Chemistry of Portuguese Water for Consumption and Potential Benefits to Human Health

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Abstract

The health benefits of water intake may result from the content of chemical elements that it carries and from its physico-chemical characteristics. Know whether and how the physical and chemical characteristics of drinking waters can influence our health is important for the well-being of society. With the development of this work it was evaluated the quality of the Portuguese drinking water, both distributed by the public network (45 samples) and by distribution at markets in bottles (24 samples), it was analyzed its origins and identified cases of relation between the drinking water's characteristics and human health. It was verified that Portuguese drinking waters present good quality, with few irregularities, and through the Piper diagram it was concluded that a significant part of the Portuguese tap water under study is calcium and sodium hydrogen carbonate facies and that the bottled water is mostly sodium hydrogen carbonate facies, with differences along the territory depending on the captured water's circulation geological environment. Based on correlation studies, among others, it is indicated that certain recurrent pathologies in Portugal may be fought with the consumption of some drinking waters. Therefore 48 % of the Portuguese tap waters may in theory provide reductions in regard to cardiovascular diseases, kidney stone and oral diseases and bottled waters can bring these benefits to various combinations of pathologies. Pedras Salgadas and Frize could be examples of waters that may provide benefits in controlling high blood pressure and circulatory diseases.

Keywords: drinking water, health, water quality, pathologies, hydrochemistry.

1. Introduction

Water is essential to life on Earth and represents 70 % of its surface. However, available freshwater represents less than 3 % of the total earth water (Mendes and Oliveira 2004). The human being is made of 65 % water and it is highly dependent of its availability (Mendes and Oliveira 2004). The lack of water intake can result in situations that lead to death (Cortez, 2012).

In developed countries there are two main ways to access water: the public water supply (tap water) and bottled water. Tap water may be derived from superficial and/or underground waters and it's subjected to treatments that guarantee its drinkability. Bottled water originates from underground waters and doesn't suffer any modifications because the preservation of its natural properties is mandatory (RASARP, 2013; APIAM, 2014[a]).

One of the essential properties of water is its great ability to dissolve different substances, which makes water a vehicle for essential nutrients for the survival of plants and animals (Cortez, 2012). The constituents of the waters can influence positive or negatively the human health and can appear naturally in the water or due to pollution phenomena. There are several national and worldwide entities that control the drinking water quality, which establish quantitative and qualitative rules and develop scientific research related with this subject's knowledge. Knowing how the waters that we drink daily influence our health is very important for the well-being of our society.

Several studies have been undertaken with the purpose of finding which water properties influence human health. For example, it was stated that waters rich in calcium are important in the human diet because of their high quantity of bio-available calcium and also that selenium is important for the immune system (Heaney, 2006; WHO, 2005). This study aims to assess the chemistry and quality of the Portuguese human drinking water (tap and bottle water) and identify whether there is some relationship between the features of the consumed water and our health, in order to identify potential benefits/harms effects resulting from its consumption. For this aim, Portuguese waters were sampled and their physical and chemical quality characteristics evaluated. At the same time, it was carried out an information gathering exercise on certain common medical conditions in Portuguese population and the characteristics of the water consumed in administrative zones were compared with the occurrence of these diseases.

2. Sampling and Methods

For this study, between 2011 and 2013, 45 tap waters from continental Portugal were sampled, in order to be representative of the water that the Portuguese consume at their homes, and 24 bottled waters were purchased in supermarkets. The tap waters represent 43 Portuguese counties (*concelhos*), scattered throughout the administrative areas NUTS II (Figure 1). The bottle waters (16 mineral waters and 8 spring waters; Figure 2) represent the countries consumption since they are freely sold in the Portuguese market.

Water samples were analysed in the laboratory of Petrology and Mineralogy at Instituto Superior Técnico (LAMPIST), for the following parameters: pH (hydrogen potential), alkalinity, electrical conductivity (CE) and dry residue (RS). The determination of the anions was performed at LAMPIST by ion chromatography using a DIONEX ICS-900 chromatograph. The cations were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, when the content is above a certain maximum value) at Actlabs Laboratory (Canada), after the preservation of the sample by acidification at pH < 2 with concentrated HNO_3. The chemical analyses were performed without prior sample filtering, to ensure the representativeness of water consumption.

The classification of the hydrochemical facies of the waters done through the Piper diagram was performed using the *RockWorks 15* software. The water hardness was calculated using the standard Method 2340 B, APHA (APHA, 1999). The diseases and mortality rates data were collected through the available online information both in independent work and in the National Institute of Statistics platform (INE). The determination of the Pearson Correlation Coefficient (or classical correlation coefficient) for a 95 % confidence interval was made with the *Statistica 12.5* software.

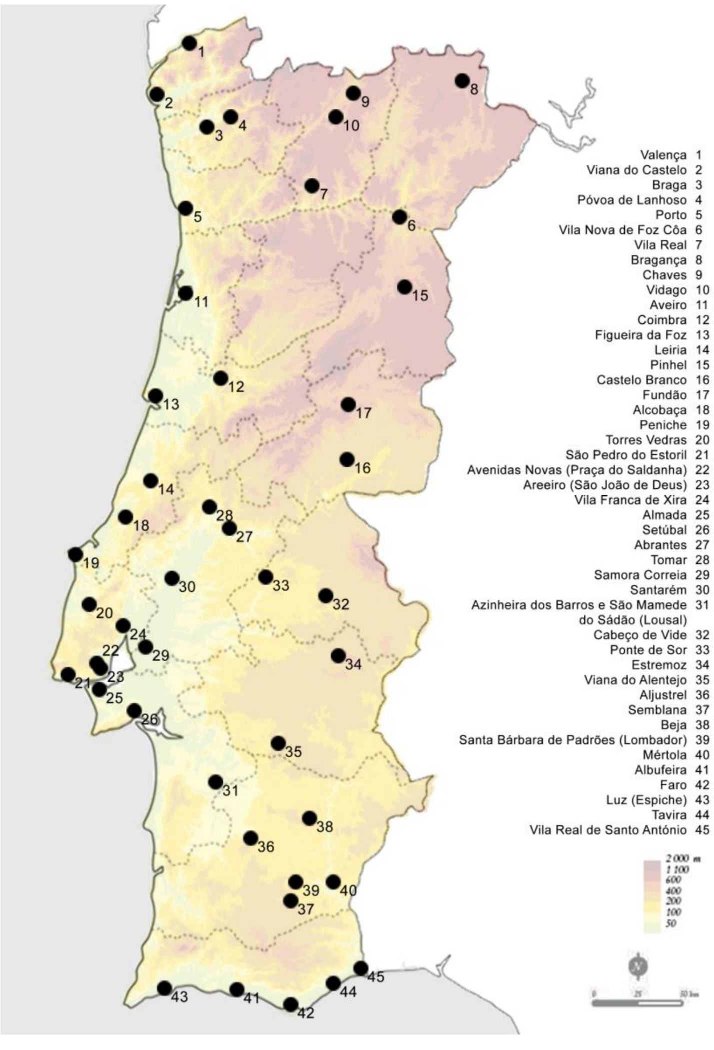


Figure 1 - Map of Portugal with the locations of the sampled public waters.

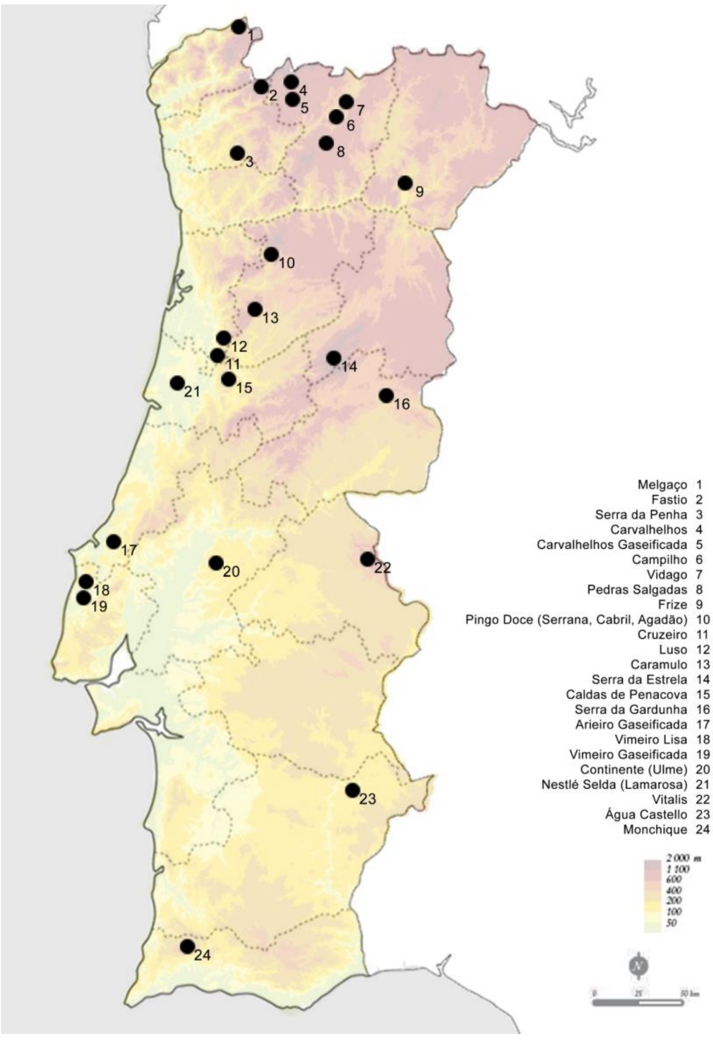


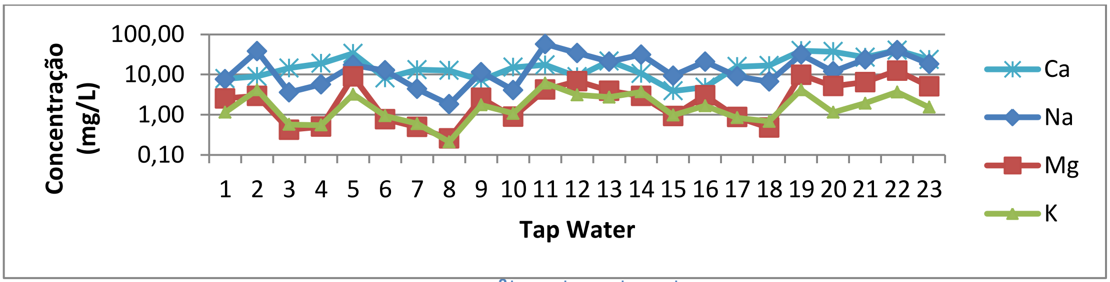
Figure 2 - Map of Portugal with the locations of the sampled bottled waters.

3. Characterization of the Waters in Study

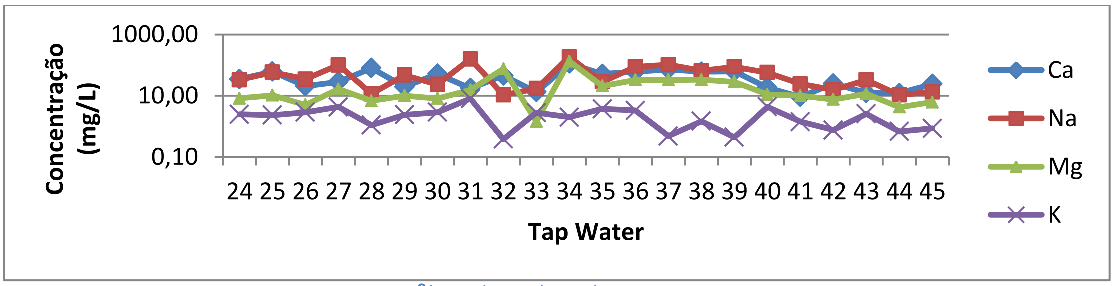
3.1. Tap Water

Regarding the pH parameter, the maximum value recorded in tap water was 9.7 (Alcobaça) and the minimum value was 5.7 (Coimbra). The average pH was 7.35 and the median 7.44. The maximum and minimum values of conductivity were recorded, respectively, in Estremoz (1970 μS/cm) and Bragança (65.7 μS/cm). The median value of the conductivity was 288 μS/cm (average of 406.01 μS/cm). Between a minimum of 50.2 mg/L and a maximum value of 154.8 mg/L, the dry residue of the public water varies widely, recording a median of 189.2 mg/L. Considering the EC values recorded, about 82.2 % of public mineral waters have low values and 17.8 % intermediate values. The public waters have a temporary alkalinity average of 123.6 mg/L of HCO_3^-, median of 76.86, with minimum e maximum of 19.52 and 495.32, respectively.

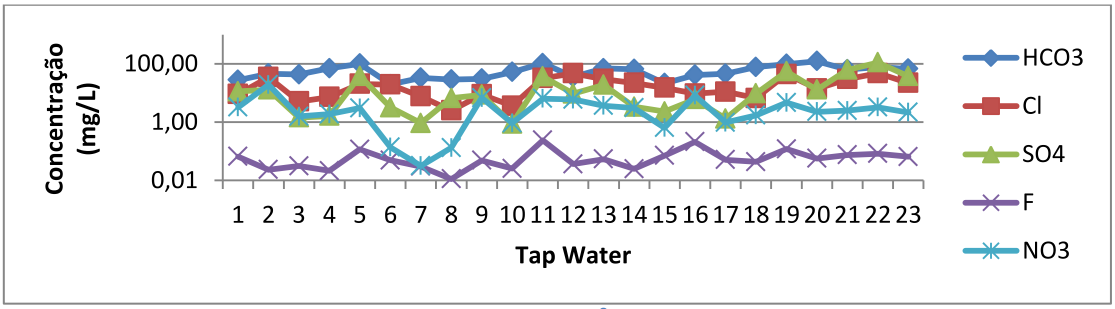
The dissolved cationic and anionic species in the studied tap water appear in several ranges of concentration, as presented in **Erro! A origem da referência não foi encontrada.** to **Erro! A origem da referência não foi encontrada.**.



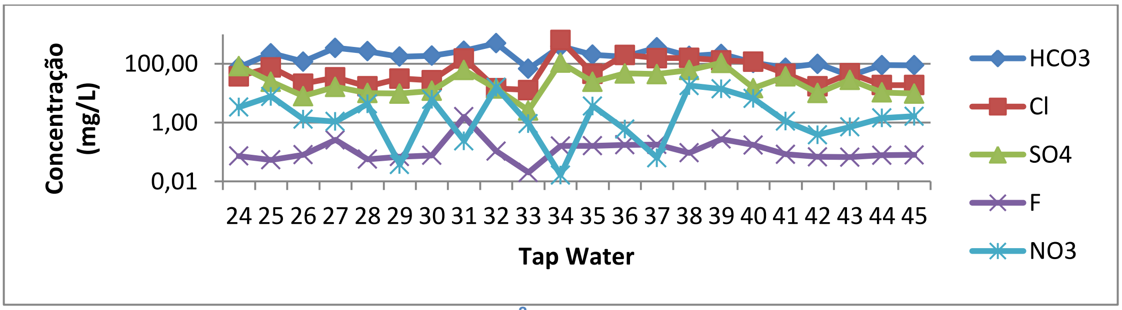
Graphic 1 - Concentration of Ca^{2+}, Na^{+}, Mg^{+} e K^{+} in the studied tap waters.



Graphic 2 - Concentration of Ca^{2+}, Na^{+}, Mg^{+} e K^{+} in the studied tap waters (continuation).



Graphic 3 - Concentration of HCO_3^-, Cl^-, SO_4^{2-}, F^- e NO_3^- in the studied tap waters.



Graphic 4 - Concentration of HCO_3^-, Cl^-, SO_4^{2-}, F^- e NO_3^- in the studied tap waters (continuation).

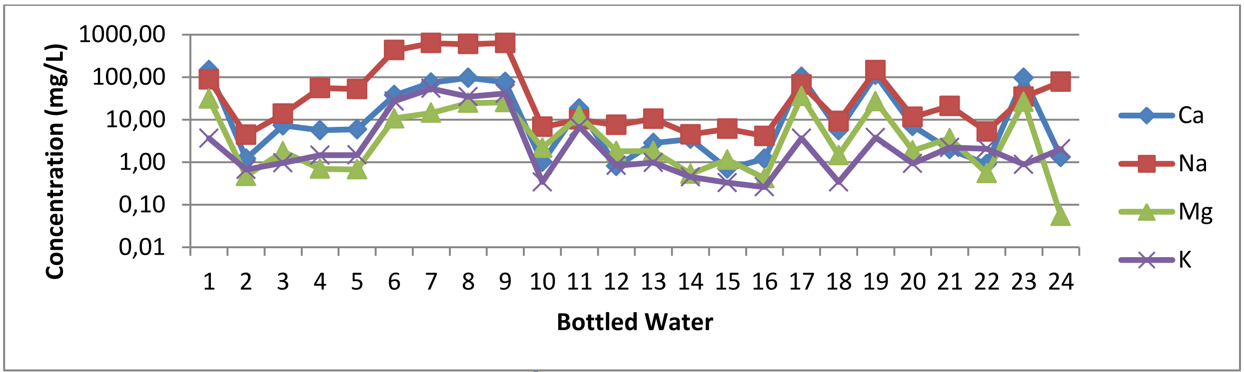
Based on the concentration of major anions and cations, the most frequent facies for tap waters was calcium hydrogen carbonate (26.7 %) and only one water had a magnesium bicarbonate facies (Aveiro).

Tap waters exhibit a varied hardness distribution: 13.3 % are hard; 20 % are very hard; 28.9 % are soft; and 37.8 % are very soft. The median and average hardness of these waters are, respectively, 80.2 mg/L and 123.78 mg/L of $CaCO_3$.

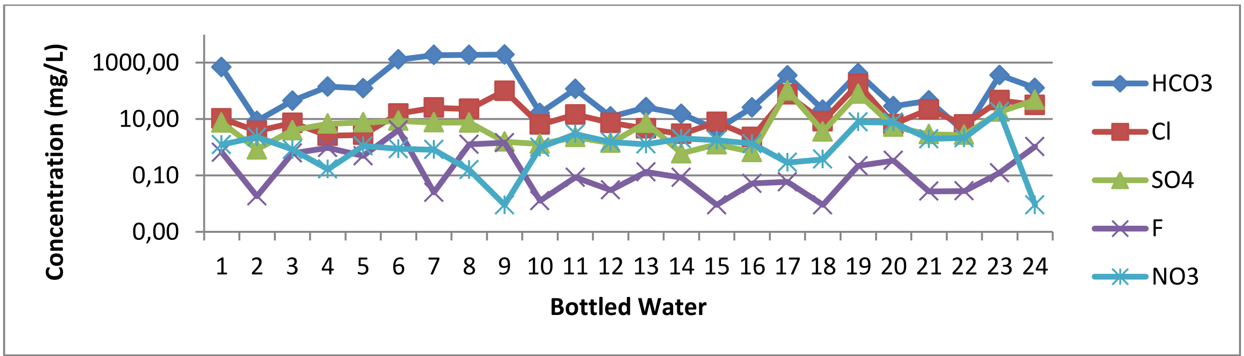
3.2. Mineral and Spring Waters

In mineral and spring waters the pH minimum values were 5.5 for plain water (Caldas da Penacova) and 5.3 for carbonated water (Carvalhelhos Gaseificada) and the maximum values were 9.4 for plain water (Monchique) and 6.5 for carbonated water (Frize). The maximum and minimum condutivity values were measured, respectively, in the Monchique water (419 µS/cm) and in the Serra da Gardunha water (33 µS/cm). These waters have a median of 82.7 µS/cm (average of 116.4 µS/cm). The plain waters have low dry residue values, with a median of 101 mg/L (average of 122 mg/L), that don't exceed 453 mg/L (Carvalhelhos water). The carbonated waters have the highest dry residue values, with a median of 1289 mg/L, a maximum of 2336 mg/L (Frize) and a minimum of 208 mg/L (Carvalhelhos Gaseificada). The carbonated waters are more mineralized than the plain waters, since 73.3 % of the plain waters have low mineral concentration and the remaining have the lowest mineral concentration. Among the carbonated waters 22.2 % have low mineral concentration, 66.6 % median mineral concentration and 11.2 % have high mineral concentration. The median value of alkalinity for plain waters was 25.9 mg HCO_3^-/L (minimum and maximum of 3.7 and 141.5, respectively) and for carbonated waters the median was 691.7 mg HCO_3^-/L (minimum of 124.4 and maximum of 1941).

The dissolved cationic and anionic species in the bottled water appear in several ranges of concentration, as it can be seen in the Graphic 5 and Graphic 6.



Graphic 5 – Concentration of Ca^{2+}, Na^+, Mg^+ e K^+ in the studied bottled waters.



Graphic 6 – Concentration of HCO_3^-, Cl^-, SO_4^{2-}, F^- e NO_3^- in the studied bottled waters.

The majority of the bottled waters are sodium hydrogen carbonate facies (62.5 %).

The median hardness of these waters, is 19.96 mg/L (average of 121.87 mg/L of CaCO3), which classifies these waters as too soft (62.5 %) and very hard (29.2 %).

3.3. Quality of the Drinking Water

Although the measured concentrations don't have a long-term significance, at the time of sampling some irregularities were found regarding the Portuguese Law and the EU Directive (Table 1). Some were worrying, like the water from Estremoz which has a concentration of silver 4.3 times higher than the maximum value allowed by Portuguese law.

Table 1 – Comparison between tap water and bottled spring water concentrations and the maximum values of the DL 306/2007 for the drinking water.

	Cl (mg/L)	F (mg/L)	Al (mg/L)	As (µg/L)	Se (µg/L)	Ag (µg/L)
Tap Water (Freguesias)						
Estremoz	633.7					4.3
Azinheira dos Barros e São Mamede do Sádão (Lousal)		1.6				
Bragança			0.41			
Alcobaça			0.27			
Castelo Branco				42.5		
Samora Correia				10.7		
Santa Bárbara de Padrões (Lombador)					39.8	
Spring Bottled Water						
Continente (Ulme)				12.8		
Portuguese Law DL 306/2007	**250**	**1.5**	**0.2**	**10**	**10**	**1**

The high concentration of Cl^- in the Estremoz water is probably due to the disinfection process that tap water is submitted with Cl^- and the high concentration of Al^{3+} (Bragança e Alcobaça waters) due to the coagulation/flocculation process that some treatment plants have done with aluminum sulfates (Mendes and Oliveira, 2004). The selenium in the water of Lombador may be due to the selenium minerals that occur with sulphides mineralisations (Lenntech, 2015) in the Zona sul-portuguesa and the silver's high concentration in the Estremoz water could be due to the silver occurrences along the metallic mines located in that zone (LNEG, 2013).

4. Health and Water Consumption

For this study, several diseases/pathologies with great relevance for the Portuguese society were analyzed: hypertension, cardiovascular diseases, kidney stones, osteoporosis, oral diseases and diseases due to mental disorders. These data were collected mostly for 2012, since the samples for this study were collected between 2011 and 2013. When there were impossibilities, due to lack of information available, the values of other years were used in order to be possible to continue the practice. However this was only done after confirming that the concentrations of the major elements in the waters don't suffer great variations along the years. This confirmation was carried out using data of the quarterly analysis by the municipal councils (*câmaras*), which are available for online consultation across several on-line platforms.

In Portugal, hypertension is a national problem since almost half the population has high blood pressure, 42 % (Nichols et al., 2012). As it has been established by several studies, the high consumption of salt is a dietary factor connected to hypertension. For example, the INTERSALT concluded that the consumption of Na higher than 2.3 g/day results in high blood pressure (PS/PD of 3-6/0-3 mmHg) (Viegas, 2008). Albertini et al. (2007) found that the elderly, with normative blood pressures, when consuming highly mineralized sodium chlorinated water have an increase in blood pressure, even when eating a diet restricted in salts.

With data from this study it was verified a positive correlation between the sodium on tap water and cases of hypertension in Portugal's population ($r = 0.93$). However, it has to be taken into account that this correlation was established with little data and that the largest share of the daily sodium intake comes from eating habits and not water consumption. Even so, EPA recommends that individuals with strict low sodium diets (< 500 mg/day) don't drink water with more than 20 mg/L Na, making several Portuguese waters not suitable for those cases (admitting a daily consume of 2 L of water).

Some studies verified that a low sodium diet (460 mg Na/day) can result in an increase in total cholesterol, which is worrisome since high cholesterol is closely related with cardiovascular risk (Park, 2011). According to Albertini et al. (2007), the consumption of highly mineralized sodium hydrogen carbonate waters in combination with a low sodium diet, is beneficial for the human health. A healthy adult that follows this diet and drinks at least 2 L of water per day, should consume waters rich in sodium (for example, the tap waters from Leiria, Abrantes and Samora Correia; or the bottled waters Frize, Monchique and Carvalhelhos).

In Portugal, the concentrations of sodium in the drinking water can be due to several factors, as for example, in the Orla ocidental and Orla algarvia zones the water from some groundwater captions runs in evaporitic formations and cases of saltwater intrusion into aquifers can also occur (Almeida et al., 2000).

The number of deaths in Portugal due to circulatory diseases has been increasing over the years and in 2012 the diseases of the circulatory system were the leading cause of death in the country (30.4 %), corresponding to a crude mortality rate of 312.6 deaths per 100 000 inhabitants (INE, 2014[b]).

There are several cases in which it was found an inverse relationship between magnesium concentration in drinking water and the prevalence of cardiovascular diseases. According to Albertini et al. (2007), the consumption of magnesium is associated with the decrease of the mortality due to stroke, but not the incidence. Also, several epidemiological studies, that took place between 1979 and 2003, showed an inverse relationship between the consumption of hard waters and death from ischemic heart disease (WHO, 2004).

Since the benefits of calcium and magnesium are only visible when water with concentrations higher than 20-30 mg/L of Ca and 10 mg/L of Mg (WHO, 2004) is consumed, the correlations established in this study, between those concentrations in tap waters and the standardized mortality rates for circulatory diseases (INE, 2014[a]), are only inverse in those conditions. So, an inverse correlation was found between the magnesium in the waters of Alentejo and the mortality for cerebrovascular diseases (r = -0.945), and between the calcium in the waters of Lisboa e Vale do Tejo and the mortality for ischemic heart disease and acute myocardial infarction (r = -0.771 e r = -0.757, respectively). The Portuguese waters that, according to these findings, have benefits for human health are: tap waters from the areas NUTS III of Península de Setúbal, Lezíria do Tejo, Alto Alentejo, Alentejo Central and Baixo Alentejo; and bottled waters Melgaço, Vimeiro Gaseificada, Arieiro Gaseificada, Pedras Salgadas, Água Castello, Frize, Vidago and Campilho.

An example of a geological factor related with high concentrations of magnesium and calcium in the drinking water can be found in the Zona de Ossa-Morena, since some of the mentioned waters were collected and distributed there. That geological factor is the multiple occurrences of dolomite ($CaMg(CO_3)_2$), which is one of the most common minerals in carbonated rocks (along with calcite and aragonite) and that can cause water rich in Mg and Ca (Almeida et al., 2000).

The European Association of Urology (EAU) (2012) estimates that about 55 million adults in Europe are affected with kidney lithiasis (or kidney stones). Some studies report that the consumption of sodium, both through water and food, indirectly increases the amount of calcium in the body and assists stone formation in the kidneys (Ravikumar et al., 2012). The consumption of waters with high calcium content (> 75 mg/L) or acidic can also assist in stone formation (Ravikumar et al., 2012). Thereby, in order to prevent the formation of kidney stones, assuming a daily consumption of at least 3 liters of water and the reduced consumption of animal protein, waters with low concentration of Ca^+ should be consumed between meals (for example, the tap waters from Leiria, Pinhel, Alcobaça, Valença and Mértola; or the bottled waters Fastio, Luso, Vimeiro Lisa, Monchique and Campilho).

Osteoporosis affects millions of people worldwide and in Portugal affects more than half a million people, especially women (INE, 2009). Although not all types of osteoporosis are due to a negative calcium balance, this is a contributory factor even when it does not have a causal role (Nordin, 1996). Another element connected to the osteoporosis problem is phosphorus, which is helpful in maintaining bone health, although its contribution only appears when there is a good calcium and phosphorus relationship – 1-2.5:1 (Morais e Burgos, 2007).

A correlation was not found between the calcium intake in the tap waters and osteoporosis cases in Portugal. This lack of a good correlation can be due to the fact that people generally do not consume enough calcium daily (Araújo et al., 2012), resulting in a calcium level in the body that is not sufficient to fight or prevent osteoporosis. Since usually there is a good intake of phosphorus in our diet (Araújo et al., 2012), it was possible to find a good inverse correlation between phosphate content in water for human consumption and the incidence of osteoporosis in men. With these results it can be suggested that waters rich in phosphate can be beneficial in the fight against osteoporosis, provided the subjects have a balanced diet in calcium and phosphorus.

Waters with a high concentration of calcium should be consumed in addition to a diet rich in calcium (~1000 mg/L), in order to help the prevention of osteoporosis derived problems (for example, the tap waters from Estremoz, Tomar, Semblana and Almada; and the bottled waters Melgaço, Vimeiro Gaseificada, Arieiro Gaseilficada and Vidago). For healthy adults with a diet that respects the recommended daily intake of calcium and phosphorus, the waters that apparently help the prevent of osteoporosis due to their good Ca:P balance are the tap water from Castelo Branco and bottled waters Luso, Caramulo, Serra da Gardunha and Vitalis.

The concentration of phosphorus in drinking water is usually low but, for example, some higher values can be found due to groundwater circulation in contact with apatite ($Ca_5(PO_4,CO_3)_3(OH,F,Cl)$), since it is a typical phosphorus mineral that occurs with granitoids in the Portuguese Zona centro-ibérica (Almeida et al., 2000).

Oral diseases such as dental cavities and periodontal diseases are a serious public health problem, since they affect most of the population and influence their levels of health, wellness and quality of life (Plano Nacional de Saúde, 2015). The beneficial effects of fluoride intake are established, because it reduces the solubility of the mineral portion of the tooth making it more resistant to the action of bacteria, reducing the prevalence and severity of dental cavities (Duarte, 2008). However, a common disease in the oral health is fluorosis, which occurs when excessive fluoride is consumed, which manifests itself in the form of stains on teeth (DGS, 2008).

According to WHO, the water consumption of 1.5 to 2 mg/L of fluoride in hot climate areas, may contribute to the occurrence of fluorosis. In continental Portugal, levels of fluorosis are low, but there are some cases in Alentejo (DGS, 2008), which is a region with moderately hot climate and occurrence of high fluoride in the tap water (Alentejo Litoral – 1.57 mg/L F).

For tap waters in study, it was found a good correlation between the fluoride concentration in the water and the percentage of children (6 years old) free of cavities. Since the external aspects (such as tobacco) have little influence on children, it was observed that in this case a higher fluoride concentration in drinking water increases the absence of cavities in children. It has to be mentioned that the limitation of our data does not allow to make an absolute statement about the relationship between fluoride consumed trough tap water and a good oral health, but to date there isn't any data corroborating this theory, provided that there is compliance with the maximum consumption figures issued by WHO.

According to the Directorate General of Health (DGS, 2005), children up to 6-7 years of age, people with diseases due to excessive fluorine and breastfeeding women should not regularly drink water with fluoride content of more than 0.7 mg/L. This means they should avoid the following bottled waters: Carvalhelhos, Monchique, Pedras Salgadas, Frize and Campilho.

The presence of fluoride in the water usually is due to the dissolution of fluorite or other minerals such as fluorapatite, muscovite and some amphiboles (Calado and Almeida, 1993), which are common on the North of the country due to the existence of a large quantity of granitic rocks.

Diseases due to psychological disorders, which are revealed with mood disorders, as the majority of the depression situations, are directly responsible for high levels of personal, family, social and occupational disability and are indirectly responsible for suicide. In Portugal, in 2010, suicide mortality rate was 3.8 for women and 13.5 for men (OECD, 2012).

Mood disorders are associated with a high suicide risk, which can be reduced by treatment based on lithium (Kabacs et al., 2011), which in the correct dosage does not alter consciousness, does not give drowsiness and is harmless to non-manic and non-depressed patients (Leal and Fernandes, 2002). In addition to its attenuating characteristics of humor, several studies have demonstrated that lithium also has anti suicide properties, and throughout the years several studies have shown an inverse correlation between the lithium in drinking waters and the mortality rates for suicide (Ohgami et al, 2009; Kabacs et al., 2011; Kapusta et al, 2011).

In this study it wasn't found any correlation between the concentrations of lithium of the studied tap water and the mortality rate for suicides, for 100.000 inhabitants, and the standardized mortality rate of intentional self-harm and consequences. The lack of correlation could be also related to the socio-economic factors, such as unemployment, per capita income, education level and others, because Portugal with the economic crises has been having a growing unemployment rate (7.6 % in 1983 to 16.2 % in 2013) (PORDATA, 2015).

Besides suicide, the study by Schrauzer and Shrestha (1990) indicated that lithium from public waters had moderating effects on violent criminal behavior. However, for the waters in study correlations between lithium's concentration of tap waters and the crimes against the estate and against people for 2011 and 2013 was not established.

In addition to the studies for the tap waters, there are other studies reporting the effects of additional lithium consumption in much lower doses than those administered therapeutically (600-1200 mg/day) (Leal and Fernandes, 2002). For example, a study with recovering drug addicts demonstrated, the existence of a positive effect on the well-being and mood of individuals through daily supplementation with 400 µg of Li (Schrauzer and Vroey, 1994). According to these studies, the daily consumption of only 0.33 L of Vidago, Frize, Pedras Salgadas or Campilho waters, can bring benefits to the welfare and mood of the consumers. These values do not represent, however, an alternative to lithium supplements administered to patients with more severe problems, since the lithium concentration in bottled water is lower than the recommended doses for therapeutic purposes. This product could, however, be regarded as a nutritional supplement.

Lithium-rich waters in Portugal may be due to several factors such as for example a deep water circulation within faults in the crust highly mineralized zones and the water-rock interaction with pegmatite, since it has a high concentration of lithium (30-70 mg of Li/Kg), as it happens in the north of the country (Salminen, 2005).

5. Conclusions

In this work it was verified that the chemicals species in drinking water, and other qualitative and quantitative characteristics, are linked with the geological environment of circulation of the ground and surface waters and with the treatment processes to which are submitted.

The chemistry of the studied tap waters differed depending on the area of water collection (NUTS III). Among them, around 57.8 % of the waters are hydrogen carbonated, 17.8 % are chlorinated and 24.4 % are sulphated/chlorinated. The hydrogen carbonated waters are mostly calcic (46.2 %) and sodic (26.9 %), the chlorinated are sodic (50 %) or calcic/magnesian (50 %) and the sulphated/chlorinated are mostly calcic/magnesian (81.8 %). It was also verified that waters from Norte are mainly calcic, from Centro are mainly sodic and the waters from Alentejo and Algarve are mainly calcic or magnesian.

The bottled waters are mostly sodium hydrogen carbonate facies (62.5 %), as the waters from the Zona centro-ibérica (for example, Pingo Doce, Serra da Gardunha, Caramulo, Fastio and Serra da Penha).

In this case study, it was indicated that the Portuguese drinking waters may provide presumed health benefits with regard to fighting at least one of the diseases/pathologies analyzed. For the tap water, it was found that 48 % can provide benefits for the health of a healthy adult individual, with respect to cardiovascular diseases, kidney stone disease and oral diseases (waters from Porto, Alcobaça, Peniche, Torres Vedras, São Pedro do Estoril, Avenidas Novas (Praça do Saldanha), Areeiro (São João de Deus), Almada, Setúbal, Abrantes, Tomar, Samora Correia, Santarém, Cabeço de Vide, Ponte de Sor, Viana do Alentejo, Aljustrel, Semblana, Beja, Santa Bárbara de Padrões (Lombador) and Mértola).

Taking into account the benefits provided to healthy adults, the bottled waters worth mentioning are: Melgaço, Areeiro Gaseificada, Vimeiro Gaseificada and Água Castello (hypertension, cardiovascular diseases and oral diseases); Carvalhelhos Gaseificada (hypertension, kidney stone and oral diseases); Campilho (hypertension, circulatory diseases and kidney stones); Pedras Salgadas and Frize (hypertension, circulatory diseases and psychological diseases); Caramulo and Serra da Gardunha (kidney stone, oral disease and osteoporosis).

This thesis constituted a preliminary study, within this thematic, made with the number of samples that were possible to collect/obtain in the country. In the future, if it is intended to proceed with a larger or more specific study in Portugal, with the aim to verify, or not, the results obtained in this work, it would have to ensure a greater database, a long term specialize medical data and correlation studies that should take into account socio-economic and/or behavioral data.

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