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The physio-chemical conditions of surface and groundwater resources in water scarce areas – how droughts affect ions migration

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ABSTRACT

Mediterranean countries are characterized by high temperatures, low rainfall along with frequent catastrophic, prolonged droughts. In the short run lack of water-limits the amount needed for domestic use, while in the long run it leads to deterioration of the quality. In addition to the quantity of available water resources, its quality is of extreme importance. The objective of the study was to compare suitability of groundwater with that of surface water in order to use it. An additional goal was to determine the possibility of estimating conservative ion migration time as well as determine nitrate ion migration cycle. Data available from 2015 to 2019 was divided into two groups: groundwater (being under limited influence of climatic conditions and not exposed to direct evaporation) and surface water (exposed to direct sunlight and significant evaporation). It has been shown that, with the exception of nitrate ions, the physicochemical composition of groundwater is less variable than that of surface waters; however, it is strongly spatially diversified across the country. It has been established that in a dry and hot climate, with a high share of artificial irrigation of crops (with deliberate limitation of evaporation and intensification of infiltration) along with the introduction of fertilizers, migration cycle of nitrogen compounds in the environment is different than that from temperate and humid climate. The final conclusion is the unexpected: surface waters are much safer when used for consumption. For irrigation of crops, groundwater with high nitrate content may also be used; however, over-fertilization should be avoided.

Keywords: Drought; Water use; Water resources; Ion-migration; Nitrogen cycle; Portugal

1. Introduction

The subject of water resources has been extensively discussed in many publications. The main reason for this interest in the availability of water to meet the demand is its undeniable priority in sustaining life. For the functioning of vital biological process plants and animals, as well as humans, need water. The universal right to water and sanitation has

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evolved from soft into hard international law, where it is now considered as a "distinct, composite human right" [1]. In 2010, United Nations General Assembly recognized "the right to safe and clean drinking water and sanitation as a human right that is essential for the full enjoyment of life and all human rights" [2]. The General Assembly's Resolution (64/292) brings significant international political weight behind the notion that access to clean, safe drinking water, and sanitation is an independent human right [2]. Hall et al. [3] noticed that focus only on the human right to safe, clean drinking water could limit the impact of water service provision if it focuses solely on domestic water supply. That is the reason that the human right to water should not be limited to safe, clean drinking water; a more progressive interpretation of existing international law, focusing on the human right to water (in general), may be a more effective way to address a comprehensive range of socio-economic rights in rural and peri-urban areas [3]. However, water plays an important role in realizing other human rights such as the right to food and livelihoods. The food producing (especially agriculture) needs much water to be sufficient. Lack of water resources sufficient to cover the needs of each of the sectors using it creates conflict situations. It is increasingly recognized that access to water could in future constitute the main cause of conflict, including global armed conflict [4–6].

In countries with high insolation and high temperatures, the fact that there is no access to water in a satisfactory and sufficient quantity is common. Drought is a natural and recurrent climate phenomenon in the Mediterranean region where Portugal is located, resulting from a temporary rainfall reduction. In the present context of climate change there is no clear trend regarding annual precipitation, but the remaining variables contribute to an overall reduction on water availability, thus reinforcing the need to promote a precautionary approach as well as risk assumption and sharing measures [7]. Climatic factors (e.g., temperature and precipitation) represented the primary cause of the uncertainty of water supply [8]. Many water-scarce countries, for example, Portugal, has severe, frequent problems in the water availability for use in diverse sectors (including agriculture and water supply for domestic use), with common and extensive periods of drought [9], very low rainfalls, and extreme hot summers [10].

Worldwide, agriculture accounts for 70% of all water consumption, as compared to 20% for industry and 10% for domestic use. However, in industrialized nations, industries consume more than half of the water available for human use. Freshwater withdrawals have tripled over the last 50 y [11].

Concerning Portugal, the yearly water used is estimated as 9,151,000,000 m^3. The daily water used per capita is 2.371 L; for comparison, in Poland, it is 763 L/person, and in the United Kingdom 348 L/person. This is due to the differences in water demand in these countries. In Portugal, up to 87% of water is sought for the agriculture sector [12]. Agriculture in Portugal is usually based on small or medium-sized family-owned dispersed units. The sector also includes larger-scale intensive farming export-oriented agrobusinesses backed by companies. Portugal's climatic and topographic conditions allow for a large number of crops, including, for example, olives, citrus, sunflowers, tomatoes, and cereals. Producing of many products like wine, table grapes, or olives are competitive in European Union, since the end of last Millenium there has been an observed increased in the demand for Portuguese products in the export market.

From the opposite point of view has been pointed out that "Portugal is living on water that it does not have," according to the Association for Nature Portugal (ANP) [13]. This has so far hindered also implementation of so many investments, among others hydropower, hydro cooling-systems in factories, or withdrawals needed for domestic use. Those investments based on running waters must factor in the absolute necessity of protection of the water environment dependant on water [14–16]. In practice, it means the obligation of leaving environmental flow in the river bed in the cross-section below the level of water abstraction [17,18]. Portugal can be very vulnerable to the impacts climate change, taking the form of rising sea levels, heat waves, flooding, and droughts; some regions are already suffering due to pressure put on water resources, and this is deepen in the face of future climate conditions [19]. Major water quality problems occur on the shared rivers bordering stretches, where water quality does not meet the standard set by the legislation, and this is the case for a number of downstream stretches and for almost all coastal areas, with values of pollutant loads exceeding the recommended for human consumption. Another problem is that found mainly in the south of Portugal, water levels significantly drop in the summer in some rivers, leading to elevated concentrations of pollutants. As to coastal waters, the quality is generally good, except of some spots of fair and poor quality, one example being Porto's metropolitan area [20]. Urban wastewaters are responsible for more than 57% of these pollutant loads [20]. Groundwater plays an important role in public, industrial, and agricultural sectors; however, they are putting pressure is increasingly being put on these resources. Climate change contributes to deepening water scarcity in Portugal, especially in arid and semi-arid cases, as is the case for some regions of south of Portugal, in Alentejo and Algarve [21]. Agriculture is usually highlighted as a major contributor to nitrogen pollution of water, although livestock and urban sectors are important contributors too [22]. The low efficiency of uptake of the nitrogen applied as chemical fertilizers and manures leads to a nitrogen surplus that can lead to underground and surface waters, reducing their quality, and putting pressure on receiving waterbodies [23]. Portugal has extensive areas of its land (almost 90%) under agricultural use. Local factors controlling nitrate leaching are the high temperatures during half of the year that promote volatilization of nitrogen and reduce losses to water [24]. On the other hand, alternating dry and wet soil conditions stimulate soil organic matter mineralization and promote nitrate leaching from mineralized nitrogen compounds [25].

The constantly expanding agricultural market requires meeting the needs of water for irrigation. In the dry, hot and virtually no-rain climate of Portugal, this is a task extremely difficult–to accomplish, however, it is also necessary to maintain agricultural production and guarantee work and earnings for many residents. In addition to the right amount of water, its quality is extremely important, and this largely depends on the source. The study analyses the spatio-temporal variability of water used to meet the needs of drinking water and irrigation, distinguishing between two sources: surface water and groundwater.

1.1. Water sources for agriculture and public water supply in Portugal

To meets its water needs, Portugal uses both surface and groundwater resources. Surface waters in Portugal are mainly associated with major rivers (Tejo, Douro, Guadiana, and Minho). Spain and Portugal share five river basins: Minho, Lima, Douro, Tagus, and Guadiana. The total area of these basins is 268.500 km^2, which represents about 45% of the Iberian Peninsula, and corresponds to 64% and 42% of mainland Portugal and Spain, respectively [26]. The exclusively national rivers are smaller and more irregular, the most important of which are Lima, Cávado, Ave, Leça, Vouga, Mondego, Lis, Sado, Mira, the Algarve, and Oeste waterways. The main Portuguese river basins are shown on Fig. 1a.

From a hydrogeological point of view, Portugal is a fortunate country for there is a large diversity of porous, karstic and fissured aquifers, where groundwater is stored in great quantities, interacting with surface water systems like rivers, estuaries, and sea in a variety of climatic conditions, from the wet North to the dry South [27]. About 20% of the geographical extension of Portugal is covered by 62 aquifer systems, of which 60% are porous [28]. According to the geological characteristics Portugal is divided into four main hydrogeological units (Fig. 1b). From an hydrogeological point of view there are porous, karstic, and fractured aquifers, which govern the conditions of storage and transmission of water. Groundwater is linked to surface water in many different forms [27].

The unit Hercynean massif shown on Fig. 1 is mainly composed of igneous and metamorphic rocks. Due to their low permeability and specific yield values, no aquifers have yet been identified in this large region; some carbonate aquifers in the Alentejo area constitute an exception. In the Western unit, there are 30 aquifer systems of sedimentary and karstic types, which may be confined or unconfined and may locally be artesian. A few aquifers are multi-layer systems, where leakages could occur, providing groundwater interchange between aquifers. The aquifer systems in the Meridional unit are carbonated ones with some karstification development. The Tagus-Sado unit includes the most important aquifer system of the Iberian Peninsula: the Tagus-Sado aquifer system, which covers a large sedimentary basin of about 8,000 km^2. This is a multi-layer system, the deepest aquifer being the most productive one. In some areas, the system displays a flowing artesian behavior. This aquifer system is an unique source of water supply for domestic, agricultural, and industrial use. There are also some small alluvial aquifers that have strong links with watercourses with frequent water exchanges [27].

With the Portuguese climate, an integrated management of water resources is highly needed. With Regarding the joint use of groundwater and surface water, Burt had already pointed out in 1976 [30] that, "the inherently random nature of surface water supplies and the natural recharge to an aquifer give groundwater stocks an important role as a contingent supply for times when surface water stocks (i.e., dams) are below average. Additionally, optimal intemporal

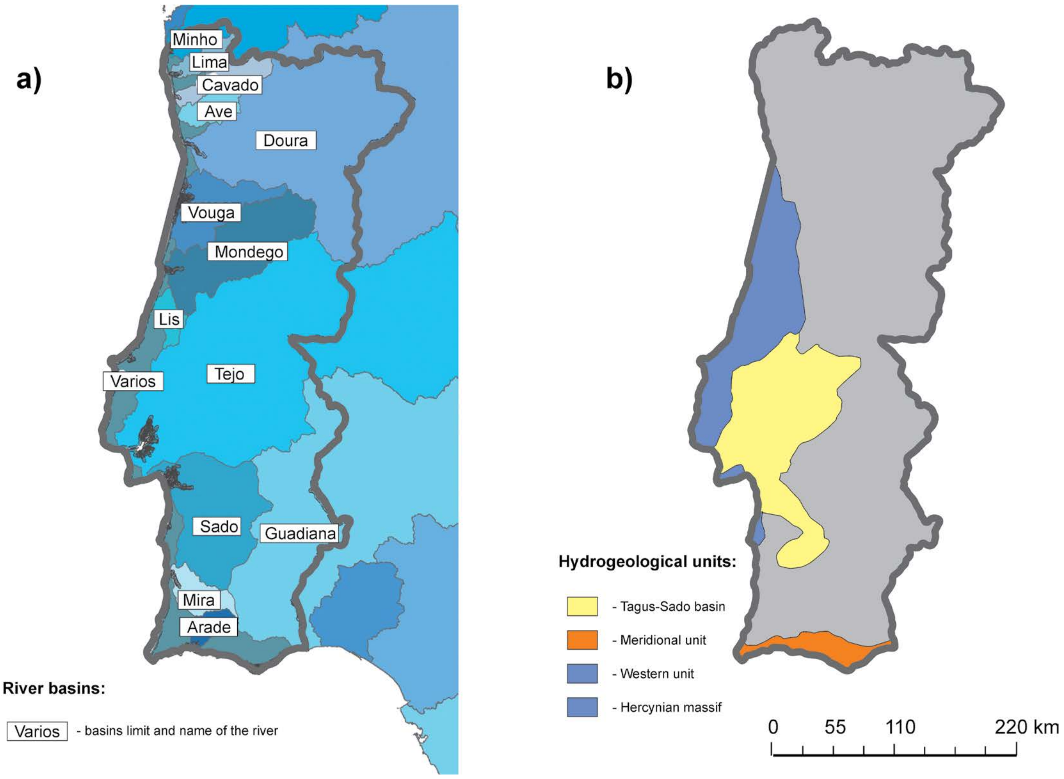


Fig. 1. Main characteristics of water sources in Portugal: (a) river basins [29 modified] and (b) main hydrogeological units [27 modified].

allocation of groundwater used conjunctively with surface water will impute a higher value to the surface water than it would have in an unmanaged basin". Groundwater plays an important role in public, industrial, and agricultural sectors, this last one being the greatest consumer of groundwater [28,31]. Data gathered in the scope of the Portuguese National Water Plan [27] indicate that the agricultural sector annually consumes about 88.7% of groundwater and 74.8% of surface water. According to the IPCC report [32], southern Iberia is projected to experience higher temperatures and lower precipitation in future, which could introduce new challenges for the regional sustainability of agriculture [33]. This is a great challenge for the agricultural sector, both in the context of ensuring the right quantity and quality of water, as well as in undertaking proper crop management. Valverde et al. [34] have evaluated the potential impacts of climate change on irrigation-based agriculture by running long-term soil water balance simulations.

2. Materials and methods

2.1. Database of surface and groundwater samples

The database used for this paper included physicochemical analyses of water samples carried out by an accredited laboratory in 2015–2019. The available data was divided into two groups: groundwater and surface water analyses. The first group includes typical groundwater abstractions (boreholes) and source abstractions (as groundwater's spontaneous outflow in places where groundwater table intersects the surface). Thus, this group consists of waters subjected to climate conditions in a limited way, not exposed to direct evaporation. The second group consisted of surface water abstractions, both flowing (natural rivers and artificial irrigation ditches in drainage network) and standing waters (lakes and ponds). The waters in this group are exposed to direct sunlight, hence subjected to significant evaporation.

All water sampling points collected in the base were plotted on the map of Portugal, subsequently location coordinates were assigned to them (Figs. 2 and 3). In addition to the breakdown into surface and underground waters, a classification has been introduced regarding the way water is used (irrigation, human consumption, animal feeding, and others). The database for groundwater built in this way included 100 abstraction points and almost 500 determinations of selected parameters. For the surface water base, there were 52 abstraction points and more than 300 determinations (which resulted from frequent sampling of the same points at particular intervals). Due to the different purposes of the analysis ordered, their scope for individual analyses included only selected determinations. For further analysis, parameters whose population size allowed for carrying out advanced analyses of time, spatial variability, or basic statistical analyses were selected.

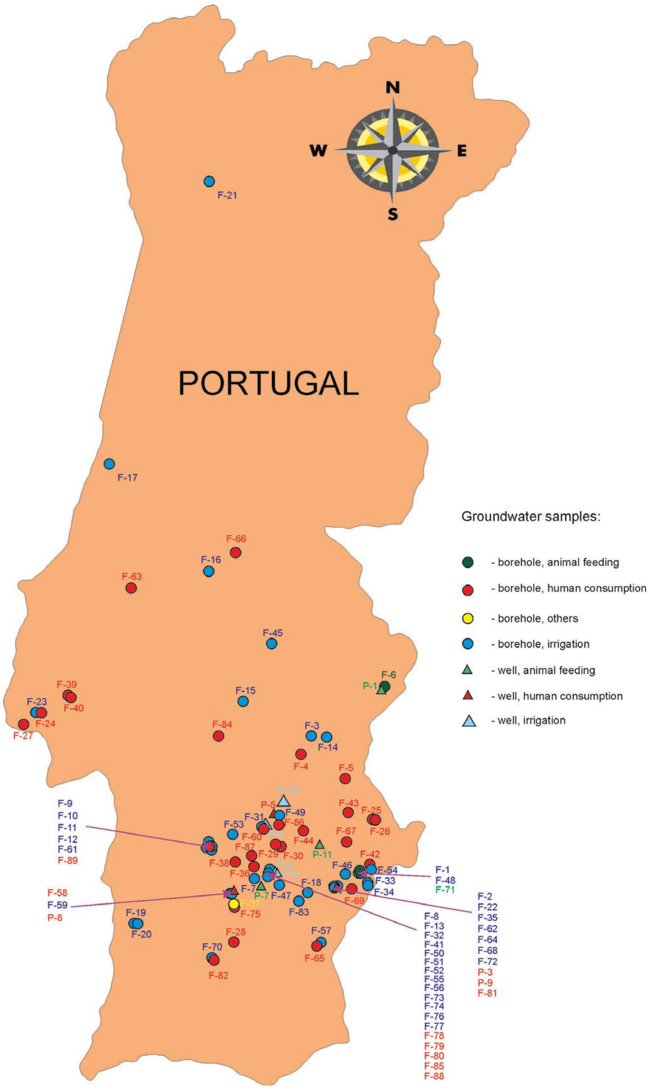


Fig. 2. Groundwater samples of database.

Table 1 summarizes the methodology for the determinations used in this publication. Most determinations are made on a modern ionic chromatography "Metrohm 930 Compact Ion Chromatography Flex" equipped with the 863 Compact Autosampler.

Due to the different purposes of the ordered analytical tests, their scope for individual tests covered only selected determinations. For the needs of these tests, a database was built and verified, and samples for each subsequent test were selected according to the relevant criterion. Thus, for example, for spatial analyses, time points were only selected for which appropriate determinations were made, with the remaining "empty" points being removed from the database.

2.2. Analytical procedures for water samples characterization

The scope of analytical tests available for this work was always subject to the order received by the laboratory. The laboratory carries out analytical tests in accordance with applicable standards using modern laboratory equipment.

2.3. Programs used for analyses

Excel program, among others, was used to analysis collected results. In order to obtain an easy and reliable analysis of the variability of the main parameters in the abstracted ions, a modified Schoeller–Berkaloff graphic method, often

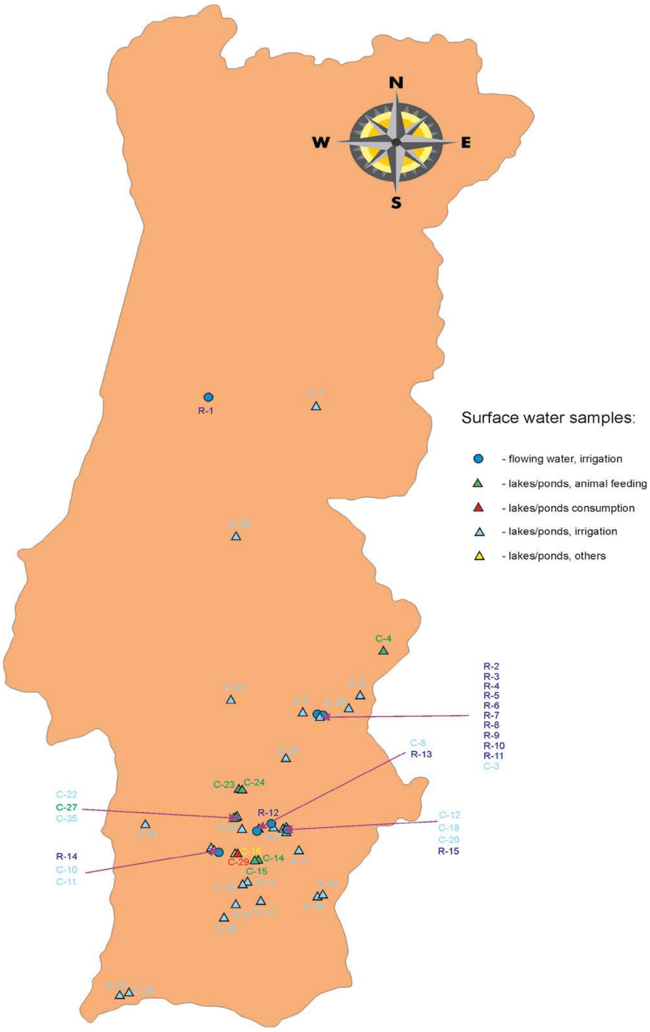


Fig. 3. Surfacewater samples of database.

employed for similar analyses [35–37], was used. The basic analysis of the variation of selected ions was also carried out using the STATISTICA platform, with the results being presented in the form of the typical box charts. The program was used to show the range of values of the observed parameters and their basic statistical characteristics.

To develop a map of spatial distribution analysis for groundwater, the SURFER® 16 program was used, it is designed for comprehensive visualization of XYZ data. In the Surfer program, the kriging method with a linear variogram was used as one of the griding methods (creating a regular value grid), while the variogram modeling procedures made it possible to pick the optimal shape. This is the most commonly used method in creating a regular value grid, as it gives the best results of modeling the course of the function $z = f(x,y)$ based on a finite number of XYZ points. Variogram modeling is an additional procedure that helps to raise the accuracy of this method.

3. Results and discussion

3.1. Groundwater variability of physiochemical parameters

Table 2 shows the physicochemical characterization of groundwater and surface water samples with all analyzed parameters. Table 2 shows only those parameters for which the size of the set of determinations made it possible to authenticate the scope of further statistical analyses. Availability of several results for the same abstraction points carried out at different sampling dates leads to the number of results exceeding the number of points sampled.

Variability of all analyzed ions has been shown on the modified Schoeller–Berkaloff chart (Fig. 4), this allows for mapping of water chemistry in a rectangular coordinate system. The concentrations of selected main ions values were plotted on vertical, auxiliary axes (determined at equal intervals) according to a logarithmic scale. The applied concentration values (in unit as mg/L) were connected with each

Table 1
Methodology of determinations

Parameter	Standard	Method
pH	PE.01.01 from 21.11.2017	Potentiometry
EC (electrical conductivity), mS/cm at 20°C	PE.02.01 from 21.11.2017	Electrometry
Total phosphorus (P), mg/L	PE.10.01 from 21.11.2017	Spectrophotometry UV-vis
Phosphates (P_2O_5), mg/L	PE.23.01 from 21.11.2017	Ion chromatography
Total nitrogen (N), mg/L	PE.03.01 from 21.11.2017	Calculation
Nitrates (NO_3), mg/L	PE.04.01 from 21.11.2017	Ion chromatography
Nitrites (NO_2), mg/L	PE.04.01 from 21.11.2017	Ion chromatography
Chlorides (Cl), mg/L	PE.04 from 23.02.2017	Ion chromatography
Sodium (Na), mg/L	PT.ME.055 (Ed. 04 2014.03.17)	Ion chromatography
Calcium (Ca), mg/L	PE.17.01 from 21.11.2017	Ion chromatography
Magnesium (Mg), mg/L	PE.17.01 from 21.11.2017	Ion chromatography
Bicarbonates (HCO_3), mg/L	PE.17.01 from 21.11.2017	Volumetry
Bor (B), mg/L	PE.18.01 from 21.11.2017	Spectrophotometry UV-vis
Ammonium nitrogen (NH_4), mg/L	PE.06.01 from 21.11.2017	Ion chromatography
Sulphur (SO_4), mg/L	PE.04.01 from 21.11.2017	Ion chromatography

Table 2
Physicochemical characterization of the surface water samples

Parameter	Units	Groundwater samples				Surface water samples			
		Average	Interval (min.-max.)	Valid number	Standard deviation	Average	Interval (min.-max.)	Valid number	Standard deviation
pH	–	7.5	5.2–8.5	77	0.51	8.1	6,9–9.5	52	0.46
EC (electrical conductivity)	mS/cm at 20°C	0.83	0.05–2.82	66	0.45	0.81	0.05–4.45	49	0.69
Calcium (Ca)	mg/L	71,2	8.4–151	44	37.50	62.15	10–165.8	45	35.53
Magnesium (Mg)	mg/L	39.7	12.2–80.7	43	21.24	43	6–134	46	26.73
Sodium (Na)	mg/L	62.5	18.8–190	46	45.27	86	25–570	43	104.99
Chlorides (Cl)	mg/L	88.7	0.015–588	55	99.39	98	21.5–487	45	99.39
Bicarbonates (HCO_3)	mg/L	290	88–499	45	117.23	14.5	2.1–45.6	16	15.61
Nitrates (NO_3)	mg/L	57	1–1,023	93	120.06	246	61–416	45	112.36

other by a broken line reflecting the chemical composition of water from one analysis, that is, the same date of sampling. Dozen analyses could be shown on one chart, making visual comparison easy. Fig. 4 features the Schoeller–Berkaloff plots for analyzed groundwater abstractions, each broken line presenting the results from one of analyzed samples, if all presented ions were available. For some of the analyzed samples, only nitrate ion determinations were carried out, the such results being shown in the graph as points.

As Fig. 4 shows, except for the concentration level of nitrate ion which shows very high variability, the concentration level of the vast majority of the analyzed ions only slightly. A conclusion that might be drawn from this is that this variability could result from the presence of anthropogenic sources of this ion, most likely related to fertilization of fields and crops. The concentration level of remaining ions assume values typical for groundwater and sources, calcium concentration is characterized by variability from a few to several hundred mg/L, which results from the time of infiltration water in the system and the time available for the water-rock reaction. The intensity of the process of saturating groundwater with calcium ions, as well as other ions, depends not just on the reaction time alone, but also on the mineralogical composition of aquifers and their solubility in water.

The relatively large number of analyses for sampling points located in known locations with assigned coordinates also made it possible to plot spatial distributions of selected ions (Fig. 5). Such distributions were presented only for those ions with sufficient data collected from the widest possible area. As for one aquifer, a decision was made to obtain isolines, introducing some systematization of hydrogeological conditions. Each sampled point abstracted water from the first aquifer or sourced it from the surface, that is, the self-outflow of the aquifer to the surface of the land. Due to the not very complicated hydrogeological structure (Fig. 1), the above simplification was introduced enabling visualization of spatial variability.

The use of the SURFER program allowed for the isolation of lines, however, it has to be remembered that accuracy decreases with decreasing distance from the groundwater abstraction points. Thus, it was impossible to cover the whole country with the isoline map, and the scope was each time imposed by the program on the basis of the database entered. For different parameters and ions, each time had a different number of results resulting directly from the available database.

3.1.1. Conservative ions migration

Conservative ions polluting groundwater, such as elevated chlorides, constitute a big problem when using them for irrigation or domestic use. Migration of chlorides in groundwater mainly takes place as a process of advection transport with infiltration water depending on the average water velocity [38]. The migration time of conservative pollutants may be approximated on the basis of the water exchange time in the rock profile assuming piston displacement. It is assumed that the conservative pollutants dissolved in water also diffuse into immobilized water located in the rock pores and migrate at such a speed as if all the

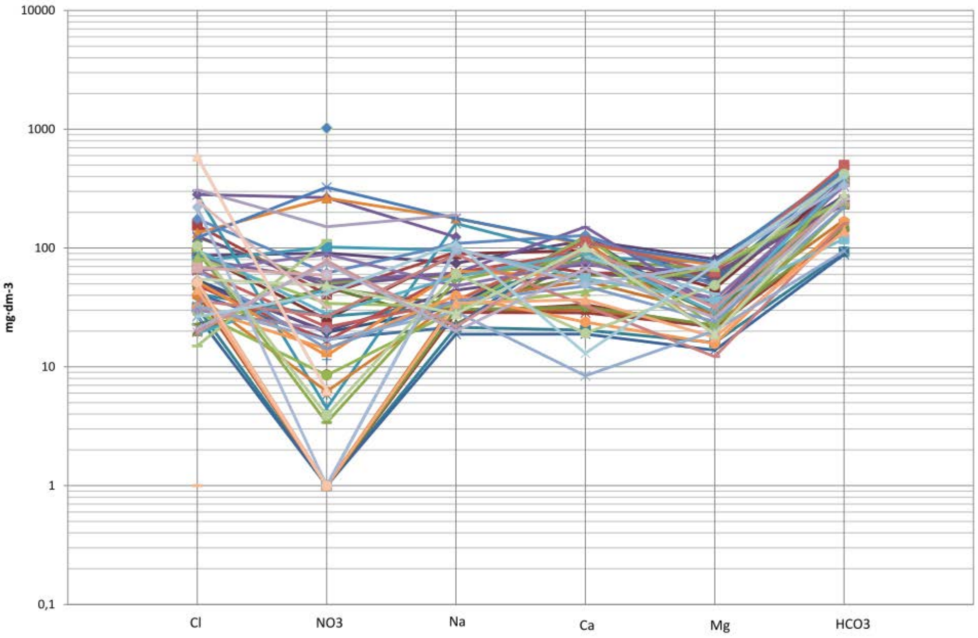


Fig. 4. Modified Schoeller–Berkaloff chart of groundwater samples.

water contained in the rock profile were displaced [39]. The filtration time through the aeration zone is determined by the formula [40]:

$$t_a = \sum_{i=1}^{n} \frac{m_i \cdot (w_0)_i}{I_e} \tag{1}$$

where: m_i is the thickness of successive layers of the aeration/vadose zone profile (m); $(w_0)_i$ is the average volume humidity of successive layers of the aeration/vadose zone (–.); I_e is the precipitation infiltration in the soil profile (m^3/m^2 y) obtained from multiplying the infiltration rate (w_i [%]) and the amount of precipitation.

On a local scale, the infiltration of rainwater by the carried conservative pollutants is a complicated process, but determining the time of water infiltration into the saturation zone is extremely important. The use of meaningful indices based on timescales is indispensable for groundwater resources management [41]. The result of the calculations make it possible, in the event of a threat to the quality of groundwater, to estimate the time of their migration from the surface to the saturation zone, and this in turn make it possible to determine measures needed to be undertaken in order to minimize contamination, for example, untypical draining barrier as a method of limiting penetration of pollutants into the groundwater reservoir [16]. In a situation where it is impossible to counteract water degradation, knowledge of the time of inflow to the intake provides a time buffer for seeking other alternative water sources.

3.2. Surface water characteristics of physiochemical parameters

Table 2 shows the physicochemical characterization of all analyzed parameters of surface water samples, for which the size of the set of determinations made it possible to authenticate the scope of further statistical analyses.

The fluctuation of the concentration level of all analyzed ions were shown on the modified Schoeller–Berkaloff chart (Fig. 6), which facilitates mapping of water chemistry in a rectangular coordinate system as shown in section 3.1 (Groundwater variability of physiochemical parameters). Fig. 6 features the Schoeller–Berkaloff plots for analyzed surface water abstractions, each broken line presenting the results for one of analyzed samples.

As Fig. 6 shows, most of the analyzed ions depict a relatively high variation, in the order of 10 or even a 100 times. This variability could result from the natural variability of surface water chemistry and, most of all, from the nature of the drained drainage basin and the supply of anthropogenic and natural ions from this area. A detailed comparison of the variability of ion content of groundwater and surface waters has been outlined in section 3.3 (Comparison between groundwater and surface water sources of water).

3.3. Comparison between groundwater and surface water sources of water

Water needed for agricultural uses, and even more for domestic use, should meet the applicable quality standards and have low variability of noted main ion content, ensuring a stable, known, and predictable physicochemical composition. The suitability of water for the above-mentioned purposes is a frequent subject of studies undertaken by many researchers [42–44]. One of the objectives of this study, was to compare the suitability of groundwater with that of surface water in order to use it for two basic purposes, domestic use and agriculture. For this purpose, using the Statistica program, a basic statistical analysis of the variability of the observed main ions (Table 2) and parameters

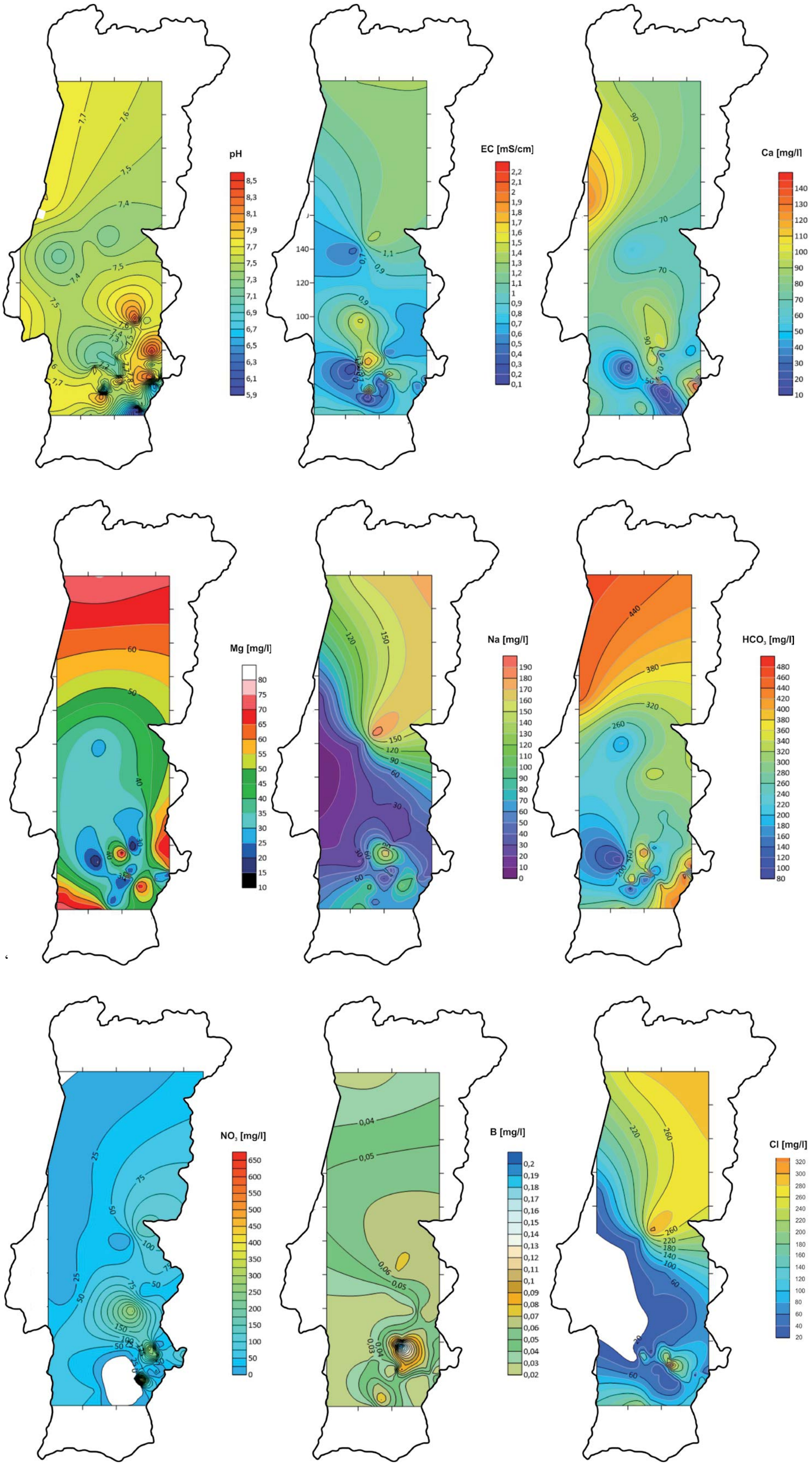


Fig. 5. Spatial distributions of selected parameters and ions from the SURFER program.

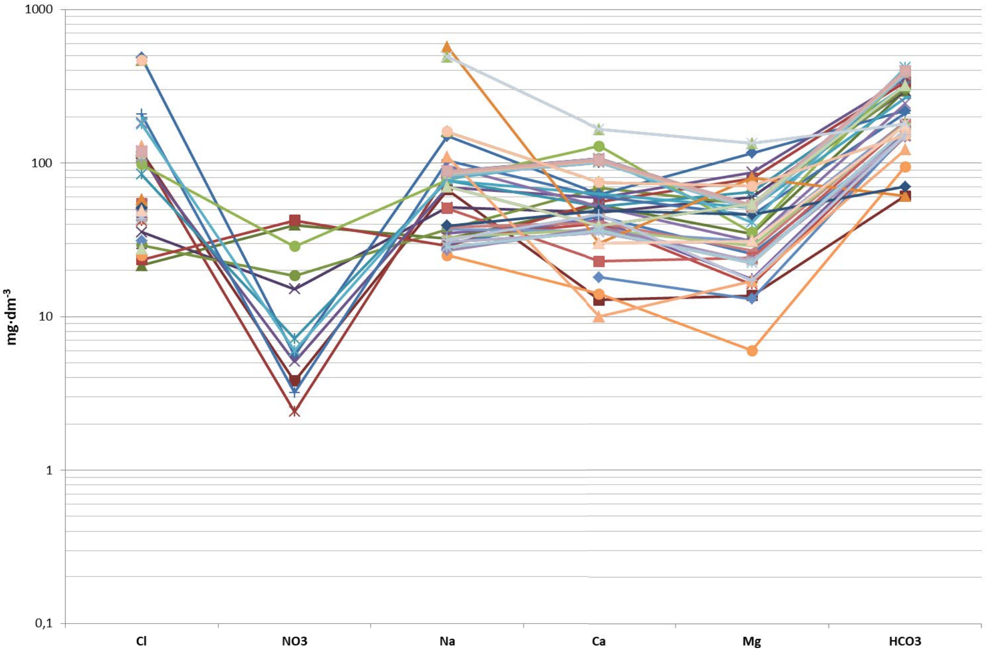


Fig. 6. Modified Schoeller–Berkaloff chart of surface water samples.

in the analyzed water samples was carried out, and distribution histograms were drawn as graphical images of the distribution of abundance (Fig. 7).

Analysis of Fig. 7 clearly indicates that the analyzed parameters and contents of selected ions are characterized by diverse empirical distributions expressed graphically in the form of histograms. Distributions of Ca, HCO_3 are unimodal. From the obtained values of parameters of pH distribution, it may be concluded that the sample is heterogeneous. For the analyzed groundwater, bimodal distributions are more frequent and include calcium, magnesium, and bicarbonate analyses. According to Table 2, the greatest variation in groundwater was shown by the following anions: chloride, nitrate, and bicarbonate ions. Cations have less varied distributions, as shown by standard deviation, while the pH and EC values are least variable. The greatest variation in surface water was observed in the case of the following anions: chloride, sodium, and bicarbonate ions (Table 2). Cations have less varied distributions, pH and EC values are least variable, just the same as in groundwater.

To better illustrate the differences in the physicochemical parameters of the waters captured, Fig. 8 presents box charts for the same analyzed parameters/main ions for groundwater and surface waters, respectively. Adopting one vertical scale facilitated for a better graphic representation of statistical variability.

Generally, the observed values of main ions are characterized by relatively high variability. Nitrate ions observed in surface waters represent the, and this has been presented in detail in section 3.3.1 (Water quality standards for human consumption). For most ions and parameters in surface waters (pH, Ca, Mg, Na, and Cl) their range of variability is greater than for groundwater, which could lead to the preliminary conclusion that using groundwater for agriculture or domestic use is safer. Analysis covering these indicators alone shows that their physicochemical composition is less variable in groundwater, while it is strongly spatially diverse across the country (Fig. 5).

As expected, the pH in surface water samples is higher than in groundwater samples, which results from different hydrogeochemical conditions. Lower pH values (corresponding to slightly acidic waters) are characteristic for groundwater, while pH values in the vicinity of neutral waters are characteristic for waters in ponds in which the equilibrium content of dissolved carbon dioxide in the form of bicarbonates and carbonates is established. In underground waters, the contents of bicarbonate ions were observed in the analyzed samples in a higher range of values than in surface waters, which is manifested by the observed lower pH of these waters. The pH is also an important indicator of the content of ammonia and nitrates. High concentrations of dissolved ions in irrigation water can negatively affect plant growth [45].

3.3.1. Water quality standards for human consumption

In Portugal, the quality of water for human consumption is regulated by Entidade Reguladora dos Serviços de Águas e Resíduos (ERSAR), which holds the status of legal authority over decision on the quality of water for human consumption. All actions are strictly bound by and inspected in accordance with the EU drinking water directive [46], and thus comply with international water quality standards. Decree-Law No. 306/2007 of August 27, on the quality of water for human consumption [47], assesses the verification of water quality/water quality control standards. Drinking water quality is an essential indicator for assessing the development of each country and the well-being of the population [48]. Results of water samples have been compared with standards (Table 3).

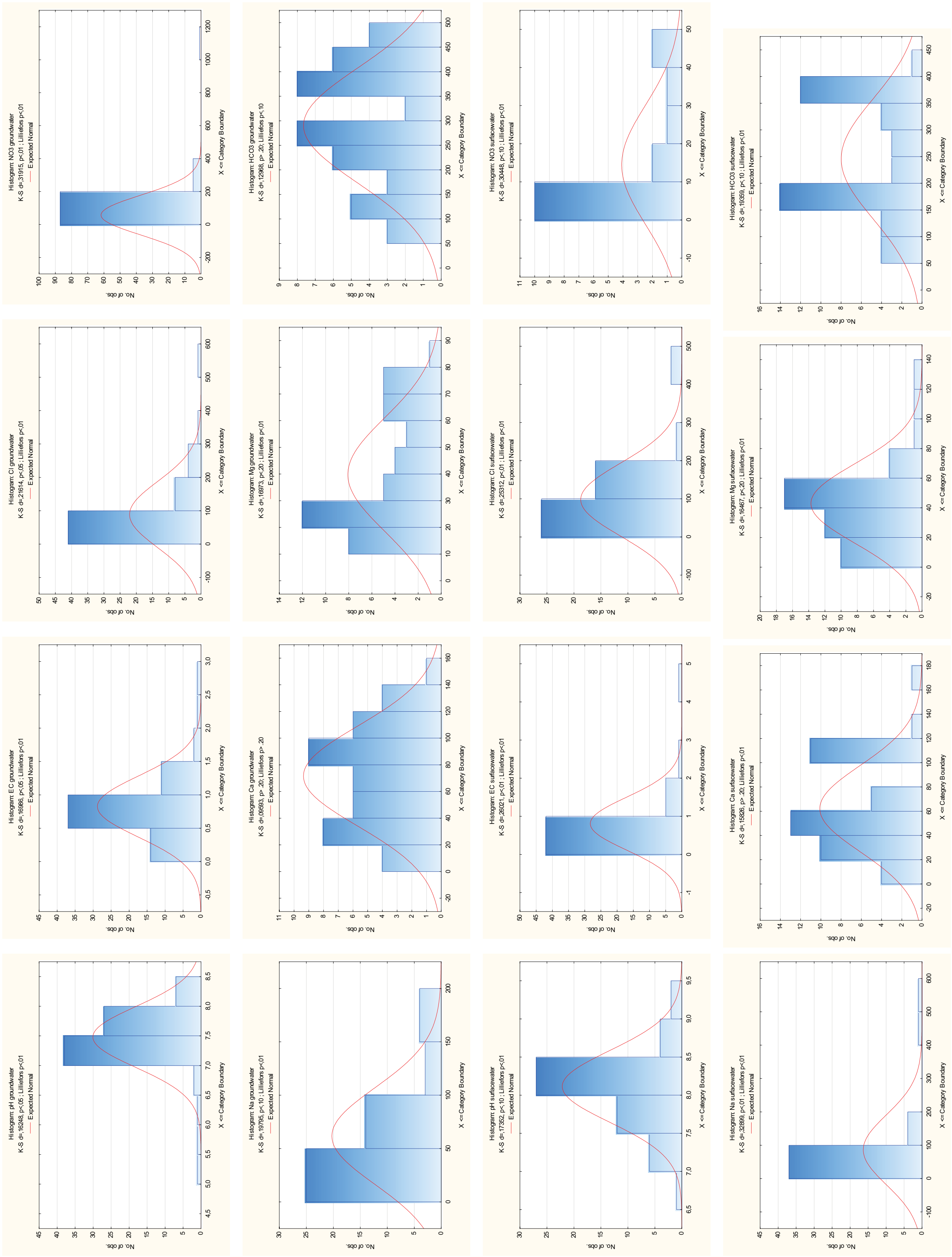


Fig. 7. Histograms of analyzed parameters and ions.

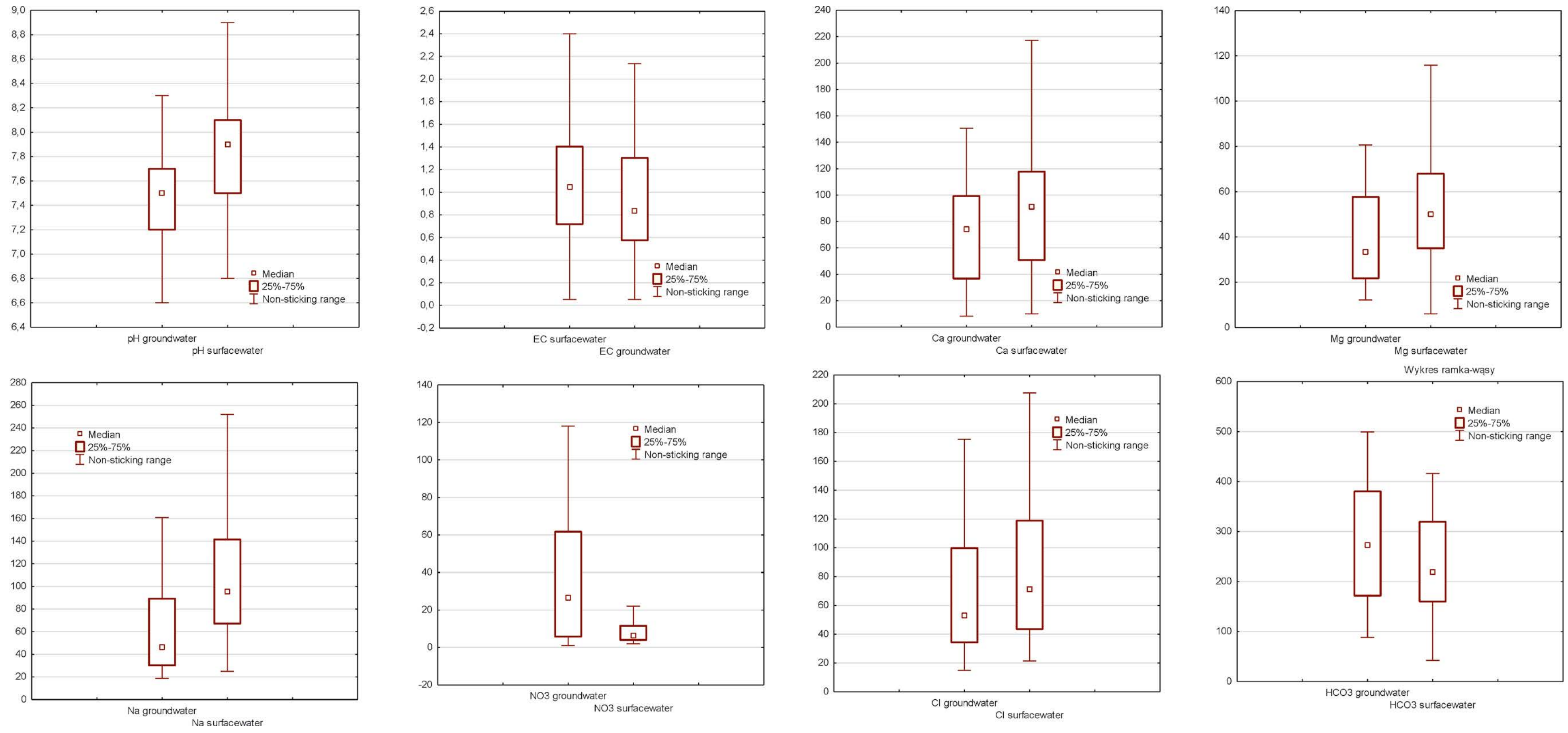


Fig. 8. Characteristic values of selected ions and parameters in comparison of groundwater and surface water.

Table 3
Water quality compared with standards for human consumption [47]

Parameter	Units	Standard	Groundwater samples that meet the standards (%)	Surface water samples that meet the standards (%)
pH	–	$6.5 < pH < 9$	96	98
EC (electrical conductivity)	mS/cm at 20°C	2.5	98	96
Sodium (Na)	mg/L	200	100	92
Chlorides (Cl)	mg/L	250	93	96
Nitrates (NO_3)	mg/L	50	71	100

Analyses of the Table 3 shows that generally both groundwater and surface water samples meet the standard set for drinking water (more than 90% of the samples) except for the nitrates in groundwater (only 71% of the samples). For the comparison, as by this criterion (nitrates standard), 100% of surface water samples meet the standard.

3.3.2. Nitrates course of migration

The level of concentration of nitrate ions in groundwater is at a higher level and shows much greater variability. In surface waters, nitrate ions are not that much sparsely distributed. In conditions of moderate and humid climate, this is a rather unexpected situation, as most nitrogen loads through surface runoff are directed to the rivers and finally to the seas or oceans. Hence, it can be concluded that in dry and hot climate conditions, the mechanism of nitrogen circulation in the water and water-ground environment is different – most pollution of nitrogen compounds infiltrates deep into the aquifer, and surface runoff is very limited. Due to limited rainfall, the runoff generation is small and the use of artificial irrigation results in an increased irrigation return flow causing the nitrate compounds to infiltrate deep in the aquifer. Thus, nitrate concentrations in surface waters are observed at low concentrations. A diagram of the conditions for nitrate ion migration to groundwater and runoff to surface water is shown in Fig. 9. The potential evapotranspiration is normally higher than 1,000 mm/y, causing a high water deficit in the soil. Portugal is a region characterised by very warm and dry summers, with the rainy season occurring in winter, with regular drought cycles that sometimes continue for 2 or 3 consecutive years [49].

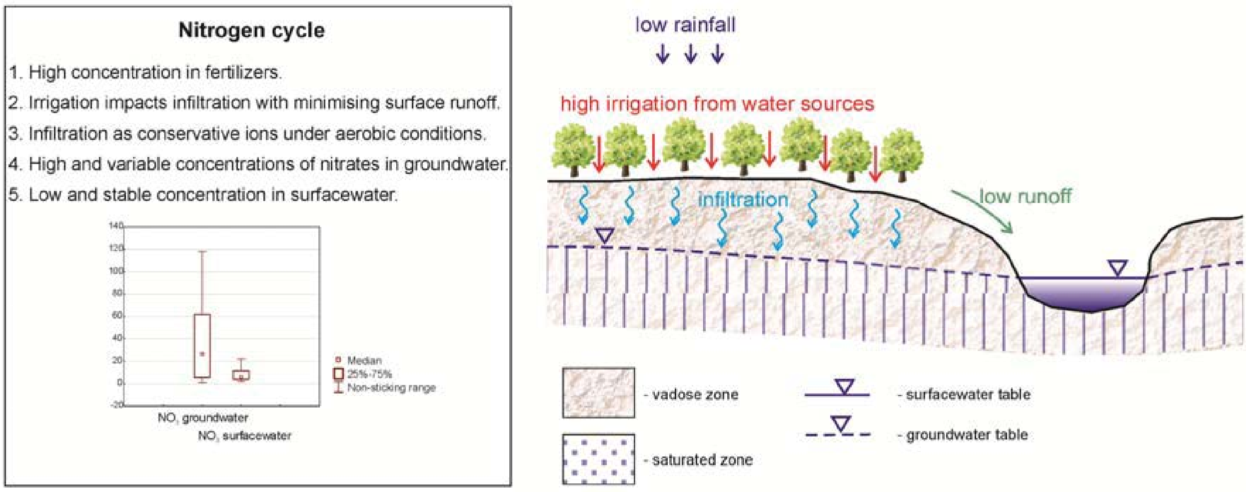
It has been be remembered that generally nitrogen compounds in the form of nitrates or nitrites constitute conservative impurities. Thus, nitrogen forms behave like conservative pollution, that is, they migrate from the surface of the land to groundwater in accordance with the actual rainwater filtration rate. For shallow waters of the first aquifer, this assumption is acceptable because they are mainly waters of open aquifers with a free water table. These waters are dominated by oxidation processes, which include the nitrification process. Denitrification processes that can reduce nitrate concentrations usually only occur in deeper waters, under anaerobic conditions. Many factors could stimulate nitrification or denitrification processes, and these have been studied, among other by Magalhães et al. [50] as effect of salinity and inorganic nitrogen concentrations. Geological and morphological conditions as well as the amount of fertilizers introduced determine the high spatial diversity and variable content of nitrogen compounds in the groundwater captured. Thus, due to the differences found in the content and characteristics of nitrate variability, it can be stated that, according this criterion, surface waters are much safer when used for consumption. Low concentrations and a small variation in nitrate concentrations in surface waters allows them to be used without the use of technologically difficult and expensive water treatment operations. Also, other forms of nitrogen (total nitrogen, nitrates, and ammonium nitrogen) in groundwater assume a much wider range of concentrations with many times higher contents (Table 2). When water is used for irrigation, low concentrations of nitrogen compounds are not so strictly observed and groundwater can often be used. Nevertheless, over-fertilization should be avoided.

Wetland system may be successfully used to reduce excessive nitrogen-compound content. Some plants like *Vetiveria zizanioides* or *Oryza sativa* could be used because of their high phytoremedation potential to nitrate removal in vertical flow constructed wetland systems [51]. Recent studies indicate that these types of facilities are better under dry climate conditions (without four seasons through the year) and should not be recommended for wider use in temperate climate conditions [52]. The reliability of pollutions removal in the constructed wetland system are higher in the stable and high temperature as it is observed in Mediterranean countries through the whole year.

The observed phenomenon of nitrogen migration in the aquatic and water-ground environment should be considered as characteristic for arid and hot regions like Portugal. With the increasing intensification of extreme drought phenomena, there will probably be a deepening intensification of the process. Based on previous reports on climate change in Portugal, the problem of drought and their negative impact is becoming increasingly important [53,54]. The frequency of droughts has significantly increased in recent years [55]. Varied drought recovery durations are perceived for different water quality variables, and in general, it takes about 2 more months for water quality variables to recover from a drought, following termination of hydrological drought [56]. The situation could even be more severe when the rainfall came after a long drought and the drought–rewetting cycle effect occurred [57].

4. Conclusions

Portugal is a Mediterranean country characterized by high temperatures and low rainfall with a predominance of evaporation over rainwater infiltration. In such dry and



Nitrogen cycle

1. High concentration in fertilizers.
2. Irrigation impacts infiltration with minimising surface runoff.
3. Infiltration as conservative ions under aerobic conditions.
4. High and variable concentrations of nitrates in groundwater.
5. Low and stable concentration in surfacewater.

Fig. 9. Cycle of nitrogen migration in the water environment.

hot regions, prolonged droughts are particularly devastating for the population. In the short run, lack of water limits its availability for domestic use, its quality deteriorates, while in the long run, it leads to shortage of food, as the lack of water for irrigation results in a lack of agricultural production, which is the dominant branch of the economy in Portugal. The effects of global warming on agriculture and water resources management is of concern in the Mediterranean climates. In countries with a dry and hot climate, climate disasters, especially the potential for prolonged drought, pose a very high risk. In addition to the criterion of access to water in the amount meeting the demand (which has been done by many researchers so far), the quality of the water taken into consideration is too of particular importance. This issue was the merits of this work. As a final conclusion, it has been pointed out that in a dry and hot climate, with a large share of artificial irrigation of crops combined with the use of fertilizers, the migration cycle of nitrogen compounds in the water and soil environment is different in the temperate and humid climate. In moderate climates, the vast majority of nitrogen compound loads are carried with rainwater through surface runoff to rivers. Nitrates, as biogenic compounds, are one of the monitored surface water pollutants in such climate with serious environmental consequences. Based on available analyses of ground and surface waters in Portugal, it was found out that in the case of semi-arid climate in conditions of intensive irrigation of crops, the nitrogen migration cycle in the environment is specific. Irrigation carried out in a way that limits evaporation, intensifies the infiltration of water from irrigation with nitrogen compounds used in fertilization. As a result, groundwater is characterized by significantly higher contents of various forms of nitrogen and their significant variability, which results from the intensity of crop fertilization. Based on the collected and developed database, a conclusion reached in this work is that surface waters are much safer when used for consumption. Low concentrations and a small variation of nitrate concentrations in surface waters means they can be used without of the need to employ technologically difficult and expensive water treatment operations. As there is no strict requirement to keep the concentrations of nitrogen compounds low when for irrigation, groundwater could also be used to irrigate the crops, however, over-fertilization should be avoided.

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