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# Post-wildfires effects on physicochemical properties of surface water: the case study of Zêzere watershed (Portugal)

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#### ABSTRACT

In Portugal, wildfires are frequent and sometimes catastrophic and responsible for high damages and human losses. They have been especially intense in the Center Region of Portugal, where the Zêzere watershed is located. This research presents an analysis of the temporal and spatial occurrence of these events within the watershed. It was observed that the extent of the burned areas has a high annual variation and is not directly related to the number of reported occurrences. However, considering these factors and the high incidence of these events in some delimited sectors, environmental stress is observed, especially on the surface water quality. Water quality deterioration in the main water bodies is particularly relevant within the areas where drinking water reservoirs are located. The water quality parameters (WQPs) collected by the water quality monitoring stations (WQSs) located in these sectors (data from SNIRH) were cross-referenced with the burned areas recorded annually. Variations in the physicochemical properties of the surface water were analyzed, depending on the occurrence of wildfires and their corresponding burned areas. The increase of certain WQP downstream of watercourses that intersect sub-basins with burned areas also demonstrates the straight relation between wildfires and an increasing risk for water quality.

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# 1. Introduction

Wildfires cause several environmental disturbances, with relevant impact on air [1] and water quality [2]. Wildfires induce water quality degradation during the first precipitation and in the consequent runoff, which transports the elements and compounds derived from burned material deposited on the soil's surface toward water bodies [3–8].

The combustion of forest material results in the emission of dioxins and ashes into the atmosphere, which are later deposited in soil, water, and vegetation. These pollutants are mostly deposited on the burned soil surface, which may reach high levels of dioxins [9].

Fire has several effects on the soil, as illustrated by Ferreira et al. [10]: direct effects due to the action of heat on organic components (mineralization of organic matter) and indirect effects due to the disappearance of ground cover and foliage protection (susceptibility of soil to erosion and changes in the hydrological regime). The authors state that these physical processes (soil erosion) are directly related to the change of soil structure and have a relevant role in the export of nutrients, thus causing impacts downstream of the burned areas. Among the various forms of water circulation in the burned slopes, surface runoff must be highlighted [11], through the transport of soil sediments and ash deposited on the soil's surface. When the presence of matter in the form of particles in the water is very high, be it scattered or from flotation, a rise in turbidity is observed [12].

The transport of the elements present on the soil's surface occurs through the runoff water coming from precipitation in the slopes [11]. This rain water has a good capacity for transporting materials and is considered one of the major transporting nutrients, sediments, solutes, and other particles into the watercourses [6,13,14-17].

According to Smith et al. [18], the pollutants are eroded and washed into streams by overland flow moving downslope in small channels (called rills) or in the unconcentrated flow. However, the largest water quality impacts result from high magnitude events, such as localized flash floods, large floods, and debris flows [17], these events being one of the consequences of the wildfires due to an increase of runoff in the burned areas [19–22].

Landsburg and Tiedemann [12] report that the factors with greatest impact on reducing the quality of water intended for human consumption are as follows: the turbidity, the content of sediments in suspension,

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the increase of nutrients in runoff, and increased water temperature. They state that the chemical constituents that cause greater concern for watercourse susceptibility are nitrates and nitrites, but there may be additional changes by modifying other parameters, such as the pH variation, sulfate concentration, chloride, iron, and total dissolved solids, among other components.

The elevated nitrate concentrations can persist for up to 10 years after the fire [23], but the nitrate concentrations in previously burned watersheds were lower than in their unburned counterparts, a fact observed by Riggan et al. [24] in the experimental watersheds in the San Dimas Experimental Forest in the Angeles National Forest, California.

In wildfires, the high production of polycyclic aromatic hydrocarbons (PAHs) caused by the natural vegetation burning process is also important. These compounds cause major environmental concerns because they can be mutagenic, carcinogenic, and teratogenic [3,25–29]. PAHs are produced by the incomplete combustion of organic matter [30]. These chemical compounds are emitted during wildfire activity, both in the form of gases and particles, and vary with the type of fire and combustion process. The formation of these compounds is maximized at combustion temperatures between 500 and 800°C [9].

Wildfires are responsible for major land cover changes (LUCCs) in Portugal, due to highest fire incidence in some regions, especially the Center and North of the country [31]. In mainland Portugal, the Mediterranean climate instigates the occurrence of wildfires, as the country has a spring rainy season favorable for vegetation development, followed by a very warm period favorable for triggering and developing fires [32].

Thus, the wildfires in Portugal are considered a phenomenon of the greatest environmental impact, contributing to an increase of the hydrological and erosion processes [33] and their implications on water quality. These implications are the result of the connectivity between the processes that occur in the slopes with burned areas and watercourses [10].

In Portugal, wildfires are responsible for several environmental problems, namely concerning watercourses pollution [34,35]. For example, Meneses and Cortez [8] assessed the effect of a wildfire on the physicochemical properties of the water of São Domingos stream (Western Region of Portugal) and noted an increase in the concentration of certain elements downstream of the burned area (e.g. Ca and Mg), which is higher after the first rains that generate runoff.

This research begins with the description of certain implications of wildfires on water quality and the high incidence of these events in some areas of the Portuguese territory, as the understanding of these consequences along watersheds, namely within important reservoirs integrating the drinking water supply, is a very relevant issue. Therefore, the main goal of this research is to analyze the temporal and spatial occurrence of wildfires in the Zêzere watershed to identify the effects of these events on the physicochemical properties of the surface water and the consequent implications on the water quality.

# 2. Materials and methods

# 2.1. Study area

The selected study area is the Zêzere watershed (covering 5063.9 km<sup>2</sup>), located in the Center Region of mainland Portugal (Figure 1). This watershed is very relevant to the country because it contains an important public reservoir for the drinking water supply (Castelo de Bode Dam), responsible for the supply of most of the Lisbon metropolitan area (approximately 29% of the Portuguese population in 2015; source: Pordata).

Upstream of the watershed is the Estrela Mountain (Serra da Estrela), with a maximum altitude of 1993 m. Downstream of the watershed, the altitude decreases, and hillsides come with smaller slopes.

The relief, latitude, and continentality factors condition the spatial distribution of the rainfall in mainland Portugal. The rainfall regime is also characterized by a high spatial and interseasonal variability [36]. The rainfall changes along the study area, with the highest values in the upstream areas (Figure 2), reflect the interference of relief and elevation. The rainfall data (available at the National System of Hydrological Resources [SNIRH], Portugal) of the meteorological stations (MS) selected by each sector delimited on the watershed (Figure 1) show this spatial variation.

However, the spatial rainfall variation in the downstream areas is smaller, and the correlation between the monthly rainfall is higher (e.g. MS Constância, Castelo de Bode, and Tomar) (Figure 3). The St. Luzia (sector B, Figure 1) has no MS.

The most relevant LUCCs in the watershed, according to the Corine Land Cover of 2012 (source: European Environment Agency [EEA]), are the coverage by scrub and/or herbaceous vegetation associations (40.5%), followed by forests (29.9%) and heterogeneous agricultural areas (17.3%). The remaining area is occupied by permanent crops, arable land, open spaces with little or no vegetation, settlements, water bodies, and pastures (4, 3.5, 1.9, 1.7, 1.0 and 0.2%, respectively). However, the LUCCs of this watershed has undergone major changes in recent years, especially in the



Figure 1. Zêzere watershed location and wildfires incidence.



Figure 2. Total annual rainfall (R) of the selected meteorological stations and annual R average (lines).

conversion and loss of forest [37], induced mainly by the frequent wildfires that occurred over these years (Figure 1).

To evaluate the post-wildfires' effects on the surface water's physicochemical properties, the watershed was split into five sectors (Figure 1), according to the WQSs, with the available data (SNIRH). Sector A comprises the area upstream of Dornelas WQS (163,092.6 ha); sector B comprises the area drained for the St. Luzia Dam (4937.5 ha); sector C comprises the intermediate area of

the watershed and integrates the Cabril Dam (73,595.9 ha); sector D comprises the reservoir of Castelo de Bode and the surrounding areas (154,819.4 ha); and sector E comprises the sub-basin of the Nabão River (109,940.7 ha), where the Fábrica da Matrena WQS is located.

# 2.2. Wildfires and water quality data

The data of the burned areas and occurrences were obtained on the Institute for Nature Conservation and



Figure 3. Relation between monthly rainfall (R) (1975–2013) of the selected meteorological stations (MS) to first downstream MS located in Zêzere watershed (Constância 17G/04UG).

Forestry (ICNF) website for mainland Portugal (vector data) for the period of 1975–2013. The Zêzere watershed boundaries (vector data) and the hydrologic data were obtained from the SNIRH database (public available data).

Since most of the WQSs in this watershed have no available data in the collection of water quality data, only the WQSs with data were chosen. Thus, there were some water quality parameters (WQPs) for which estimation was necessary due to missing data, in particular from 2011, using a linear regression with data from the closest WQS. The WQSs selected are located downstream of each delimited sector. The St. Luzia, Cabril, and Castelo de Bode WQSs are located in dam reservoirs, while the Fábrica da Matrena and Dornelas WQSs are located in main rivers (Nabão and Zêzere, respectively).

The selected WQPs (1993–2013) at these stations are as follows: pH (an important operational WQPs [38]), 5-day biochemical oxygen demand (BOD5), electric conductivity in the field (20°C) (EC), total suspended solids (TSS), total nitrate ( $NO_3^-$ ), and total nitrite ( $NO_2^-$ ). The PAH data are only available for 1990–1993 and 1999–2004 in the Castelo de Bode Dam WQS. Given the relevance of these WQPs to the wildfires' effects analysis on surface water's physico-chemical properties, the available data were used for the identification of possible water quality implications.

# 2.3. Spatial and statistical analyses

The ArcGIS 10.3 software was used for the spatial analysis of wildfires and to determine the incidence of these events. For the assessment of incidence, each annual event (single layers) has been assigned a value: "1" in case of a burned area and "0" for an unburned area. All the wildfire features were combined using a union operation, resulting in a new feature dataset, where the number of occurrences for the 1993–2013 period can be calculated for each line (polygon in the map) in the attribute table.

The fire frequency was evaluated in several studies using the Weibull function [39–43]. This procedure was also used in this work to analyze the incidence interval of wildfires (burned areas and occurrences), with the data series from the previously defined 1975–2013 interval, and to evaluate the probability of the determined number of occurrences ( $P_O$ ) and burned area ( $P_B$ ) to be exceeded. These probabilities were used to calculate the return periods:

$$P_O = 100 * (1 - (r_O/(N_O + 1))) \tag{1}$$

$$P_B = 100 * (1 - (r_B/(N_B + 1)))$$
(2)

Here,  $r_O$  and  $r_B$  are the order number of occurrences and the burned area, respectively;  $N_O$  and  $N_B$  are the total records of occurrences and the burned area, respectively.

However, only the period of 1993–2003 integrated the analyses performed with the WQPs (data available for the period).

For the sectors (Ss) delimited in the Zêzere watershed, the burned area was calculated, and combined statistical analyses (descriptive and analytical) were performed using the water quality's physical and chemical indicators.

In each sector, the burned areas were split as a function of the distance to the main watercourses, obtaining variables for each year (between 1993 and 2013) and the total burned area for multiple distances (ring buffers: 22, 4, 6, 8, 10, and 12 km). The distance (along the watercourses) to the burned area ( $\geq$  1 ha) closest to each sector's WQS was also determined for each year.

To identify the wildfires' effects on the physicochemical properties of the surface water, the software Statistica 7 was used. First, the correlation between the burned areas and rainfall in the sectors with the WQP variations (maximum values) was determined; later, the Principal Components and Classification (PCA) were used to analyze the distribution of the variables (WQPs and burned areas) from all sectors, to determine whether there are implications on the water quality between the burned areas observed by each sector, and if they are higher in sectors located downstream. All data were previously standardized.

The total burned area, annual rainfall, minimum distance between burned area (minimum 1 ha), and the total burned area in different buffers (2, 4, 6, 8, 10, and 12 km obtained with Geographic Information System--GIS) of the main watercourses were correlated with the maximum annual WQPs values.

# 3. Analysis of results

#### 3.1. Wildfires in the Zêzere watershed

In the early 1990, the forest of this watershed was composed mainly of conifers (Corine Land Cover, 1990), hence the easy spread of wildfires and their difficult extinction (also due to uneven relief), resulting in large expanses of burned areas [44].

Currently, this watershed's forest is composed mainly of scrub and/or herbaceous vegetation associations, pastures, and other tree species [45], the result of wildfires and the burned areas' extension (Figure 1, with special emphasis on the 2003-2007 subperiod, Figure 4(a)) but also of the incidence of these events (Figure 1), which do not allow the forest, particularly resinous trees, to regenerate.

According to the burned area data and the occurrence of wildfires in the Zêzere watershed, we can conclude that these events are recurrent in this territory and can be regarded as one of the main events in the LUCCs that occurred here. However, the total number of occurrences has no direct relationship with the total burned area registered in this watershed. This is in line with the straight relation between wildfires and the existence of combustible material. In recent years, there have been more fires, but the burned area is smaller compared to that of previous years (Figure 4(a)). The year 2003 was notable, considering the high burned area and large burned areas near the water bodies (Castelo de Bode and Cabril Dams) (Figure 4(b)). The incidence of wildfires is also a common phenomenon in the watershed, especially in its upstream sector (Figure 1).

One of the most relevant reservoirs of drinking water in mainland Portugal, the Castelo de Bode Dam, is located within this watershed. The LUCCs from wildfires can affect the quality of surface water, due to the constant loss of vegetation cover, which results in the drag of certain chemical and physical elements from the burned soil surface through runoff, increasing their concentrations in downstream waters [8,37]. It also leads to a lower water infiltration capacity of the soil and water retention over the watershed.

The analysis of the incidence interval of wildfires shows that the Zêzere watershed had a gradual increase to approximately 100 occurrences in a return period of four years. At this point, a natural break occurs to higher return periods and larger number of occurrences (Figure 5(a)). However, the probability of the determined number occurrences being exceeded is quite high for short periods. The number of



Figure 4. Burned area and number of wildfires (1975–2013) in Zêzere watershed (a) and burned area by sectors delimited in Zêzere watershed (b). Data source: ICNF.

occurrences is important in this type of research because, if many wildfires surrounding water bodies occur annually, even though each may have a reduced burned area, the sum of the burned area of the total wildfires can be high.

In the analysis of the burned area return interval (Figure 5(b)), the more extensively burned areas beyond the 15 years stand out. This analysis highlights the likelihood of wildfire occurrence in small areas with short return intervals, but illustrates that the occurrence of these devastating events, by the extent of the burned area, has a longer return period, a favorable factor for the regeneration of natural vegetation. On the other hand, the higher the plant productivity (biomass), the greater the accumulation of forest fuel, with the associated increase of wildfire consequences, depending on the severity and intensity of these events [46].

# **3.2.** Variation of the physicochemical properties of the surface water

The selected WQPs varied differently in the sectors defined in the Zêzere watershed, but they also show many irregularities in the period under analysis (Figure 6).

In the case of the BOD5, the Fábrica da Matrena WQS presents the highest values, especially in 1994, 1999, 2002, and 2008. In the sector where this WQS is located (E), there are many industrial activities and media reports about illegal discharges in the Nabão River. Thus, the presented values may reflect these activities, which contributed in some ways to the reduction of the surface water quality in this river. However, it was found that, in 1999, there were many wildfires in this sector, which resulted in an extended burned area. These events could also partially

contribute to the increase of the BOD5 registered in the Nabão River. The remaining WQSs' registered values indicate concentrations lower than 10 mg  $L^{-1}$ .

The EC also stands out in sector E (Fábrica da Matrena WQS), but this WQP has the highest registered values in sector A (Dornelas WQS) for the considered time series, especially for 2000 and 2005. The latter year also presents a considerable burned area in sector A, which can be reflected in the variation of this WQP in this sector.

The concentrations of  $NO_3^-$  and  $NO_2^-$  are also very fickle in the considered period, especially the former WQP in sector E in 2000 and the latter WQP in sector B in 1997.

The pH parameter presents, in general, the maximum values in the Castelo de Bode Dam, with a highlight on 1993. The water from this dam comes from the waters drained from sectors A, B, and C and the respective area of sector D. Thus, assessing the implications of burned areas on the physicochemical properties of the surface water exclusively in this sector is complex. This WQP is also highlighted in the St. Luzia WQS (sector B), with the maximum values observed in several years.

The high concentration of TSS stands out in the upstream sector (A) of the Zêzere River water in 2009, coinciding with the high burned area in this sector that year. Regarding the burned areas recorded in this sector, the relevant years (2000, 2001, 2003, and 2005) also reflect the maximum values of TSS recorded in this sector, demonstrating the interference of water drained from the burned areas in the increase of solid load matter in the water of this river.

In the Castelo de Bode reservoir, a high increase in the concentration of PAH was also observed in 2003 (Figure 7), coinciding with the high burned area recorded that year. The increase of this concentration



**Figure 5.** Wildfires (occurrences) return interval (Ori) and the probability of the determined number of occurrences to be exceeded (P) in the Zêzere watershed (Graph A). Burned area return interval (Bri) and the probability of the determined burned area to be exceeded (P) in the Zêzere watershed (Graph B). Linear trends of occurrences and burned area are represented using a dashed line.



🗆 Dornelas (Sector A) 🗏 Alb. Santa Luzia (Sector B) 🗏 Alb. Cabril (Sector C) 🗮 Alb. Castelo de Bode (Sector D) 🖷 Fábrica da Matrena (Sector E)

Figure 6. Maximum annual value of WQP for the surface water quality stations selected within the Zêzere watershed.

reflects the dragging of PAH by runoff that occurred in the burned areas upstream of this reservoir. In 1999, many illegal discharges (domestic and industrial effluents) into the urban sewage network or water lines were identified, which, together with the near absence of urban wastewater treatment systems, led to the discharge of high pollutant loads into the Zêzere River [47]. This fact can explain the PAH fluctuation verified in this year.

# 3.3. Interference of wildfires on the physicochemical properties of the surface water

The average annual WQPs and the annual burned areas for the five sectors were compared, but the results

did not reveal any consistent relation. As a consequence, it was decided to cross the maximum annual WQPs value and the annual burned areas, since the availability of certain chemical compounds or elements in the burned areas is higher after wildfires, and these are easily dragged by the first rains capable of generating runoff [2,8], considering that input of these compounds or elements is identifiable in the analysis of the maximum WQPs annual value in the Zêzere watershed's surface waters. However, the relationship between the WQPs (maximum values) and burned areas in each sector is not always evident. In some cases, negative correlations were also found. The positive correlations between the burned areas with some WQPs are worthy of being highlighted: the EC and TSS in sector A, NO<sub>3</sub><sup>-</sup> in Albufeira de St. Luzia (sector B)



**Figure 7.** Variation of contents of polycyclic aromatic hydrocarbons—PAH ( $\mu$ g L<sup>-1</sup>) in the Castelo de Bode dam reservoir and burned area (1998–2004).

and Cabril (sector C), the BOD5 in Castelo de Bode (sector D), and the EC in sector E (low positive correlation) (see Table 1).

It should also be noted that, in some cases, the burned area near the watercourses is important for certain WQP concentrations in the surface water, with this influence reducing with the increasing distance of the buffer around these watercourses (Table 1), for example, the EC in sectors A and E, and the  $NO_3^-$  in sector B. On the other hand, for the WQSs in sectors C and D, some WQP correlations tend to increase when considering the burned area of wider buffers, for example, the  $NO_3^-$  and BOD5, respectively.

In the case of the MDBA variable (minimum distance between burned area, with minimum 1 ha) and WQS, the interest lies on the negative correlations because the higher concentration of determined WQPs can be related with the reduced distance to the burned areas. However, the results do not have very strong relations with the proximity of the burned areas.

The rainfall presents very low correlations with WQPs, and in some cases, they are even negative. Positive correlations for these variables only occur in sectors D (pH) and E ( $NO_3^-$ ).

The water runoff generated in the burned areas and the consecutive drag of compounds or chemical elements resulting from the wildfires to the rivers or reservoirs may not be reflected in the reference point (localization of the WQS) of each sector but may contribute to the detected increased concentration of these elements in the downstream sectors.

The Castelo de Bode Dam contains drained water from sectors A, B, C, and D. In this dam, the influence of the upstream sectors' drained waters on the increase of some WQPs was verified; hence, some established correlations between WQPs and the total burned area of these sectors also increased (Table 2). In an advanced PCA factor analysis, the results allow the identification of groups of variables (Figure 8) that demonstrate the interference of wildfires on the physicochemical properties of the surface water. First, an interconnection or continuity is observed between sectors A, C, and D (see Figure 1) in the burned areas (main watercourse––Zêzere River), forming groups with some WQPs of these sectors (G1 and G2 in Figure 8).

For example, the TSS in Dornelas (sector A) and Cabril (sector C) integrate this grouping and demonstrate the interference of water runoff from these sectors on the increase of the solid load in the Zêzere River waters, highlighting the increased soil erosion by water as a function of the burned areas, involving the dragging of sediments by waters that run superficially downstream. The TSS in Castelo de Bode (sector D) stands out in this analysis as a function of the burned areas of St. Luzia (sector B), hence the proximity between the TSS observed in this sector (D) and the burned areas of St. Luzia.

In the projection of the variables (Figure 8), the EC observed in Cabril is also strongly connected to the burned areas recorded in this sector (C) and the upstream sector (A). This result indicates that the more burned area, the greater the concentration of dissolved minerals in the surface water within these sectors.

The variation of concentration of the WQPs  $NO_3^$ and  $NO_2^-$  observed in each sector has no direct relationship with the burned areas, except for  $NO_3^-$  in sectors A, B, and C. In most years, the concentration of these WQPs in the upstream sectors (A and B) is higher compared with the downstream sectors (particularly in sector D). This may be due to the dilution effect on reservoirs that these sectors comprise. However, an elevated  $NO_3^-$  concentration in Castelo de Bode was punctually found, which may be the result of the concentration of waters from the upstream

**Table 1.** Pearson's correlation coefficients (*r*) between maximum annual value of WQP and annual burned area (1993–2013) of the sectors delimited in Zêzere watershed (significance level p < 0.05).

|   | Variable                 | BOD5   | EC (20°C) | $NO_3^-$ | $NO_2^-$ | pН     | TSS    |
|---|--------------------------|--------|-----------|----------|----------|--------|--------|
| Sector A  | ТВА                      | -0.089 | 0.588     | 0.404    | -0.054   | -0.073 | 0.581  |
|   | R                        | -0.112 | 0.014     | 0.199    | 0.083    | 0.056  | 0.122  |
|   | MDBA                     | 0.308  | -0.186    | 0.137    | 0.278    | -0.235 | -0.008 |
|   | BABW 2km                 | -0.065 | 0.606     | 0.448    | -0.071   | -0.112 | 0.542  |
|   | BABW 4km                 | -0.091 | 0.574     | 0.395    | -0.060   | -0.101 | 0.601  |
|   | BABW 6km                 | -0.093 | 0.587     | 0.398    | -0.071   | -0.075 | 0.602  |
|   | BABW 8km                 | -0.089 | 0.592     | 0.407    | -0.074   | -0.073 | 0.586  |
|   | BABW 10km                | -0.087 | 0.594     | 0.408    | -0.076   | -0.070 | 0.583  |
|   | BABW 12km                | -0.088 | 0.594     | 0.408    | -0.076   | -0.069 | 0.582  |
| Sector B  | ТВА                      | 0.115  | -0.085    | 0.570    | 0.006    | -0.015 | 0.335  |
|   | MDBA                     | -0.178 | -0.178    | -0.079   | 0.111    | -0.157 | -0.082 |
|   | BABW 2km                 | 0.214  | -0.069    | 0.588    | -0.008   | -0.035 | 0.340  |
|   | BABW 4km                 | 0.181  | -0.074    | 0.574    | 0.024    | -0.035 | 0.360  |
|   | BABW 6km                 | 0.140  | -0.082    | 0.572    | 0.013    | -0.024 | 0.345  |
|   | BABW 8km                 | 0.115  | -0.085    | 0.570    | 0.006    | -0.015 | 0.335  |
|   | BABW 10km                | 0.115  | -0.085    | 0.570    | 0.006    | -0.015 | 0.335  |
|   | BABW 12km                | 0.115  | -0.085    | 0.570    | 0.006    | -0.015 | 0.335  |
| Sector C  | TBA                      | -0.328 | 0.291     | 0.438    | 0.168    | 0.081  | 0.158  |
|   | R                        | 0.180  | -0.092    | -0.424   | -0.268   | 0.051  | 0.172  |
|   | MDBA                     | 0.150  | 0.180     | 0.189    | -0.333   | 0.139  | -0.033 |
|   | BABW 2km                 | -0.306 | 0.284     | 0.402    | 0.173    | 0.114  | 0.101  |
|   | BABW 4km                 | -0.311 | 0.297     | 0.414    | 0.174    | 0.105  | 0.125  |
|   | BABW 6km                 | -0.325 | 0.294     | 0.432    | 0.169    | 0.088  | 0.152  |
|   | BABW 8km                 | -0.328 | 0.291     | 0.438    | 0.168    | 0.081  | 0.158  |
|   | BABW 10km                | -0.328 | 0.291     | 0.438    | 0.168    | 0.081  | 0.158  |
|   | BABW 12km                | -0.328 | 0.291     | 0.438    | 0.168    | 0.081  | 0.158  |
| Sector D  | TBA                      | 0.532  | 0.110     | -0.113   | 0.092    | 0.120  | 0.017  |
|   | R                        | -0.087 | 0.142     | 0.093    | -0.090   | 0.340  | -0.003 |
|   | MDBA                     | -0.253 | -0.193    | 0.174    | -0.032   | 0.320  | -0.114 |
|   | BABW 2km                 | 0.509  | 0.133     | -0.131   | 0.120    | 0.100  | 0.060  |
|   | BABW 4km                 | 0.522  | 0.119     | -0.115   | 0.106    | 0.115  | 0.040  |
|   | BABW 6km                 | 0.527  | 0.114     | -0.112   | 0.098    | 0.121  | 0.025  |
|   | BABW 8km                 | 0.532  | 0.112     | -0.113   | 0.093    | 0.120  | 0.020  |
|   | BABW TUKM                | 0.533  | 0.111     | -0.112   | 0.093    | 0.119  | 0.018  |
| Conton F  |                          | 0.533  | 0.111     | -0.112   | 0.093    | 0.119  | 0.018  |
| Sector E  | I DA<br>D                | -0.133 | 0.343     | -0.006   | 0.151    | -0.050 | -0.266 |
|   |                          | -0.204 | -0.255    | 0.302    | -0.191   | -0.046 | 0.209  |
|   |                          | -0.276 | -0.202    | -0.055   | -0.309   | -0.016 | -0.501 |
|   |                          | -0.162 | 0.127     | -0.111   | 0.192    | -0.100 | 0.175  |
|   | BARW 6km                 | -0.135 | 0.202     | 0.007    | 0.240    | -0.115 | -0.15/ |
|   | BABW OKIII               | -0.133 | 0.202     | 0.020    | 0.195    | -0.000 | -0.210 |
|   | BABW OKIII               | -0.132 | 0.330     | _0.009   | 0.101    | -0.032 | -0.245 |
|   | BABW TUKITI<br>BABW 12km | -0.130 | 0.347     | -0.001   | 0.155    | -0.045 | -0.239 |
|   |                          | -0.131 | 0.545     | -0.002   | 0.150    | -0.040 | -0.204 |
| IBA, total burned area; K, annual rainfall; MDBA, minimum distance between burned area (minimum 1 ha) and WQS; BABW, total burned area in different buffers of main watercourses. |                          |        |           |          |          |        |        |

**Table 2.** Pearson's correlation coefficients (r) between maximum annual value of WQP of Castelo de Bode WQS (sector D) and the total annual burned area (upstream sectors A, B and C, including the sector D) (significance level p < 0.05).

| WQP                          | Burned area of the sectors<br>(A + B + C + D) |
|------------------------------|---|
| BDO5                         | 0.52  |
| EC (20°C)                    | 0.16  |
| NO <sub>3</sub> <sup>-</sup> | -0.16   |
| NO <sub>2</sub> <sup>-</sup> | 0.03  |
| рН                           | 0.14  |
| TSS                          | 0.10  |

sectors and the runoff water to the sector where this reservoir is located.

The analysis of the projection of the variables shows that the pH values recorded in Cabril are related with the proximity of its the burned areas. The wildfires that occurred in this sector (B) and the vast extension of burned area (mainly from 2003 to 2005) had interference on the variation of this WQP in the downstream (Cabril reservoir).

Other evidence of the post-wildfires' effects on the physicochemical properties of the surface waters is the case of Castelo de Bode, with the BDO5 very close to the variable of this sector's burned areas (Figure 8).

#### 4. Discussion

The study area presents a marked contrast between the upstream and downstream sectors, in particular, the slope of hillsides, the type of land use, and land cover and the spatial distribution of environmental factors (rainfall, humidity, and wind exposition, among



**Figure 8.** Projection of the variables (maximum annual value of WQP and burned area of each sector) on the factor-plane. BUR, burned area. BOD5, 5-day biochemical oxygen demand; EC, electric conductivity in field ( $20^{\circ}$ C);  $NO_{3}^{-}$ , nitrate;  $NO_{2}^{-}$ , nitrite; pH; TSS, total suspended solids. Places: DORN, Dornelas (sector A); SLUZ, Alb. St. Luzia (sector B); CABR, Alb. Cabril (sector C); CAST, Alb. Castelo de Bode (sector D); MATR, Fábrica da Matrena (sector E).

others). The upstream and downstream sectors can also be differentiated according to the area affected by wildfires, which varies along the watershed, and where the previously mentioned factors also have implications on the extent of the burned areas.

The processes that occurred post-wildfires affect the water quality, especially due to the input of certain elements or substances through runoff from the burned areas. However, these effects can vary depending on the different characteristics of the fire and the environmental factors specific to the conditions of the place where these occurred (slope of hillsides, land cover, precipitation, and temperature, among the more relevant). This happens because the intensity, severity, and processes or treatments during and after a fire can have implications on the water quality [48], according to the various abovementioned processes that interconnect the hill-sides with burned areas and watercourses.

In this research, an immediate increase of the concentration of  $NO_3^-$  and  $NO_2^-$  was not observed after the occurrence of wildfires in the monitored areas. These results may reflect the reduced drag of these chemical constituents from the burned areas to the water bodies but also the dilution effect caused by the water stored in reservoirs, a fact also observed in other research performed in on the São Domingos stream (located in the Western Region of Portugal) [2].

Sector E of the Zêzere watershed does not really reflect the correlation of wildfires with the variation of WQPs. Surface water in this sector is drained in its area of influence. This sector has a strong influence from anthropogenic activities (agriculture, artificialization of the soil with industrial areas, homes, roads, or similar land uses) with implications on the water quality [37,45]. However, the projection of the variables showed that the closer variables to the burned area in this sector are  $NO_2^-$  and  $NO_3^-$ . The projection of the variables also showed that these WQPs have greater proximity to the burned areas established in sectors A, B, C, and D, although there is no direct interference between these sectors and the waters of sector E.

The more visible effects, after removing the vegetable or organic material layers due to wildfires, are water erosion and the occurrence or amplification of floods, causing excess transport of sediments (source of diffuse pollution) and nutrients or compounds, such as  $NO_2^$ and  $NO_3^-$ , which are subsequently deposited in the waterbodies [7,12]. However, in this research, it was found that, according to existing data, the increase in the concentration of these WQPs in surface waters after the Zêzere watershed wildfires is negligible, not requiring major concerns, but the persistence of these WQPs over several years post-wildfires must be taken into consideration [23]. The increase in concentration of these two WQPs should be a concern when wildfires occur in areas with a high nitrogen concentration [12].

The reduction of water quality occasionally occurred in this watershed after the occurrences of certain wildfires, especially those with large extensions of burned area, with a highlight on, for example, the increase of the TSS content. The increase of this WQP after the wildfires and the respective implications on the water quality, as well as the variation of other WQPs (pH, sulfate concentration, chloride, and iron, among other components), is also denoted by Landsburg et al. [12] and is partly explained by the increased water erosion that occurred in the burned areas and the respective dragging of sediments to the water bodies. This dragging also provides the increased turbidity of water bodies (caused by suspended material).

The correlation between the BDO5 and the burned areas was higher in sector D (Castelo de Bode). This sector also contains water drained from upstream sectors (where the incidence of wildfires is higher). This fact may reflect this WQP's increase in this area, but there may also be other factors at play, since some studies suggest the increase of this WQP is a function of the industrial and urban runoff [37,49], land use and land cover types existing in the aforementioned upstream sectors. However, the BDO5 concentration observed in Castelo de Bode can also reflect the TSS of the waters drained from the upstream sectors, where the TSS concentration is quite high and has a positive correlation with the burned areas recorded in these sectors, hence the proximity to enter these WQPs presented on the projection of the variables (Figure 8). According to Dolloff [50], the increase of suspended solids and dissolved organic matter (which is predominantly organic) contributes to the biological oxygen demand in the receiving waters.

In this research, it was observed that the EC presents a positive correlation with the burned areas (except St. Luzia), indicating the interference of water drained from the burned areas in the increase of this WQP. In contrast, pH has no relationship with the burned areas, or it is very low (Table 1). This parameter does not constitute a health concern at the levels found in the waters analyzed (the pH must be between  $\geq$  6.5 and  $\leq$  9 in conformity with the Portuguese Decree-Law 306/2007 of 27 August [51]), except for in Albufeira de Castelo de Bode in 2003 with a pH > 9. However, the research presented by Pereira et al. [52] for the northeast of the Iberian Peninsula demonstrated an increased concentration of EC and pH post-wildfire because, according to these authors, the mineralized nutrients contained in ash are easily leachable, increasing the EC.

Ash resulting from wildfires can form a significant component of suspended material flux within the first year after a fire [17]. The events of rainfall and wind postwildfire acquire significant importance in the removal of ash on the hillslopes [53], and this ash can also transported to water bodies. Additionally, the wind impacts the wildfires' behaviors by supplying the fire with additional oxygen, which pushes it to move faster across the land [54]. However, there is a lack of data, as the effects derived from wind action are not studied in this research, but they can also contribute to increasing the compounds concentration verified in the water of the reservoirs analyzed because burned areas surround them.

There are other variables that can explain the variance of the analyzed WQPs in this watershed, i.e. fire intensity and permanence time may result in a variable severity of their consequences. This is the response of ecosystems to fire, but it can also be used to describe fire's effects on the soil, hydrological systems, fauna and flora, in the atmosphere, and also in society [55].

Many studies have demonstrated the increase of PAH in the water after wildfires [3,26,28,30]. The high concentration of PAH observed in Castelo de Bode in 2003 is a reflection of the direct and indirect implications of wildfires that occurred in this watershed on the water quality of this reservoir. This water is important for the public water supply, requiring prior treatment to prevent public health consequences, according to the PAH effects previously referenced.

According to Ferreira et al. [10], one of the most important consequences of fire passing through an area is the export of large amounts of nutrients, which may trigger downstream pollution problems, especially if there are dams and water catchment in proximity to the burned areas. This fact is confirmed in this research, but the different variations of the WQPs analyzed in the study area should be noted because there has not been an increase or reduction in parallel of all the WQPs in the surface waters after the occurrence of wildfires. The individual variation of verified WQPs may also reflect the interference of the stream waters of other sub-basins, where there may be a greater availability of the element in question, and thus lead to a concentration increase of these WQPs in water bodies from the point of where these watercourses intersect.



Figure 9. Barriers in burned areas (in gullies and slopes) of Gerês mountain, North of Portugal, constructed post-wildfires with materials of burned trees.

The rainfall that occurred in the watershed, although important for the runoff formation, has little relation with the variation of the WQPs analyzed. It would be interesting, in further work, to elaborate the analysis of this variable (R daily) and compare it with the variation of WQPs (also daily) after the wildfires.

It is worth highlighting that the effects of wildfires on surface water were only observed when analyzing the maximum values of the WQPs, not the annual average of each WQP. This somehow reflects the higher drag of the elements or chemical compounds resulting from the wildfires occurring in a very specific period (in particular, the first rainfall after the wildfires able to generate surface runoff) [8,56] but also the stability of ecosystems on the retention of these elements, dissipating this dragging to the water bodies over time. This happens because, on one hand, the greatest concentration of WQPs occurs during the first rains (by dragging in the water runoff and leaching), and on the other hand, because there is retention or assimilation by vegetation that grew in the burned areas [2]. In this sense, the post-wildfire precipitation can explain the degree to which wildfires degraded the water quality and supply, but this factor cannot be analyzed independently, i.e. a group of multiple factors that explain the water quality and supply variations (e.g. the extent and intensity of the wildfire, the watershed topography, and the local ecology) must be integrated [17].

Developing a system of mitigation measures is important to the water quality supply. Sham et al. [57] relates some measures, for example, properly designed forest riparian buffer strips that can protect source waters from wildfire-related runoff problems. Limiting the scope and burn intensity of wildfires can also significantly mitigate the sediment problems of these watercourses.

The magnitude of the effects on water quality increases with burn severity [57], but the reduction and maintenance of the forest materials available can minimize this severity, and this constitutes a simple measure that can be implemented by forest owners. On the other hand, if the replanting of burned areas is done using pyrophytes species, forest owners can introduce corridors of species more resistant to fire (e.g. *Quercus sp.*), thus contributing to minimizing large wildfires. The creation of barriers with forest material post-wildfire in watercourses or slopes (Figure 9) can provide the reduction of soil loss and, consequently, of the particles suspended in water.

Preventing the flow of burned areas from occurring directly into water bodies would be essential to avoid increasing the concentration of certain WQPs. In this sense, some preventive short-term post-fire measures may be drainage through artificial channels, the application of straw on the burned areas, and placement of barriers in the water lines, among others. In the long term, it may be forest management, namely avoiding reforestation with flammable species in the vicinity of water bodies. It is also important to mention that drinking-water treatment must always be adjusted in accordance with changes in source-water chemistry.

# 5. Conclusions

This work presents research on the distribution of wildfires (spatially and temporally) over the Zêzere watershed, in mainland Portugal, and their implications on the surface water quality. Wildfires were responsible for large LUCCs in this watershed, and the sector upstream was where there has been greater incidence of these events. Due to the high number of annual occurrences and the extension of the burned areas and their incidence, most of these events are considered catastrophic, not only because of the material damage, but also because it reduces the surface water quality. This is considered an important environmental problem because the Zêzere watershed comprises the main reservoir of drinking water in mainland Portugal (Castelo de Bode Dam).

Further, it was verified that the return period for the wildfires with reduced burned areas is very short, this type of event having a high probability of recurrence. The statistical methods applied in this research confirm the impacts of the wildfires on the physicochemical properties and changes in the surface water. In some cases, there have been changes in the physicochemical properties of the water directly in the watercourses closest to the burned areas, while in other cases, there were changes in the water bodies located downstream of the point of monitoring (WQS). These results indicate that there is a continuity of the effects of wildfires along the watercourses but also the increase of certain WQPs after the intersection of several streams draining sub-basins within the burned areas.

The year 2003 was particularly catastrophic in this watershed, with extensive burned areas, and the effects of wildfires were very evident in the increase of the concentration of PAHs and other WQPs in the Castelo de Bode Dam. These results indicate that these events impact the surface water quality.

The results of this work are important for the management of the water bodies of the Zêzere watershed and others but also for forest management, especially in the reforestation of burned areas with fire-resistant species. This may contribute to the reduction of the incidence of these events, thus reducing possible implications of these events on the water quality.

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