Surface water is defined as any water body that is found flowing or standing on the earth surface, such as streams, rivers, and lakes. Surface water is the most productive ecosystem and receives the inputs of pollutants, because it is often located around highly populated and industrialized areas (Selvam et al. 2011; Mustapha et al. 2013). Consequently, surface waters are highly vulnerable to contamination due to the easy accessibility for wastewater disposals, since alluvial plain of rivers generally constitute the areas with a high population density, owing to the favourable living conditions, such as the availability of fertile lands, water for irrigation, industrial, or drinking purposes (Vega et al. 1998; Zhang et al. 2019). Over the last decades, the increase in population, as well as the occurrence of water stress areas, have constituted an important source of contamination for surface water and groundwater. The water quality could be indicated by the physical, chemical, and biological parameters (Liu et al. 2009; Barakat et al. 2016), which are mainly controlled by human activities and natural processes, and directly or indirectly influenced by the surface activities (Pratt and Chang 2012; Ai et al. 2015; Vasconcelos 2015).

The water quality is determined by numerous factors, including land use, hydrological conditions, and anthropogenic activities. The identification of the contamination sources in the Vizela river and the potential effects on water quality will promote efficient watershed management. The spatial and temporal variability of surface water was analysed through the physicochemical parameters, including: temperature, pH, Total Dissolved Solids, electrical conductivity, redox potential, and chloride, fluoride, bromide, nitrite, nitrate, sulfate, and phosphate content. The microbiological parameters *Escherichia coli* and *intestinal enterococci* were monitored over time. The obtained results show that the water located downstream the Vizela river is the most contaminated, although there has been an improvement in the water quality over time. The microbiological values are higher than the Portuguese parametric values defined for human consumption, and often also for recreational water activities. Continuous spatial and temporal water monitorization including the physicochemical and microbiological parameters is recommended as a preventive and monitoring measure.

**Keywords**: surface water; urban areas; industrial activity; contamination; Vizela; Portugal

**ABSTRACT**

The water quality is influenced by different factors, including land use, hydrological conditions, and anthropogenic activities. The identification of the contamination sources in the Vizela river and the potential effects on water quality will promote efficient watershed management. The spatial and temporal variability of surface water was analysed through the physicochemical parameters, including: temperature, pH, Total Dissolved Solids, electrical conductivity, redox potential, and chloride, fluoride, bromide, nitrite, nitrate, sulfate, and phosphate content. The microbiological parameters *Escherichia coli* and *intestinal enterococci* were monitored over time. The obtained results show that the water located downstream the Vizela river is the most contaminated, although there has been an improvement in the water quality over time. The microbiological values are higher than the Portuguese parametric values defined for human consumption, and often also for recreational water activities. Continuous spatial and temporal water monitorization including the physicochemical and microbiological parameters is recommended as a preventive and monitoring measure.
different climate scenarios (Motew et al. 2019). Moreover, the predictor of land use for the water quality parameter is dependent on multiple spatial and temporal scales. Land use in urban areas and water management require a multi-scale approach, especially in a watershed scale management.

Monitoring water bodies is not only a scientifically relevant task, but also legally imposed in several countries [Water Framework Directive (WFD) and the European Marine Strategy Framework Directive (European Commission 2000)]. The surface and groundwater contamination have been protected and replaced in the Union European Union (EU), mainly through the implementation of national and international policies (Directive 2000/60/EC; Directive 2006/118/EC). However, in the current scenario, climate change, water scarcity, population and urbanization represent challenges for water supply and availability systems, considering that until 2025, about half of the world’s population will live in the areas affected water stress in terms of its quantity and quality (WHO 2019).

An inadequate water management – quantity and quality of water resources – has a serious impact on sustainable development (Taiwo et al. 2010; Mustapha et al. 2013; Bon et al. 2020). Meeting the water quality goals to sustain the environmental quality on a large scale, the multi-state water system is a challenge (Fernandez and McGarvey 2019).

The industrial activities concentrated in the Valley of Ave river and the proliferation of energy production units have intensified the sources of contamination, mainly the industrial and domestic ones. In 1999, a regional program “Vale de Ave’s depollution system” was implemented, to restore the natural conditions of the Ave River. However, after the application of this project, the ecological status of the river did not go beyond the classification of “poor quality”, according to the Portuguese Environment Agency (Rong et al. 2019). The aim of this research was the spatial and temporal water monitorization, regarding the contamination sources located in the Vizela River, to improve the river water quality.

MATERIALS AND METHODS

The Ave river is located in the North of Portugal, in the Baixo Minho region (Fig. 1a), in the districts of Braga and Porto, being bordered to the north by the Cávado river watershed, to the east by the Douro river watershed and, to the south by the Leça river watershed (Silva 2004). The area is included in the Portuguese Hydrographic Region (RH2) – River Cávado, Ave and Leça (APA 2015).

The Ave river has an extension of about 100 km and a drainage watershed area of 1340 km². The headwaters are in Cabreira Mountain (1260 m above mean sea level, a.m.s.l.), and the estuary is in Vila do Conde, along the Atlantic coast. The most important tributaries are the Este and Vizela rivers at the right and left banks, respectively (Fig. 1b).

The Vizela river is about 33 km long, with the source in the mountains located NW of Fafe (altitude of 894 m) and confluences with the Ave river in Vila das Aves at an altitude of 92 m, with an altimetric variation of 802 m (Fig. 2a). The Vizela River watershed is an elongated basin, with an elongation ratio of 0.97, and a drainage density about 0.89, and is not conducive to the occurrence of floods (Monteiro 2015). The average flow in the Ave river was 2.96 m³/s in the dry season (September 2016) and 63.08 m³/s in the wet season (February 2017) (www.snirh.pt accessed in May 2020).

The geographical position and the proximity of the Atlantic Ocean will control the dominant meteorological conditions, but the influence is also exerted by the mountains in northwest Portugal. In the study area, the total annual rainfall is over 1400 m, with the highest temperature in June (19.9°C) and the lowest one in November (11.5°C; IPMA 2018).

The soils on the valley of the river Ave have a potential for agricultural development, with high population density and concentration of industrial activities (Bento-Gonçalves et al. 2011). The land use is dominated by artificial, agricultural, and forest and semi-natural areas (Fig. 2b). The urbanized zones are included in artificial areas, located predominantly around water courses, including the riverbanks. The textile industry and agriculture are the main activities in the area.

The water resources are used for manufacturing and irrigation of rural activities. Most of the river watershed area is used for agricultural and livestock activities (Ribeiro et al. 2016). In the Ave river watershed, there are water quality problems, mainly associated with the high industrial density, including the textile sector (largest industry), leather tanning, rubber manufacture, and plastic production. Some industrial effluents are still...
illegally discharged into the water courses without treatment (Rocha et al. 2013; Barbosa et al. 2018).

The discharge of pollutants in a water course in a specific location is a contamination source and could be classified as a local (identified) or diffuse (dispersed), mainly related to different human activities. The area is characterized by a disorganized land use, with different occupation types interleaved, and consequently with different water contamination sources, mainly associated with urban occupation, industrial and commercial activities, heterogeneous agricultural areas, with permanent crops and arable land (Antunes et al. 2019).

A total of ten water samples were collected and analyzed during two sampling campaigns, between July and October 2018. The two water sampling campaigns were carried out on the hydrological year of 2017/2018, which included a rainy season longer than usual followed by a dry period. Consequently, the samples collected in October 2018 will represent the dry period. Five water points are located in the Vizela river watershed (Fig. 1b) and are distributed from the Vizela river source (point VR1) to the confluence with the Ave river (point VR5). The surface water samples VR2, VR3 and VR4 are spatially distributed, between VR1 and VR5, along the Vizela River. The five sampling points promote a spatial and temporal water characterization as well as identification of potential contamination sources. The samples were collected about 20 cm below the water level. Temperature, pH, Eh, electrical conductivity (EC)
and total dissolved solids (TDS) were measured in situ with a multiparameter equipment (HANNA INSTRUMENTS, the HI 98129 and HI 98120 models). The samples were filtered through 0.45 μm pore size membrane filters, whereas alkalinity and anions (Cl\(^-\), F\(^-\), Br\(^-\), NO\(_2^-\), NO\(_3^-\), SO\(_4^{2-}\), PO\(_4^{3-}\) ) were determined by ion chromatography (Metrohm, model 761 Compact IC) at the University of Minho (Braga, Portugal). Total alkalinity was determined by automatic titration (Orion titrator, model 950) with 0.01M HCl (APHA et al. 1992).

Duplicate blanks and a laboratory water standard were analyzed for quality control. The microbiological parameters *Escherichia coli* and intestinal enterococci were determined between 2012–2017, in the water points VR3, VR4, and VR5 (Câmara Municipal Vizela 2018).

**RESULTS AND DISCUSSION**

The five-surface water are in the Vizela and Ave river with coordinates, altitude, and main land use types of the watershed presented in Table 1.

| Water points | Latitude     | Longitude     | Altitude (m) | Land use types          |
|--------------|--------------|---------------|--------------|-------------------------|
| VR1          | 41.5052437°  | - 8.1600960°  | 422          | Forest and semi-natural |
| VR2          | 41.4147665°  | - 8.2160362°  | 190          | Agricultural            |
| VR3          | 41.3731549°  | - 8.3074263°  | 132          | Artificial (urban)      |
| VR4          | 41.3624588°  | - 8.3734916°  | 94           | Artificial (urban and industrial) |
| VR5          | 41.3621109°  | - 8.4317627°  | 54           | Artificial (urban and industrial) |

The surface water physicochemical parameters and anion contents were represented by their descriptive statistics (Table 2). Water temperature is an indicator of water quality and will affect the dissolved oxygen and pH values. The highest temperature value was obtained in October (VR5 = 22.5 °C), while the lowest one in July 2018 (VR1 = 12.6 °C).

The pH value ranges between 6.9–7.9, without a significant temporal variation. Total dissolved solids (TDS) vary between 423 mg/L (point VR5) and 17 mg/L (point VR1), with a similar variation in electrical conductivity (EC; Fig. 3). The highest EC, TDS, Cl\(^-\), NO\(_2^-\), Br\(^-\), PO\(_4^{3-}\), SO\(_4^{2-}\), and alkalinity were obtained in October (Table 2; Fig. 3). The highest chloride water content was detected in October as well, although in the water points VR2 and VR1, no significant temporal variation was observed. The water sample VR5 has a maximum content of 160.1 mg/L Cl\(^-\), with a significant temporal variation (Fig. 3).

The nitrite water content is higher in October than in July 2018, except for the water point VR3. The water content shows a maximum of 4.5 mg/L

**Table 1.** Coordinates, altitude, and land use types around surface water sampling locations

**Table 2.** Descriptive analysis of the water quality parameters

| Parameter | July (2018) | October (2018) |
|-----------|-------------|----------------|
|           | Minimum     | Maximum        | Mean  | Std. Deviation | Minimum     | Maximum        | Mean  | Std. Deviation |
| Temp. (°C)|             |                |       |               |             |                |       |               |
| 12.6      | 18.2        | 14.1           | 2.18  | 18.2          | 22.5        | 19.8           | 1.56  | 1.56          |
| pH        | 6.9         | 7.8            | 7.3   | 0.32          | 7.0         | 7.9            | 7.3   | 0.37          |
| EC (µS/cm)| 35          | 420            | 315   | 168.66        | 38          | 844            | 437   | 325.96        |
| Eh        | 96          | 114            | 101   | 6.91          | 100         | 125            | 115   | 10.62         |
| TDS (mg/L)| 17          | 209            | 156   | 87.52         | 18          | 423            | 219   | 163.69        |
| BOD (mg/L)| 3.9         | 7.8            | 5.6   | 1.62          | 3.8         | 6.5            | 5.4   | 1.12          |
| F (mg/L)  | -           | 0.026          | -     | 0.012         | -           | 0.09           | 0.03  | 0.04          |
| Cl\(^-\)  | 4.0         | 64.5           | 48.1  | 28.82         | 4.4         | 160.1          | 74.7  | 63.54         |
| NO\(_2^-\) | 0.06        | 1.54           | 1.08  | 0.67          | 0.05        | 4.52           | 0.82  | 1.85          |
| NO\(_3^-\) | 1.46        | 10.97          | 8.66  | 3.64          | 0.73        | 10.28          | 9.67  | 4.05          |
| Br\(^-\)  | -           | 0.024          | -     | 0.011         | -           | 0.14           | 0.02  | 0.07          |
| PO\(_4^{3-}\) | -         | 0.15           | 0.10  | 0.07          | -           | 0.77           | 0.07  | 0.33          |
| SO\(_4^{2-}\) | 1.60        | 21.15          | 14.43 | 8.70          | 1.53        | 27.77          | 19.74 | 10.80         |
| Alkalinity*| 5.4         | 46.0           | 31.1  | 18.0          | 7.4         | 85.9           | 46.4  | 32.4          |

Std. Deviation – standard deviation; Temp. – Temperature; EC – electrical conductivity; TDS – total dissolved Solids; BOD – Biological Oxygen Demand; * mg/L CaCO\(_3\).
NO₂ (point VR5) and a minimum of 0.050 mg/L NO₂ (point VR1).

The microbiological parameters *Escherichia coli* and *intestinal enterococci* determined in the sampling points VR3, VR4 and VR5, show a variation in the minimum and maximum values recorded for the period between 2012 and 2017. The water points VR3 and VR4 tend to present the highest values, particularly between 2012-2014 (Table 3).

The water quality classes were evaluated in accordance with Portuguese Regulation of the water quality for human consumption and agricultural irrigation (Portuguese Decree 2007; 2009; 2012). The water from VR5, VR4, and VR3 are unsuitable for human consumption because the NO₂ content

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**Fig. 3.** Seasonal variation of water from the Vizela river
is above the Portuguese parametric value (0.5 mg/L) (Brás 2018). The highest SO$_4^{2-}$ water content is observed in October (points VR5 and VR2) and the lowest one in the water from VR1 (Fig. 3).

The microbiological parameters have a minimum value for the occurrence of *Escherichia coli* and *intestinal enterococci* below the parametric value for recreation activities (Portuguese Decree 2009, 2012). However, the three water samples show a maximum value above it, between 2012 and 2016, and must not be used for the recreation activities (Table 3).

**CONCLUSIONS**

The water quality was strongly impacted by land use, and the influence varies on time and space scales. The obtained results show that the water downstream the Vizela river is the most contaminated, although there has been an improvement in the water quality in the river watershed over time, mainly since the creation of the regional programme, in 1999. Otherwise, the upstream river water shows the lowest contents in most analyzed parameters, because it is located closest to the natural spring of the Vizela river. The water contamination increases with the distance from the Vizela River source. The microbiological parameters *Escherichia coli* and *intestinal enterococci* water contents are higher than the parametric Portuguese legislated values indicated for human consumption and are also above the parametric value defined for the recreation activities.

The monitorization of the physicochemical and microbiological parameters of water is strongly recommended in the Vizela river watershed, including a spatial and temporal water network. Further works with more data, including a temporal and spatial variability, are urgently needed to unravel the interactions of the human activities and water quality, which would improve the watershed water management.

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| Year | Min. (ufc/100mL) | Max. (ufc/100mL) | Min. (ufc/100mL) | Max. (ufc/100mL) | Min. (ufc/100mL) | Max. (ufc/100mL) |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2012 | 270             | 70000           | 200             | 14000           | 210             | 18000           |
| 2013 | 54              | 8800            | 54              | 8800            | 37              | 8100            |
| 2014 | 260             | 9200            | 200             | 5500            | 240             | 7000            |
| 2015 | 180             | 5000            | 210             | 7700            | 130             | 5300            |
| 2016 | 210             | 880             | 250             | 1600            | 130             | 930             |
| 2017 | 46              | 840             | 110             | 1700            | 46              | 760             |
| 2012 | 110             | 13000           | 150             | 14000           | 150             | 8700            |
| 2013 | 25              | 4000            | 25              | 4000            | 24              | 3100            |
| 2014 | 37              | 7900            | 54              | 3500            | 220             | 3700            |
| 2015 | 43              | 2400            | 72              | 4800            | 80              | 3600            |
| 2016 | 55              | 940             | 150             | 940             | 46              | 820             |
| 2017 | 51              | 410             | 79              | 590             | 46              | 560             |

Min. – minimum; Max. – Maximum. The values higher than the parametric value for *E. coli* = 1800 ufc/100 mL and *intestinal enterococci* = 660 ufc/100 mL (Portuguese Decree 2009, 2012) are in bold.
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