MSc Thesis Proposal: Submarine Fresh Groundwater Discharge Study, Algarve, Portugal:

How the groundwater flow in carbonated rocks affect the spatial extent, the hydro-chemical pattern and the isotopic signature of submarine groundwater discharge?

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Chapter 1

Background

1.1 Introduction

The research supported by the hereby proposal concerns a study of the Submarine Groundwater Discharge (SGD) in Algarve, Portugal. SGD is defined has all the discharge of subsurface fluid across the sea floor. It is composed of two components, the first is the submarine fresh groundwater discharge and the second is the recirculated seawater (UNESCO, 2004). The study will take place in the region of Olhos de Água, about 30 km West from the city of Faro. It will focus on how the groundwater flow in carbonated rocks affect the spatial extent, the hydro-chemical pattern and isotopic signature of submarine discharge. This research is elaborated in the scope of MSc. thesis in Hydrology and is incorporated within the on-going project named FREEZE (Submarine FREshwater dischargEs: characteriZation and Evaluation study on their impact on the Algarve coastal ecosystem). The FREEZE project aims a better understanding of SGD along the Algarve coast via the mapping of the intertidal area where SGD occurs, the quantification of the freshwater discharge, the impacts of SGD on coastal ecosystems a remote sensing test to detect SGD occurrence and finally a methodology for the detection of SGD offshore Instituto Nacional de Engenharia [2009]. To achieve this research, 6 month will be required, from February to July and will require one month and half of fieldwork during the period of March and April.

1.2 Research area

The research will take place around Olhos de Água (OdA), the beach area of this resort municipality had been showing the occurrence of SGD phenomenon on a 400 m stretch in the inter-tidal and sub-tidal zone. This area is included within the Albufeira coastal aquifer as shown in Figure 1.1.
1.2.1 Vegetation and Land use

The southern coast of Portugal is characterized by an important development of the tourism sector, particularly demanding in water supply directly but also indirectly for the irrigation of the numerous golf courses flanking the coast of the area. Furthermore the water abstraction for agricultural purpose, such as the irrigated market gardening, represents a significant need of water. The vegetation is mainly composed by citrus tree used for cultivation and other commercially attractive trees such as olive, almond and cork oak trees are also common.

1.2.2 Geomorphology

The Algarve littoral is characterised on the East by a shore line of sandy deposit and the West by a platform of secondary and tertiary terrain forming a cliff, those cliffs can reach several meters and are well observed between Albufeira and Olhos de Água [Razack et al., 1980]. Inland, the area can be described as coastal plain with low relief, bordered on the north by Jurassic limestone with a more pronounced relief. Several characteristic karstic features can also be observed such as doline and dry valleys [Bronzini, 2011].
1.2.3 Geology

Here is a short description of the stratigraphy found in the research area:

1. The Jurassic formations: It is dominated by a calcareous and dolomitic matrix. It is composed of

   (a) *Marga e Calcários arenosos de Albufeira* (Sandstone and limestone from the Oxfordian to the Kimmeridgian, thickness ranging from 80 to 100 m)

   (b) *Calcários recifais da Ribeira de Quarteira* (Siliceous limestone of the Kimmeridgian, the unit can be around 20 m thick)

   (c) *Calcários e dolomitos do Escarpão* (Dolomitic limestone and compact dolomite from the Kimmeridgian and Thithonian, around 650 m thick).

2. The Cretaceous formations: they are all part of the lower Cretaceous and are dominated by a marly limestone and sandstone matrix.

   (a) *Arenitos do Sobral* (Sandstone with clayey components and conglomerates, up to 50 m in the study area)

   (b) *Margas com Choffatella decipiens* (Marls, sandstone and marly and dolomitic limestone from the Barremian, 25 m thick)

   (c) *Calcários e Margas com Paloribitolina lenticularis* (Compact limestone and sandstone from the Aptian, 10 m thick).

3. The Miocene formations: mainly sandy limestone and detritic matrix with a maximal thickness of 85 m in the South 35 m in the North. The research will be strongly focused on this formation due to the fact that SGD are discharging for that aquifer. The map in Fig. X presents the depth of the aquifer’s base. The latter is constituted of:

   (a) *Formação Lagos-Portimão* (Sandy limestone, sandstone and yellow bio-calcarenite)

   (b) *Calcários lumachélicos da praia da Rocha* (Fossil-filled limestone).

4. The Quaternary formations: detritic deposit composed of coarse sand with a thickness varying from 10 to 300 m.

   The Albufeira aquifer presents one major tectonic events close to the research area: The *S. Marcos da Serra or Quarteira* fault. The latter has a NW-SE orientation and his partially responsible of the path taken by the Quarteira river. During the previous geological survey undertaken under the FREEZE project, this fault has been suspected to be responsible of the origin of the inland springs close to Olhos de Água. The report also supposed that the fault could also be responsible for the offshore springs [Dill, 2013]. The results of this survey are explained in Geophysics survey section 3.2.2, in the subsection Strategy.
1.2.4 Hydrogeology

The simplified cross-section in Figure 1.2, despite representing a North-South profile further East of Olhos de Água, summaries well the local geology. The profile location can be found in Fig. 1.3. In the profile, we can distinctively see the two main aquifers of the area; the Jurassic and the Miocene aquifer. Two other minor aquifers can be found in the area. First, the Upper Miocene that lies on the top of marly limestones and marls of low resistivities and under the Plio-Pleistocene layers. This aquifer is locally present, only fed by rainwater and has a short residence time explaining why this aquifer dries out in the summer. The SGD are supposed to drain that aquifer. Natural seawater intrusion has been reported during high tide. Secondly, the Cretaceous aquifer, which is constituted of small karstified members and of its sandy base. Despite forming a minor aquifer, the formation in general, separates the Miocene from the Jurassic aquifer. The VU Universities has done an extensive research work in the area, among them, Elsendoorn et al. (1982) interpreted a North-South profile of the area in Fig. 9.1 which include the Upper
Miocene aquifer. However the spatial extent of the Upper Miocene is discussable and in contradiction with Kleinendirst et al. (1985) (Fig. 1.5, Fig. 1.6, Fig. 1.5) who assumes that the Upper Miocene is present until the ocean. The location of the profile can be found in the Appendix 9 with the results of VES in Appendix 10.
Figure 1.4: N-S Hydrogeological profile A on Olhos de Água by Elsendoom et al. (1982).
Figure 1.5: N-S Hydrogeological profile on Olhos de Água by Kleinendirst et al., 1985).

1.2.5 SGD

The springs that will be studied occurs in the Miocene limestone that in topped by Pleistocene red sands. Any spring discharge was observed in the latter and neither between the two geological unit [Amaral et al., 2012]. Eleven inter-tidal springs appear on a 400 m coastline line, sub-tidal springs have also been detected.

Three main (non exhaustive) mechanisms are link to the origin of SGD in carbonate coastal aquifers. The first is tectonic constraints, creating a secondary permeability through the less permeable matrix. Secondly, karstification can also explain the occurrence of SGD, the latter is controlled by the flux of water, the dissolved CO$_2$ and the potential hydraulic gradient between recharge area and outlet zone. In coastal aquifer, the outlet is defined by the sea level where springs are likely to occur. During eustatic change, at falling sea level, the original base outlet is abandoned for deeper network but will still remain connected to the original network [Fleury et al., 2007]. During rising network, the springs are submerged under the sea. Fleury et al. [2007] defines three resulting situations:

- (i) The submerged networks can continue to discharge the groundwater, creating submarine springs.
- (ii) They may let in seawater.
- (iii) The outlets and the conduits may become partially or totally clogged either by marine sediments or by deposits from inside the karst, i.e., karstic clogging. The
last is due to the presence of an impervious layer underlying the aquifer. Concerning their driving mechanisms Burnett et al. [2006] list six of them:

1. The terrestrial hydraulic gradient (gravity) that results in water flowing downhill

2. Water level differences across a permeable barrier

3. Tide, wave, storm, or current-induced pressure gradients in the near-shore zone

4. Convection (salt-fingering) induced by salty water overlying fresh groundwater in some near-shore environments

5. Seasonal inflow and outflow of seawater into the aquifer resulting from the movement of the freshwater-seawater interface in response to annual recharge cycles

6. Geothermal heating
Figure 1.7: N-S Hydrogeological profile C on Olhos de Água by Kleinendirst et al., 1985).
Chapter 2

Research Project Goals

The thesis has for main purpose to give an insight in how the groundwater flow in carbonated rocks affect the spatial extent, the hydro-chemical pattern and the isotopic signature of submarine discharge. To answer the latter question the four following issues will be addressed during the research:

1. **Issue 1**: What is the spatial 3-D configuration of the fresh/salt water interface and how does carbonated rocks affect the interface. Can geophysical surveys help to localise the main coastal conduits connecting the carbonated aquifer to the sea. What is the spatial extent of the freshwater discharge, can it be related to the eye spotted intertidal springs? What are the mechanism underlying the origin of the springs in Olhos de Água? How does the tide cycle affect the interface and the submarine discharge’s the temporal variation?

2. **Issue 2**: Is it possible to characterize the hydro-chemical and isotopic signature of the inter-tidal and sub-tidal springs, and also to relate it with inland water. Could the mechanism of salinization of the springs be determined based on the hydro-chemical and isotopic data and also be confirmed by the geophysical results. Can the hydro-chemical evolutions throughout the four seasons be related to the karst network structure?

3. **Issue 3**: Can the system be described by an inverse hydro-chemical and groundwater flow model?

4. **Issue 4**: Is it possible to relate and compare the studied carbonated aquifer and its SGD to other coastal aquifer already studied, maybe classify it under the list elaborated by Fleury et al. [2007]. Can this comparison give a guideline regarding its management.
Chapter 3

Methodology

3.1 Preliminaries

3.1.1 SGD formation

This part of the research will be a literature review focused on the development of SGD. The understanding of their formation process can give significant information for the extent of the discharge zone and explain the mixing process answering to the different salinities of the intertidal springs. Among them, aquifer fracture and karstification plays a large role. The latter is strongly depending on eustatic changes that are responsible for development of the SGD, it can give a rough estimation range regarding the karst network’s extension depth. Afterwards, this review can be compared to the results of the geophysical surveys and the hydrochemical samplings. Razack et al. [1980] estimates that the sea level variation after the Miocene deposition as attained 50 m below today’s sea level, the marine regression has probably induced the development of the karstification of the Miocene. He also adds that the deep karstification had been developed during tectonic constrain during the upper Miocene and the Pliocene.

3.1.2 Structural geology of the Algarve

Not available yet.

3.1.3 Resistivity to expect

Based on old surveys in the area, a literature review has been done in order to estimate the different formation resistivity to expect. Table 3.1.3 shows the different range expected.

Old resistivity of the Miocene aquifer filled with brackish water displayed values around 15 Ωm, this can imply equivalence problem with the marly limestone and marly layer of the Miocene that can be around 20 Ωm.
<table>
<thead>
<tr>
<th>Formation</th>
<th>Resistivity Range (Ωm)</th>
<th>Kleinendirst et al., 1985</th>
<th>Elsendoorn et al., 1982</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plio/Quaternary</td>
<td>27 - 400</td>
<td>80 - 450</td>
<td></td>
</tr>
<tr>
<td>Fresh Upper Miocene</td>
<td>20 - 42</td>
<td></td>
<td>34 - 40</td>
</tr>
<tr>
<td>Local Upper Miocene</td>
<td>350 - 800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brackish Miocene</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt Intruded Miocene</td>
<td>2 - 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh Miocene</td>
<td>75 - 105</td>
<td>100 - 115</td>
<td></td>
</tr>
<tr>
<td>Upper Cretaceous</td>
<td>20 - 50</td>
<td>20 - 35</td>
<td></td>
</tr>
<tr>
<td>Lower Cretaceous</td>
<td>4 - 15</td>
<td>60 - 100</td>
<td></td>
</tr>
</tbody>
</table>

### 3.1.4 Forward Modelling

Preliminary modelling has for goal to have an approximation of the model to determine the best electrode distances and configurations. It will allow to analyse the least dimensions and resistivity contrast detectable by the CVES campaign.

### 3.2 Issue 1: The fresh/salt water interface

Two procedures will be followed to study the fresh salt/water interface. First, a theoretical approach will be followed in order to estimate the boundary of the salt/fresh water interface with the Ghyben - Herzberg relation. Then, a more precise look will be given with the help of geophysics surveys.

#### 3.2.1 Ghyben - Herzberg

**Theory**

Although this model neglects convection, dispersion and diffusion phenomena and assumes a static contact between the fresh and salt water, it can give an overall idea of the salt/fresh water boundary. Later in the research, knowing the overall interface distribution will help for the understanding of the salinization of the springs (See Section 3.3.6).

\[
\frac{1}{h_s} = \frac{\rho_f}{\rho_s - \rho_f} \cdot h_f
\]  

(3.1)

Where \(h_f\) is the height of the water table above the mean sea level (a.m.s.l), \(\rho_f\) and \(\rho_s\) is the density of freshwater and seawater respectively. The depth of the seawater \(h_s\) can then be estimated. Considering \(\rho_s = 1.025 \ g/cm^3\) and \(\rho_f = 1.00 \ g/cm^3\), Equation 3.1 can be simplified as:

\[
h_s = 40 \cdot h_f
\]  

(3.2)
Strategy

To answer the equation, the head of the coastal wells should be measured. When values will be assessed, a profile of the salt/fresh water interface can be done.

3.2.2 Geophysics Surveys

Theory

The spatial configuration of the fresh/salt water interface will be achieved by the mean of geophysical surveys. Sea water contain a high concentration of dissolved ion (around $3.5 \times 10^4$ mg l$^{-1}$) allowing a high electricity conductance (around 50 mS cm$^{-1}$) however fresh water has a much lower concentration of dissolved ions (lower than $10^3$ mg l$^{-1}$) implying a lower conductance. This contrast allow the elaboration of the spatial distribution of the salt/fresh water at different depth through the geologic media. Those measurements would allow displaying the salt/fresh water interface and the zone of fresh water discharge. Regarding the temporal variation of the interface, the idea would be to also to effectuate those measurements at low and high tide level. Previous studies has shown that SGD shown from measurement during low tide can reveal to be obstructed by salt intrusion through the conduits preventing the flow of fresh water towards the sea. Knowing that the discharge of SGDs are only effective at certain time would be valuable information for the research. The information gathered by the geophysical surveys would also be significant information for the understanding of the different SGD’s salinities. Two different geophysics equipment will be used:

1. **Time Domain Electromagnetic Method** (TDEM), or Transient Domain Electromagnetic Method (TEM) TDEM works according to the following principle. A loop is disposed on the ground and a current is passed through it creating a primary magnetic field. After around tens of milliseconds the current is stopped creating a secondary current through the subsurface producing a secondary magnetic field, measured by the receiving loop[4] [Kontara and Ozorovich, 2006][Reynolds, 1997].

2. **Continuous Vertical Sounding** (CVES) CVES is a geoelectrical method allowing the combination of profiling and sounding, the result is a 2D coverage of profile displaying the resistivity along a profile. Measurements will be done from the beach but also offshore with the help of a submarine cable with a fixed electrode distance of 5 m. The geo-electrical method will require basic field data such as the Electrical Conductivity (EC) of the SGD, of the seawater and also of the fresh aquifer water. The formation factor should also be determined. Formation resistivity from previous measurement will also be needed. According to Archie’s law (1942), the specific resistivity ($\rho_s$; units $\Omega m$) can be obtained by multiplying the formation factor which depend on the nature of the material, the texture of the matrix and the medium in the pores (F; units $-$) with resistivity of the pore water ($\rho_w$; units $\Omega m$):
\[ \rho_s = F * \rho_w \quad [\Omega m] \quad (3.3) \]

Where:

\[ \rho_w = \frac{1000}{EC} \quad (3.4) \]

Electrical conductivity (EC; units (µS)/cm) [van Breukelen et al., 2007].

**Strategy**

The strategy concerning the geophysics survey will be based on the preliminary research done in the area. The inland area as already been investigated under the FREEZE project with Radio Frequency-Electromagnetic (RF-EM) with frequency ranging from 12-300 kHz as a preliminary overview of the study area’s geology. The reported results present that the inland springs are strongly dependent of the local Quarteira fault system: the springs seem to be parallel to the fault system. This particularity raises two hypotheses: The first would be that the fault act as a barrier to the groundwater flow causing the inland springs. The second would be that the Quarteira fault would be a graben constituted of several parallel draining groundwater [Dill, 2012]. Based on the assumption that the springs origin inland can be reproduced offshore, the CVES survey will be performed following this observation. The TDEM campaign as already been performed and will need to be reviewed. Previous geophysical surveys from the VU University will also be consulted. A special attention will be given to the interface between the Miocene aquifer and the underlying Lower Cretaceous layer since SDG might occur at the base of the Miocene due to the underlying poorly permeable layer. According to Bronzini [2011] and Razack et al. [1980] the Miocene layer should have a thickness around 85 m in the coastal area around Olhos de Água. Although de Vries and Schwan [2000] on Fig. X estimate it between 100 and 150 m. Two different type of CVES measurement will be undertaken. First, the intertidal zone will be investigated during low tide period with a Terrameter SAS 4000, max of 400 m profile length with an electrode distance of maximum 5 m. Secondly, offshore measurements will be performed with the mean of a marine cable with a fixed electrode distance of 5 m and a maximum of 400 m profile. The two main question of this part of the research will be address the following way:

1. Fresh/salt water interface: will require transversal survey which can be performed next to OA4 and OA3 (Fig. 3.2.2 by Francés [2013]). A focus on the relation between the slope of the fresh/salt water interface with the hydraulic gradient should also be address (why), This aspect is also important for the SGD which are more evident with significant hydraulic gradient. This will also require measurement of head inland (measure head in Upper Miocene or Miocene). This part will require a large amount of water for the electrode.
2. Identification of fresh discharge: Verify the hypothesis that fresh discharge occurs several kilometres from the shore. This will require CVES parallel to the coastline.
Figure 3.1: Map of the preliminary geophysical surveys.
Interpretation

CVES allow a 2-D profile, so in order to interpret them in 3-D, a manipulation is needed. 3-D profiles should generally be carried with rectangular grid of electrodes, however with a certain amount of parallel 2-D surveys and perpendicular tie lines if needed, a 3-D profile can be obtained. This method require to collate RES2DINV data into a RES3DINV format. Nevertheless this operation is not always recommended. Firstly, there should be at least 5 parallel lines, and the separation between the lines should not be more than twice the unit electrode spacing along the lines [GEO, 2011].

CVES planning

1. Monday 1st to Friday 5th: Onshore CVES, perpendicular to the coastline.
2. Friday 5th to Monday 8th: Marine cable following the tide
3. Monday 8th to Friday 12th: Marine cable, using the boat.

3.3 Issue 2: Hydro-chemical and isotopic signature

To answer this issue, this part of the research requires sampling of the intertidal, sub-tidal springs and also inland coastal well. The idea would be to continue the analysis of the basic physiochemical analysis of the intertidal springs already measured (T, pH, Salinity, Alkalinity, NO$_3^-$, NO$_2^-$, NH$_4$), Discharge) and to complete them with further analysis such as major ions, minor ions and natural isotopes ($\delta^{2}H$ and $\delta^{18}O$).

Two field campaign will be required: First in the end of March, only sampling the inter-tidal spring and limited to the physiochemical analysis (T, pH, Salinity, Alkalinity, NO$_3^-$, NO$_2^-$, Discharge). The next one will be in the end of April beginning of May, it will require sampling of the coastal wells, sub-tidal and intertidal springs for isotopic signature but also minor and major ions analysis. The intertidal springs will be localised with the GPS measurements gathered by FREEZE team. Due to beach dynamics some are expected to change the location and will require field observations. The confirmation can be established with the physiochemical parameters previously measured. The sub-tidal springs sampling will be done by a diver. 100 samples for the major ion and minor ion are available, another 50 are also available for the natural isotope analysis. Knowing that here is at least 11 different inter-tidal springs to sample, the rest of the available samples will be divided for the sub-tidal and well sampling.

3.3.1 Analytical procedure

1. Anions (Cl$^+$, NO$_3^-$, NO$_2^-$, SO$_4^{2-}$) and nutrients (NH+, PO$_3$) are analysed on a 324 44 Labmedics Aquakem 200 discrete analyser (DA). Alkalinity is mea-
Table 3.1: Physicochemical, hydrochemical, isotopes parameters measured in the VU laboratory

<table>
<thead>
<tr>
<th>Isotopes</th>
<th>$\delta^2H$, $\delta^{18}O$ [%]</th>
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<tbody>
<tr>
<td>Anions</td>
<td>Cl, Br, NO3, NO2, SO4, HCO3 [mg l$^{-1}$]</td>
</tr>
<tr>
<td>Cations</td>
<td>Na, K, Mg, Ca, Fe, Al, Si [mg l$^{-1}$]</td>
</tr>
<tr>
<td>Trace elements</td>
<td>B, Ba, Be, Sr, Li, Mo, As, Cd, Co, Cr, Cu, Ni, Pb, Se, Sb, V, Zn [mg l$^{-1}$]</td>
</tr>
<tr>
<td>Physicochemical</td>
<td>Temperature (T)[C], pH[-], EC[$\mu$S cm$^{-1}$], salinity [g/L], TDS [ppm], discharge [L/s], coordinates</td>
</tr>
</tbody>
</table>

sured via inflection point titration on a Radiometer Titralab TIM840 titration workstation (automatic titrator). All DA methods are based on colorimetry, i.e., the adsorbance of a sample at a certain wave length (colour) after addition of certain reagents is taken as measure of the concentration of a certain chemical. Anion Br$^+$ can be determined via ion chromatography (IC; Figure 11.5) on a Dionex DX-120 IC equipped with Ion Pac AS14 column [van Breukelen et al., 2007].

2. Cations (Ca, Mg, Na, K, Fe, Mn, Al and Si) are determined using the acidified samples by means of a Varian 730-ES inductively coupled plasma-optical emission spectroscopy (ICP-OES) [van Breukelen et al., 2007].

3. Trace metals: ICP-OES can also simultaneously measure a whole suite of spore elements and heavy metals (B, Ba, Be, Sr, Li, Mo, As, Cd, Co, Cr, Cu, Ni, Pb, Se, Sb, V, Zn) [van Breukelen et al., 2007].

4. Strontium: To be defined

5. Isotopes: Description needed

Here is a recap in Table 3.1 of all the parameter measured:

### 3.3.2 Identification of the SGD

The identification of the SGD will be first based on the EC measure and is expected to range from 2,300 to 14,000 $\mu$S cm$^{-1}$ according to Amaral et al. [2012]. In this area, seawater EC ranges approximately from 29,000 to 51,000 $\mu$S cm$^{-1}$. Secondly, temperature is also a useful tool for the verification of the spring origin, the sea has been in direct contact with the atmosphere respond to the seasonal temperature variation, groundwater should therefore present cold anomalies in summer and warm anomalies during the winter UNESCO [2004]. Sampling the spring can appear to be a complicated manipulation to avoid direct mixing with seawater, Bronzini [2011] used a 5 L plastic PET bottle but did not fully succeed, a better solution should be thought. Alkalinity should be measured in-situ by the mean of a
field titration kit, NO$_3^-$ and NO$_2^-$ as well with strips. Regarding the sampling, they will be filtered by a 0.45 mm before being stored in plastic tubes, cation sample will be acidified with HCl and isotopes will be stored in 30 mL amber-coloured glass bottle. All the samples will be shipped to the VU University Laboratory for analysis.

3.3.3 The characterization of the springs

Seawater contribution:

Natural isotope as been describe as a useful tool for characterizing SGD [Schiavo and Povinec, 2009] such as $\delta^{18}O$ and $\delta^2H$. Their variations will be studied and allow to estimate the seawater contribution to the spring. Karst aquifers SGD are likely to display large variation of sea water contribution, in Schiavo and Povinec [2009], $\delta^{18}O$ ranged from -5.6 ‰ and +1.0 ‰ while $\delta^2H$ ranged between -30 ‰ and +5.0 ‰ supposing a sea water contribution varying from 0 % to 60 %. This method is only valid for high EC value.

Hydro-chemical process:

Major ion ratios, such as Na$^+$/Cl$^-$, Mg$^{2+}$/Cl$^-$, Ca$^{2+}$/Mg$^{2+}$, SO$_4^{2-}$/Cl$^-$, Ca$^{2+}$/Cl$^-$ are often used to identify processes within the mixing zone. Cation exchange, precipitation and dissolution divert those ratios from the pure mixing line between the seawater and freshwater end-members in distinct directions [Povinec et al., 2006]. A special interest will be given to saturation index (SI). SGD can be fed by two aquifers. First, the Upper Miocene aquifer. The latter is directly fed by rainwater and having a short residence time. Secondly, the Miocene aquifer. This aquifer outcrops on a very limited spatial area and studies has shown that it might be fed by the Jurassic aquifer further north between Mosqueira and Pata de Cima where the Cretaceous barrier is not present (Kleinendirst et al., 1985). Therefore, if the SGD are fed by the Upper Miocene, the equilibrium with the calcite would not be reached, and hence SI would be negative. On the other hand, is SGD are fed with the upper Miocene, the equilibrium would be reached and the SI would approach 0.

Strontium isotope

Theory Strontium is a minor constituent of groundwater. It readily substitutes calcium ions in calcium. Hence it participates in the water-rock interactions. No natural fractionation of stable strontium isotope was observed during natural processes. This property makes the isotopic ratio of strontium a reliable candidate for tracing strontium of different origin, for evaluating mixing of ground waters and for studying a state of isotopic equilibrium between groundwater and strontium bearing minerals and rocks. A precise mixing balance can be set up for two aqueous end members with different $^{87}$Sr/$^{86}$Sr values. Information on this process and
on the extend of water-rock interactions is obtained from comparing the $^{87}\text{Sr}/^{86}\text{Sr}$ values in the primary minerals of the host rock with those in the groundwater and in the secondary minerals on the surface of fractures, joints and pores. Strontium and calcium have similar geochemical properties. Therefore, the strontium isotopic composition serves to study the weathering of calcium bearing rocks and the biogeochemical recycling of calcium [Mook and Groen, 2004].

**Strategy** To be defined.

### 3.3.4 Evolution along the flow path

This section will target to understand the water signatures evolution, from the rainwater, through the aquifer until the springs. Two origins can be attributed to the SGD. First, the Upper Miocene aquifer. The latter is directly fed by rainwater and having a short residence time. Secondly, the Miocene aquifer. This aquifer outcrops on a very limited spatial area and studies has shown that it might be fed by the Jurassic aquifer further north between Mosqueira and Pata de Cima where the Cretaceous barrier is not present (Kleinendirst et al., 1985), this theory was also supported by [Bronzini, 2011]. This section will require sampling of rainwater in the recharge area of the Jurassic aquifer, the Upper Miocene and Miocene aquifer. The samplings will be done following a North-South transect aligned to the Olhos d’Água. Fig. 3.2 show the groundwater flow of the Albufeira aquifer and the two selected transects.

### 3.3.5 Geochemistry analysis of the different formations

Geochemical analysis of the rocks from the Miocene, upper Miocene and the Jurassic aquifer. The purpose would be to eventually link the geochemical analysis to the hydrochemistry characterisation of the sampled SGD to have a better insight of the groundwater’s origin. This part of the research will require the sampling of the different rocks in the region where they outcrop. In Fig. X, the different rock’s sampling locations are pointed. The analysis of the rack samples can be done ate the VU University laboratory. Strontium analysis could also be an option to characterize the different aquifers and therefore have a better indication of the groundwater’s origin.

### 3.3.6 Determination of the SGD salinization

Various theories tries to explain the salinization of the SGD in karst aquifers, here is the three reported by Fleury et al. [2007]. Based on the geophysics surveys, this part of the research will try to answer which mechanism is involved in the salinization of the springs of Olhos de Água.
Figure 3.2: Sketch of the groundwater flow around Olhos de Água, if no pumping Monteiro et al. (2007) in [Bronzini, 2011].

**Venturi effect**

A narrow passage in the main conduit, together with a narrow secondary conduit connected to the sea, (Fig. 3.3) lets the water through but causes a depression that sucks in seawater. The Venturi effect increases the flow rate of the entering seawater when the freshwater discharge increases. This mechanism is thought to be responsible for the seawater intrusion. According to Mijatovic (1962), this mechanism is not compatible with the morphology of karst because the karstification tends to eliminate the connections in this type of system. If it were present it would, in his view, be very unusual [Fleury et al., 2007].

**Density driven effect**

Since the Venturi effect cannot be generalised to explain the salinity in the karstic coastal springs, Djurasin (1942) in Mijatovic, 1962 suggested that the saline intrusion was due to the difference in density between the freshwater and the seawater. Thus, the coastal and submarine springs are linked to a deep conduit ending in the sea (Fig. 3.4). As long as the hydraulic head of the seawater is higher than that of the freshwater at the junction of the two conduits, the seawater enters and contaminates the aquifer [Fleury et al., 2007].
Density stratification

The phenomenon of density stratification in the flow occurs in sub-horizontal karstic conduits (...). A flow of fresh or brackish water leaves the top of the conduit or channel at the same time as a flux of seawater enters at the base. A saline wedge becomes established in the conduit. Its position depends on the outgoing flow rate and the dimensions of the conduit. As the karst conduits can develop at depth, the network of functioning conduits may cross the zone contaminated by the saline intrusion in the micro-fissures of the matrix. The saline wedge then becomes highly perturbed by the fresh-water flux in the conduits crossing it. The hydraulic head of the aquifer controls the exchanges between the matrix and the conduits. When the hydraulic head in the conduit is higher than that of the seawater in the matrix, part of the freshwater passes from the conduit into the matrix, forcing out the seawater. When the hydraulic head gradient is reversed, seawater enters the conduit [Fleury et al., 2007].

3.3.7 Evolution of the SGD

Time series of various parameters can give important information:

Seasonal Time Series

1. EC times series can give information on the karst network structure: The springs with branching inferior to 100 m are likely to present sudden increase in salinity in light of the fact that secondary vein act has a siphon during period of low discharge (Bonacci [1987] in Fleury et al. [2007]). Springs with branching of greater depth have more regular salinity variation. Its variation can also give an insight regarding the spring’s response to rainfall regime.
2. **Temperature**: to verify their response to seasonal air temperature variation

3. **pH**: Can give information of the meteoric imprint of the groundwater hence give information on the residence time of the water.

**Hourly Time Series**

In order to be able to interpret the seasonal time series, variation of the basic physico-chemical parameter on smaller time step should be done. This can be done with the mean of a CTD diver which will allow measurements of conductivity, temperature and pressure. The diver could be placed before April and measure during the whole month.
3.4 Issue 3: Modelling

To be discussed and defined with Rui Hugman and Prof. Jos Paulo Monteiro.

3.4.1 Inverse hydro-chemical model

3.4.2 Groundwater flow model

3.5 Issue 4: Coastal karst aquifer management

This part of the research will focus on the comparison of the studied aquifer with other coastal karst aquifer regarding their level of karstification and fracturation. Based on those parameter, this section will give an insight of is vulnerability and give a management perspective. This chapter will be inspired by Fleury et al. [2007] who has already elaborated a classification of aquifer on this topic. If possible a rough estimation of the SGD outflow will be defined and an overview on the management implication will be address. This part of the research can also use the groundwater flow model in order to estimate the aquifer vulnerability to climate change. Seawater level, precipitation, pumping rate, and land use change can have a major impact on the coastal aquifer, knowing that ASG has been supposed to limit seawater intrusion, this aspect should therefore be studied.
Chapter 4

Material

See the following page.
<table>
<thead>
<tr>
<th>GPS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Well sampler</td>
<td>Map: locate wells and verify GPS data for head calculation</td>
</tr>
</tbody>
</table>

- **Geophysics**
  - Submarine cable CVES
  - LUND cable (for CVES only)
  - 4 hammers
  - Cable reels and steel/brass electrodes
  - Connection cables (and spare connector plugs)
  - Battery packs and charger (2)
  - ABEM Terra meter
  - Submarine cable
  - Calculator
  - "Measuring tape
  - Log-log paper for drawing field curve"
  - 10 L bucket for wetting dry soil around electrodes
  - Screwdrivers, pliers, and a multimeter

- **Hydrochemistry:**
  - Shuffle to put electrodes deeper
  - NO3 and pH strips
  - EC meter
  - pH meter + calibration fluids"
  - 50 ml syringes (2)
  - Milli-pore nitrate-cellulose filter (150)
  - Titration Kit (Alkalinity)
  - Sampling bottles plastic (5)
  - Major ion sampling tubes (50)
  - Minor ion sampling tubes (50)
  - Amber glass sampling bottles for isotope (50)
  - Cool box
  - Marker stiff

- **Software**
  - ArcGIS
  - "ModFLOW SEAWAT - groundwater flow model"
  - Hyca - Hydrochemistry plot
  - RES2DMOD, RES2DINV and RES3DINV - CVES interpretation

- **Technical Equipped:**
  - 26 buckets for the submarine cable (4)
## Chapter 5

### Cost

<table>
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<th>Description</th>
<th>Cost</th>
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<td>Sending samples to the VU laboratory</td>
<td>20 - 30$^1$</td>
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<tr>
<td>Major and Minor ion analysis (50+50)</td>
<td>To be determined by Koos</td>
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<td>Plane ticket</td>
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<td>Isotope analysis (50)</td>
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<td><strong>Total [Euros]</strong></td>
<td><strong>300-325</strong></td>
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$^1$From 0 to 5 kg 20 euros and from 5 to 10 kg 30 euros  
$^2$If the preparation is done by the student, analysis are free.
Chapter 6

Deliverables

1. A proposal
2. A hydro-geological N-S profile
3. Ghyben - Herzberg salt/fresh water interface
4. Mid-term report after all the field measurements with the thesis outlines and the complete Research Area part and the Methodology
5. CVES profile
6. Inverse hydro-chemical model
7. A groundwater flow model
Chapter 7

Bottleneck

1. CVES hydro-geological interpretations: Contrast in karst not significant (between brackish Miocene and fresh marly of the Upper Miocene). Also, numerous parameters are likely to change drastically: water quality change, lateral change and porosity.

2. Determine the smallest conduits detectable.

3. Topography variation and rocks for submarine cable (CVES)

4. Detect shallow fresh water due to fixed resolution of the marine cable of 5m.
Chapter 8

Planning

See the following page.
<table>
<thead>
<tr>
<th>Month</th>
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<td>March</td>
<td>9</td>
<td>Proposal</td>
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<td>10</td>
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<td></td>
<td>11</td>
<td>Prep. CVES</td>
</tr>
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<td></td>
<td>12</td>
<td>Prep. CVES + Prep. sampling campaign</td>
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<td>Sampling campaign + send samples to VU</td>
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<td></td>
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<td>Return to A'dam</td>
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<td>23</td>
<td>Process hydrochemical data 1 and 2</td>
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</table>

¹: Buffer week: week meant to absorb eventual delay
Bibliography


Rapid 2D Resistivity and IP inversion using the least-squares method Wenner. GEOTOMO SOFTWARE MALAYSIA, 115 Cangkat Minden Jalan 5, Minden Heights, 11700 Gelugor, Penang, Malaysia, July 2011.


Chapter 9

Appendix I

Location of the N-S Hydrogeological profile on Olhos de Água by Elsendoorn et al. (1982).
Figure 9.1: N-S Hydrogeological profile location on Olhos de Água by Elsendorn et al. (1982).
Chapter 10

Appendix II

VES results by Elsendoorn et al. (1982)
Figure 10.1: VES 113 by Elsendoorn et al. (1982).
Figure 10.2: VES 114 by Elsensohn et al. (1982).
Figure 10.3: VES 115 by Elsenborn et al. (1982).