0.57	0.82	0.88	1.13	1.61
Total P (mg/L)	0.02	0.03	0.02	0.03	0.13

Again, as indicated in the second sampling campaign, water from points 1 to 4 could be used as a human drinking source after class A2 treatment, as pointed in the attachment I of the Decree-Law n.^{0} 236/98 (considering only analyzed parameters). All measured parameters, except for fecal coliforms, are within the limits even for a less severe treatment (class A1). Point 5 shows much higher values of turbidity, fecal coliforms, BOD_5 and total solids compared to the past campaigns.

5.1.4 Fourth campaign

The fourth sampling campaign was made on a registered temperature of 13 ºC, but the previous days were hotter, with temperatures reaching up to 25 ºC and no rain. The river flow was low. The results from the analysis performed in the fourth sampling campaign are presented in Table 9.

Table 9. Parameters analysis results for the fourth sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	7.75	7.99	8.11	7.93	8.12
DO (% sat)	92.7	94.5	93.1	88.8	84.3
Turbidity (NTU)	1.35	1.49	1.14	1.41	158.33

Table 9. Parameters analysis results for the fourth sampling campaign (cont.)

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
Temperature (ºC)	11.3	12.3	12.3	13.4	14.8
Total Solids (mg/L)	285	219	239	229	696
FC (CFU/100 mL)	16,133	5,700	5,167	4,500	566,667
BOD_5 (mg/L)	0.00	1.20	0.63	2.33	128.33
Nitrates (mg/L)	0.54	0.75	0.88	1.16	1.95
Total P (mg/L)	0.04	0.03	0.07	0.09	1.32

In this campaign, it is possible to notice an increase in the measured values of total solids, temperature, total phosphorus and fecal coliforms of all points. Assessing the factors that may influence fecal coliforms indexes in the Pearl River Delta region in China, Hong et al. (2009) concluded that the increase of temperature and total solids can influence the number of fecal coliforms in water, as both phosphorus and fecal bacteria tend to be pounded by particles. Generally, total solids values in surface water is associated with external causes, such as receiving the runoff from drainage basin and re-suspension of sediments.

In addition, this campaign shows that water from points 1 to 4 could be used as a drinking water source only after class A3 treatment, as pointed in the attachment I of the Decree-Law n.^{0} 236/98 (considering only analyzed parameters). Water from point 5 couldn't be used as a drinking water source in any case, with some values (BOD_5) even exceeding the limits for wastewater discharge, shown in the attachment XVIII of the Decree-Law n.^{0} 236/98.

5.1.5 Fifth campaign

In Table 10 are presented the results from the analysis performed in the fifth sampling campaign.

Table 10. Parameters analysis results for the fifth sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	7.68	7.67	7.83	7.69	8.23
DO (% sat)	88.6	83.3	85.8	80.2	91.2
Turbidity (NTU)	2.07	0.95	1.13	3.53	10.40
Temperature (^{0}C)	13.6	14.8	14.4	16.6	17.5
Total Solids (mg/L)	155	190	189	212	337

Table 10. Parameters analysis results for the fifth sampling campaign (cont.)

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
FC (CFU/100 mL)	1,117	1,707	667	7,067	20,367
BOD_5 (mg/L)	0.00	1.00	0.67	0.67	17.53
Nitrates (mg/L)	0.54	1.16	1.31	1.49	2.24
Total P (mg/L)	0.05	0.06	0.08	0.19	1.38

Fifth campaign was made under a temperature of 14 ºC, and previous days reaching up to 25 ºC, with no rain recorded. The river flow was low. Made in the middle of the spring season, the river's riparian forest was well developed, which represents a physical barrel in the retention of sediments.

Following the limits described in the attachment I of the Decree-Law n.^{0} 236/98, and considering only the measured parameters, water from points 1, 2 and 3 could be used as a source for drinking water after treatment A2. Point 4 fits in the limits of treatment A3, and some parameters of point 5 (total phosphorus and fecal coliforms) exceed the limits for any treatment class, being undesirable for this purpose.

5.1.6 Sixth campaign

Sixth and last sampling campaign was made in the second day of summer season, under a temperature of 16 ºC, and the previous week with temperatures reaching up to 35 ºC. No rain was recorded in the previous days and the river flow was low. The results from the analysis performed in the sixth sampling campaign are presented in Table 11.

Table 11. Parameters analysis results for the sixth sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	7.77	7.74	8.09	8.19	7.61
DO (% sat)	66.4	64.1	68.2	68.0	65.3
Turbidity (NTU)	2.74	1.51	0.98	2.01	18.17
Temperature (ºC)	14.3	15.4	15.3	19.0	19.0
Total Solids (mg/L)	300	308	344	397	413
FC (CFU/100 mL)	79,000	330	513	140	86,000
BOD_5 (mg/L)	10.30	6.37	3.70	4.80	58.30
Nitrates (mg/L)	0.55	0.99	1.34	1.41	4.21
Total P (mg/L)	0.07	0.06	0.07	0.13	0.75

Following this sampling campaign results, it is possible to notice a reduction in the dissolved oxygen rates and an increase of BOD_5 values for all five points, comparing to the past five campaigns. This can represent a rising bacteria activity decomposing organic matter and an influence of increasing temperature.

Also, this campaign shows an unusual elevation in the values of fecal coliforms, BOD_5 and nitrates on point 1. Located in a rural area, this can be caused by the presence of animal's feces and an indicator of farming activities, sources of organic matter and nitrogen.

In the sixth campaign, considering only the measured parameters, points 1 and 5 couldn't be used as a drinking water source, point 2 only after a class A3 treatment, and points 3 and 4 after class A2 treatment, based on the attachment I of the Decree-Law n.^{0} 236/98. Again, like the fourth campaign, the values of BOD_5 at point 5 (located after the city's wastewater treatment plant) exceeded the limits for wastewater discharge, shown in the attachment XVIII of the Decree-Law n.^{0} 236/98.

5.2 WATER QUALITY INDEX

With the results obtained experimentally for each parameter (Tables 6-11), and the calculation procedure presented on item 2.3 of the present work, it was possible to obtain the NSFWQI for the five different sampling places, from January/2022 to June/2022 (Tables 12-17).

Table 12. Water Quality Index for first sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	10.8	9.9	10.1	10.1	10.3
DO	16.3	16.4	14.8	14.6	14.2
Turbidity	7.9	7.1	7.9	7.8	5.5
Temperature	9.3	9.3	9.3	9.3	9.3
Total Solids	6.4	5.5	6.5	6.5	6.2
FC	6.0	3.3	3.8	1.6	0.5
BOD_5	8.1	6.6	8.6	7.3	0.7
Nitrates	9.7	8.3	9.5	9.4	9.2
Total P	9.1	8.7	8.7	8.8	2.7
NSFWQI	**84**	**75**	**79**	**75**	**59**

Table 13. Water Quality Index for second sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	10.9	10.4	10.6	10.2	10.2
DO	14.8	14.9	14.9	14.6	14.9
Turbidity	7.9	7.9	7.9	7.9	6.9
Temperature	9.3	9.3	9.3	9.3	9.3
Total Solids	6.8	6.0	5.6	6.1	6.0
FC	2.8	6.2	4.2	4.7	2.5
BOD_5	9.9	5.9	8.8	6.6	2.6
Nitrates	9.8	9.6	9.7	9.5	9.3
Total P	9.8	9.6	9.6	9.3	5.4
NSFWQI	**82**	**80**	**81**	**78**	**67**

Table 14. Water Quality Index for third sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	11.0	11.1	11.1	11.1	11.0
DO	14.5	14.4	14.7	14.3	14.5
Turbidity	7.8	7.8	7.7	7.5	4.3
Temperature	9.3	9.3	9.3	9.3	9.3
Total Solids	6.6	6.5	6.4	6.3	5.1
FC	2.9	2.5	2.3	2.8	0.5
BOD_5	9.9	9.9	9.9	9.9	0.2
Nitrates	9.8	9.6	9.6	9.4	9.2
Total P	9.8	9.5	9.7	9.6	8.4
NSFWQI	**82**	**80**	**81**	**80**	**63**

Table 15. Water Quality Index for fourth sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	10.9	10.5	10.4	10.6	10.3
DO	16.1	16.3	16.2	15.7	15.0
Turbidity	7.7	7.7	7.8	7.7	0.4
Temperature	9.3	9.3	9.3	9.3	9.3
Total Solids	5.0	5.7	5.5	5.6	2.5
FC	1.0	1.6	1.6	1.7	0.4

Table 15. Water Quality Index for fourth sampling campaign (cont.)

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
BOD_5	9.9	8.9	9.4	7.8	0.2
Nitrates	9.7	9.6	9.6	9.4	9.0
Total P	9.4	9.5	9.1	8.9	3.3
NSFWQI	**79**	**79**	**79**	**77**	**50**

Table 16. Water Quality Index for fifth sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	10.9	10.9	10.8	10.9	10.1
DO	15.7	15.1	15.3	14.7	16.0
Turbidity	7.6	7.8	7.8	7.3	6.1
Temperature	9.3	9.3	9.3	9.3	9.3
Total Solids	6.4	6.0	6.0	5.8	4.4
FC	3.0	2.6	3.5	1.4	0.9
BOD_5	9.9	9.1	9.4	9.4	1.5
Nitrates	9.7	9.4	9.4	9.3	8.9
Total P	9.3	9.2	9.02	7.9	3.2
NSFWQI	**82**	**79**	**80**	**76**	**60**

Table 17. Water Quality Index for sixth sampling campaign.

Parameter	Point 1	Point 2	Point 3	Point 4	Point 5
pH	10.9	10.9	10.4	10.2	11.0
DO	11.9	11.3	12.3	12.3	11.7
Turbidity	7.5	7.7	7.8	7.6	5.1
Temperature	9.3	9.3	9.3	9.3	9.3
Total Solids	4.8	4.7	4.3	3.7	3.5
FC	0.5	4.4	3.8	5.5	0.5
BOD_5	3.2	5.0	6.8	6.0	0.2
Nitrates	9.7	9.5	9.3	9.3	7.9
Total P	9.1	9.2	9.2	8.4	4.8
NSFWQI	**67**	**72**	**73**	**72**	**54**

The final National Sanitation Foundation Water Quality Index, for each sampling point, of the campaigns made from January/2022 to June/2022, are presented in Table 18.

Table 18. Monthly water quality index for each sampling point.

Date	Point 1	Point 2	Point 3	Point 4	Point 5
JAN/2022	84	75	79	75	59
FEB/2022	82	80	81	78	67
MAR/2022	82	80	81	80	63
APR/2022	79	79	79	77	50
MAY/2022	82	79	80	76	60
JUNE/2022	67	72	73	72	54

For better comprehension and comparison of the results, the final values for the Water Quality Index for the five sampling places, from January to June, are shown in Figure 13.

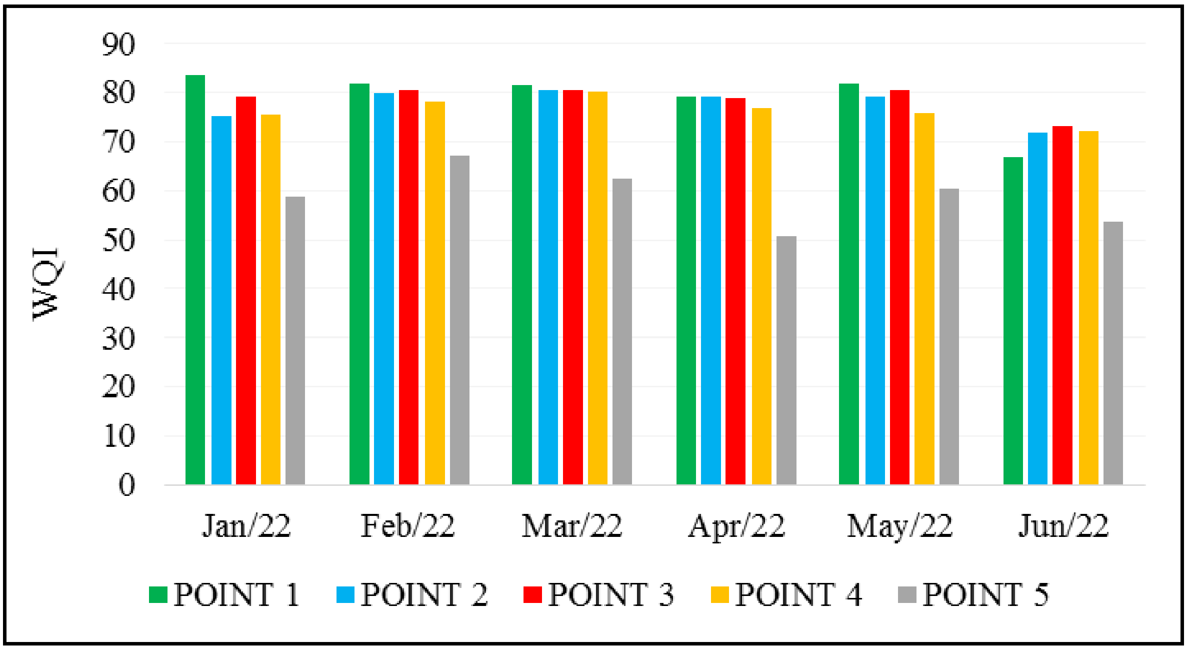

Figure 13. Comparison of water quality indexes for each month.

Finally, based on Table 3, it is possible to classify the water quality index results in different quality classes (Table 19).

Table 19. Quality class for each river location.

DATE	Point 1	Point 2	Point 3	Point 4	Point 5
JAN/2022	Good	Good	Good	Good	Regular
FEB/2022	Good	Good	Good	Good	Regular
MAR/2022	Good	Good	Good	Good	Regular
APR/2022	Good	Good	Good	Good	Bad
MAY/2022	Good	Good	Good	Good	Regular
JUNE/2022	Regular	Good	Good	Good	Regular

In general, comparing the results, with exception to the Point 5, the Fervença River showed good quality of water in the analyzed period. From January to May (2022), it is possible to see for points 1 to 4 very level water quality indexes, with low variations, both in terms of location and temporal evolution.

The month with the worst water quality index results for the majority of the analyzed river points was June (campaign 6), with notable lower scores for dissolved oxygen, BOD_5 and total solids (Table 17). This can be explained by a natural increase in water temperature, which compromises dissolved oxygen indexes, and by a possible increase in bacteria activity decomposing organic matter.

Unfortunately, the winter period was marked by a severe drought, which compromised the expected results in terms of temporal evolution. Figure 14, data provided by the Portuguese Institution of Sea and Atmosphere (IPMA), compares the total volume of rain in 2022 with the average from 2011 to 2021. It is possible see a huge difference in January and February, as the volume of rainfall in 2022 represents only 6,5% and 6,9% from what was expected, respectively. March, April, May and June also didn't have the expected amount of rainfall, with very discrepant values.

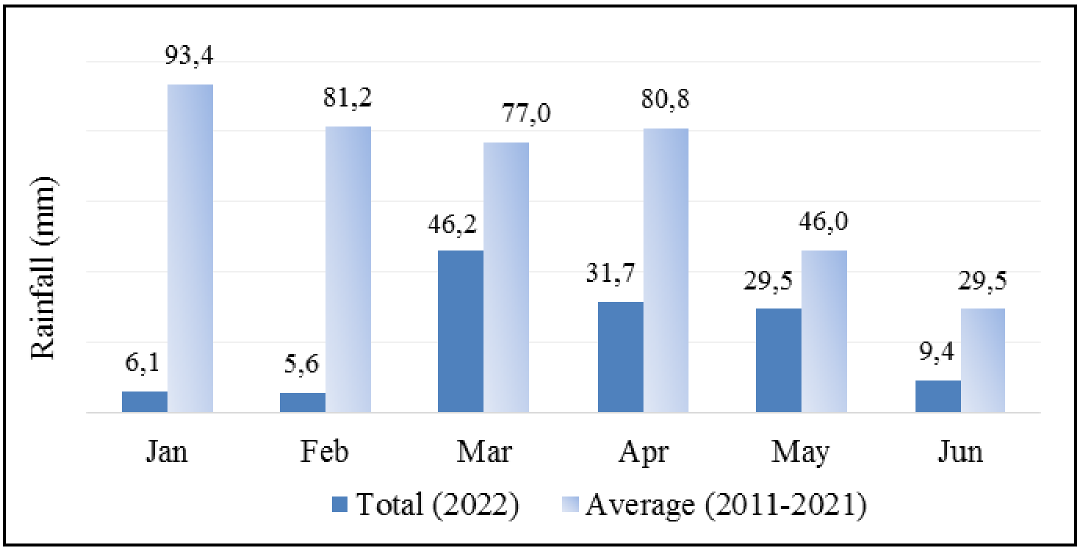

Figure 14. Rainfall of 2022 (total volume) compared to the average of 2011-2021 (IPMA).

As already mentioned, rainfall has direct relation with surface water quality and is one of the most influential seasonal factors. It is possible to conclude that having low rainfall rates during the whole analyzed period, especially in winter (which was expected to be the rainiest period), is the biggest reason for almost equality in the water quality index results, in terms of monthly evolution comparison. In general, it wasn't possible to detect any influence of rainfall on obtained results.

Another seasonal factor that couldn't be detected any influence in the water quality index results is the riparian forest growth. Expected to protect the river from sediment-laden runoffs on rainy periods, especially in spring, the results were also compromised by the lack of rain.

In regard to land use influence and location comparison, point 5 has the worst water quality index scores in every month. Located around just 200m after the Bragança's wastewater treatment plant, it is possible to confirm that it has total relation to the "Regular" and "Bad" water quality status obtained during the analyzed period. In addition, the Point 1 "Regular" status in the month of June, caused by lower indexes in parameters like fecal coliforms, dissolved oxygen and BOD_5, is possibly related to the sources of organic matter that the region has more tendency to have.

Also, it is possible to notice a slight superiority in Point 1 water quality indexes (with exception to the month of June) compared to point 4, for example. This was already expected, considering that Point 1 is located in the rural area, and Point 4 is located in Bragança's center area, with more potential to come into contact with cities pollutants.

In conclusion, according to the obtained results for water quality indexes, the city of Bragança had direct negative influence in the Fervença's River water quality status, in the first six months of 2022.

6 CONCLUSION AND FUTURE RESEARCH

6.1 CONCLUSION

The application of the Water Quality Index to assess the water quality of the Fervença River in Bragança, Portugal, was successful. The results could be compared over time, in different locations and with the Portuguese legislation that defines the requirements for different uses of water.

In general terms, the results showed “good” quality of water for points 1 to 4, based on the water quality classes. Considering the analyzed parameters (9), water for all six sampling campaigns from points 2, 3 and 4 could be used as a source for drinking water production after treatment class A2 or A3, defined in the Decree-Law n.^{0} 236/98. For point 1, water couldn’t be used for this purpose only in the last campaign, due to the high values of fecal coliforms and BOD_5.

For point 5, water quality index results showed “regular” to “bad” status in the quality of water. Located just hundreds meters after the Bragança wastewater treatment plant, this confirms the bad influence that it has on the Fervença River water quality. In two of the campaigns, some water quality parameters values even exceeded the limits for wastewater discharge, shown in the Decree-Law n.º 236/98.

The campaign conducted in June had the lowest overall status of all, which may have been influenced by the greater temperatures of this month. Temperature has direct relation to the dissolved oxygen, the parameter with the highest weight value in the WQI determination. Rainfall influence couldn’t be observed in the results due to the low pluviometry values registered in Bragança in the first six months of 2022, marked by an intense drought.

The present study confirmed the expected bad influence that the city of Bragança has on the Fervença River water quality, which is small from point 1 to 4 as the river flows into the city, but considerable after point 5, receiving discharges of treated effluents from the wastewater treatment plant.

6.2 FUTURE RESEARCH

As promoting clean water for all of society is one of the biggest challenges today, this study represents only a small portion of the actions that need to be taken. Monitoring surface water quality is a study that has to be done continuously, in order to monitor pollution caused agents and proceed with urgent actions. In addition, governmental actions to inform and educate society about water pollution and how everyone can do their part should be more present.

This study can lead to further researches, and following the conclusions obtained, these are some suggestions:

- Do longer studies;
- Cover more water quality parameters;
- Try to identify the biggest causes of fecal contamination in Bragança;
- Verify the influence of the Fervença River water in the Sabor River water quality;
- Promote this type of study to other universities along the country, so more rivers can be evaluated;

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ANNEXES

ANNEX 1: Description of analytics methods

BOD5

Materials:

- 15 glass bottles with the OxiTop measuring system;
- Magnetic bars;

Reagents:

- Sodium Hydroxide tablets;

Equipment:

- WTW TS 606/3 incubator;
- Magnetic boards;

Procedure:

- For each of the samples, three glass bottles were filled with the sample, with a volume defined by the manufacturer;
- 2 to 3 Sodium Hydroxide tablets were added in a recipient that is placed inside the bottle for the absorption of the released CO2;
- Magnetic bars were also placed in the bottles for agitation;
- Bottles were placed inside the incubator, on magnetic boards;
- After 5 days, the values were read.

Total Phosphorus

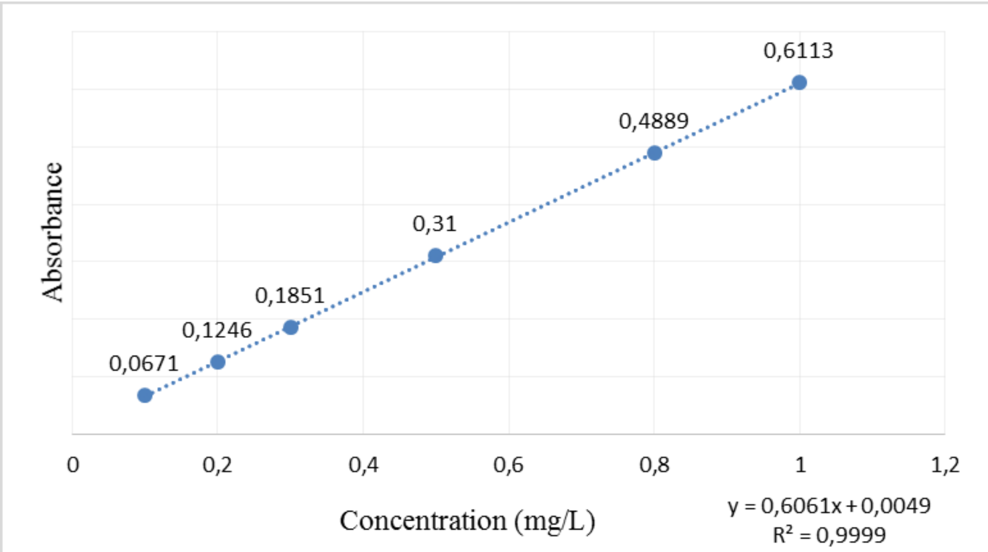
Reagents:

- Sulfuric Acid (H_2SO_4) 5N
- Ammonium molybdate solution (40 g/L)
- Potassium Antimonyl tartrate solution (2,74 g/L)
- Ascorbic Acid 0,1 M
- Combined Reagent

- Standard Phosphate Solution (0,0025 mg P/mL)

Preparation of calibration curve:

From a series of six standards within the phosphate range (0,1, 0,2, 0,3, 0,5, 0,8 and 1,0 mg P/L), calibration curves of absorbance x phosphate concentration were plotted using distilled water with the combined reagent.



Procedure:

- 50 mL of sample were pipetted into a 125 mL beaker
- 1 drop of phenolphthalein indicator was added, and when red colored 5N H_2SO_4 was added just to discharge the color.
- 8 mL of combined reagent were added.

After 10 minutes, absorbance of each sample was measured at 880 nm.

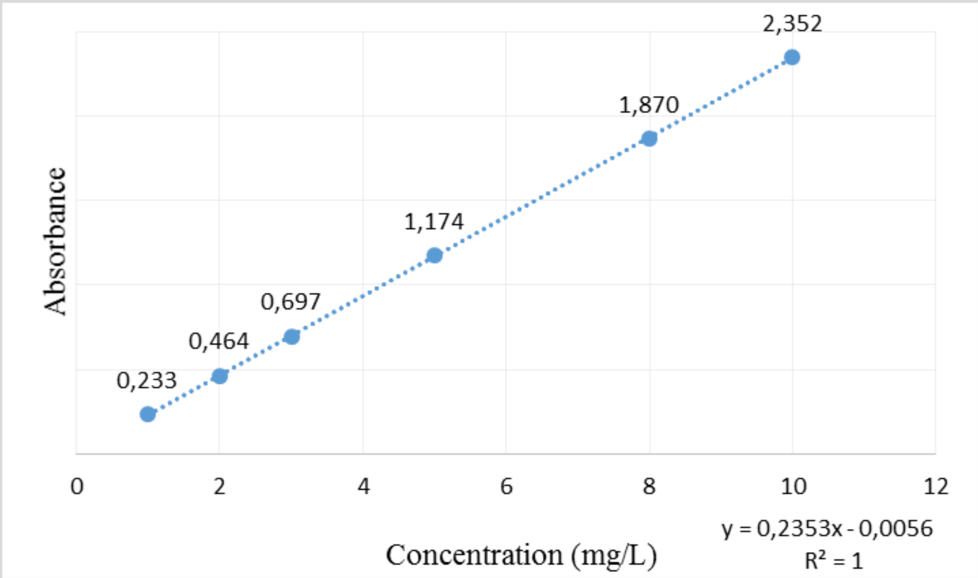
<u>Nitrates</u>

Reagents:

- HCl 1N;
- Stock Nitrate solution;

Preparation of calibration curve:

A series of standards (1,0, 2,0, 3,0, 5,0, 8,0 and 10,0 mg/L) covering the range 0 – 11 mg/L NO_3^- were prepared, treated the same way as samples. The absorbance x NO_3^- concentration curves were plotted.



Procedure:

- 1 mL of HCl 1N was added to 50 mL of sample;
- After 10 minutes, the absorbance was measured at 220 and 275 nm (the wavelength of 220 nm to obtain NO_3^- reading and 275 nm to determine interference due to organic matter).

To obtain the corrected sample absorbance, it is necessary to subtract two times the absorbance at 275nm from the reading at 220nm.

Fecal coliforms

Material:

- Petri plates;
- Filter membrane 47 mm;
- Vacuum filter;

Equipment:

- Laboratory oven at 44^0C

m-FC agar base preparation:

52 g of m-FC agar base were added in 1000 mL of distilled water and diluted with magnetic bars and heating. 10 mL of Rosolic Acid were added. This mixture was distributed in Petri plates and stored in low temperatures.

Preparation of dilutions:

In 100 mL Erlenmeyer flaks were added 99mL and 90mL volumes of distilled water and placed in autoclave for sterilization. In the 99mL volume flasks, 1 mL of sample was added to produce a 10^{-2} dilution and in the 90 mL volume flasks, 10 mL of sample were added to produce a 10^{-1} dilution. If a higher dilution was needed, a certain volume was removed from a pre-diluted sample.

Procedure:

- With the vacuum filter and the membrane, the 100 mL diluted or non-diluted sample was filtered;
- The membrane filter was placed in the petri plate and stored in the lab oven at 44^0C.
- This procedure was repeated in triplicate for three different dilutions, for each one of the samples.
- After 24 hours, the bacterial colonies on the plates were counted (only blue ones).

Calculation:

The following equation was used for determination of UFC/mL:

$$\frac{\in C}{V(n1 + n2 \ldots) * d} = UFC/mL$$

Where:

C = Counted colonies on each plate

V= Volume filtered (100mL)

n= number of plates

d = used dilution

<u>Total Solids</u>

Procedure:

- In a drying oven at 105ºC, evaporating dishes of 100mL were placed for 1 hour for a heat clean;
- Dishes were stored and cooled in a desiccator until needed, and the weigh was done right before use.
- The volume of 100 mL of sample were placed in the dishes, three for each sample.

- Samples were evaporated to dryness on a water bath, and the residue in the dishes was placed in the drying oven for 1 hour.
- After that, weight was measured again, and the total solids weight is defined as the subtraction of first weight from the final weight, as shown in the following equation.

$$\frac{(A - B)\ x\ 1000}{sample\ volume\ (mL)} = mg\ total\ solids/L$$

Where:

A = weight of the dish + dried residue, mg.

B = weight of the dish, mg.