Impacts of climate changes in groundwater quality of Portuguese karstic aquifers

Oliveira, J.

1. Goals
This project intends to be an initial approach to the study of climate change in quality and saturation state of groundwater sources, facing karstic Portuguese aquifers. Therefore, three aquifers were selected to analyze the viability of water quality for integrated management of surface and ground water resources in the public supply network.

2. Introduction
Groundwater resources are a renewable water source an human scale, but are strongly controlled by climate then, the impacts of climate change on this resource becomes essential to take a proactive and preventive in a long-term protection. The aquifers most vulnerable to climate change are the karstic carbonate aquifers where water chemistry and fast circulation, make them extremely vulnerable to contamination and extreme climatic regimes. Climate change may be felt in the aquifers at hydrochemical and hydrodynamic levels. The change in temperature, the increase of CO₂ dissolved in rainwater and the change in rainfall pattern can promote a greater dissolution or precipitation of carbonate minerals along the karst conduits. Extreme drought conditions increase the residence time of groundwater, with consequences on water quality by increasing the reaction time of the water with the rock. In terms of hydrodynamics, the quick response of the aquifer systems of precipitation extremes can result in large variations in the flow of springs and flooding depressed areas of the aquifer. In terms of water quality, the prevision is a general reduction in quality, where the surface water resources are the most vulnerable, followed by karst aquifers. Thus after appropriate treatment of groundwater, it can be integrated into the public supply network, mixed with surface water, to ensure the public water supply in drought situations. This project leads the study of climate change on groundwater quality in karst carbonate aquifers of Portugal, focusing on hydrochemistry and processes of dissolution and precipitation of carbonate minerals, as well as the evolution of water quality with these changes.

3. Methodology
First, it was made an initial characterization of the saturation state of carbonated species in all karstic carbonate aquifers of Portugal provided a spatial distribution of the saturation index. Three aquifers were selected for a detailed study of the evolution of hydrochemical characteristics relating that evolution to the climate change in order to understand how temperature and precipitation affect the water quality, adopting a climatic evolution model. In all three case studies, Sicó-Alvaiázere, Estremoz-Cano and Querença-Silves aquifers, a geological, climatic, hydrodynamic and hydrochemical characterization was made in order to assess the sensitivity of the aquifer to these factors. It was verified that the waters of the three systems present mainly calcium bicarbonate facies and there were some stations with sodium chloride facies in the extreme SW Querença-Silves aquifer that correspond to karst cavities with sea water entry. The evolution of the saturation indexes with an increasing temperature and reduced precipitation under climate model HadCM3-A2c was studied and, therefore, initially evaluated the correlation between climate and hydrochemical parameters through linear
correlations. By studying the evolution of partial pressure of carbon dioxide (P_{CO2}) due to climate change, it was observed a tendency for increased water solubility, thereby increasing the water dissolution capacity.

The quality of drinking and irrigation water was also studied, according to the legislation in force, and the SVI quality index (Stigter, et al 2008) was applied to determine the potential water withdrawals for human consumption.

4. Impacts of climate change in groundwater quality

4.1. State of act

For being the most visible short-term, the first studies of the impacts of climate change on water resources, were focused on surface water resources. Where were evaluated changes in rainfall patterns and runoff, flooding and droughts, and extreme precipitation events.

It also began studying impact of rising sea levels in coastal regions, considering the loss of landmasses, destruction of coastal ecosystems and increased erosion. After, coastal aquifers and advancement of saline interface became an important study subject. In groundwater, the study of climate change began recently, because it is a resource whose changes are observed in the long term. The carbonate aquifers have deserved more attention due to their high sensitivity to variable precipitation regimes.

4.2. Impacts of climate change

Climate models indicate an overall increase in atmospheric temperature, reduction of annual rainfall, but also an increasing of the frequency of extreme precipitation events.

The effects may lead to a reduction of annual recharge providing a reduction in the flow of aquifer discharge into the rivers, the residence time of water will be higher, degrading the quality of water both for greater interaction of water with the rock (greater mineralization of water) or by increasing the concentration of pollutants.

The coastal near aquifers may be affected by the advance of saline interface, caused by the rise in the sea level. May still occur carbonate dissolution processes by mixing corrosion.

The increasing of greenhouse emissions, including CO₂, can affect the pH of rain water and enhance the dissolution of karst cavities.

4.3. Selection of climate model

To calculate the evolution of hydrochemical parameters with weather, it was necessary to select a climate model. The project SIAM II (Santos et al, 2006) includes several models of weather prediction. The selected model was the HadCM3-A2c, this model fits well to the national climate scenery, is considered the most pessimistic model, within the models that best correlate with historical data in order to highlight more clearly the potential impacts of climate change in groundwater.

5. Dissolution and precipitation carbonate processes

The high reactivity of water gives a great capacity of water to mineral dissolution, in this way, natural water contains large amounts of dissolved substances. Water can dissolve gases, liquids and solids, making it possible to infer its way underground through the concentration of dissolved species.

The composition of groundwater depends on factors which affect the chemical balance of the solution. The extrinsic factors include the climate, the thickness and type of land use, the residence time of groundwater, the pressure and the characteristics of the rock (nature and weathering). The intrinsic factors are related to water chemistry and their reactions on the surface of the mineral.

The intrinsic factors affect the precipitation or dissolution of the mineral are temperature, pressure, pH and ionic strength waters. In the area of contact with the mineral water, the reactions are conditioned
by the effect of common ion, the complex formation reactions, redox reactions, adsorption and ion exchange.

The solubility of a mineral is the maximum concentration of its elements in the water. Solubility equilibrium exists when a chemical compound in the solid state is in chemical equilibrium with a solution of that compound, it can be measured by the saturation index.

In the case of carbonate minerals, calcite has a solubility similar to dolomite, but the kinetics of the reactions is different, so that the reaction with calcite is faster than with the dolomite and may thus give rise to water supersaturated in calcite, but undersaturated in dolomite. Thus, the solubility of calcite and dolomite increases with increasing $P_{\text{CO}_2}$, pH drop, corrosion by mixing of seawater and freshwater, and decreases with increasing temperature and the common ion effect.

6. Saturation state of Portuguese carbonate aquifers

24 of the 62 Portuguese aquifers are carbonate type and some have karstic systems characteristics. These aquifers are the subject of study when it comes to climate change because they are most vulnerable to rising temperatures and carbon dioxide in the atmosphere and soil, which may cause an intensive weathering of carbonate rocks.

713 saturation indexes were calculated at the national level, most of the values indicates that the waters tend to precipitate calcite and dolomite, indicating a significant tendency to dissolution of calcite and dolomite, and only a residual percentage of water is in equilibrium.

In the Occidental Border (OB), Meridional Border (MB) and Ancient Massif (AM), most of the analysis indicates a tendency for the supersaturation of water in calcite. In the same study, there is a tendency of water to the dissolution of dolomite on the Occidental Border and the other hideogeologic units, for the precipitation of this mineral, which may be related to more abundant precipitation observed on the Occidental Border.

The investigation of seasonality effects in carbonated species saturation index (SI) is showed on Figure 1 and Figure 2.

7. Case studies

7.1. Sicó-Alvaiázere aquifer system (OB)

7.1.1. Caracterization

This aquifer system, occupies 332 km$^2$ overlapping several territorial small divisions in Coimbra, Leiria, and Santarém districts.

Supported by midle Jurassic limestones (from Batoniano to Bajociano), the aquifer have a karstic circulation, where subsurface drainage is done to a small number of permanent and temporary springs, located east of the system. The recharge is directly
from rainfall. The most productive areas are located at west and east of the system. The recharge is directly from rainfall. The most productive areas are located at west and east of the system. This aquifer is influenced by atlantic climate, where accumulated annual rainfall is between 700mm and 1400mm, and the temperatures between 12.5°C and 17.5°C.

**7.1.2. Hidrochemical facies**

This system is dominated by calcic bicarbonated facies (Figure 3).

![Figure 3 - Stiff diagram](image)

**7.1.3. Hydrochemical indexes**

The rMg/Ca, rK/Na, rCl/HCO₃, rSO₄/Cl indexes and others calculated by AquaChem software indicates that the origin of groundwater is relacionated with limestones weathering and cationic change phenomena.

**7.1.4. Current status and evolution of water saturation state in respect to calcite and dolomite**

The current status of SI calcite and dolomite, Figure 4, shows that groundwater is in equilibrium with calcite SI, and underssaturated in respect to dolomite. This difference in saturation state can be related with the different kinetics reaction of this carbonated species and with low residence time of groundwater.

**7.1.5. Water quality**

For the application of Decree-Law (DL) 306/2007 and 236/1998, there was just too much calcium hardness affecting the quality of drinking water at the stations represented in red in Figure 5.

![Figure 4 – current state of calcite and dolomite saturation indexes in this aquifer.](image)

**Table 1 - Weather forecast to 2050 and 2100**

<table>
<thead>
<tr>
<th>Climate Model</th>
<th>Year</th>
<th>North Prec.</th>
<th>North Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HadCM3-A2c</td>
<td>2050</td>
<td>-11%</td>
<td>+2.5 ºC</td>
</tr>
<tr>
<td></td>
<td>2100</td>
<td>-13.6%</td>
<td>+4.5 ºC</td>
</tr>
</tbody>
</table>

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**Figure 4**

- **Water quality**
  - For the application of Decree-Law (DL) 306/2007 and 236/1998, there was just too much calcium hardness affecting the quality of drinking water at the stations represented in red in Figure 5.

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- **Weather forecast to 2050 and 2100**
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  - |               | 2100 | -13.6%      | +4.5 ºC     |

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**Figure 5**

- **Current status and evolution of water saturation state in respect to calcite and dolomite**
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**Figure 4**: Current state of calcite and dolomite saturation indexes in this aquifer.

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**Table 1**

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Applying the DL 263/1998, the water from all stations is able for irrigation. The SVI index allows to determine the stations with quality for human consumption and type of contamination that affects them (Table 2).

<table>
<thead>
<tr>
<th>SVI class</th>
<th>%Viol</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVItot</td>
<td>11.0%</td>
</tr>
<tr>
<td>SVItoxic</td>
<td>0.0%</td>
</tr>
<tr>
<td>SVIMicrobial</td>
<td>61.3%</td>
</tr>
<tr>
<td>SVINO3,Cl</td>
<td>0.0%</td>
</tr>
<tr>
<td>SVIFe-Mn</td>
<td>1.9%</td>
</tr>
</tbody>
</table>

Table 2 - SVI index for classes of contaminants considered.

Most of the contamination found is microbial type, thus, most stations only require a microbiological treatment to achieve drinking water quality (Figure 6).

7.1.6. Evolution of water hardness

Applying the climate model considered to the evolution of hardness, an increase in temperature enhances the hardness increase between 0.2 mg / l to 0.8 mg / L per year until 2050 and between 0.17 mg / l 0 and 51 mg / l until 2100. Considering the isolated influence of rainfall in water hardness, there is a trend where it is expected that by 2050, the increase in hardness can be done at an annual rate of 0.34 mg / l to 1.78 mg / l, while that for 2100, forecasts point to an annual increase of this parameter from 0.39 mg / l and 1.78 mg / l.

7.2. Estremoz-Cano aquifer system (AM)

7.2.1. Characterization

This aquifer system is supported by dolomites and limestones of Estremoz formation (Cambrian) and the volcanic-sedimentary complex of Estremoz, better known as Estremoz marble (Ordovician). In the region of Cano, the most recent geologic unit date Pleistocene, is formed by the limestone of the Cano-Casa Branca formation, as Paleozoic formations are directly superimposed by Cano-Casa Branca limestones, there is hydraulic connection between those aquifers. The aquifer system is composed by free karstic aquifers, in some confined spaces, due to interbedded shale and metavulcanites. It is integrated into an anticline structure (Estremoz Anticline), oriented NW-SE, contemporary of Variscan orogeny.

7.2.2. Hydrochemical facies

The waters of this aquifer are classified as calcic and magnesium bicarbonate, a characteristic that identifies the type of carbonates that water passes through and dissolves, where the limestone releases calcium cations and dolomites and magnesium cations.

7.2.3. Hydrochemical indexes

The HCO₃/SiO₂ index indicates that all samples may result from weathering carbonates, this origin is
supported by other indices (\(r_{\text{Mg/Ca}}, r_{\text{K/Na}}, r_{\text{Cl/HCO}_3}, r_{\text{SO}_4/\text{Cl}}\)) that indicates the dissolution of dolomite and precipitation of calcite as the main factors for the composition of the water provided. Some samples may have been affected by cation exchange and presence of ferromagnesian minerals.

7.2.4. Current status and evolution of water saturation state in respect to calcite and dolomite

In all stations, the water is undersaturated in calcite and dolomite (Figure 8) and is normal the seasonal variations of this indexes. The saturation index values in calcite and dolomite are very low, maybe due to errors in analysis.

![Figure 8 – Current status of calcite and dolomite SI](image)

Considering the projected climate changes in the model HadCM3-A2C (Table 3), increasing temperature promotes a decrease in SI of calcite and dolomite. An increasing of \(P_{\text{CO}_2}\) increases the solubility of water in relation to carbonated species. On the other hand, the reduction of precipitation expected promotes a slight increase in SI of calcite and dolomite, and a decrease in \(P_{\text{CO}_2}\).

<table>
<thead>
<tr>
<th>Climate Model</th>
<th>Year</th>
<th>Prec.</th>
<th>Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>HadCM3-A2c</td>
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<td>-18%</td>
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</tr>
<tr>
<td></td>
<td>2100</td>
<td>-28%</td>
<td>+5.1 °C</td>
</tr>
</tbody>
</table>

Table 3 – Weather forecast to 2050 and 2100

7.2.5. Water Quality

The quality of drinking water is regulated by DL 306/2007 and 236/1998, thus, the parameters that exceed the parametric values are the hardness, the magnesium and nitrates. The first exceed the PV due to the nature of these carbonate rocks, while nitrates are related to agricultural activity in the region.

![Figure 9 – Spatial distribution of quality for drinking water. In red and orange are the stations unable for consumption, and red represents the water with quality for that use.](image)

Most of the contamination has an excessive concentration on microbiological parameters, the rest are divided between the excess of chlorides and nitrates, iron and manganese (Figure 10).

![Figure 10 - SVI on water quality stations](image)

7.2.6. Evolution of water hardness

Considering the hardness as the main natural factor influencing water quality for human consumption, it was studied its temporal evolution. Thus, the hardness tends to increase between 0.2 \(\text{mg} / \text{L}\) to 0.8 \(\text{mg} / \text{L}\) per year until 2050 and 0.17 \(\text{mg} / \text{L}\) and 0.51 \(\text{mg} / \text{L}\).
mg / l until 2100, considering only the increase in temperature. Considering the reduction of precipitation, there is a growing trend in hardness with decreasing precipitation. At 2050, the increase in hardness can be made at an annual rate of 0.34 mg / l to 1.78 mg / l, while for 2100, forecasts point to an annual increase of this parameter from 0.39 mg / l until 1.78 mg / l.

7.3. Querença-Silves aquifer system (MB)

7.3.1. Characterization

Occupying an area of 318 km² in the municipalities of Albufeira, Lagoa, Loulé and Silves, the aquifer system Querença-Silves is an important reservoir of groundwater from the Meridional Border, the largest and most productive in this region. It is backed by limestone, dolomite and mixed formations, covering various formations of the lower, middle and top Jurassic.

The aquifer has a karst circulation, is unconfined and confined in some places.

The distribution of climatic parameters throughout the year indicates a typical Mediterranean climate.

7.3.2. hydrochemical facies

The dominant hydrochemical facies in the Querença-Silves aquifer is the calcium and magnesium bicarbonate, by the movement of water in limestone and dolomite of Barrocal Algarvio. There are, however, three stations where the facies sodium chloride, indicate a possible contamination of seawater in karstic holes (Figure 11).

7.3.3. hydrochemical indexes

Hydrochemical indexes of this aquifer system indicate the likely origin of the waters as phenomena resulting from the dissolution of gypsum, weathering of limestones, dolomites and dolomitic limestones. In some stations, the software AquaChem identifies cation exchange phenomena.

7.3.4. Current status and evolution of water saturation state in respect to calcite and dolomite

In this study, it was observed that Querença-Silves aquifer has saturation index of dolomite higher than calcite, and above the threshold and is visible that the amplitude of variation of the saturation index of dolomite is greater than in saturation in calcite (Figure 12). It is also noteworthy that the waters analyzed in this graph show a wide geographical spread, due to the data treatment sets with only one measurement and data with some continuity over the time.

![Figure 12 – Current status of calcite and dolomite SI.](image)

Considering the projected climate changes in Table 5, with that increasing temperature, it is expected a significant decrease in the calcite and dolomite SI, and an increase in P\textsubscript{CO2}. The reduction in rainfall tends to promote a slight increase in the calcite and dolomite SI, as well as reduction of P\textsubscript{CO2}.

<table>
<thead>
<tr>
<th>Climate Model</th>
<th>Year</th>
<th>South Prec.</th>
<th>Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HadCM3-A2c</td>
<td>2050</td>
<td>-28%</td>
<td>+2.6 °C</td>
</tr>
<tr>
<td></td>
<td>2100</td>
<td>-42%</td>
<td>+4.9 °C</td>
</tr>
</tbody>
</table>

Table 5 - Weather forecast to 2050 and 2100

7.3.5. Water Quality

The application of DL 306/2007 and 236/1998 for drinking water, has shown an excess of hardness in 96% of the tests, corresponding to natural causes. In four stations there is an excess of potassium
chloride, sodium sulfate, and conductivity, corresponding to the stations affected by sea water. Some stations have excessive nitrates from farming deriving site (Figure 13).

Figure 13 – Spatial distribution of water quality. In red, orange and purple are the water unable to drink, and the green represents the stations with water quality for human consumption.

The quality of water for irrigation is defined by DL 236/1998, three abstraction were identified unable for irrigation due to high conductivity and sodium hazard. The remaining water withdrawals are moderate to high salinity hazard and can be used for irrigation in certain types of soils and crops.

To set the water quality index and type of treatment that should be used to integrate the public supply network, it was used the methodology developed by Stigter, et al (2008), through analysis of parameters that exceeds the standard violation index (SVI), with the values obtained that are shown in Table 6.

<table>
<thead>
<tr>
<th>SVI</th>
<th>%Viol</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVItot</td>
<td>13.3%</td>
</tr>
<tr>
<td>SVIToxic</td>
<td>0.1%</td>
</tr>
<tr>
<td>SVIMicrob</td>
<td>26.3%</td>
</tr>
<tr>
<td>SVINHCl</td>
<td>10.8%</td>
</tr>
<tr>
<td>SVIFeMn</td>
<td>3.1%</td>
</tr>
</tbody>
</table>

Table 6 – SVI index for classes of contaminants considered.

The microbiological contamination is most significant, with 26.3% of the analysis with values above the PV, followed by contamination of nitrates and chlorides, which reach 10.8% of the tests. Excess of iron and manganese translates into 3.1% of the analysis. In general, it is found that 13.3% of the tests carried out at the waters of this aquifer system, have some kind of contamination (Figure 14).

Figure 14 – SVI on water quality stations.

7.3.6. Evolution of water hardness

Considering the hardness as the main natural factor influencing water quality for human consumption, it was studied its temporal evolution with climate change predicted by the model HadCM3-2AC. There is a very significant increase of hardness in 2050 and 2100. The hardness may increase annually of 0.14 mg/l and 0.31 mg/l by 2050 and between 0.1 mg/l and 0.19 mg/l as until 2100. Regarding the impact of the rainfall reduction in hardness, it tends to increase annually between 0.34 mg/l and 1.06 mg/l by 2050 and between 0.24 mg/l and 0.53 mg/l in 2100.

9. Conclusions

It was found that SI of dolomite is more sensitive to the climate that SI of calcite.

On the characteristics of water in all aquifers to water facies is predominantly calcium bicarbonate, however, the aquifer Estremoz-Cano there is an enrichment of magnesium in the stations who contact metavulcanitos. Querença-Silves aquifer in some stations has sodium chloride facies, corresponding to the salt water intrusion in karst cavities that in this way can influence the dissolution of carbonate rocks through the process of weathering by mixture.

The impacts of increasing temperature can be translated by the reduction of the saturation index of dolomite and calcite, in terms of rainfall is expected a growing trend in calcite and dolomite saturation index. The water solubility tends to increase with the increase of $\text{P}_\text{CO}_2$, thereby increasing the dissolution of carbonate rocks.
In Sicó-Alvaiázere aquifer system the quality for human consumption is conditioned by natural factors, in this case, the high hardness and calcium concentration are related to the weathering of carbonate rocks. These waters are considered able for irrigation in all soil types. According to the SVI index, 5 of 9 quality stations can be integrated into the public supply network.

In Estremoz-Cano aquifer system the quality for human consumption is affected by excess of nitrates, chlorides, hardness and high conductivity only in certain stations. The salinity hazard is medium to high conditioning this water for agricultural practices. About SVI index, 16 of 26 quality stations can be integrated into the public supply network, through a basic disinfection.

In Querença-Silves aquifer system water quality is affected by a general excess of hardness (mg / l CaCO3), is locally affected by excessive chloride, potassium, sodium, sulfate, and conductivity at stations with salinity intrusion, and the excess nitrates in some stations. The stations with an average salinity hazard are able for irrigation, while the waters with a high to extremely high salinity hazard, cannot be used. Applying the SVI index, were identified 44 of the 58 stations able for integration into the public supply network, through a basic disinfection.

Overall, the quality of water in the case studies aquifers is considered well, where the percentage of infected analysis in Sico-Alvaiázer system is 11%, 9.4% in the Estremoz-Cano aquifer, and 13.3% in Querença-Silves aquifer.

Thus, this project aims to contribute to the study of climate change on groundwater in Portugal, hoping that future developments will pass through a management of this resource in a rational and integrated with the capture of surface water, enhancing public supply network in order and ensuring continuous supply even under extreme drought.

10. Bibliography

