Exploratory Socio-hydrogeological Assessment of the Long-term Effects of Groundwater Contamination to Improve Population Resilience

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Thesis to obtain the Master of Science Degree in

Environmental Engineering

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Abstract

Contamination of groundwater can pose serious challenges especially in environment where hydrogeological conditions increase the vulnerability level of the aquifer to contamination. The Estarreja region, Northwest of Portugal is an example where an industrial complex is located within a highly vulnerable environment, thereby triggering the effects of long-term groundwater contamination resulting in threats to the inhabitants (humans and ecosystems) and triggering various socio-economic challenges. In this study, we combined hydrogeological information of the environment with social data (perceptions and reactions) information of some inhabitants (respondents) for the purpose of understanding the existing challenges towards improving the population resilience. Vulnerability analysis of the aquifer showed that the area is highly vulnerable to contamination activities especially areas around the chemical complex (high to extremely high vulnerability) .The results from hydrogeochemical analyses showed that the area is still undergoing varying levels of contamination activities as indicated in the major processes controlling groundwater chemistry in the area. Major water types identified was NaCl types combined with $CaCl_2$ and Na_2SO_4 sub-types, which points to the process of local salinization in the aquifer system. Analysis of sea water contribution on samples, ion ratios calculations showed that most of the groundwater samples with NaCl water type are not caused by sea water mixing but as a results of other reaction processes on-going in the aquifer system. Major of the reactions are cation exchange processes, simple dissolution of silicate weathering and carbonates processes, which can be linked to interactions between the surface waters (contaminated water channels) with the groundwater system and geology of the area. Multivariate statistical analysis using principal component analysis (PCA) further confirmed the major hypothesis of the study that groundwater is influenced by anthropogenic contamination mainly from surface waters in channels located in the study area. Further analysis of the groundwater quality status by comparing with WHO and Portuguese drinking-water standards showed that all groundwater samples exceeded the recommended limits of both standards. But, only 5 % of the groundwater samples were below the limits the Portuguese maximum permissible standards. For irrigation water quality assessed based on standard methods only 75 % were suitable for irrigation purpose. Combining the hydrogeological information and social information presented a complex link between the data that does not follow a rational line of thoughts, which could be possibly due to the fact that there are no effective communication of risks and possible precautions that could results from using the groundwater resources in its contaminated state. Therefore the need for effective stakeholder participatory campaigns and awareness to improve the population resilience.

Keywords: Groundwater contamination, socio-hydrogeology, hydrogeochemistry, vulnerability, Estarreja Chemical Complex (ECC), Northwest Portugal, multivariate statistical analysis, groundwater quality

Resumo

A contaminação das águas subterrâneas pode representar sérios desafios, especialmente em ambientes onde as condições hidrogeológicas contribuem para o agravamento do nível de vulnerabilidade do aquífero à contaminação. A região de Estarreja, no noroeste de Portugal, é um exemplo de um complexo industrial que está localizado num ambiente altamente vulnerável, aumentando os efeitos da contaminação nas águas subterrâneas a longo prazo, resultando em ameaças aos habitantes (humanos e ecossistemas) e desencadeando vários desafios socioeconómicos. Neste estudo, combinam-se informações hidrogeológicas com informações sociais (percepções e reações) de alguns habitantes (entrevistados) com o objetivo de compreender os desafios atuais para melhorar a resiliência da população. A análise de vulnerabilidade do aquífero mostrou que a área é altamente vulnerável a atividades que resultem em contaminação, especialmente as áreas em redor do complexo químico (vulnerabilidade alta a extremamente alta). Os resultados das análises hidrogeoquímicas mostram que a área ainda está a associada a níveis variáveis de atividades contaminantes, conforme indicado nos principais processos que controlam a química das águas subterrâneas na área. Os principais tipos de água identificados foram os tipos de NaCl combinados com os subtipos de $CaCl_2$ e Na_2SO_4, que apontam para um processo de salinização local no sistema aquífero. Analisando a contribuição da água do mar nas amostras, as taxas de iões mostraram que a maioria das amostras de água subterrânea com o tipo de água NaCl não está associada à mistura com a água do mar, mas sim com o resultado de outros processos de reação em desenvolvimento no sistema aquífero. As principais reações são processos de troca catiónica, dissolução simples de intemperismo de silicato e processos de carbonatos, que podem estar relacionados com as interações entre as águas superficiais (valas de efluentes industriais) com o sistema de águas subterrâneas e a geologia da área. A análise estatística multivariada, particularmente a análise de componentes principais (PCA) confirmou a principal hipótese do estudo, nomeadamente de que a composição das águas subterrâneas são influenciadas pela contaminação antropogénica derivadas das águas superficiais nas valas localizadas na área de estudo. Uma análise mais aprofundada do estado da qualidade da água subterrânea, comparando com os padrões da WHO e os padrões de água potável em Portugal, mostrou que todas as amostras de água subterrânea excederam os limites recomendados para ambos os padrões. Porém, apenas 5 % das amostras de águas subterrâneas estavam abaixo dos limites dos padrões máximos permitidos em Portugal. Relativamente à qualidade da água usada para irrigação, avaliada com base em métodos padrão, apenas 75 % das amostras eram adequadas para fins de irrigação. A combinação de informações hidrogeológicas e sociais resultou num elo complexo entre os dados que não seguem uma linha racional lógica, o que possivelmente se deve ao facto de não haver uma comunicação efetiva dos riscos e possíveis precauções resultantes do uso de águas subterrâneas contaminadas. Portanto, há a necessidade de realizar campanhas participativas eficazes e de consciencialização para melhorar a resiliência da população.

Palavras Chave: Contaminação água subterrânea, socio-hydrogeologia, hidrogeoquímica, vulnerabilidade, Complexo Químico de Estarreja (CQE), análise estatística multivariada, qualidade água subterrânea

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Acronyms

APA	Agência Portuguesa do Ambiente
AQP	Aliada Química de Portugal
ASE	Average Standard Error
BLUP	Best Linear Unbiased Predictor
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
EPA	Environmental Protection Agency
EU	European Union
EU-EIR	European Union Environmental Implementation Review
HDPE	High Density Poly Ethylene
MSE	Mean Square Error
MTBE	Methyl Tertiary Butyl Ether
NPS	Non Point Source
NUTS	Nomenclature of Territorial Units for Statistics
PCA	Principal Component Analysis
PCB	PolyChlorinated Biphenyls
PTEs	Potentially Toxic Elements
PVC	PolyVinyl Chloride
RMSE	Root Mean Square Standardized Error
RMSSE	Root Mean Square Standardized Error
SI	Susceptibility Index
SPSS	Statistical Packages for Social Sciences
TCE	TriChloroEthylene
US EPA	United States Environmental Protection Agency
VCM	Vinyl Chloride Monomer

Chapter 1

INTRODUCTION

1.1 Research background

The increasing demand for water resources imposed by population growth, intensive agriculture, and industrial progress poses serious threats to the available groundwater resources globally. Groundwater is subjected to many pressures as a result of global changes in human activities on the environment and as such, putting the limited groundwater resource often at risk. Therefore, the quality status and sustainable use of water has become a major issue, and also one of the major environmental challenges of this present century.

Most industrial activities are often located nearby rivers, and seas to facilitate easy transport operations of industrial products. As a result, numerous industrial sites exist in vulnerable areas, surface and shallow groundwater bodies. Contaminants emerging from old industrial activities are posing major risks to the environment and surrounding ecosystems at large. The contamination is complex due to the interaction between these contaminated surface water bodies and underlying groundwater systems.

Several environmental assessment reports published by international institutions such as the European Environment Agency (EU-EIR, 2019), the United States Geological Survey and the United States Environmental Protection Agency (US-EPA, 2019) reported that, an increasing number of chemical substances such as; fertilizers, pesticides, organic and inorganic compounds have been detected in soil and groundwater by changing its natural composition. These chemical substances limit the use in irrigation and public supply, and create serious problems for terrestrial ecosystems and associated aquatic lives. Fertilizers, in particular nitrogen, appear to be contaminants in more widespread distribution.

Contamination with herbicides and other very persistent organic compounds in the environment such as polychlorinated biphenyls (PCB), benzene, toluene, ethylbenzene, xylene (commonly referred to as BTEX), methyl tertiary butyl ether (MTBE), trichlorethylene (TCE), mononitrobenzene (MNB), among others, have been detected in a large scale and in different hydrogeological environment. These organic compounds have the long-term toxicity, and some of them are even carcinogenic, endocrine disruptor and have effects on the nervous system (ATSDR, 2010); so its presence in groundwater is a risk for public health and for the most vulnerable ecosystems.

In addition to the already known contaminants, there are also new contaminants (emerging organic contaminants) recognised by the scientific community to represent potential health hazards (Sethi and Di Molfetta, 2019). Emerging organic contaminants include, among others, pharmaceuticals, illegal drugs, micro-plastics, personal care products, food preservatives and additives, and engineered nanomaterials (Postigo and Barceló, 2015; Cosenza et al., 2018)

Contamination can have a long term negative effect on soil quality, water quality and also threaten human health or dependent ecosystems in the environment. A recent report of the European Commission estimated that, potentially polluting activities have taken or are still taking place on approximately 2.8 million sites in the European Union (EU). At EU level, 650,000 of these sites have been registered in national or regional inventories. About 65,500 contaminated sites already have been remediated. Portugal has registered 181 sites where potentially polluting activities have taken or are taking place, and already has remediated or applied after-care measures on 83 sites (EU-EIR, 2019).

In the North-western part of Portugal is located an industrial zone - Estarreja Chemical Complex (ECC). The region of Estarreja has always had a strong connection with different industries. Since the 1930s, several units of the agro-food industries (e.g. Nestlé, Avanca) and the chemical industry (SAPEC) have been installed in the area (Ordens, 2007; Ribeiro and Coelho, 2015). It also attracts a high social and ecological penalty due to the presence of contamination. Therefore, it has been one of the first cases of pilot study on local management of contaminated sites in Portugal.

At present, the main companies within the ECC produce chemicals such as: polyvinyl chloride (CIRES); nitrobenzene, aniline, cyclohexilamine, cyclohexanol, sulphuric acid, nitric acid and sulphanilic acid (Bondalti). Also, methyl diphenyl isocyanate (DOW Portugal); pure and mixed gases for industrial and medical uses (Air Liquide); aluminium sulphates and polyaluminum chlorides in liquid form (AQP) are produced. The production of these chemicals within the ECC require the use of a long list of potential hazardous substances, which have left contamination footprints in the surrounding environment over the years. In addition, the indiscriminate release in the past of these hazardous substances into the environment has led to high levels of soil, surface and groundwater contamination by potentially toxic elements (PTEs).

Although, scientific studies and rehabilitation measures have been implemented for the past 20 years in a bid to restore the environment. Groundwater contamination levels have remained high for some PTEs, whose concentrations may be several orders of magnitude higher than human consumption and irrigation standards. some of these PTEs are known to be potential threat to human and ecosystem health due to direct or indirect exposure to contaminated groundwater and can lead to long-term carcinogenic and non-carcinogenic health risks. The local population surrounding ECC still traditionally rely on groundwater resources for basic human uses (cooking, bathing), and agricultural uses (cattle rearing and irrigation activities) despite having assess to safe public water supply (mostly for drinking purpose). There are many research that have been executed in this area over the years. However, the link between groundwater contamination and human health risks still remains poorly understood. Also, there is neither any existing established scientific framework to address these problems, nor to improve social awareness amongst the local populace who are in direct or indirect contact with the contamination activities.

1.2 Problem statement and motivation

The Aveiro Quaternary shallow unconfined aquifer surrounding the ECC is very vulnerable to point and diffuse contamination. It is formed by high permeability hydrogeological formations, with high recharge rates and interacts with surface water bodies (lagoons and irrigation channels) and dependent ecosystems. The aquifer is located in areas with strong agricultural, domestic and industrial pressures that contaminated groundwater. The aquifer has already been defined as a nitrate vulnerable area following the implementation of the Nitrates Directive (Directive et al., 1991), which aims to protect water quality across Europe by preventing nitrates from agricultural sources polluting ground and surface waters and by promoting the use of good farming practices.

The production of hazardous chemicals within the ECC has left a contamination footprint in the surrounding environment, leading to high levels of soil, surface and groundwater contamination by potentially toxic elements. Despite the confinement of wastes and investment in improved technologies within the industrial complex which includes: less contaminant production processes; confinement of open dump waste in ERASE facility (ERASE, 2000); impermeabilization of industrial areas; removal of burial pipes to control leakages and improved monitoring of air, soil and water quality. There are still reported cases of high level contamination activities in the environment. These contamination activities could be traced to long history of contaminant in the environment (unsaturated zone and groundwater) from past years (decades). Current research Neves (2015); André (2016) and Marques (2017); have reported cases of acid drainage (pH values less than 4.0) in most channels around the study area. These observed low pH values, could be as a result of untreated effluents still being discharged into some of the drains or the long-term effect of the contamination still persist.

However, research and rehabilitation efforts have been implemented around the ECC to understand and clean-up the environment respectively. These efforts aimed at restoring the environment around ECC have not been so effective in tackling the challenges and improving the livelihood of the populace so far. For example, the studies of Senos et al. (1994); Leitão (1996); Taunt (2001); Ordens (2007); Neves (2015); André (2016) and Marques (2017); have focused on evolution of the contaminant plume close to ECC in the study area. These studies applied common methods (geophysical, hydrogeological, hydrogeochemical and modeling approach) to delineate and map contaminated areas. Some recent studies have focused on linking the contamination (especially groundwater resource) in the region with human health risk (Pinto et al., 2019). However, studies linking contamination and human social perception have not been reported in the area. Hence, engaging in such studies would provide a better understanding of the current problem and possibility of effectively tackling this issue in the study area.

In the light of above stated situation being faced by the population around ECC, there is need for a detailed regional study to understand the link between long-term contamination activities, the impact on groundwater resources in the area and perception of the population. Thus, an interdisciplinary socio-hydrological approach is needed to bridge the gap between science and society in order to protect the environment and inhabitants in the long-run, which is the main goal of this study.

1.3 Research aim and objectives

The overarching aim of this study was to explore the benefits of integrating hydrogeological with the perceived knowledge of humans (sociology) approach to understand the effects and human perception of long-term groundwater contamination on the inhabitants (humans) for the purpose of improving the population resilience.

Specifically, the objectives were to:

(a) conduct regional field studies by measuring/mapping field parameters; thereby identifying contaminated hotspots;

(b) identify major hydrogeochemical processes controlling groundwater chemistry in the area, using hydrogeochemical (graphical) and multivariate statistical analysis methods;

(c) assess the current groundwater quality status, by comparing with standard water quality guidelines (drinking and irrigation purposes);

(d) evaluate the vulnerability of the underlying shallow aquifer in the area to contamination activities, using susceptibility index (SI) method;

(e) assess the level of perception (informed knowledge) by inhabitants (humans), as regards the contaminated groundwater resource in the area; and

(f) Proffer practical measures to improve the population resilience in the long-run.

Therefore, to achieve the stated aim and objectives, the following specific research questions were formulated:

① What are the impacts of (contaminated) surface water in channels used to discharge industrial effluents in the past ?

② What is the level of groundwater (aquifer) vulnerability to contamination activities in the area ?

③ What is the current groundwater quality status, as regards suitability for major water uses (drinking and irrigation purposes) ?

④ Is there any connecting link between the current groundwater quality status and inhabitants perception (informed knowledge) to possible risks ?

⑤ What are the strategies that could be implemented to achieve a long-term solution to the issue ?

Major hypothesis

Groundwater contamination in the study area is predominantly caused by, interaction of the (contaminated) surface water in channels used to discharge industrial effluents in the past.

1.4 Outline of the thesis

The thesis is structured as a series of seven different interconnected chapters, that aim to provide justified answers based on the research goal to each of the specific stated objectives of the study. Hence, chapter 1 provide a background and scope of the study; whereas chapter 2 gives a brief introduction about the study. Meanwhile, chapter 3 gives a brief review of past studies done in the study area and basic concepts and theories related to the study; whereas, chapter 4 gives detailed description of all materials and methods applied in the study. Also, chapter 5 and chapter 6 present all results and discussion of the research. Finally, the thesis closes with chapter 7, highlighting the main message of the study, and then supported with some recommendations.

1.5 Project framework and funding information

The project was funded under the Soil Take Care project, an international project co-financed by the European Regional Development Fund (ERDF) through the Interreg Sudoe initiative. It aims to improve the management and rehabilitation of contaminated soils and waters in the southwestern region of Europe involving partners and intervention sites from Spain, Portugal and the South of France.

The Portuguese partners CERIS-IST, was responsible for the task number GT.6: Numerical modelling of transfers of pollution through soil, air and water. Therefore, methods and objectives of this study were framed under the project and in agreement with the Portuguese research team.

Chapter 2

RESEARCH AREA

2.1 General overview

This chapter presents a brief description of the study area; which include the physical settings, climatic conditions, hydrological, hydrogeological and land use characteristics of the study area.

2.2 Description of study area

2.2.1 Geographical location

The study area (Figure 2.1) is geographically located in Northwest of Portugal between latitude 40° 74’ 90” N and 40° 79’ 74” N, and longitude 08° 62’ 91” W and 08° 56’ 45” W Greenwich meridian in the WGS84 geographical coordinate system. The study area is located in the Aveiro region of Portugal, more specifically in the sub-region of Baixo Vouga (Northwest of NUTS II, according to European Community Regulation number 1059/2003 of the European Parliament and Council of 26 May 2003; which established a common classification of territorial units for statistics - NUTS I, II and III) (André, 2016).

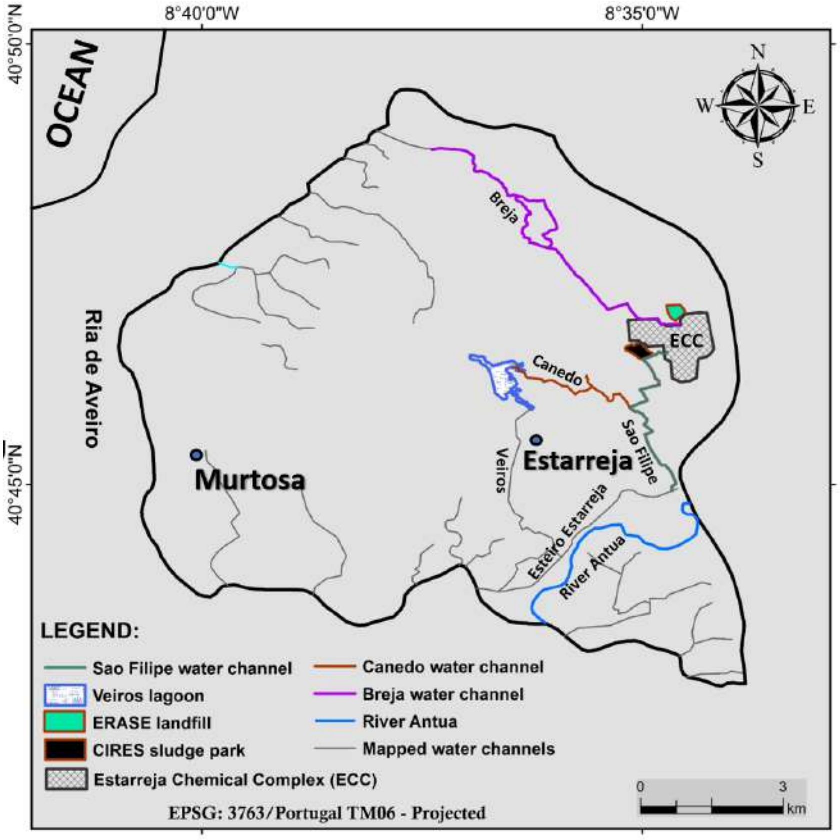
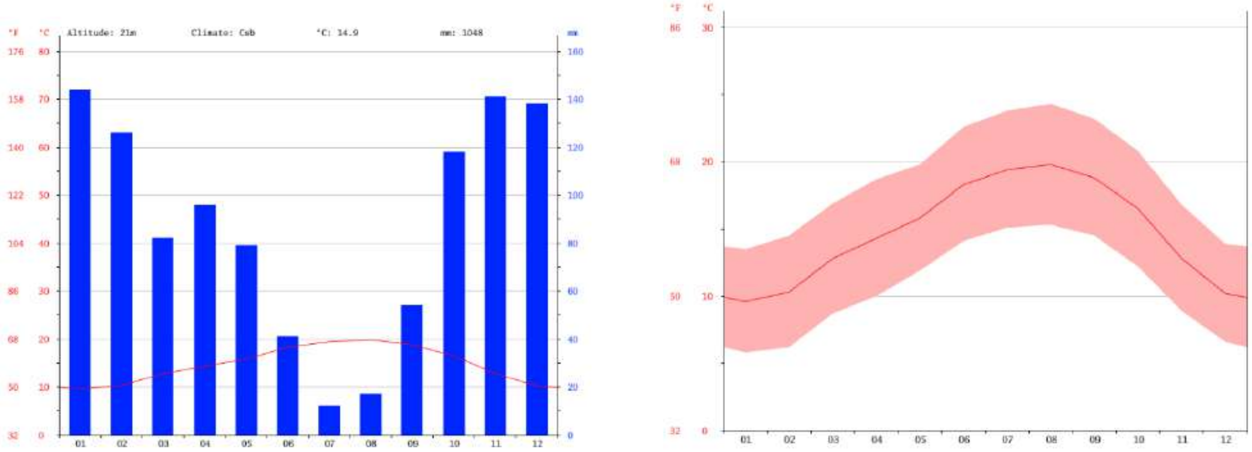


Figure 2.1: *Location of study area showing locations of water channels, lagoons, rivers in (Estarreja and Murtosa regions), Aveiro District, North-West of Portugal*

The study area comprises of two major municipalities; Estarreja and Murtosa regions (Figure 2.1), with a land surface area of approximately 84 km^2 and a polulation of 27000. The Estarreja municipality is located in the district of Aveiro and is limited by Ovar municipality at the North-Northeast area; by Oliveira de Azeméis municipality in the Northeast area; to the East by the Albergaria-a-Velha municipality and by Aveiro municipality to the South and Murtosa South-west. The region of Murtosa, covers the municipalities; Avanca and Pardilhó to the North; Beduído and Veiros at the center; and Salreu, Canelas and Fermelã to the Southern part of the study area (Figure 2.1).

2.2.2 Climate

The climate is warm and temperate in Estarreja. In winter, there is much more rainfall in Estarreja than in summer. The Köppen-Geiger climate classification is "Csb" (Climate Csb: Mesothermal Temperate Humid Climate; s-dry season in summer; b-bit hot summer, but extensive (Kottek et al., 2006)). The average annual temperature in Estarreja is 14.9 °C. About 1048 mm of precipitation falls annually. The driest month is July, with 12 mm of rainfall. Most precipitation falls in January, with an average of 144 mm (Figure 2.2a). The warmest month of the year is August, with an average temperature of 19.8 °C (Figure 2.2b). In January, the average temperature is 9.6 °C. It is the lowest average temperature of the whole year. The difference in precipitation between the driest month and the wettest month is 132 mm. The average temperatures vary during the year by 10.2 °C (CLIMATE-DATA, 2019).



(a) Average precipitations (mm) for each months

(b) Average temperatures (°C and °F) for each months

Figure 2.2: *Variations in climatic condition and patterns of: (a) Average precipitations (mm) for each months; and (b) Average temperatures (°C and °F) for each months in Estarreja (Source: from (CLIMATE-DATA, 2019))*

2.2.3 Land use and Topography

The study area has specific land use patterns that show the major activities done in the area. Land use of the are is divided into four major types; forested areas, agricultural areas, urban areas and industrial areas (Figure 2.3). Agricultural areas occupy most of the study area followed by forested areas and industrial areas. Forested areas are more distributed towards the Northern part of the study area whereas, agricultural areas are more towards the Southern part and Western part of the study area.

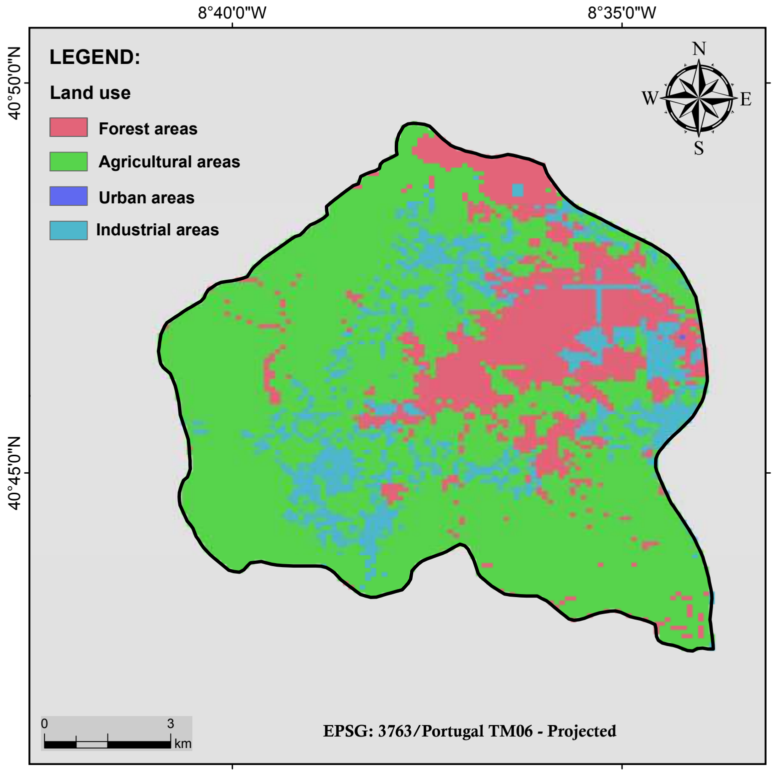


Figure 2.3: *Distribution of land use patterns in the study area*

The altitude of the study are (Figure 2.4) can be divided into three different zones with each having unique features and land use pattern.

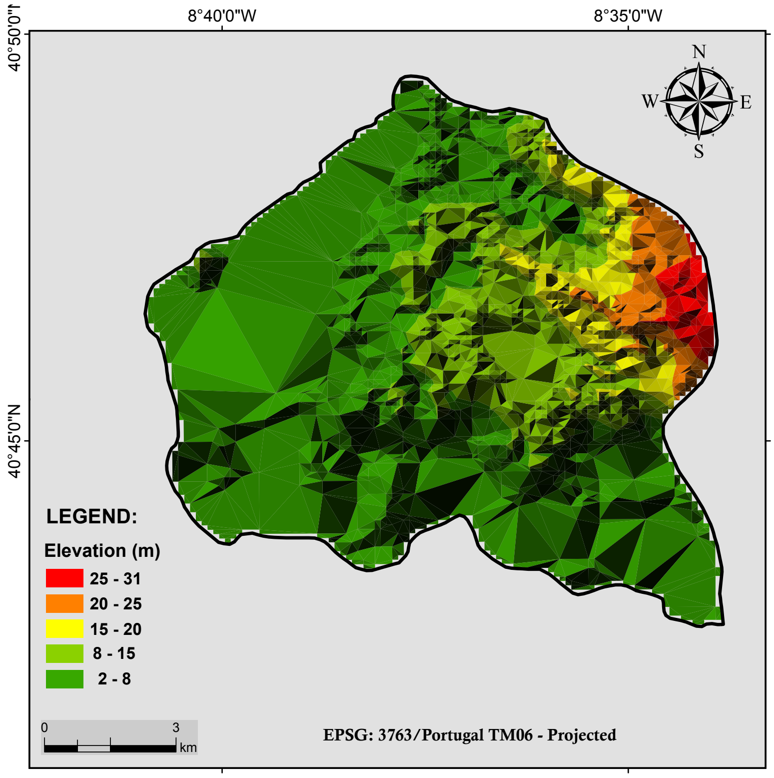


Figure 2.4: *Distribution of elevation in the study area*

The first zone is towards the West side of the study area with altitudes between 2 and 15 m. In this zone, irrigated agriculture is the major land use pattern. The intermediate zone is located around the centre of the study area having elevation between 15 and 20 m. The major land use pattern in this zone are industrial and forested areas. Finally, in the study area the highest portions are located in the East part of the study area. This zone is dominated by forested, low density urban areas and also has the industrial complex.

2.3 Hydrogeological setting of the study area

2.3.1 Geology

Generally, the geologic formations that support this aquifer system are all detrital in nature (Figure 2.5), and can be individualized into three large units:

- river terraces and ancient beaches, of Pliocene age, ;
- a gravelly sequence, and mostly covered by one or more layers of organic sludge, known for basic formation of quaternary (Pleistocene), and;
- a dune mantle and modern alluvium, of Holocene age.

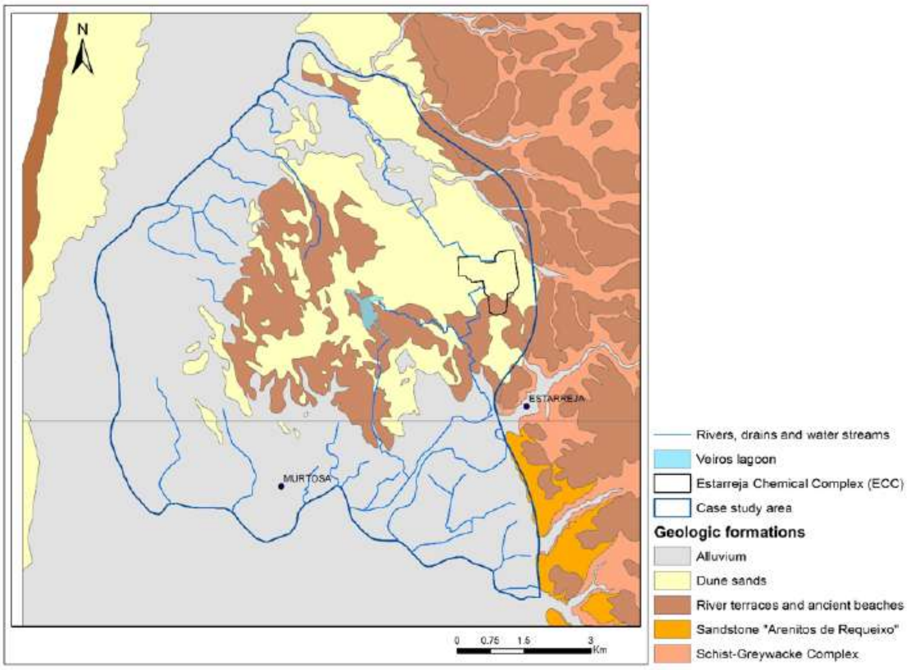


Figure 2.5: *Geology of the study area, digitalized from the geologic maps 13 C – Ovar and 16 A – Aveiro (scale 1:50k) (Source: from Barreiras (2019))*

In the study area, these deposits settle discordantly on a substrate consisting of either lower cretaceous clayey formations, or schist-greywacke, belonging to the Schist-Greywacke Complex (SGC), from the Precambric age.

The Cretaceous formation that forms the substrate for the Holocene and Plio-Pleistocene detrital sedimentary is “Arenitos de Requeixo”, a clay, conglomerate stoneware with intercalations of clays, sands and pebbles (quartz or quartzite), also with light colour. This sandstone emerges near Estarreja train station, and further south of the study area (Ordens, 2007). The study area covers only an area where debris deposits arise from Plio-Pleistocene and Holocene ages (Figure 2.6). The ages of the geological formations in the region are located in a wide time interval, that started in the Pre-Cambrian and ended in Quaternary (Barradas, 1992b).

(a) Dune sands immediately West of ECC

(b) Terrace located immediately East of the study area

Figure 2.6: *Major formations which include: (a) Dune sands; and (b) Terrace outcrop; located West and East of the study area respectively (Source: from Ordens (2007))*

The Holocene age formations are sand dunes and modern alluvium. The dune and beach sands cover all the study area. These are very fine to fine sands, with low clay component and usually clear, white or yellowish in colour (Figure 2.6a). The formation of the alluvium (muddy sands and muds) is in close relation to the evolution of a river that flows South from the study area and of the Ria de Aveiro lagoon.

The Pleistocene age formations are fluvial terraces and old beaches formed by fine to coarse sands, often with intercalation of muddy or clayey sands and with pebbles at the bottom part (Figure 2.6b).

(a) Cretaceous outcrop located immediately South-east of the study area

(b) Shale outcrop located immediately East of the study area

Figure 2.7: *Examples of outcrops of major formations which include: (a) Cretaceous outcrop; and (b) Shale outcrop; located South-east and East of the study area respectively (Source: from Ordens (2007))*

Rocha (1993) conducted studies to determine the mineralogical constituents of the sedimentary basin of Aveiro, which includes the study area. He employed X-ray diffraction analysis and transmission electron microscopy to study soil fractions found in the study area. The results revealed that, the main mineralogical components associated with the Holocenic and Plio-Pleistocenic formations are largely identical but corresponding relative abundances may vary from level to level. The mineralogical composition of these sediments are: quartz, plagioclase, potassium feldspar, calcite and dolomite as principal minerals; gypsum, opal, and zeoliths, among others, as secondary minerals; and illite, kaolinite and smectite as principal clay minerals (Rocha, 1993).

In the eastern part of the study area, the bedrock consists of Pre-Cambrian schists or mica schists (Figure 2.7b); while on the western part of the area it is formed by consolidated sandstones from the Lower Cretaceous (Figure 2.7a).

2.3.2 Lithostratigraphy

The lithostratigraphy of the study area was established by Moitinho d' Almeida and Zbyszewski (1947, 1949), based on numerous surveys conducted in the 1940s, at various points on the coastal plain, especially in the region where the Old Massif can be found in shallow depth. These surveys were made in the context of research works to the construction of boreholes for urban and industrial water supply. The surveys provided very important data for the geological and hydrogeological knowledge of the quaternary formations, and several detailed geological profiles were made. A sedimentary sequence with great vertical and lateral heterogeneity was shown by these surveys, in which an alternation of nine layers of more or less sandy sands and muds is observed. These layers settle discordantly on a deeply altered substrate of schists and clay sandstones.

Base on the work of Moitinho d' Almeida and Zbyszewski (1947, 1949), a thorough lithostratigraphic characterization was done by Ordens (2007). Spatial integration of fifty-six borehole logs available for the study area were analysed, which allowed for the definition of a seven layer sequence of Holocene and Pleistocene formations, from top to bottom (Figure 2.8). This listostratigraphy descriptions has serve as a basis for many studies in the area and well accepted in the scientific community (Neves, 2015).

The lithostratigraphic sequence (top to bottom, indicating in parentheses the correspondence to the units proposed by Moitinho d' Almeida and Zbyszewski (1947, 1949) are:

(1) **Superficial Sands** (Layer 8 and 9): Unit consisting of dune sands that cover most of the study area. Included in this unit are some levels of compact clay and humus;

(2) **Sludge with vegetable remains** (layer 7b): unit consisting of dark gray sludge with vegetal remains. To the east, this unit presents lateral variation for gray sandy clays with vegetal remains;

(3) **Fine sand** (layer 7 and 7a): this unit consists of fine sand (layer 7) in the base, sometimes with small rolled stones on top (layer 7a). It is not always possible to distinguish this unit from layer 9, especially when no rolled stones are present and layer 7b is not present;

(4) **Sludge and sandy sludge with vegetable remains and lamellibranchs** (complex 6): unit consisting of sludge, sandy sludge and fine muddy sands, always dark gray in color, with vegetable remains and lamellibranchs. To the east, this unit presents lateral variation for gray sandy clays with vegetable remains;

(5) **Fine to coarse sands with rolled stones** (layer 5): unit consisting of fine to coarse sands with presence of rolled stone. From East to West, the pebble size and layer thickness increases;

(6) **Sludge with vegetal remains** (layers 3 and 4): unit consisting of sludge, sandy sludge and very muddy fine sands, always of dark gray color, with vegetable remains. To the east this unit presents lateral variation for clays, sometimes sandy, dark gray, with vegetal remains;

(7) **Medium to coarse sands with rolled stones** (layer 2): Unit consisting of medium to coarse sands with small and large rolled stones. Sometimes when sludge from layer 3 and 4 are not present, it may be difficult to distinguish layer 5 from this layer.

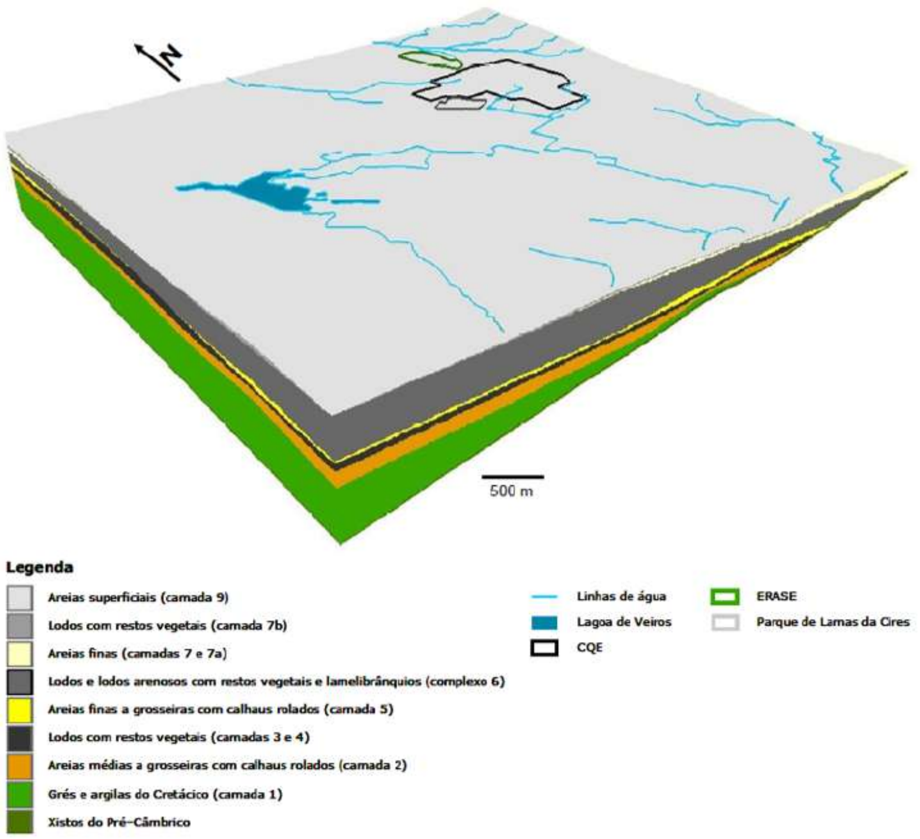


Figure 2.8: *3D diagram describing the lithostratigraphy of the study area (Source: from Ordens (2007))*

Ordens (2007), extract some cross-sections from the 3D lithostratigraphy model (Figure 2.8) of the area. The cross-section (Figure 2.9), to the south of the ECC, with the direction E - W and N - S, shows the structure and geometry of the lithostratigraphy of the Aveiro Quaternary.

- dune and beach sands;
- muds;
- fine sands;
- muds and sandy muds with shells
- fine to coarse sands with gravel;
- muds;
- medium to coarse sands and gravel.

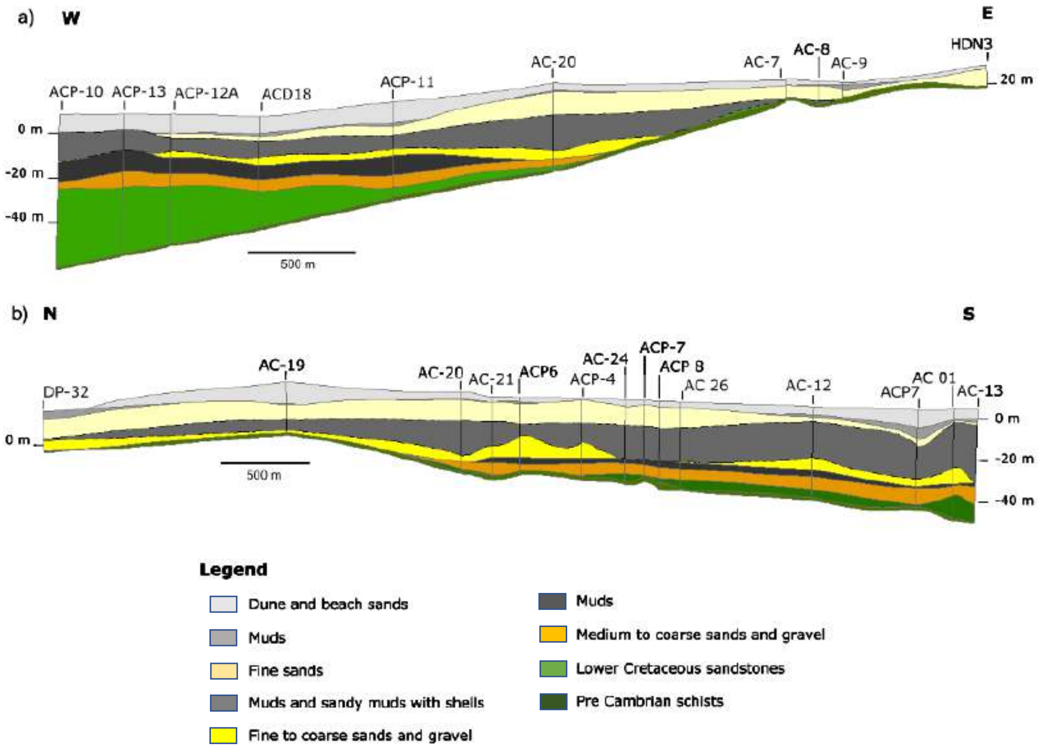


Figure 2.9: *Interpretative cross-sections of the study area showing the litostratigraphic sequence. (a) E - W cross-section (b) N - S cross-section (Source: from Ordens (2007))*

The entire sedimentary sequence is only present in the western and southern parts of the study area. In the Northern and Western parts of the study area just the first layers of the sequence are observed. The schists are the bedrock in the Eastern and Northern parts of the study area, while the deeper Lower Cretaceous sandstones are the bedrock in the West and South parts of the study area (Ordens et al., 2007).

2.3.3 Hydrogeologic units

The study area is located in the region covered by the Aveiro Quaternary Groundwater Body (Figure 2.10) (AQGB) , as defined by the Portuguese Environmental Agency (EU-WFD, 2000).
The sets of defined lithology occurring in the study area, in conjunction with analyses data obtained in hydraulic construction water collection reports, make it possible to consider the existence of two main aquifer units with different hydraulic and hydrogeological characteristics (Moitinho d' Almeida and Zbyszewski, 1947, 1949).

The two units present in the study area, belonging to the Aquifer of the Quaternary System are:

- **Shallow aquifer unit:** It is a phreatic surface aquifer, lithologically installed from the top to the bottom in shallow sand (dune), fine sand sometimes with small pebble, interleaves sludge and muddy sands with plant residues. This unit has great permeability (25 - 65 $m.d^{-1}$) and porosity which makes it very vulnerable to pollution. The recharging is accomplished by precipitation
- **Deep aquifer unit ("Base Quaternary"):** It is a semi-confined aquifer, lithologically installed from top to bottom in fine to medium and coarse sand with rolled stones. It presents intercalated

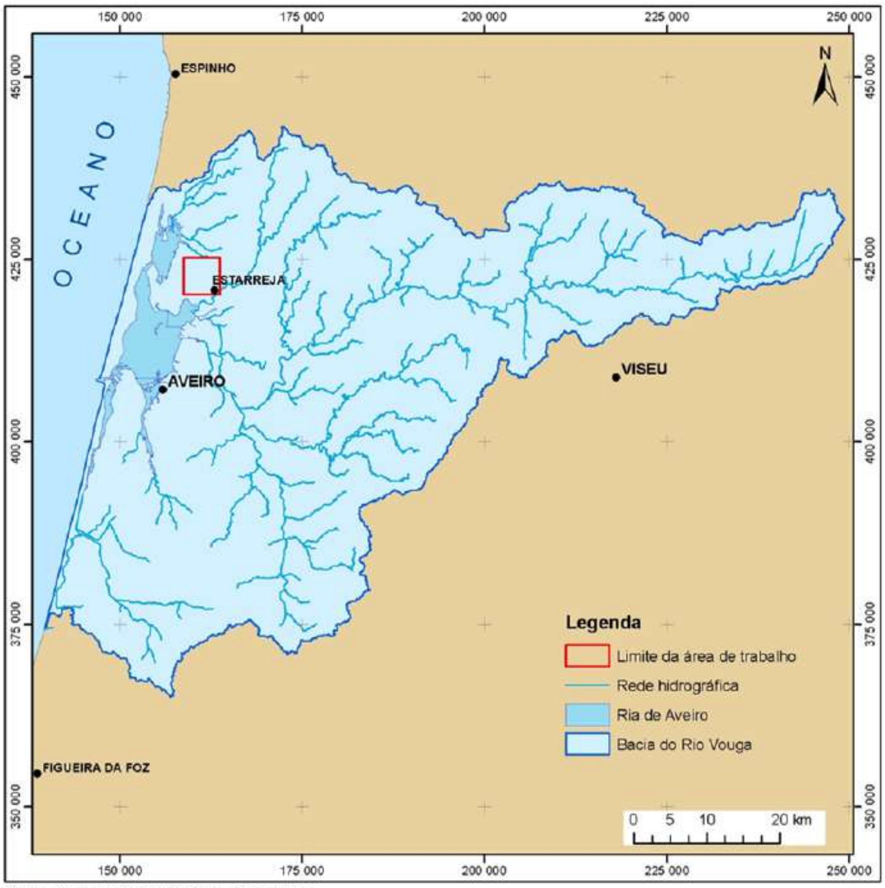


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Figure 2.10: *Location of Aveiro Quanternary Groundwater Body (AQGB) in the River Vouga basin of the study area (Source: from Neves (2015))*

mud and muddy sands with plant debris, with a hydraulic conductivity between 25 - 40 $m.d^{-1}$. Its recharge depends primarily on water infiltration from precipitation.

The two aquifer units are separated by a semi-confining layer (with hydraulic conductivity less than 1) consisting of sludge and slimy sand with variable thickness. Moreover, in some sites it may not be present, particularly in the North-east region of the study area. Therefore, the absence of the semi-confining layer in some area, places the two units into contact and increasing possible contamination of the second aquifer unit (Ordens, 2007).

Chapter 3

LITERATURE REVIEW

3.1 Overview on contamination and remediation activities in the study area

The main source of groundwater contamination in the study area is largely associated with the operation of an industrial chemical complex (Estarreja Chemical Complex - ECC) over the years. In the past, the industrial activities and processes often results in the discharge of liquid and dumping of untreated solid waste into the environment (IDAD, 2000; ERASE, 2000). In addition to the industrial origin of contamination, agriculture and the use of septic tanks for domestic waste storage also contribute to the contamination of groundwater in the study area.

Since the mid thirties and until beginning of the new millennium, the chemical industries at the ECC have disposed solid and liquid effluents without adequate treatment to remove pollutants (heavy metals, metalloids and organic compounds). The liquid effluents were usually ejected into the São Filipe, Breja and Canedo water channels. Also, the solid residues were deposited in two major areas without proper confinement: which are mud park belonging to CIRES (chemical industry) and the ERASE landfill (Fig. 1) (Leitão, 1996; IDAD, 2000; ERASE, 2000).

The principal pollutants present in the liquid effluents can be divided in two major groups:

- **inorganic pollutants:** Chloride, Sodium, Sulphate, Nitrate, Nitrite, Mercury;
- **organic pollutants:** Nitrophenols, Nitrobenzene, Aniline, Vinyl chloride, Benzene, Chlorobenzene, and Hydrocarbons.

The solid residues were mainly muds with high concentrations of; sodium chloride, calcium sulphate, calcium carbonate, magnesium hydroxide, iron, mercury, arsenic, zinc, chromium, copper, vanadium, acetylene and carbon tetrachloride.

Other anthropogenic activities (agriculture, cattle raising, use of septic tanks at local households) around the Chemical Complex also contribute to further soil and groundwater contamination (Ordens et al., 2007).

3.1.1 The industries

Most of the chemical industries are located inside the ECC. The industrial area of 2 km^2 is 1 km away from the Estarreja town. The major industrial units working for many decades inside the industrial complex (Figure 3.1) are :

- **UNITECA (currently BONDALTI):** It has been in operation since 1956. The company used to produce sodium and chlorate compounds from rock salt through electrolytic cells using mercury cathodes (Costa and Jesus-Rydin, 2001). Over a long period, the effluent enriched in chlorides, sulfates and liquid mercury were discharged into the São Filipe water channel. At present, the industrial processes have been replaced with modern technologies that are harmful to the

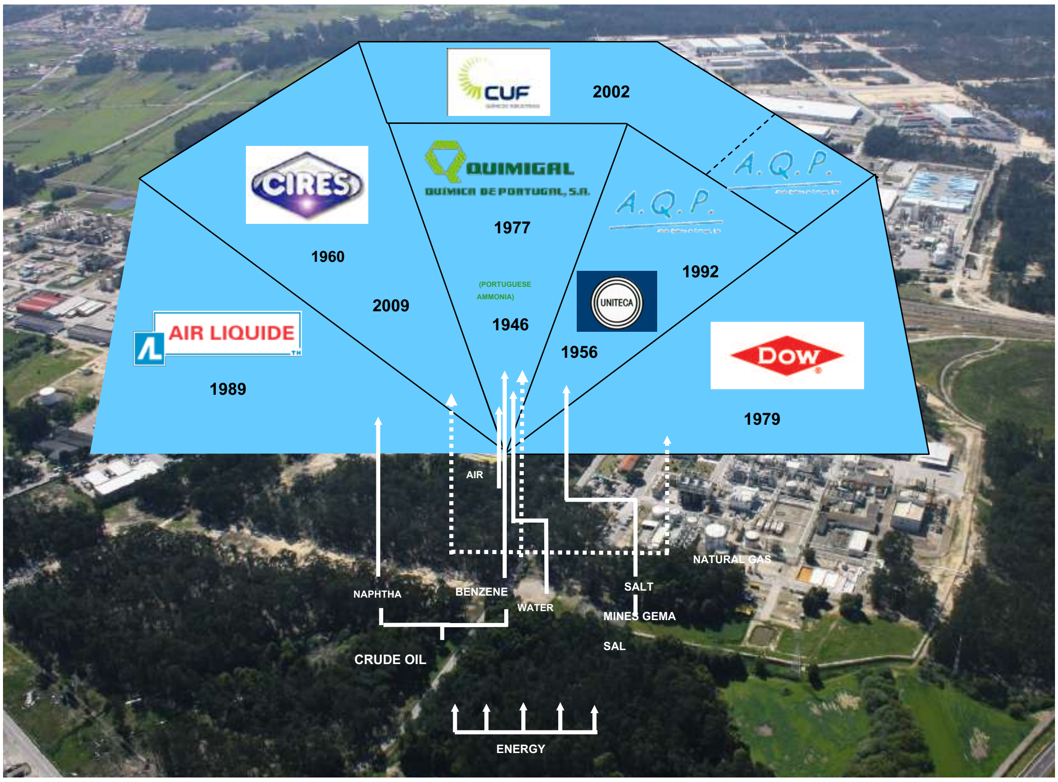


Figure 3.1: *Aerial view showing Estarreja Chemical Complex, various industrial units and their products (Source: from (Pacopar, 2001))*

environment. In the Industrial Chemicals business unit, Bondalti mainly focuses on the following two supply chains: Aniline and derivatives in the organic chemicals sector and Chlor-alkalis in the inorganic chemicals sector.

- **Química (currently BONDALTI):** Established in 1946, produced ammonium sulphate, from sulphuric acid and ammonia. In 1974, it began production of nitric acid and ammonium nitrate. These productions stopped in the early 1990s, for the rebirth of a new unit. The new unit (Anilina de Portugal), started in 1978 as an off-shoot of Química. The new unit was involved in the production of nitric acid, aniline and nitrobenzene (Figure 3.1), which is still in operation till date.

  In addition, QUIMIGAL was responsible for the deposition of about 150,000 tonnes of sludge rich in arsenic, mercury, zinc, copper, vanadium and iron, originating from combustion of pyrites and de-dusting method into the environment. The sludge was dumped in a portion of land (sludge park) with no evidence of sealing over the years (Leitão, 1996). The sludge generated were usually channelled into the water channels through a buried pipeline.

- **CIRES:** Established in 1963 to produce synthetic resins, mainly PVC (polyvinyl chloride) from vinyl chloride monomer (VCM). These raw materials were also produced in this plant until 1986. In 1986, the company decided to end the production of VCM, preferring to buy the same compound (Ordens, 2007).

  Since 2009, CIRES has been part of Shin-Etsu Chemical Co. Ltd., the world leader in PVC production. Founded in 1960 as a joint venture between a Portuguese company and two Japanese industrial companies, CIRES was the first Portuguese-Japanese industrial joint venture in Europe, a pioneer in the production of thermoplastic materials in Portugal. The only PVC producer in

Portugal, CIRES has a strong position in the Iberian market, as part of Shin-Etsu's worldwide commercial strategy, namely in the production of PVC specialities (CIRES, 2019).

In the past, the company's effluents were discharged into the portion of the water channels close to Ria de Aveiro lagoon. The effluents are enriched in vinyl chloride and mercury (IDAD, 2000). However, at present, wastewater is sent to SIMRIA for treatment prior to discharge into the environment (Ordens, 2007).

- **DOW Portugal:** Producing since 1978 isocyanide polymers of aromatic base. It uses aniline, formaldehyde, chlorine, synthesis gas and caustic soda as raw materials for its production (IDAD, 2000). The effluents from this industrial plant are enriched in monochlorobenzene, aniline, methanol, hydrocarbons, mercury and sodium chloride. These fluids undergo treatment by activated sludge rich in mercury, chromium and sodium chloride, which are part of the solid residue. In the past, wastewaters from the industrial processes were discharged to the treadmill of Estarreja through buried conduits (Leitão, 1996; IDAD, 2000).

These industrial units are greatly inter-dependent for the exchange of raw materials and sub-products (Figure 3.2).

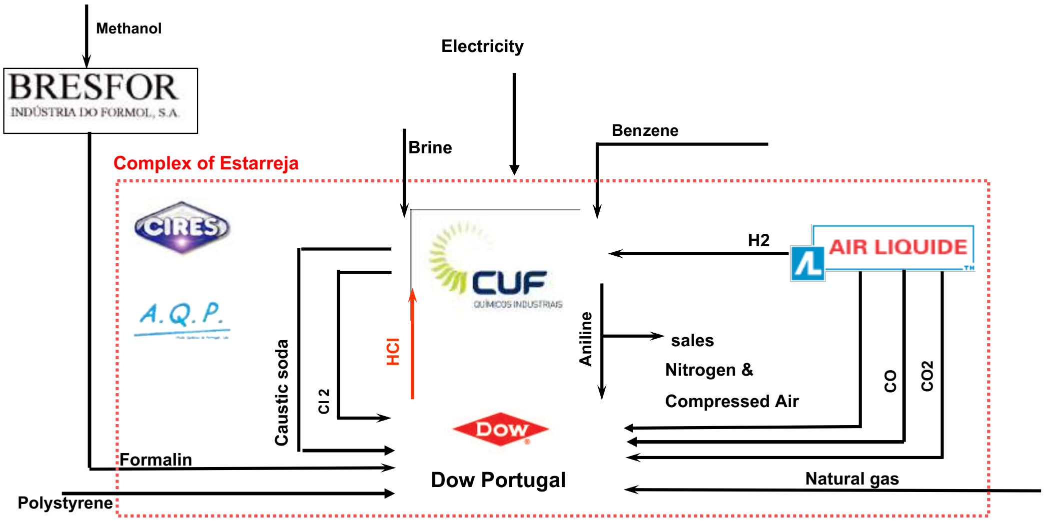


Figure 3.2: *Sketch showing various industrial units in Estarreja Chemical Complex and their productive interconnection (Source: from (Pacopar, 2001))*

3.1.2 ERASE project

At present, soil, surface and groundwater contamination risks have been minimized by prior treatment of the industrial effluents to reduced the contaminant concentrations. Also, the industrial effluents are sent to an inter-municipal sewage system for treatment (Ordens et al., 2007).

In 1994 the ERASE (Regeneration Company for Water and Contaminated Soil Estarreja) project was proposed. The need for a systematic approach to contaminated soil and groundwater became clear to the parties involved, particularly after the studies carried out by the Laboratorio Nacional de Engenharia Civil (LNEC, 1994). These studies urged the treatment and clean-up of land, water streams and the aquifer affected by the CQE industrial pollution (ERASE, 2000).Due to the high level of environmental degradation, and their high impact on social, ecological and economic level. The Estarreja region and environs were considered contaminated area requiring priority intervention. This intervention was proposed to focus on environmental remediation of hydraulic channels that crosses the area surrounded the ECC and have been used to drain the terrain (EP Solos e Sedimentos, 2012).

To remediate the area, an association was created between industry and local authorities - ERASE. The main goal of this association was to find, in co-operation with the Portuguese Environmental Ministry, a cost-effective solution for this environmental problem. The measures to be implemented should prevent contamination of soil and groundwater, from the leaching process and recover the surrounding areas that functioned as the basis for the accumulation of toxic waste (Ordens, 2007).

The solution proposed by ERASE and validated by Atkins (1997) was to design and build a landfill, in the area of pyrite wastes from Quimigal. Three different cells, to dispose off separately pyrite waste, mercury sludge waste, and contaminated soil/sediments from the water streams and the Esteiro river branch, would constitute this landfill. Calcium hydroxide, which is a waste from the CIRES production, mixed with sand, would be used to neutralise the acidic percolating liquids and separate (rather than isolate) these cells (Figure 3.3). Subsequently, a site investigation programme was proposed in order to re-validate the ERASE solution and calculate the volume of material to be disposed of in the landfill, namely (Costa and Jesus-Rydin, 2001):

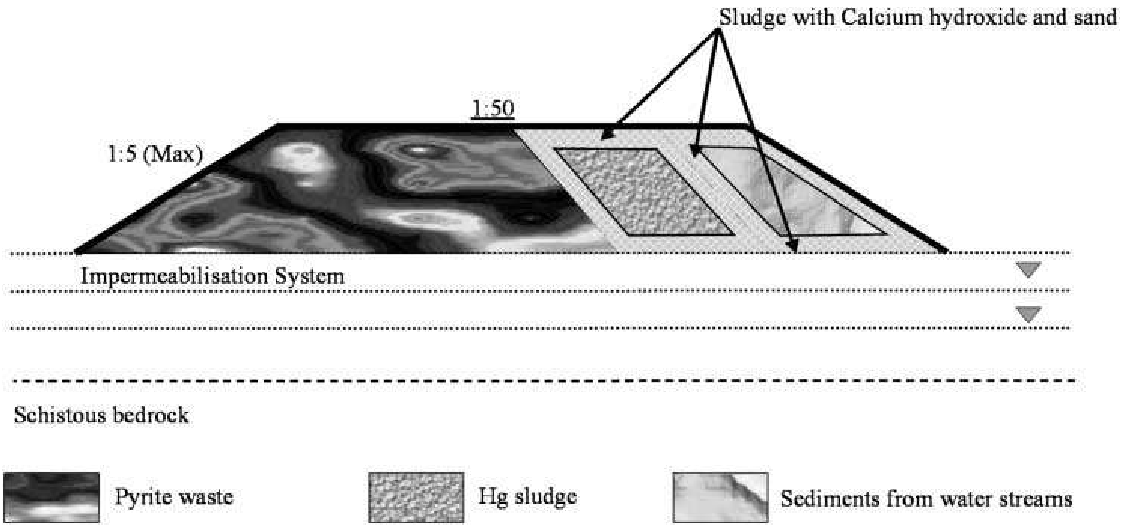


Figure 3.3: *Sketch of the proposed landfill (modified after WS Atkins 1997, Source: from (Costa and Jesus-Rydin, 2001))*

- exact volume of wastes and underlying contaminated soils to be excavated inside the ECC;
- exact volume of contaminated soil/sediments to be removed from water streams (along an 8.5 *km* extension) and the Esteiro river branch (along the first 2 *km* upstream);
- physical and chemical characteristics of contaminated soil/sediments and estimation of its ‘workability’ for landfill disposal.

3.2 Overview on groundwater contamination

Groundwater is an important source of water supply. As a water supply source, groundwater has several advantages when compared to surface water; it is generally of higher quality, better protected from pollution, less subject to seasonal and perennial fluctuations, and more uniformly spread over large regions than surface water (Zektser et al., 2004). There are many countries in the world where groundwater is one of the major sources of drinking water (e.g., Denmark, Malta, and Saudi Arabia). Groundwater also provides the largest amount of the total water resources in other countries. For example; in Tunisia it is about 95 % of the total water resources, in Belgium it is 83 %; in the Netherlands, Germany and Morocco it is 75 %; in Portugal 60 % irrigation, 65 % water supply and 50 % industry (Zektser et al., 2004). Groundwater is also a major source of industrial and agricultural uses in many countries. Continuously increasing development has led to overexploitation of groundwater resources and growing impacts of human activities on aquifers in many countries, such as decline in groundwater levels and deterioration of groundwater quality.

Groundwater is said to be contaminated when contaminant concentration levels restrict its potential use. The contamination of groundwater resources by chemicals is a growing concern and poorly understood as compared to freshwater resources. Groundwater provides the most reliable perennial source of fresh water on the Earth. It maintains flows and levels in rivers and lakes (Daughton and Ternes, 1999). Hence, it is essential for the health of groundwater-dependent ecosystems.

3.3 Sources and pathways for groundwater contamination

Contaminants can be natural or human-induced, as from leaking fuel tanks or toxic chemical spills. Pesticides and fertilizers applied to lawns and crops can accumulate and migrate to the water table. Leakage from septic tanks and waste-disposal sites also can introduce bacteria to the water, and pesticides and fertilizers that seep into farmed soil can eventually end up in water drawn from a well. Groundwater pollution caused by human activities usually falls into two categories: *point source* pollution and *non-point source* pollution (Sharma et al., 2018).

3.3.1 Point source

Point source refers to contamination originating from a single tank, disposal site. Industrial waste disposal sites, accidental spills, leaking gasoline storage tanks, and dumps or landfills are examples of point sources. Waste water sources are considered as the important point sources in the aquatic environment (Glassmeyer et al., 2005). Díaz-Cruz and Barceló (2008) studied the occurrence of organic micro pollutants such as pesticides, pharmaceuticals, industrial chemicals and their metabolites in different source of waters which is used for artificial recharge purpose. Aquifer managed recharge groundwater resources minimizes the impacts of compounds of concern. This is due to the biological and geochemical degradation and adsorption processes occur in the shallow soil zone and unsaturated zone, and these zones are partially or completely bypassed when recharge occurs directly to the aquifer (Sharma et al., 2018).

Landfill sites have also been shown to be important sources for contaminants in groundwater. However, in many developing countries there is limited effective regulation regarding groundwater protection from landfill sources. Many early studies reported a wide range of pharmaceuticals in groundwater down gradient of landfills receiving domestic and industrial waste (Eckel et al., 1993; Holm et al., 1995; Ahel et al., 1998; Ahel and Jeličić, 2000).

Septic tanks remain important sources of groundwater pollution, particularly where groundwater tables are shallow and aquifers have high transmissivity. It is very difficult to monitor and regulate contamination from septic tanks, due to the huge number of these point sources, and widespread use in rural settings. A detailed study carried out in Canada was shown that septic tank samples contained elevated concentrations of several pharmaceutical compounds (Carrara et al., 2008).

3.3.2 Non-point source

The non-point source pollution (NPS) is defined as diffuse discharges of pollutants throughout the natural environment. Chemicals used in agriculture, such as fertilizers, pesticides and herbicides are examples of non-point-source pollution (Bianchi and Harter, 2002). Similarly, runoff from urban areas is a non-point source of pollution. Fertilizers and pesticides applied to crops may reach underlying aquifers. Drinking water wells located close to crop-land sometimes are contaminated by agricultural chemicals. Because, non-point source substances are used over large areas, they can have a larger impact on the quality of water in an aquifer than point sources. If impacts from individual pollution sources such as septic system drain fields occur over large enough areas, they are treated as a non-point source of pollution (Sharma et al., 2018).

3.3.2.1 Natural substances

Some groundwater pollution occurs naturally and toxic arsenic metal is commonly found in the sediments. Hence, it can be present in groundwater at concentration that exceeds safe levels for drinking water. The same for Fe, Mn, Al Ba, Be, As, F, Radon and some radionuclide may occur naturally in the earth crust (Amrani, 2002; Cevik et al., 2005).

3.3.2.2 Petroleum-based fuels

Groundwater contaminant includes petroleum-based fuels such as gasoline and diesel. Benzene, a common component of gasoline, is considered to cause cancer in humans. Aquifers in industrialized areas are at significant risk of being contaminated by chemicals and petroleum products (Bowers and Smith, 2014). In most developed countries, various laws attempt to prevent land and water pollution, and to clean up contaminated areas when they occur (Stout et al., 1964; Thornton et al., 2013). Developing countries in economic distress are less likely than developed nations to assess the risk of groundwater contamination by land-use activities.

3.3.2.3 Chlorinated solvents

The chlorinated solvents are similar to petroleum hydrocarbons in that they are made up of carbon and hydrogen atoms, but the molecules also have chlorine atoms in their structure (Bradley and Chapelle, 2011). Unlike petroleum-based fuels, solvents are usually heavier than water, and thus tend to sink to the bottoms of aquifers (EPA, 2012). This makes solvent-contaminated aquifers much more difficult to clean up than those contaminated by fuels. In Portugal, most petrol stations have to monitor soil and groundwater due to leakage problems despite the improved confine conditions. Chlorinated solvents can be divide into LNAPLs (Less dense non-aqueous phase liquid) and DNAPLs (Dense non-aqueous phase liquid).

3.3.2.4 Heavy metals and metalloids

Heavy metal represents the metallic chemical element that has a relatively high density (specific density of more than 5 mg/L and is toxic at low concentration (Amrani, 2002). Examples of heavy metals include arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), and thallium (Tl). Heavy metals are natural components of the earth's crust. They cannot be degraded or destroyed. To a small extent they enter human and animal bodies via food, drinking water, and air. However, higher amounts of pollutants from these heavy metals are occurred due to technological progress and it is linked to the ability to extract and process metals.

Therefore, already several thousands of years ago, polluted zones were identified and some effects of metal poisoning were known during the period of development of methods for use of metals (Nriagu, 1996; Maskall and Thornton, 1998; Järup, 2003). The average subsurface abundance of arsenic is 5 – 10 µg/L (Han et al., 2003), and it is present in more than 200 mineral species. Inorganic arsenic of geological origin is found in groundwater used as drinking water in several parts of the world (Smedley and Kinniburgh, 2002). Organic arsenic compounds are found mainly in marine organisms. Arsenic levels in groundwater average about 1 – 2 µg/L except in areas with volcanic rock and sulphide mineral deposits where arsenic levels can reach up to 3 µg/L. The daily intake of total arsenic from food and beverages generally is between 20 and 300 µg/day. Lead particulate from the combustion of leaded gasoline and ore smelting can contaminate local surface water by surface run-off. A wide distribution in sedimentary rock and soils has been reported, with an average lead content of 10 mg/kg in top soil, and a range of 7 – 12.5 mg/kg in sedimentary rock.

Nickel is a ubiquitous trace metal that occurs in soil, water, air, and in the biosphere. The average content in the earth's crust is about 0.008%. Nickel enters groundwater and surface waters from erosion and dissolution of rocks and soils, as well as from biological cycles, atmospheric fallout, industrial processes, and waste disposal. Acid rain has a tendency to mobilize nickel from soil and increase nickel concentrations in groundwater, leading eventually to increased uptake and possible toxicity in micro-organisms, plants, and animals. Depending on the soil type, nickel may exhibit a high mobility within the soil profile, finally reaching groundwater, rivers, and lakes. Drinking water generally contains less than 10 µg/nickel/L, but nickel may occasionally be released from plumbing fittings, resulting in concentrations of up to 500 µg/nickel/L (Sharma et al., 2018).

3.4 Groundwater vulnerability

Foster (1987) defined vulnerability as "the intrinsic characteristics which determine the sensitivity of various parts of an aquifer to being adversely affected by an imposed contamination load". Groundwater vulnerability is a relative, dimensionless and non measurable feature which relies on geological and hydrogeological properties of an aquifer (Antonakos and Lambrakis, 2007; Fijani et al., 2013).

Assessment of vulnerability gives researchers the opportunity to evaluate the natural conditions of an aquifer sensitivity to get contaminated and constitutes an essential component of management options to preserve the groundwater quality (Worrall et al., 2002). Vulnerability assessment must be objective, scientific and based on accurate evidence (Mohammadi et al., 2009). As such, aquifer vulnerability assessment is an inexact estimation Li and Heap (2008); and, can be viewed as a tool for predicting potential to contamination, but never highlighting the degree or level of contamination.

Modeling of large scale groundwater contamination and the need for strategic planning for aquifers protection have received considerable attention in recent years (Amini et al., 2008a,b). However, groundwater can be contaminated by an endless list of inorganic and organic contaminants; such as: arsenic, aluminium, lead, mercury, fluoride, iron, nitrate, pesticides, plasticizes, and chlorinated solvents (Gogu and Dassargues, 2000). As such, effective monitoring and regular evaluation of groundwater quality in regions where groundwater is the main source of water supply for drinking, irrigation, and domestic purposes.

The concept of groundwater vulnerability to contamination was developed by McLay et al. (2001), which provides a better understanding of groundwater sensitivity against pollution with respect to geological, hydrological and meteorological conditions. Many aquifers are permeable, shallow, unconfined and highly susceptible to contamination and therefore, groundwater vulnerability assessment could be considered as a powerful measure in planning for protection of aquifers.

The best way to map aquifer vulnerability is the evaluation by a three dimensional model which takes into account all characteristics of aquifer and its variability with space and time. In practice, due to amount and quality of available data, budget and time constraints, the output of vulnerability assessment would be a two dimensional map where at each point different properties of aquifer be integrated to predict the potential pollution (Gheisari, 2017).

3.4.1 Groundwater vulnerability mapping

In recent years, several groundwater vulnerability and risk mapping approaches have been developed to estimate the sensitivity of groundwater to contamination. As such, vulnerability mapping is a valuable tool for environmental planning and decision making using indexing methods coupled with GIS-based spatial analysis commonly relied upon to ascertain aquifer vulnerability (Gheisari, 2017). This method divides a region to several hydrogeological areas with various levels of sensitivity from contamination point of view (Al-Rawabdeh et al., 2013). Groundwater vulnerability can be categorized into intrinsic vulnerability and specific vulnerability (Council et al., 1993). Intrinsic vulnerability is independent of particular contaminants and assesses sensitivity of aquifer to human activities or nature (Metni et al., 2004), while the latter considers vulnerability to one or more contaminants (Gogu and Dassargues, 2000). Intrinsic vulnerability parameters, such as soil media, depth to water and net recharge have been changed extensively due to anthropogenic activities. Moreover, specific vulnerability is used to define groundwater vulnerability to a specific contaminants by taking into account the contaminants physico-chemical properties and their relationships (Gogu and Dassargues, 2000).

Basically, there are three available techniques for creating vulnerability maps: overlay and index based techniques (Aller et al., 1987; Daly et al., 2002; Foster, 1987; Margane, 2003); process based simulation techniques (Gheisari, 2017; Kauffman and Chapelle, 2010; Rao et al., 1985; Tiktak et al., 2006); and statistical techniques (Burkart et al., 1999; Masetti et al., 2009; Teso et al., 1996; Troiano et al., 1997). Although, with respect to particular factors and under specific circumstances they have strengths and weaknesses.

3.5 Socio-hydrogeology concept

According to Hynds et al. (2018), the term socio-hydrology; which was first coined by Sivapalan et al. (2012), refer to the myriad of interactions and feedback loops between social and hydrological processes and pressures. Moreover, the term was introduced to the hydrological lexicon as a response to the discipline's perceived failure to adequately examine and address human-modified water sources. At its core, socio-hydrology comprises two social components: (i) absorption of people and their activities into hydrological science, and (ii) ensuring that water-related decision take the stakeholder perspective into consideration, that is how and why water is used (Gober and Wheater, 2014). Furthermore, socio-hydrology focuses on observing, understanding, and predicting future trajectories of human-water system interactions and the relationships between the two (Sivapalan et al., 2012; Sivapalan and Blöschl, 2015). Socio-hydrology thereby represents an interdisciplinary field that attempts to integrate the dynamic reactions and interactions between water and people.

In the same way, Hynds et al. (2018) stated that, with the continuous refinement of socio-hydrology, it was perhaps inevitable (and necessary) that a groundwater specific branch would develop. While Burke et al. (1999) were perhaps the first to make the distinction between socio-hydrology and socio-hydrogeological systems and processes, the term "socio-hydrogeology" was first introduced by Re (2015) in the *Hydrogeology Journal*. Also, Re (2015) presented the *"Bir Al-Nas"* (bottom-up integrated approach for sustainable groundwater management in rural areas) approach; which seeks to integrate socio-hydrological and science-based groundwater management practices. The *Bir Al-Nas* (Arabic translation-"the peoples well") approach comprises a strong social component (Figure 3.4), including stakeholder network analysis. In addition, the approach comprises; public engagement, and socio-economic assessment, and as such, differ from many developed socio-hydrology models (Elshafei et al., 2014) in that it places a particular emphasis on surveying, stakeholder network analysis, and local consultation. Likewise, Re (2015) refers to socio-hydrogeology as *"a way of incorporating the social dimension into hydrogeological investigations"*. Similarly, Limaye (2017) reported that the basis for any socio-hydrogeological intervention is effective communication. As such, and as substantiated by Re (2015), this represents one of the primary differences between socio-hydrology and socio-hydrogeology;

because of widespread misunderstanding of hydro-geological principles (irrespective of location, socio-economic status, and/or geological settings), higher levels of awareness nurturing via translation and communication are required.

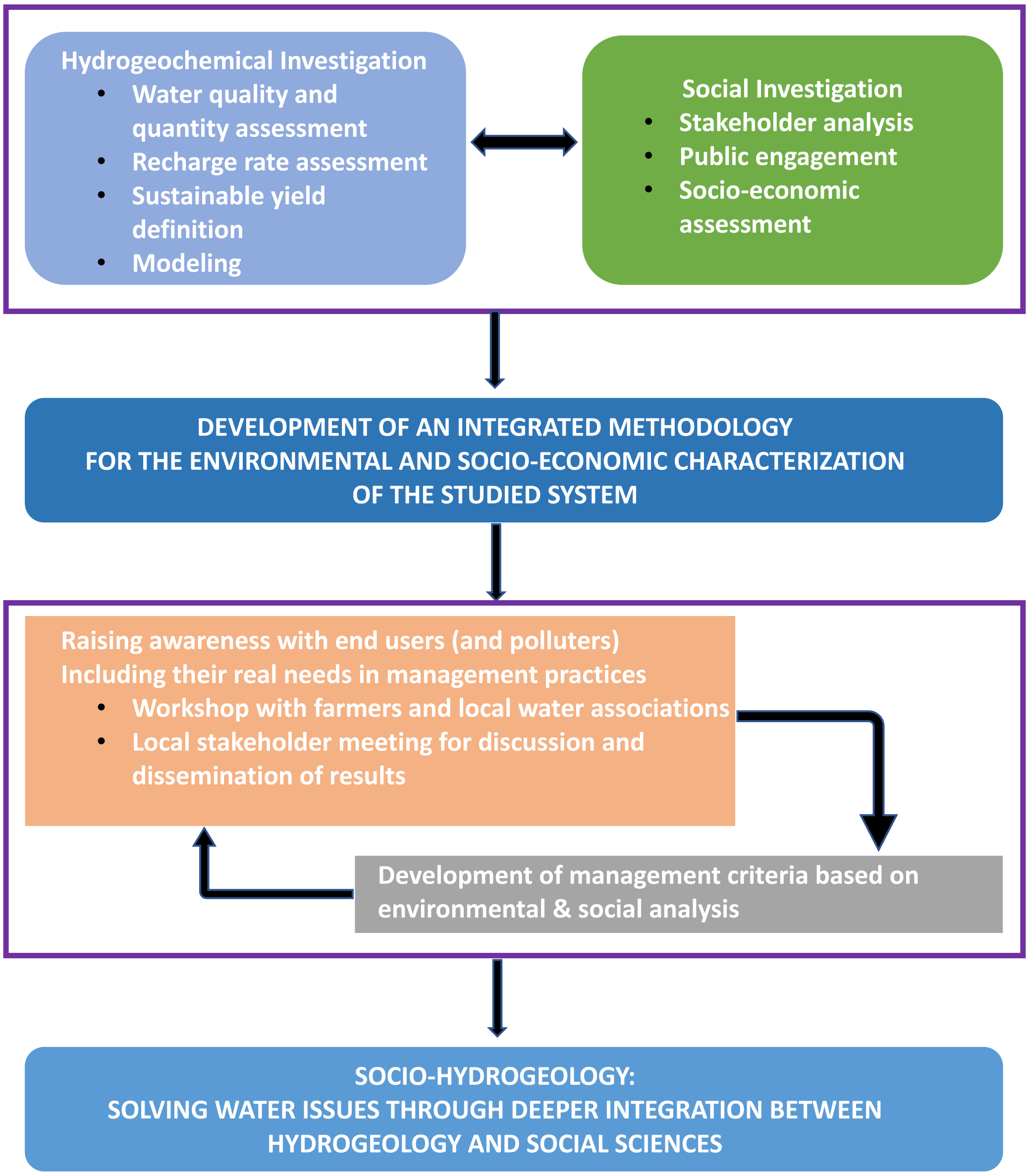


Figure 3.4: *Schematic description of the bottom-up integrated approach for sustainable groundwater management in rural areas (Bir Al-Nas) approach for socio-hydrogeology, (Source: according to Re (2015))*

Chapter 4

RESEARCH MATERIALS AND METHODS

4.1 General overview

This chapter presents various research approaches and techniques adopted to achieve the different objectives of the study. The research project is funded by Soil Take Care project, an international project co-financed by the European Regional Development Fund (ERDF) through the Interreg Sudoe initiative (SUDOE). Methods and objectives were framed under the project and in agreement with the research team.

The research was designed and conducted in four major phases. The three major research phases are;

- **Phase 1:** This phase was mainly about desk study and planning of the fieldwork campaigns. During this phase detailed reviews on available literatures as regards fieldwork already carried out in the study area was done. In addition, field maps were prepared and optimized for easy data collection on the field.
- **Phase 2:** This part of the study was mainly undertaken on the field. The activities that were undertaken include, high density campaign over the study area to measure field parameters from large diameter wells using water level meter and Hanna HI9828 multiparameter water quality meter. The field parameters measured include: groundwater level, pH, Temperature, Electrical Conductivity (EC), Oxidation-Reduction Potential (ORP), Total Dissolved Solids and Dissolved Oxygen (DO).

  In addition, the water channels around the study area were mapped by measuring the field chemical parameters to determine the level of contamination. The chemical parameters in the water channels that were used in the past to drain the area, and into which industrial effluents were discharged were monitored. From Google earth and prepared maps, new water channels were identified. These new channels were mapped on the field and thereafter the chemical parameters were measured.
- **Phase 3:** In this phase, all the preliminary data during high density sampling were optimized using Geostatistical analyses (variogram and kriging modeling). Thereafter, areas of high contamination activities were identified for low density field sampling.
- **Phase 4:** The last phase of the study was focused on low density field campaign, which involved groundwater sampling from boreholes for hydrochemical analyses and conducting structured interviews (from borehole owners) in the same location where groundwater samples were collected.

  Finally, detailed data analyses were carried out (hydrochemical, sociohydrological, statistical and vulnerability analysis) on the collected data to interpret the data in connection with the outlined objectives of the study.

4.2 Fieldwork campaigns

The fieldwork was planned to focus on contaminated areas in the region, as it would be practically and economically impossible to collect and analyse samples from all locations in the study area. Therefore, simple and cheap methods to measure field parameters (groundwater level and in-situ water quality parameters) were adopted for the study.

The first field campaign was targeted at mapping the aquifer at regional scale in order to identify contaminated areas in the study area, by measuring in-situ field chemical parameters (pH, EC, ORP and DO) which could serve as indirect indication of contamination. Thereafter, low density campaign, which include groundwater sampling and socio-hydrogeological studies (in form of structured interviews) relating to perception about the contamination activities were conducted in the identified contaminated areas.

4.2.1 High density field parameters campaign

The high density field campaign, was planned by creating a sampling map over the study area with the help of google earth and satellite imagery. The sampling map consisting of large diameter wells (over 700) scattered over the study area (Figure 4.1) was made by Barreiras (2019) as part of the Soil Take Care Project. The large diameter wells found in the study area were used in the past by farmers

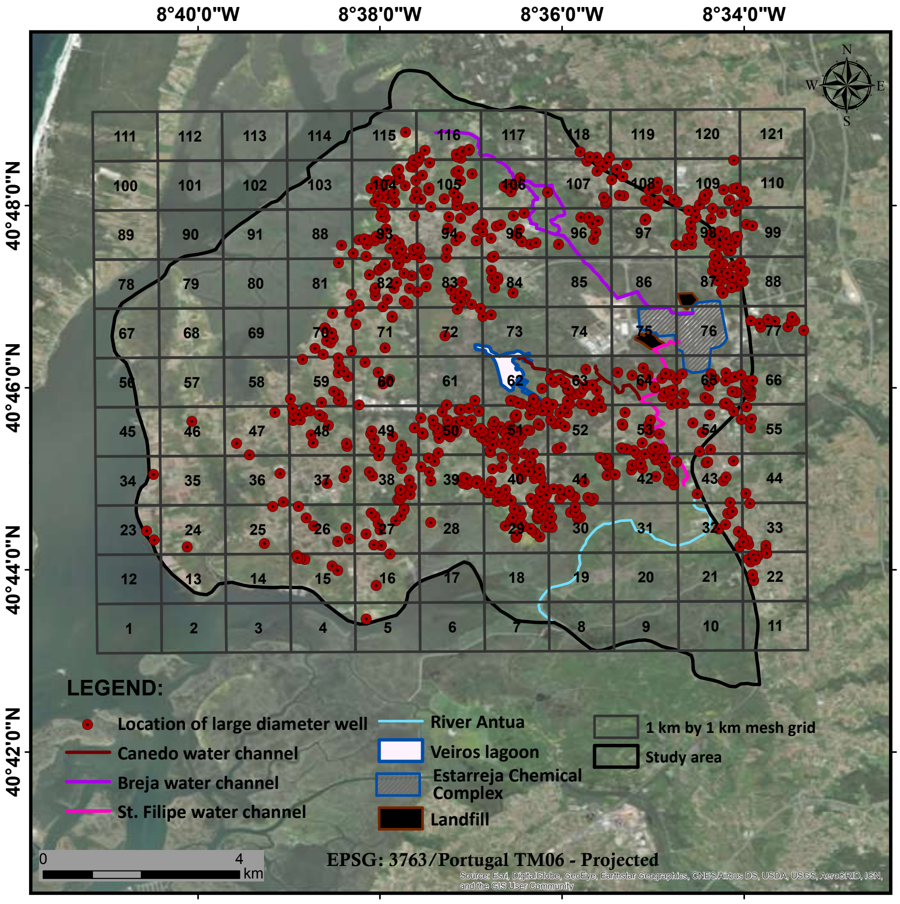


Figure 4.1: *Inventories of all large diameter wells mapped in the area using google earth (Source: from Barreiras (2019))*

to irrigate their cropped land and show high vulnerability to contamination and pumping. The study area, which extended until the natural boundaries as defined in the project were divided into a regular sampling mesh of 1 km by 1 km grid size (Figure 4.1). The natural boundaries consist: the rivers to the North and South; and the Ria Aveiro lagoon towards the west. The regular grid sampling mesh was necessary for fair statistical treatment of data in the study area. Hence, dividing the area into regular grid mesh, made it possible to measure field parameters from wells at interval distance not more than 500 m apart. The distance between two wells (approximately 500 m) was adopted, as this can be justified on a large scale (84 km^2). Also, the interval between two wells is needed to obtain reliable results when analyzing the data using geostatistics.

During the high density field campaign undertaken in May 2019, at least two large diameter wells were chosen from each grid of the sampling map. Making it it possible to measure a total of 120 large diameter wells (Figure 4.2). These wells were easily located on the field with the help of their corresponding geographic coordinates, after which in-situ field parameters (groundwater level and chemical parameters) were measured (Figure 4.3). Groundwater levels were measured from each of the large diameter wells with a sensor-type water level meter, and thereafter recorded on a field record sheet. In addition, Hanna HI9828 multiparameter water quality meter was used to measure; pH, Temperature, EC, ORP, TDS and DO from selected large diameter wells. Multiparameter probes were always calibrated against standard buffer solutions before any measurement was made on the field.

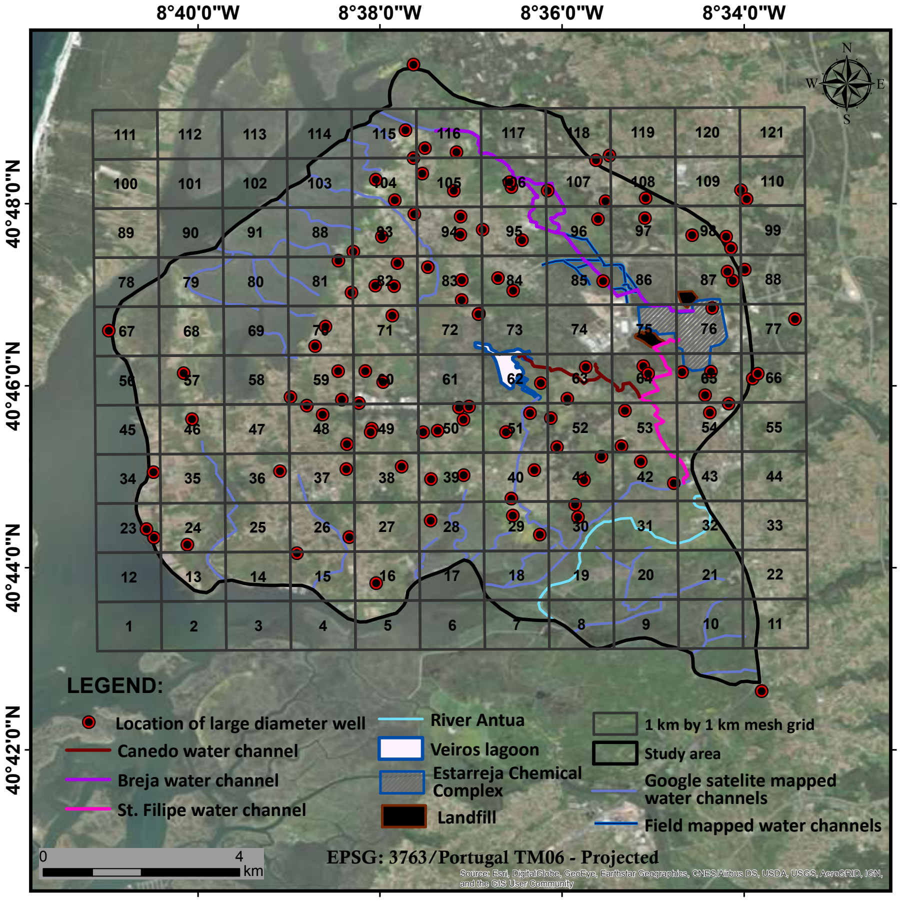


Figure 4.2: *Actual number of large diameter wells mapped during high density sampling in the study area*

Figure 4.3: *Pictures showing different activities carried out during high density sampling of large diameter wells, to determine field parameters in the study area*

4.2.2 Data optimization using Geostatistics

Variogram is the cornerstone of many geostatistical applications. The experimental variogram and any model fitted to it should be accurate. Only then can the model describe the variation reliably. Kriging requires a variogram, and it is by ensuring its accuracy that a minimum-variance predictions by kriging is obtained. If the variogram describes the variation poorly, then the kriged predictions are likely to be poor.

Also, they might have little or no validity no matter how ‘pretty’ the map looks. Further, the parameters of the variogram model may be used later for sample design and the kriged estimates for decision-making. Therefore, computing experimental variograms and modelling them should not be treated in a cavalier fashion (Oliver and Webster, 2015).

The first task in turning theory into practice is to estimate the variogram from sample data (Experimental Variogram). For example, $z(\mathbf{X}_1)$, $z(\mathbf{X}_2)$,..., where $\mathbf{X}_1$, $\mathbf{X}_2$, denote the positions of the sample in two-dimensional space. We assume that those positions have been selected without any bias. They need not be random, as in design-based estimation, because we treat the variables as the outcomes of random processes. Therefore, we can take a relaxed attitude to the sampling design, which may be systematic, random, nested or some combination (Oliver and Webster, 2015).

The usual equation to compute the variogram is the Matheron’s method of moments (MoM) estimator:

$$\hat{\gamma}(\mathbf{h}) \quad = \quad \frac{1}{2m(\mathbf{h})} \sum_{i=1}^{m(\mathbf{h})} \{z(\mathbf{X_i}) - z(\mathbf{X_i} + \mathbf{h})\}^2 \tag{4.1}$$

where $z(\mathbf{X}_i)$ and $z(\mathbf{X}_i + \mathbf{h})$ are the observed values of z at places $\mathbf{X}_i$ and $\mathbf{X}_i + \mathbf{h}$, and $m(\mathbf{h})$ is the number of paired comparisons at lag $\mathbf{h}$. By changing $\mathbf{h}$, we obtain an ordered set of semivariances. These constitute the experimental or sample variogram for the observed data set. The way Equation (4.1) is implemented as an algorithm depends on whether the data are regularly spaced in one dimension, are on a regular grid or are irregularly distributed in two dimensions (Oliver and Webster, 2015).

Several mathematical interpolators and regression (trend surface analysis) have been used with varying success for making maps from sparse data. Nevertheless, none provides sound estimates of the errors in its interpolations. However, Kriging, as a geostatistical method of interpolation performs better compared to the aforementioned methods. In addition, it minimizes the errors and is best in that sense, and because its predictions are also unbiased, it is often known as a Best Linear Unbiased Predictor (BLUP) (Oliver and Webster, 2015).

Kriging predicts values at unvisited sites from sparse sample data based on a stochastic model of continuous spatial variation. Kriging takes into account knowledge of the spatial variation as represented in the variogram or covariance function. Ordinary kriging requires no other information than that plus the measurements and their geographic coordinates. Ordinary Kriging is by far the most popular kind of kriging. In addition, with good reason; it serves well in most situations with its assumptions easily satisfied (Oliver and Webster, 2015).

Hence, geostatistics (variogram and kriging prediction) was applied on some of the measure field parameters (groundwater level, pH, ORP and EC), for the purpose of optimizing the data for low density sampling in the study area. The optimization of the measured field data using geostatistics was necessary to identify the highly contaminated areas in the region. Thereafter focused studies, which involves groundwater sampling from boreholes and conducting socio-hydrogeological interviews at groundwater sampling locations were carried out in these areas.

4.2.3 Mapping field chemical parameters in surface water bodies

The surface water bodies in the study area, which include water channels used to drain the area and the lagoon (Veiros lagoon) where some water channels discharge into were mapped. Mapping the water channels and lagoon, field chemical parameters were also measured at predefined points on the water channels and lagoon.

Hence, the existing water channels already mapped in the area were divided into 500 m intervals from the start to the end point (Appendix A.1c). Also, predefined points were located inside the lagoon (areas in connection with the water channels). These points (water channels and lagoon) were marked out on an overlay google satellite basemap (Appendix A.1c). The prepared field map was used to locate the water channels and lagoon points on the field, after which chemical parameters (pH, Temperature, EC, ORP, TDS and DO) were measured using the Hanna HI9828 multiparameter water quality meter (Figure 4.4). During in-situ measurement of chemical parameter from the water channels and lagoon, new water channels were mapped that were not part of the (existing) water channels shown on the prepared field map. The geographic coordinates of these new water channels were noted and subsequently updated on the field map.

Figure 4.4: *Pictures showing mapping/measuring activities to determine field chemical parameters from (contaminated) water channels and Veiros lagoon located in the study area*

4.2.4 Low density field parameters campaign

The low density campaign involved groundwater sampling for hydrochemical analysis from predefined locations in the study area (Figure 4.5). The selected locations were chosen from the combined kriging estimate maps of pH, EC, and ORP prepared after optimization of the high density sampling data using geostatistics.

4.2.4.1 Groundwater sampling and analysis

Groundwater samples were collected from boreholes located at predefined locations in the study area (Figure 4.5). Before samples were collected from the boreholes, water from the borehole was allowed to flow continuously while monitoring its chemical parameters (pH, Temperature, EC, ORP, and DO) using the multiparameter cell until they are relatively stable (Figure 4.6). At the point of sampling, Nalgene HPDE bottles were thoroughly rinsed two to three times with the groundwater (filtered through 0.45 µm hydrophilic filter) to be sampled. Thereafter, samples were collected for anion and cation analyses using different sampling bottles. The samples to be used for anions analyses was filtered through 0.45 µm millipore cellulose filter, stored in a 60 mL Nalgene HPDE bottle, labelled and taped appropriately to minimise air exposure and finally stored in an iced cooler box. Also, for the cations analyses, samples was filtered through 0.45 μm hydrophilic filter, acidified with three drops of HNO_3 (nitric acid) before storing in a 30 mL Nalgene HPDE bottle, labelled and taped appropriately to minimise air exposure and

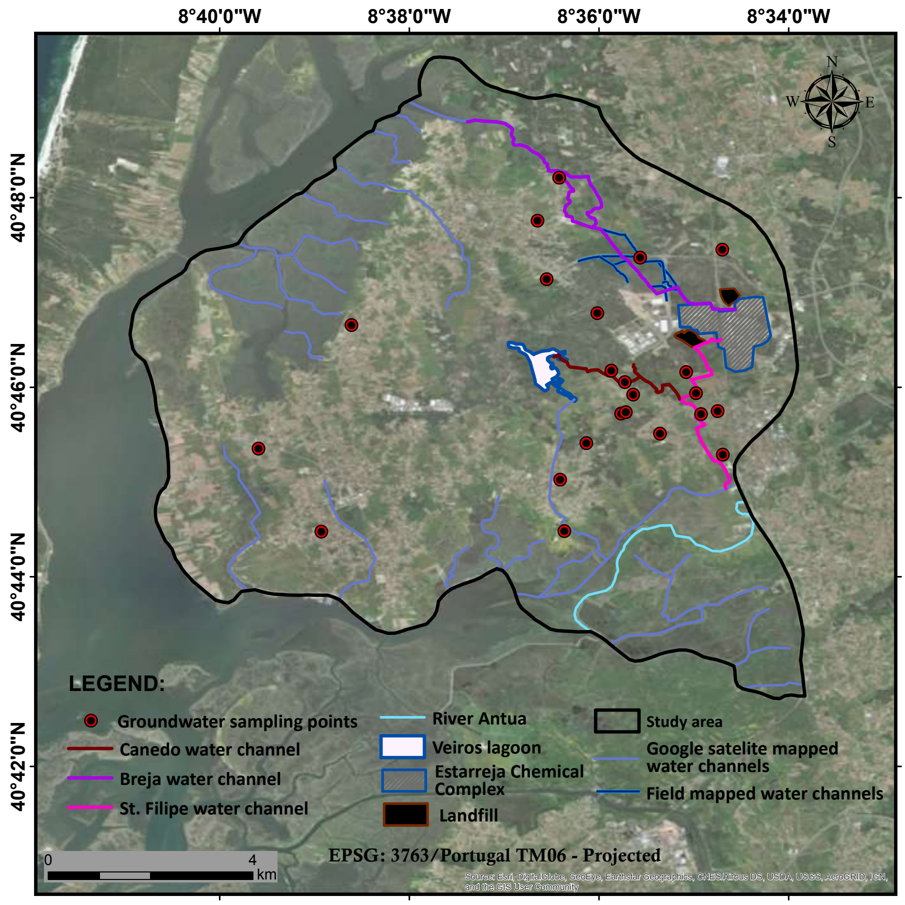


Figure 4.5: *Groundwater sampling points from which water samples were collected for analysis, and socio-hydrogeological interviews conducted during low density campaign in the study area*

finally stored in an iced cooler box. At the end of the groundwater sampling campaign, a total of 25 water samples were collected. The water samples comprises of 24 groundwater samples and only one surface water sample. The collected samples were stored in ice-boxes, brought to the laboratory and then stored in a freezer at 4 °C for further chemical analyses.

4.2.4.2 Field chemical analyses

During groundwater sampling, parameters that are know to fluctuate and change easily due to changes in the environment were measured in-situ in the field. These parameters include; temperature (Temp; °C), electrical conductivity (EC; $\mu S/cm$), pH, dissolved oxygen (DO; mg/L), oxidation-reduction potential (ORP) and alkalinity. Hence, measurement of these parameters except alkalinity were done in-situ with well calibrated Hanna HI9828 multiparameter.

Furthermore, alkalinity was measured immediately (after stability of some specific chemical parameters) using the field titration HACH kit (Figure 4.6). The processes followed in the field for alkalinity measurement were: 100 mL of the groundwater sample was measured into a beaker and bromocresol green powder (indicator) was added. Thereafter, the solution was titrated using 1.6 M of H_2SO_4 (sulphuric acid) until a colour change (pink) was observed. Immediately the colour change (pink) was noticed, the digits on the titration cartridge was recorded as the alkalinity value. However, the concentration of titration acid was changed to 0.16 M of H_2SO_4 (sulphuric acid) when less than 10 titration cartridge units was needed for colour change. Also, each alkalinity titration measurements, were repeated until two results are within 10 units (five units preferred). Moreover, the field titration cartridge gives alkalinity measurements in digit of units. Therefore, the relationship given in (Equations 4.2 and 4.3), were used to convert the digit units for 1.6 M of H_2SO_4 and 0.16 M of H_2SO_4 to concentration units in mg/L respectively.

$$\mathrm{HCO_3}^- = digits \times 1.2192 \tag{4.2}$$

$$\mathrm{HCO_3}^- = \frac{digits}{10} \times 1.2192 \tag{4.3}$$

$$pe = \frac{(E_h \times 96.42)}{[(2.303) \times (273.15 + T) \times (8.314/1000)]} \tag{4.4}$$

Where: pe is the redox potential in volts; T is the temperature in °C and E_h is the measured ORP in %.

4.2.4.3 Laboratory analysis

The water samples collected were properly labelled, packed in an ice-cooled box (Figure 4.6) and transported to Activation Laboratories in Canada for further chemical analyses. The samples were analysed in Activation laboratories for various chemical constituents using standard internationally recognised methods.

Figure 4.6: *Pictures showing different activities carried out during low density sampling; which include groundwater sampling procedures and in-situ field chemical parameter determination of water samples in the study area*

4.3 Socio-hydrogeological field study (Interviews)

Qualitative interviewing approach was employed in the field to extract information from respondents, as regards their perceived knowledge about the contamination status of the area. However, the main focus of the study; which is contamination of groundwater resource in the region constitute a major part of the interview questions. As such, qualitative interviewing was adopted; which is the most commonly used method in qualitative research to get information from people as regards a particular subject of study. The term 'qualitative interviewing' is usually intended to refer to in-depth, semi-structured or loosely structured forms of interviewing (Mason, 2017). However, Mason (2017), also stated that, using the term 'unstructured' interviewing in place of 'qualitative interviewing', can be seen as a misnomer because no research interview can be completely lacking in some form of structure. On the other hand, open-ended questions in an otherwise structured interview structure are sometimes assumed to constitute qualitative interviewing. Nevertheless, using both terms interchangeably to mean the same thing is also a misnomer, because the logic, rationale and approach used in such interviews (open-ended structured questions) are derived from survey, and not qualitative methodology (Mason, 2017).

Furthermore, Mason (2017) in his book on 'Qualitative Researching', suggested some core features of a qualitative interview approach:

- The interactional exchange of dialogue. Qualitative interviews may involve one-to-one interactions, larger group interviews or focused groups, and may take place face to face, or over the telephone or the internet.
- A relatively informal style, for example, with the appearance in face-to-face interviewing of a conversation or discussion rather than a formal question and answer format. Burgess's term 'conversation with a purpose' captures this rather well.
- A thematic, topic-centred, biographical or narrative approach, for example; where the researcher has a number of topics, theme or issues which they wish to cover, or a set of starting points for discussion, or specific 'stories' which they wish the interviewee to tell. In this case, the researcher is unlikely to have a complete and sequenced script of questions. Therefore, most qualitative interviews should be designed to have a fluid and flexible structure, and also allow researcher and interviewee(s) develop unexpected themes.
- Most qualitative research should operate from the perspective that knowledge is situated and contextual, and therefore the job of the interview is to ensure that the relevant contexts are brought into focus so that situated knowledge can be produced. According to this perspective, meanings and understandings are created in an interaction, which is effectively a co-production involving researcher and interviewees. Therefore, qualitative interviewing tends to be seen as involving the construction or reconstruction of knowledge more than the excavation of it (Mason, 2017).

4.3.1 Socio-hydrogeological (qualitative) interview conducted in the Study Area

The qualitative interviewing approach adopted in the study area, can be termed a 'modified' form of a qualitative interview. This particular approach adopted in this study entails, engaging the respondents (locals) in an open conversation (Figure 4.7) based on some sets of structured questions. However, the purpose of the structured questions regarding different aspects of groundwater contamination in the area, was just to guide each theme discussion with the respondents, rather than a question and answer kind of interview. As such, the respondents were allowed to expressed their views freely without any form of bias or suggesting some preconceived line of answers to each structured interview questions. During the interview section it was observed that some respondent discussed related issues regarding each interview questions.

Figure 4.7: *Interactive qualitative interview section with a respondent in the study area during socio-hydrogeological study*

In addition, each interview was recorded with a mp3 recorder, and responses entered immediately into the appropriate field sheet to keep track of all information from each respondent. During the interview (in Portuguese language), each interviewee (well owners), were engaged in an open discussion by one or two interviewers on different questions bothering on their perceived knowledge of contamination situation in the region, especially linked to contamination of groundwater resources.

The interview was very interactive, allowing interviewers to study body language, articulations and other behaviours displayed by each respondent.

Besides, the interview questions (Table 4.1), consist of questions relating to personal and social characteristics of each respondent, interaction with the groundwater resource, and other questions of their knowledge about the contamination activities in the area. Respondents interviewed were not preselected, but guided based on groundwater sampling location scattered over the study area of

Table 4.1: Summary of interview questions administered on the locals to retrieve information about their perceive knowledge of contamination activities in the study area (modified from *Bir Al-NAs* Socio-hydrogeology structured questionnaires Re (2015))

Structure of Interview theme (questions)	Proposed Information to be retrieved from respondents	Information retrieved from the field interviews
Personal and social information of respondents	Retrieve basic information (but will be treated anonymously) about the locals living in the area	Name, contacts, age gender and occupation
Perception about contamination status of groundwater	Retrieve basic information concerning inhabitants knowledge about the contamination issue	Information about; the existence of contamination activities, and likely sources of contamination in the area
Groundwater use	Retrieve information concerning groundwater use by locals	Information about; if water from well is currently being used, for what purpose, type of crop irrigated, and any noticeable changes in crops after irrigation
Personal stewardship practices towards adaptation/mitigation	Retrieve information from locals on their efforts to mitigate or adapt to the challenges	Information about; any water analysis, special treatment being applied to the water, and what to do in case of industrial accidents
Role of municipality, industries and civil society	Information to assess the impacts and participatory involvements various of society in the region	Information about; who pays for their water use, relatives working in any of the industries, and any contacts with associations in the region
Health challenges	Retrieve information about common health challenges faced in the area	Information about any health issue in their family
Personal suggestions/actions	Get information as regards suggestions to deal with the situation	Information about; if they would allow closure of their wells, and also like to receive the outcome of the study

Estarreja and Murtosa region. As such, each water analysis results can be matched with information provided by respondents. In total, 24 respondents cutting across different social and personal status were successfully interviewed in the study area.
After the interview conducted in the field, retrieved data (recorded voice messages and field sheets) were transcribed following standard transcription procedures. Thereafter, qualitative and quantitative analyses were carried out to understand and interpret the responses retrieved from the respondents.

4.4 Analysis of groundwater quality data

There exist several conventional tools and techniques ranging from graphical to statistical that have been used by various researchers for interpreting groundwater quality (Freeze and Cherry, 1979; Karanth, 1987; Güler et al., 2002; Machiwal and Jha, 2015). However, for this study, only graphical and statistical methods in-line with the overall objective of the study were preselected and appropriately applied on the groundwater quality data.

4.4.1 Graphical method

Most of the graphical methods are designed to simultaneously represent the total dissolved solid concentration and the relative proportions of certain major ionic species (Hem, 1987). All the graphical methods use a limited number of parameters, usually a subset of the available data, unlike the statistical methods that can utilize all the available parameters (Güler et al., 2002). An overall characterization of hydrochemical data can be achieved by determining the hydrochemical facies, generally known as water type. The different water types can be determined by plotting individual sampled chemical parameters on various plots, such as Durov (1948), Piper (1944) and Schoeller (1965) diagrams.

Piper and Durov plots were used in this study, because they are the most widely used for interpreting hydrochemical data. Piper diagram consists of two triangular fields and a central diamond-shaped field. In the two triangular fields, percentage meq/L values of major cations and anions are plotted separately and then projected onto the central field for the representation of overall characteristics of water. This plot reveals useful properties and relationships for large sample groups (Srivastava and Ramanathan, 2008). Also, groundwater samples were plotted on the Durov diagram (Durov, 1948; Lloyd and Heathcode, 1985), for the purpose of determining the domain hydrochemical processes and type of ion exchange processes on-going in the aquifer system.

4.4.2 Multivariate statistical techniques

Another approach to understanding the chemistry of water samples is to investigate statistical relationships among their dissolved constituents and environmental parameters, such as lithology, using multivariate statistics (Drever et al., 1988). Statistical associations do not necessarily establish cause-and-effect relationships, but do present the information in a compact format as the first step in the complete analysis of the data and can assist in generating hypothesis for the interpretation of hydrochemical processes (Güler et al., 2002).

According to Güler et al. (2002), statistical techniques, such as cluster analysis, can provide a powerful tool for analysing water chemistry data. These methods can be used to test water quality data and determine if samples can be grouped into distinct populations (hydrochemical groups) that may be significant in the geologic context, as well as from a statistical point of view. The assumptions of cluster analysis techniques include homoscedasticity (equal variance) and normal distribution of the variables (Alther, 1979). However, equal weighing of all variables requires the log-transformation and standardization (z-scores) of the data. Hence, comparisons based on multiple parameters from different samples are made and the samples grouped according to their “similarity” to each other. The classification of samples according to their parameters is termed Q-mode classification. This approach is commonly applied to water-chemistry investigations in order to define groups of samples that have similar chemical and physical characteristics because rarely is a single parameter sufficient to distinguish between different water types (Güler et al., 2002).

Another type of data analysis sometimes used is principal components analysis (PCA). This technique reduces the number of dimensions present in data. The PCA-defined new variables can then be displayed in a scatter diagram, presenting the individual water samples as points in a lower-dimensional (generally 2-D) space. This technique, strictly speaking, is not a multivariate statistical technique, but a mathematical manipulation that may provide a certain amount of insight into the structure of the data matrix (Davis, 1986) by reducing the dimensions of the data matrix (Güler et al., 2002).

However, for this study only the principal component analysis (PCA) was used to classify the samples into distinct hydrochemical groups based on their similarity. In order to determine the relationship between classified groups, the $(r \times c)$ data matrix (r samples with c variables) were imported into the Statistical Package for the Social Sciences (SPSS 25.0) for PCA analysis. Similarly, the principal component analysis was performed using R-mode factor analysis (Varimax Rotation with Kaiser's Normalization), which was also implemented using the SPSS statistical software. In addition, suitability of the sampled groundwater for use as drinking and irrigation purposes were analysed in accordance appropriate specific standards.

4.5 Groundwater vulnerability assessment

Vulnerability is not an absolute characteristic, but rather a relative, non-measurable, dimensionless property indicating where contamination is most likely to occur (Stigter et al., 2006b). According to Stigter et al. (2006b), the first attempts to represent it in maps were made by Margat (1968) in France. Since then, many methods and techniques concerning its graphical and numerical representation, which can be used for managerial or decision making purposes, have been developed. These methods can be grouped into three basic groups, namely: hydrogeological setting methods, parametric methods and numerical models (Vrba and Zaporozec, 1994).

4.5.1 Method of DRASTIC and susceptibility indices

DRASTIC was developed by Aller et al. (1987) for the US EPA, with the purpose of creating a methodology that would permit a systematic evaluation of the groundwater pollution potential of any hydrogeological setting. The most important assumptions made when assessing vulnerability with DRASTIC (Aller et al., 1987) are that the contaminant is introduced at the ground surface, flushed into the groundwater by precipitation and has the mobility of water.

The seven hydrogeological factors that form the acronym DRASTIC are defined in Table 4.2. Each factor is subdivided into ranges or significant media types that are rated between 1 and 10 according to their relative impact on the pollution potential, as indicated in Table 4.3. The final index is obtained by the weighted sum of the factors, different weights being assigned in the assessment of the pesticide contamination potential (Table 4.2). Values range from 23 to 226 (highest vulnerability) and are distributed among eight classes. The DRASTIC index can be calculated for various hydrogeological settings and subsequently mapped (Stigter et al., 2006b).

Susceptibility Index (SI), an improved version of the DRASTIC method because it considers the impact of land cover, was developed with the intention of evaluating aquifer vulnerability on a large to medium scale, 1:50000 - 1:200000 (Ribeiro, 2000), with respect to diffuse agricultural pollution in hydrogeological settings typically found in Portugal. In addition, Stigter et al. (2006b) pointed out

Table 4.2: Definition and weights of DRASTIC and SI parameters (adopted from (Stigter et al., 2006b))

Letter	Meaning	Weight	Pesticide weight	SI weight
D	Depth to water	5	5	0.186
R	Net recharge	4	4	0.212
A	Aquifer media	3	3	0.259
S	Soil media	2	5	-
T	Topography	1	3	0.121
I	Impact of the vadose zone media	5	4	-
C	Hydraulic conductivity	3	2	-
LU	Land use	-	-	0.222

that, the inclusion of a parameter defining land cover, thus abandoning the concept of a purely intrinsic vulnerability assessment method. The index name is in harmony with the definition of susceptibility, i.e. the lack of ability to resist the impact of contaminants on the quality of groundwater, provided by Vrba and Zaporozec (1994). The principal types of land use and their assigned ratings provided by a team of Portuguese scientists (Ribeiro, 2000) are shown in Table 4.4.

Moreover, detailed descriptions of the susceptibility index (SI) methodology and procedures are given by Ribeiro (2000), Stigter et al. (2006a), Stigter et al. (2006b) and Ribeiro et al. (2017). Hence, the study area for this research was subjected to Susceptibility Index (SI) rather than the DRASTIC index assessment. The SI method was chosen rather than the DRASTIC method, because it was important to consider land use and a tribute to two authors that developed the method who are also coordinators of the GroundwatCH Erasmus Mundus Programme.

Stigter et al. (2006b), highlighted the main differences between DRASTIC and SI indices. The relative weights (r.w.) of the first two parameters (depth to water and recharge) in the final index are comparable, amounting to 22 and 17 % in DRASTIC and 19 and 21 % in SI, respectively. Aquifer media (and its attenuation capacity) has twice as much weight in SI (26 % r.w.) than in DRASTIC (13 % r.w.), but hydraulic conductivity is not considered by SI and has the same weight as aquifer media in DRASTIC. Topography has a bigger influence in SI, namely 12 % r.w. against only 4 % in DRASTIC. Finally soil media (9 % r.w.) and vadose zone media (22 % r.w.) are DRASTIC parameters left out by SI, which has incorporated a land use parameter with 22 % r.w. In other words, the importance of the hydro- logical setting is inevitably lower in SI (Stigter et al., 2006b).

Table 4.3: Ranges and ratings of the DRASTIC and SI parameters (adopted from (Stigter et al., 2006b))

D^a (m)	**F**$_c$	**R**^{a} (mm)	**F**$_c$	**F**^{a} ($\%$)	**F**$_c$	**S**	**F**$_c$
< 1.5	10	< 51	1	< 2	10	Thin or Absent	10
1.5 - 4.6	9	51 - 102	3	2 - 6	9	Gravel	10
4.6 - 9.1	7	102 - 178	6	6 - 12	5	Sand	9
9.1 - 15.2	5	178 - 254	8	12 - 18	3	Peat	8
15.2 - 22.9	3	> 254	9	> 18	1	Shrinking and/or aggregated clay	7
22.9 - 30.5	2					Sandy loam	6
> 30	1					Loam	5
						Silty loam	4
						Clay loam	3
						Muck	2
						Non-shrinking and non-aggregated clay	1

C (m/day)	**F**$_c$	**A**^{ab}	**F**$_c$	**I**^{b}	**F**$_c$
< 4.1	1	Massive shale	1 - 3 (2)	Confining layer	1
4.1 - 12.2	2	Metamorphic/igneous	2 - 5 (3)	Silt/clay	2 -6 (3)
12.2 - 28.5	4	Weathered metamorphic/igneous	3 - 5 (4)	Shale	2 - 6 (3)
28.5 - 40.7	6	Glacial till	4 - 6 (5)	Limestone	2 - 7 (6)
40.7 - 81.5	8	Bedded sandstone, limestone and shale sequences	5 - 9 (6)	Sandstone	2 - 7 (6)
> 81.5	10	Massive sandstone	4 - 9 (6)	Bedded limestone, sandstone and shale	4 - 8 (6)
		Massive limestone	4 - 9 (8)	Sand and gravel with significant silt and clay	4 - 6 (6)
		Sand and gravel	4 - 9 (8)	Sand and gravel	4 - 6 (8)
		Basalt	2 - 10 (9)	Basalt	2 - 10 (9)
		Karst limestone	9 - 10 (10)	Karst limestone	8 - 10 (10)

[a] For SI the ratings are multiplied by 10
[b] Typical ratings between brackets
F$_c$: DRASTIC Ratings

Table 4.4: Land use classes and respective ratings use in Susceptibility (SI) method (adopted from (Stigter et al., 2006b))

Land use	**Rating**
Agricultural areas Irrigation perimeters (annual crops), paddy field	90
Permanent crops (orchards, vine yards)	70
Heterogeneous agricultural areas	50
Pastures and agro-forested areas	50
Artificial areas Industrial waste discharges, landfill	100
Quarries, shipyards, open-air mines	80
Continuous urban areas, airports, harbours, (rail)roads, areas with industrial or commercial activity, laid out green spaces	75
Discontinuous urban areas	70
Discontinuous urban Natural areas Aquatic environments (salt marshes, salinas, intertidal zones)	50
Forests and semi-natural zones	0
Water bodies	0

Chapter 5

REGIONAL FIELD STUDIES & VULNERABILITY ANALYSIS

This chapter presents detailed analyses of results and discussions of the regional studies (high density sampling and geostatistical analyses), and vulnerability analysis of the underlying aquifer in the region to contamination. The chapter is divided into two major sections; which include the regional field studies, and thereafter the vulnerability analyses including their respective discussions.

5.1 Results and discussion of regional field studies

Results presented in this section include, the outcome of mapping field parameters from large diameter wells, and also surface water (drains and lagoon) in the study area. In addition, the geostatistical analyses results of the collected data is presented.

5.1.1 Geostatistical models approach

There are several techniques available in literatures for interpolation of sampled data, but kriging methods are the best for normally distributed data (Soares et al., 1996; Aidoo et al., 2015). Therefore, kriging approach was applied to understand the spatial variation of the sampled data set, and thereafter predictions were made at locations where samples could not be collected in the study area. The three steps: Data analysis exploration, Structural Analysis and Estimation, suggested by Ribeiro (2014), were applied on the sampled data set. Geostaistical analyst wizard in ArcGIS 10.5 software was used to model the experimental variogram, and also to make prediction (kriging) maps of the different sampled parameters.

5.1.1.1 Exploratory data analysis

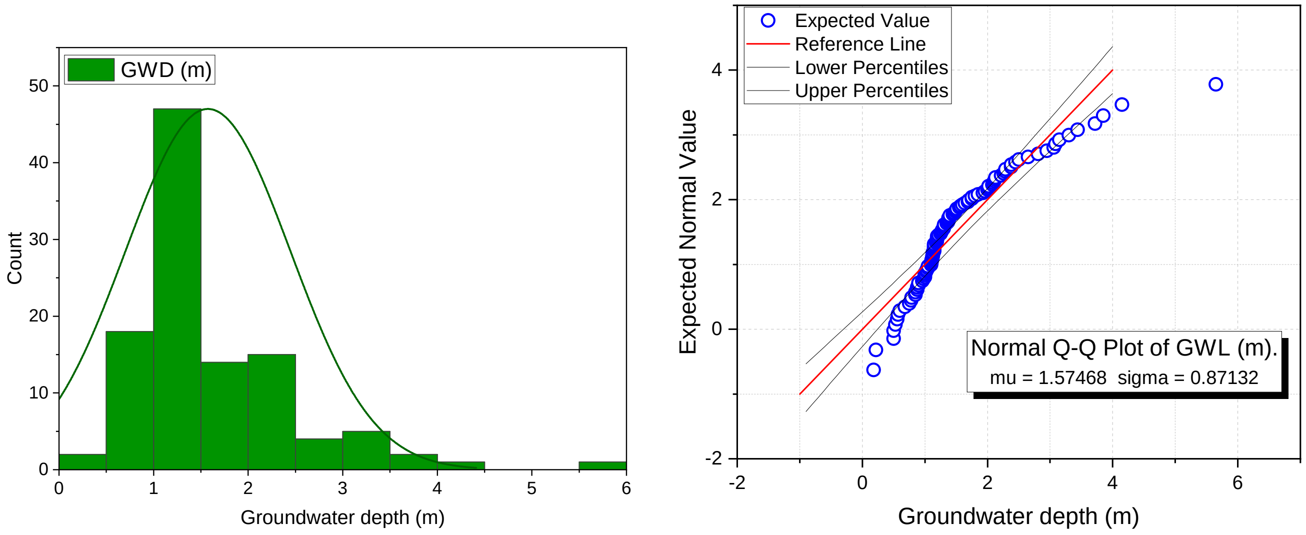
Exploratory data analysis was carried out on the sampled data to confirm normality, consistency, and the validity of applying parametric statistical methods on the data. Also, this step was necessary to identify and appropriately treat possible outliers contained in the data set. The summary statistics shows all measured field parameters do not follow the normal distribution, as indicated by their mean, median, skewness, and kurtosis values (Table 5.1). Groundwater level, pH, total dissolved solid, electrical conductivity, oxidation-reduction potential and dissolved oxygen parameters show some level of skewness (positive or negative) as observed from the analysed statisical parameters (Table 5.1).

Table 5.1: Descriptive Statistics of measured Field Parameters from large diameter wells located at different points in the study area

Statistical Parameters	**Measured Field Parameters**					
	GW level (m)	**EC** ($\mu S/cm$)	**pH**	**ORP** ($\%$)	**DO** (mg/L)	**TDS** (mg/L)
No. of Data	120	120	120	120	120	120
Minimum	0.18	20	4.5	-58	0.00	10
Maximum	9.10	7340	8.66	78	18.48	3674
Mean	1.74	646	6.45	62	5.52	323
Median	1.38	504	6.58	65	5.37	252
Std. deviation	1.24	782	0.87	18	4.29	391
Skewness	2.86	6	-0.64	-4	0.56	6
Kurtosis	11.78	51	0.12	22	0.01	51

GW - Groundwater; **EC** - Electrical Conductivity; **ORP** - Oxidation Reduction Potential;
DO - Dissolved Oxygen; **TDS** - Total Dissolved Solids

Furthermore, the histogram distributions and normal Quantile-Quantile plot (QQ plots) were plotted (Figure 5.1, 5.2 and Appendix B.1); which confirms the measured parameters have non-symmetric distributions. Also, the Shapiro-Wilk test for normality, shows that at the 0.05 confidence level, the data was not significantly drawn from a normally distributed population.

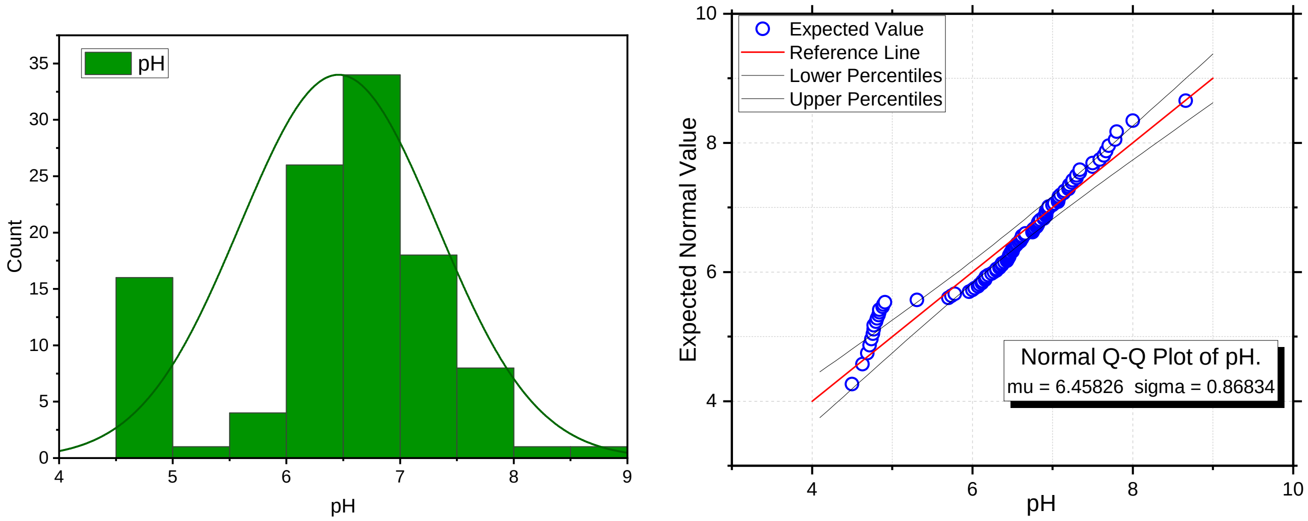


(a) Histogram and cumulative plots showing distribution of measured groundwater levels

(b) Q-Q plot of measured groundwater levels

Figure 5.1: *Plots to check normality of measured field data using (a) Histogram and cumulative plots showing distribution, and (b) Q-Q plot of measured groundwater levels in the study area*

Moreover, the variogram is sensitive to outliers in the data, i.e. unexpectedly large or small values beyond the limits of the main distribution. Therefore, all outliers should be investigated and considered as potentially erroneous values before they are allowed to remain as part of the data set. For contaminated sites, the largest values will be of most interest. However, the same data (largest values)



(a) Histogram and cumulative plots showing distribution of measured pH values

(b) Q-Q plot of measured pH values

Figure 5.2: *Plots to check normality of measured field data using (a) Histogram and cumulative plots showing distribution, and (b) Q-Q plot of measured pH values in the study area*

can contribute to several estimates of variogram $\hat{\gamma}(\mathbf{h})$, and so outliers inflate the averages. Moreover, If there are few outliers relative to the whole data, removing them often reduces skewness, and this is a reasonable approach. The values removed can be returned to the data for kriging if desired (Oliver and Webster, 2015). Therefore, the method of treating outliers suggested by Oliver and Webster (2015) was adopted and applied to the measured field parameters before performing variogram and kriging prediction.

5.1.1.2 Structural analysis of data

This stage involves performing spatial continuity correlation analysis on the data set, by calculating the experimental variogram. A variogram refers to the degree of variance of the observed values at a different location. Through a variogram, it is possible to know the distance from which the variable is no longer spatially correlated. For estimation purposes, the experimental variogram functions must be fitted by theoretical models and cross-validated with experimental data (Ribeiro, 2014).

Experimental semivariogram of each of the measured parameters (EC, pH, groundwater depth and ORP) were created with no detrend data. Thereafter, four different semi-variogram models (Spherical, Exponential, Gaussian, and Circular), were fitted to each measured parameters (pH, Groundwater level, EC and ORP) (Appendix **??**). The modelled semivariogram was necessary to provide spatial structure for performing kriging interpolation. However, the best model for each of the measured parameters were chosen based on predictive performances of the fitted models on the basis of spatial cross validation tests. The values of mean square error (MSE), root mean error (RMSE), average standard error (ASE) and root mean square standardized error (RMSSE) were estimated (Table 5.2) to choose the best model for each of the parameters.

Table 5.2: Summary of characteristics parameter of different variogram models fitted to measured field parameters in the study area

Parameter	Fitted model	Nugget (C_0)	Sill ($C_0 + C$)	Lag size (km)	Range (km)	RMSE	ASE	MSE	RMSSE
GW level	Gaussian	0.015	0.85	1354.60	6587.32	-0.0120	3.7564	-0.0012	1.0025
EC	Spherical	0.55	0.92	584.18	2704.73	0.6860	0.5902	-0.0052	1.1766
pH	Spherical	0.59	1.20	527.60	4308.05	0.3879	0.3656	0.0310	1.0705
ORP	Spherical	0.47	1.11	224.25	2242.45	2.2992	1.8327	0.0365	1.2721

RMSE - Root Mean Square Standardized Error; **ASE** - Average Standard Error; **MSE** - Mean Square Error; **RMSSE** - Root Mean Square Standardized Error; **GW** - Groundwater; **EC** - Electrical Conductivity; **ORP** - Oxidation Reduction Potential;

5.1.1.3 Estimation

Kriging interpolation was used as an estimation method to predict values in places where measurements were not carried out in the study area. This estimation is done based on spatial correlation obtained from the experimental variogram and using geostatistical methods such as kriging, which is flexible and accurate gridding method to produce good maps for most data sets (Ribeiro, 2014).

Kriging estimate maps (Figures 5.3, 5.4, and 5.5) of measured parameters (groundwater level, EC, pH and ORP) were generated, which shows a visual representation of the spatial distribution of the measured parameters in the study area.

5.1.1.4 Piezometric kriging estimate map

The piezometric kriging estimate map (Figure 5.3) shows the direction of groundwater flow in the study area. Groundwater flow direction is predominantly from the East part, majorly around the Chemical complex and directed towards the South-West part of the study area towards the lagoon(Figure 5.3). The observed groundwater flow direction is expected as a result of the progressive increase in the measured groundwater levels from East to west (Figure 5.3). This is because groundwater in this region is mainly influenced by the topography, and the east part is relatively higher compared to the west part of the study area.

In addition, groundwater flow direction North of the ECC shows a movement (contour lines) directed predominantly East-West in the central area. On the other hand, the Southern part of the study area depicts a direction as observed from the contour lines, which is directed mostly towards the North-East and South-West of the study area. Moreover, the groundwater flow geometry shown in Figure 5.3 is similar to all flow networks built on the basis of campaigns over the past decades as reported by Barradas (1992a), Ordens (2007) and Marques (2017).

5.1.1.5 pH kriging estimate map

Electrical conductivity (EC) and pH, can serve as good indicators for potential contamination activities on-going in a particular area. Therefore, mapping in-situ pH and EC in soil or water bodies (surface or

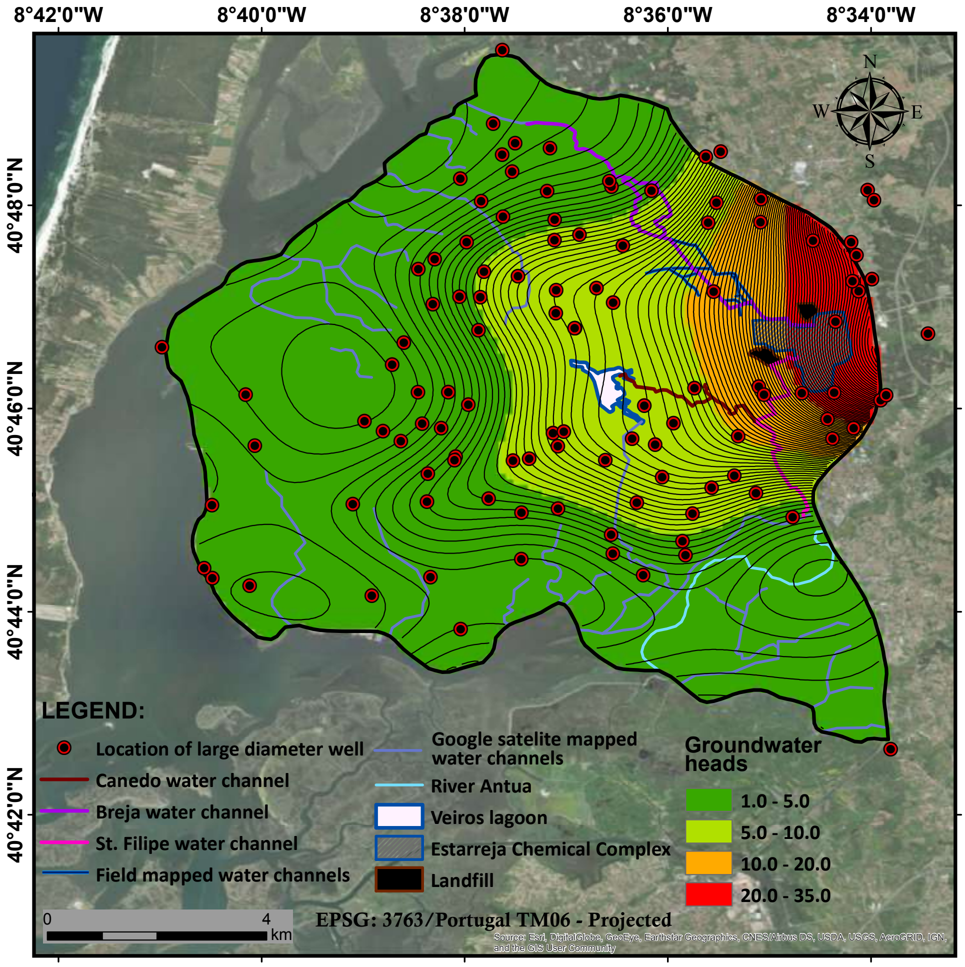


Figure 5.3: *Kriging piezometric map showing groundwater flow direction and corresponding sampling points (large diameter wells) in the study area*

groundwater), can indicate the level of contamination in different location of an area.

The pH kriging map (Figure 5.4) shows the general spatial distribution of pH in the study area. Since groundwater flows away from the eastern part towards the South-West direction as observed in the piezometric map (Figure 5.3). This peculiar groundwater flow direction in the study area, influences the general movement of the contaminants as seen in the spatial distribution of pH in the study area (Figure 5.4).

The area South of the study area, and immediately South-West to the chemical complex shows the presence of acidic waters with pH value below five.

The low pH values observed in this area (South-West of the chemical complex) were expected. The observed low pH values is likely due to two major official water channels (Canedo and São Filipe water channels) that were used in the past to discharge contaminated waste waters from the chemical complex, which coincides with the area. This also suggest that there is an interaction between the surface water in the channels and the groundwater resource in the area.

On the other hand, the Western and Northern part of the study area shows same distribution of a relatively higher pH in the range between six and eight. Moreover, there is a great possibility that the measured

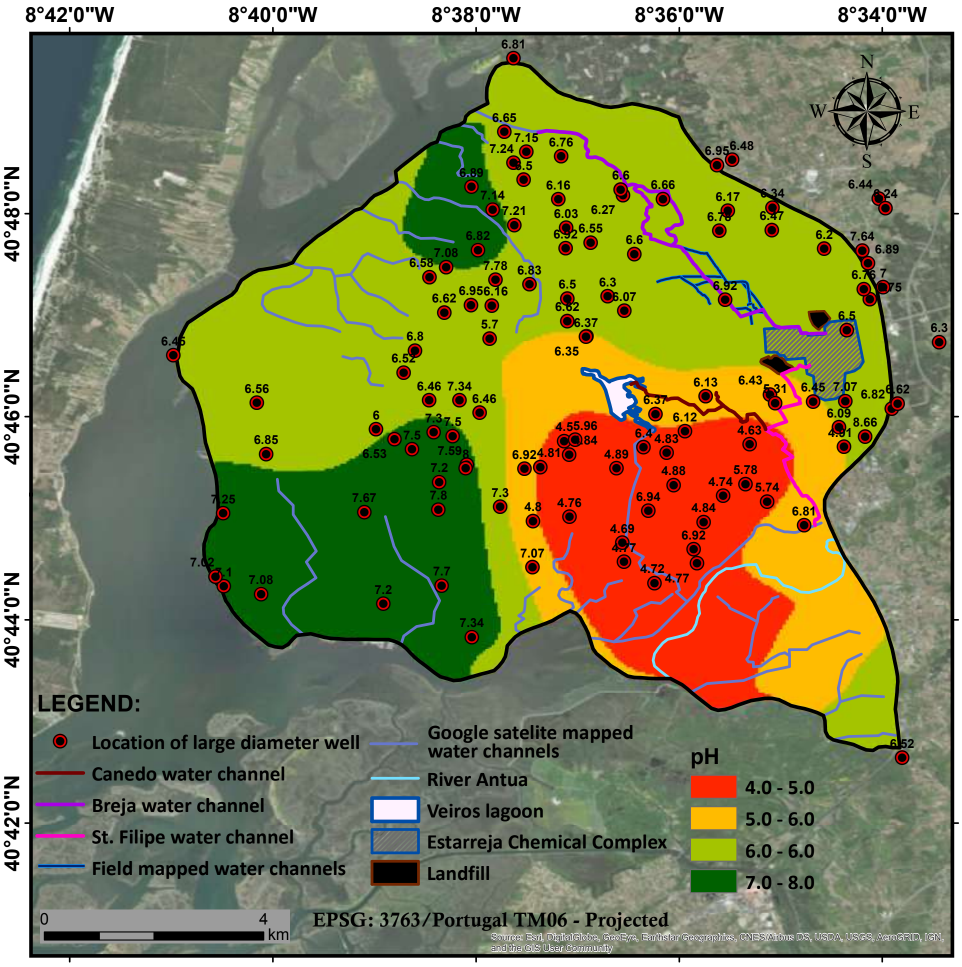


Figure 5.4: *Kriging map showing distribution of pH and corresponding sampling points (large diameter wells) in the study area*

groundwater pH in this area could be influenced by the nearby coastal lagoon (Ria de Aveiro).

5.1.1.6 Electrical conductivity (EC) kriging estimate map

The EC kriging map (Figure 5.5) shows the general spatial distribution of EC in the study area. Electrical conductivity shows no clear pattern as observed in the pH distribution over the study area. The distribution of electrical conductivity is localized to some specific areas, which coincides with areas close to the coastal lagoon or along one of the contaminated water channel in the region.

Despite the influence of the coastal lagoon, which can be clearly seen from the relative higher EC values (measured along areas close to the coastal lagoon) compared to other areas in the study area. Likewise, South of the chemical complex shows a high EC value of (7340 $\mu S/cm$).
This particular portion coincides with the São Filipe water channel; which suggest the influence of the contaminated water channel in the observed high EC value. Also, this particular pattern is observed at different areas in the region where the official water channels are localized. Therefore, it can be clearly seen that the relative high EC values measured in some areas far away from the coastal lagoon is as a result of the water channels (contaminated) located in this areas. Hence, there is a close link between

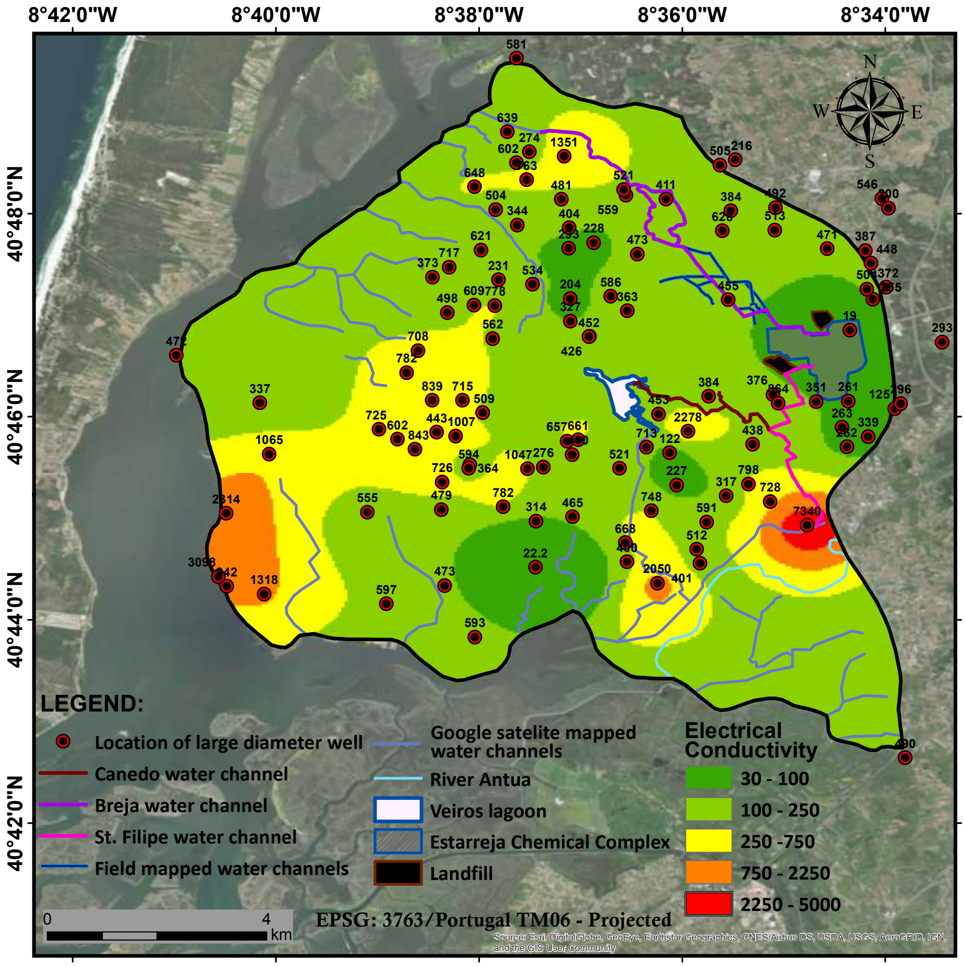


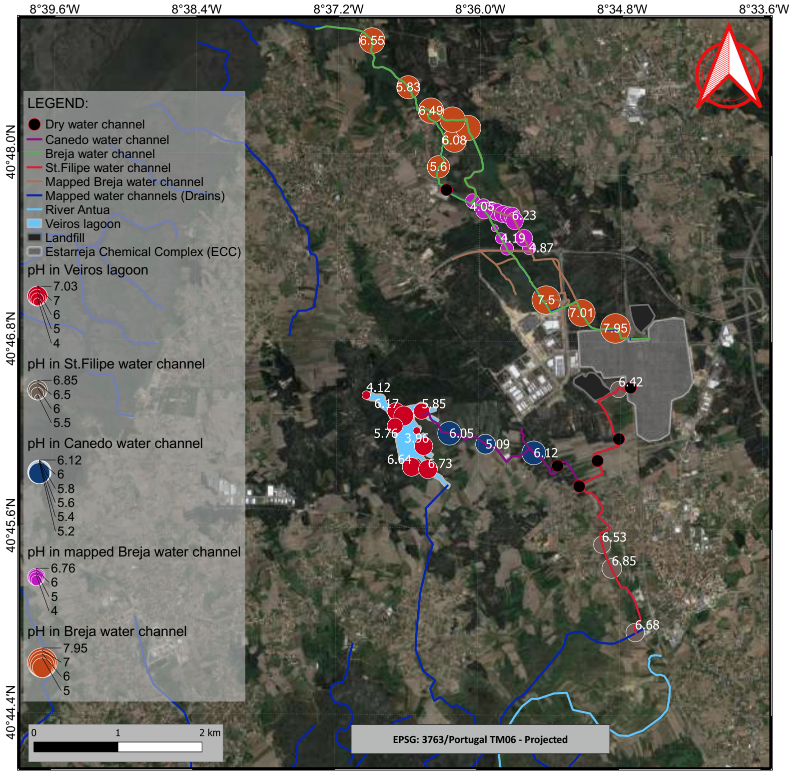
Figure 5.5: *Kriging map showing distribution of Electrical Conductivity (EC) and corresponding sampling points (large diameter wells) in the study area*

the official channels used in the past to discharge untreated waste waters into the environment, and the quality of groundwater resource in the area. Electrical conductivity and pH were also measured along the water channels and at some selected point in a popular lagoon in the region (veiros lagoon). There is an observed varying quality based on EC and pH along the water channels and lagoon (Figure 5.6).

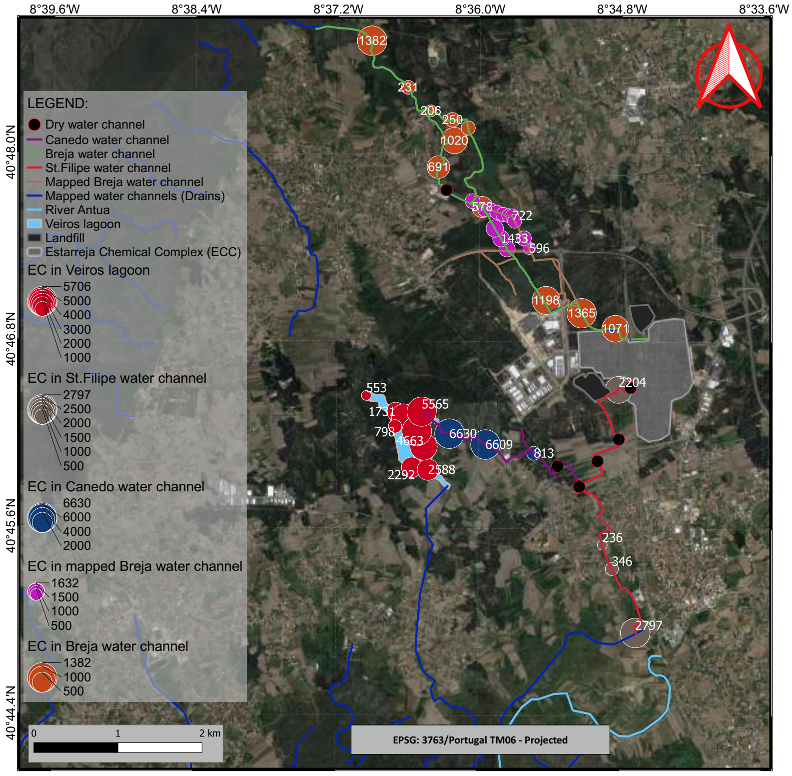
Some part of the channels were dry, because of the season during which the measurements were made (April - May). pH values measured along water channels located North of the ECC range from 6.5 to 7.95 (signifying slightly acidic to slightly basic waters). pH below five (acidic waters) were measured in water channels originating from the chemical complex towards North-West (Breja water channel) of the study area.

Similarly, pH below five were mapped along the Canedo water channel (Figure 5.6a), which originates in a swampy area near São Filipe and flows towards North-West into Veiros lagoon. Moreover, the lowest pH of less than four was measured around the Veiros lagoon.

Electrical conductivity values mapped along the three official water channels (Canedo, St.Filipe and Breja) were relatively high (Figure 5.6b). The average EC value mapped along these water channels are over 1000 $\mu S/cm$. Moreover, the highest EC values ranging between 5000 and 6600 $\mu S/cm$ were measured around the entry point connecting Breja water channel to Veiros lagoon. Hence, this suggest that, the water channels are still contaminated, even though the chemical industries have stopped discharging waste water through these channels.



(a) pH mapped along water channels and Verios lagoon in the study area



(b) EC mapped along water channels and Verios lagoon in the study area

Figure 5.6: *Distribution of chemical parameters in surface water bodies: (a) mapped pH values; and (b) mapped EC values in the study area*

5.1.2 Application of susceptibility index (SI) to the study area

The study area for this research was subjected to Susceptibility Index (SI) rather than the DRASTIC index assessment. The SI method was chosen rather than the DRASTIC method, because of the less complex nature (Table 5.3) of data needed and the study area location (which is located in same Country-Portugal, where the SI method was originally developed). In this study, ArcGIS 10.5 functionalities were utilized to create all layers of the SI model, and also to perform the necessary computations (raster overlay, raster calculation, and others) of all generated raster files (maps).

Table 5.3: Sources of data for susceptibility index (SI) parameters used to generate vulnerability map for the study area (adopted and modified from Stigter et al. (2006b))

Parameter	Data source
D	High density field measurement of 120 large diameter wells between April and May 2019
R	made for the Soil Take Care (2016 - 2019) project by Barreiras (2019); calculated using WetSpass program (Batelaan and De Smedt, 2007) using the following information: DEM, land-use, soil type, evaporation, irrigation, precipitation, and groundwater depth maps
A	1:50,000 Geological map of Portugal (Teixeira and Torre de Assuncao, 1963; Teixeira and Zbyszewski, 1976)
T	made by calculating percentage slope map using ArcGIS software from 30 m resolution digital elevation model (DEM) of the area
LU	made for the Soil Take Care (2016 - 2019) project by Barreiras (2019); produced using information from the report by Vale (2014)

D - Depth to water; **R** - Net recharge; **A** - Aquifer media; **T** - Topography; **LU** - Land-use; **DEM** - Digital elevation model

5.1.2.1 Depth to water (D)

The upper (first) aquifer unit in the study area has been defined to be a phreatic surface aquifer ((alias?)). Therefore, the depth to water is considered as the depth of the water table beneath the surface in the area. As such, the groundwater levels were measured from large diameter wells located at different points in the study area. These measurements were done between April and May 2019, and groundwater level from a total of 120 large diameter wells were measured.

Furthermore, the Geostatistical Analyst toolbox in ArcGIS 10.5 GIS software, was used for interpolation of measured well points, from which groundwater level raster map of 100 by 100 m pixel size was produced. Coupled with the large amount of measured (120) wells over the area, groundwater levels for some points in area were not available. Therefore, kriging interpolation method using variogram modeling was applied to predict groundwater levels for those areas. Thus, a variogram model was first fitted (exponential variogram) to the measured groundwater levels. Thereafter, simple kriging interpolation method was applied to predict groundwater levels at points where groundwater levels were not measured in the study area.

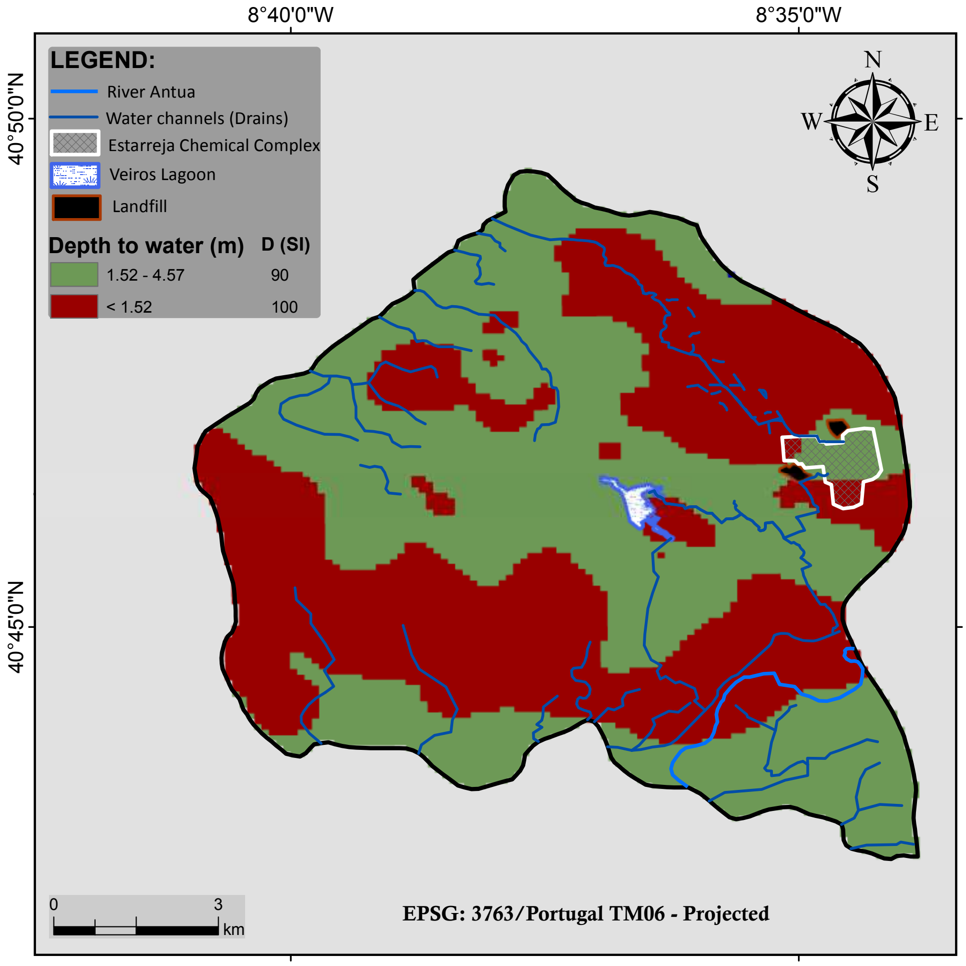


Figure 5.7: *Classified interpolated depth to water ranges and corresponding SI ratings over the study area*

The classified SI depth to water map (Figure 5.7), shows it follows the observed topography of the area. The smallest depths to groundwater values (< 1.52 m) were observed around the ECC towards the North of ECC. Also, some parts spanning from south of ECC towards south-west of the study area close to the lagoon, shows a relative low depth to groundwater. Therefore, these areas received a SI rating of 100. Moreover, the highest depth to groundwater range (1.52 - 4.57 m) are located away from the Estarreja chemical complex (ECC) towards North-west of the study area; which receives a SI rating of 90.

5.1.2.2 Net recharge (R)

Precipitation is the main source of groundwater that infiltrates through ground surface to reach water table. In general, rainfall infiltration, irrigation return flow, and absorption wells are defined as the net recharge (Aller et al., 1987). Also, Aller et al. (1987) stated that, recharge would facilitate the transportation of pollution to reach water table thus, the aquifers with more net recharge have higher vulnerability to contamination.

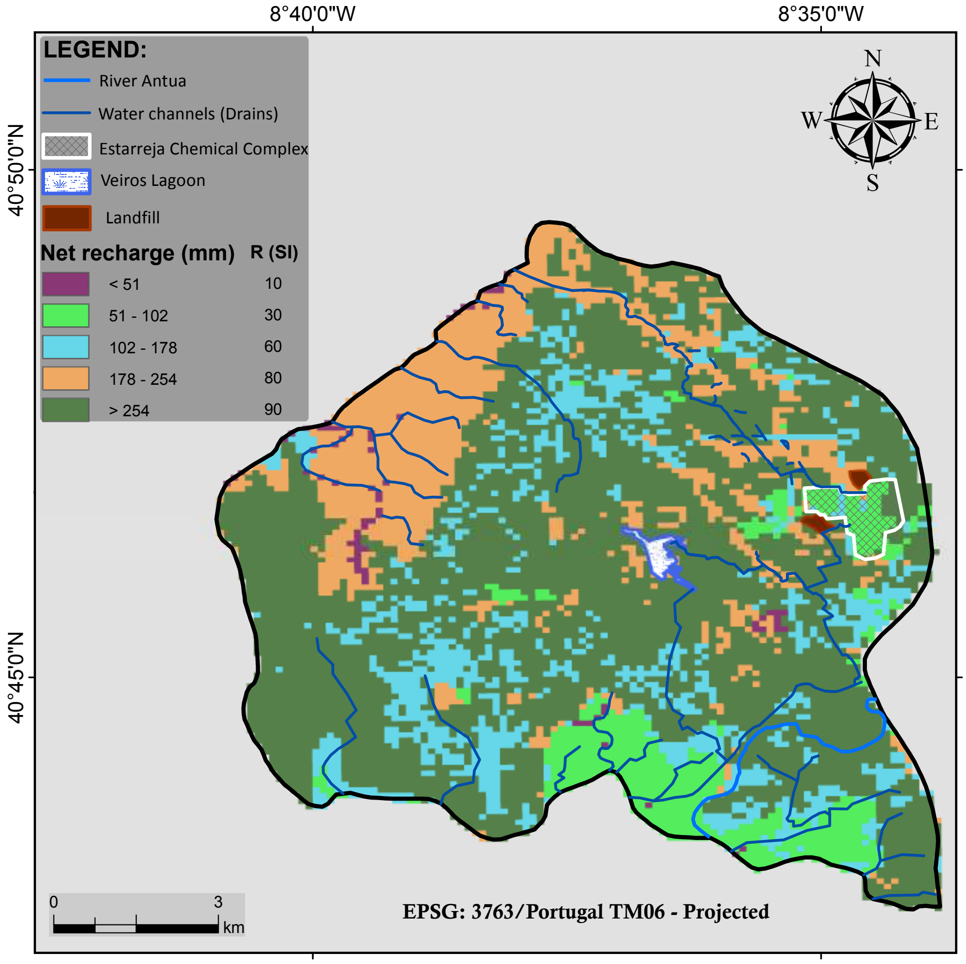


Figure 5.8: *Classified net recharge ranges and corresponding SI ratings over the study area*

The net recharge map was prepared by Barreiras (2019) using WetSpass software. WetSpass is a steady state spatially distributed water balance model for simulating yearly or seasonal averages of groundwater recharge, evapotranspiration (soil evaporation and transpiration also as separate outputs), runoff, and interception (Batelaan and De Smedt, 2007).

Classification of net recharge raster map (100 by 100 pixel) using the SI ratings was done using ArcGIS 10.5 GIS software. The SI classified net recharge map (Figure 5.8), shows most of the area have net recharge of above 254 mm/year, whereas some areas were observed with patches of intermediate net recharge values (51 - 254 mm/year). The high net recharge values over the are is connected to the type of soil predominant in the area (fine alluvium sand). As such, high recharge is expected, and will contribute to high vulnerability to contamination.

5.1.2.3 Aquifer media (A)

The classification of aquifer media was done with the use of national geology map in form of different shapefiles over the study area. The raw geology map was first grouped into major geological classes, before classifying using the SI rating.

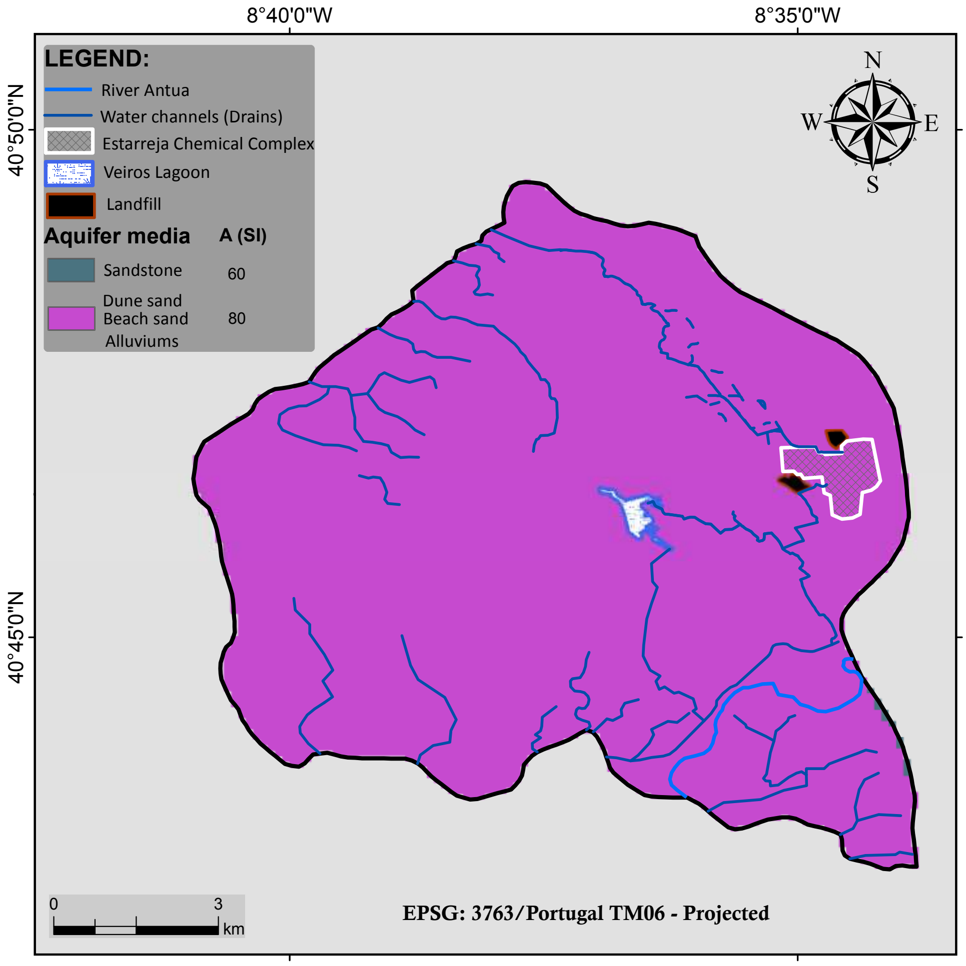


Figure 5.9: *Classified aquifer media type and corresponding SI ratings over the study area*

Furthermore, the classified aquifer media (Figure 5.8), shows the area is dominated by sand deposits (dunes, beach and alluvium sands), having high SI rating (80) and contributing to the vulnerability of the area.

5.1.2.4 Topography (T)

Topography indicates the slope of land which controls the probability that a pollutant will run off or remain on surface to infiltrate (Aller et al., 1987). Steeper topographic surfaces are less vulnerable to contamination compared to flat topographic terrains. The topography raster map was produced from a 30 m resolution Digital Elevation Model of the area. Spatial analyst tools in ArcGIS was used to derive the percentage slope map from the DEM.

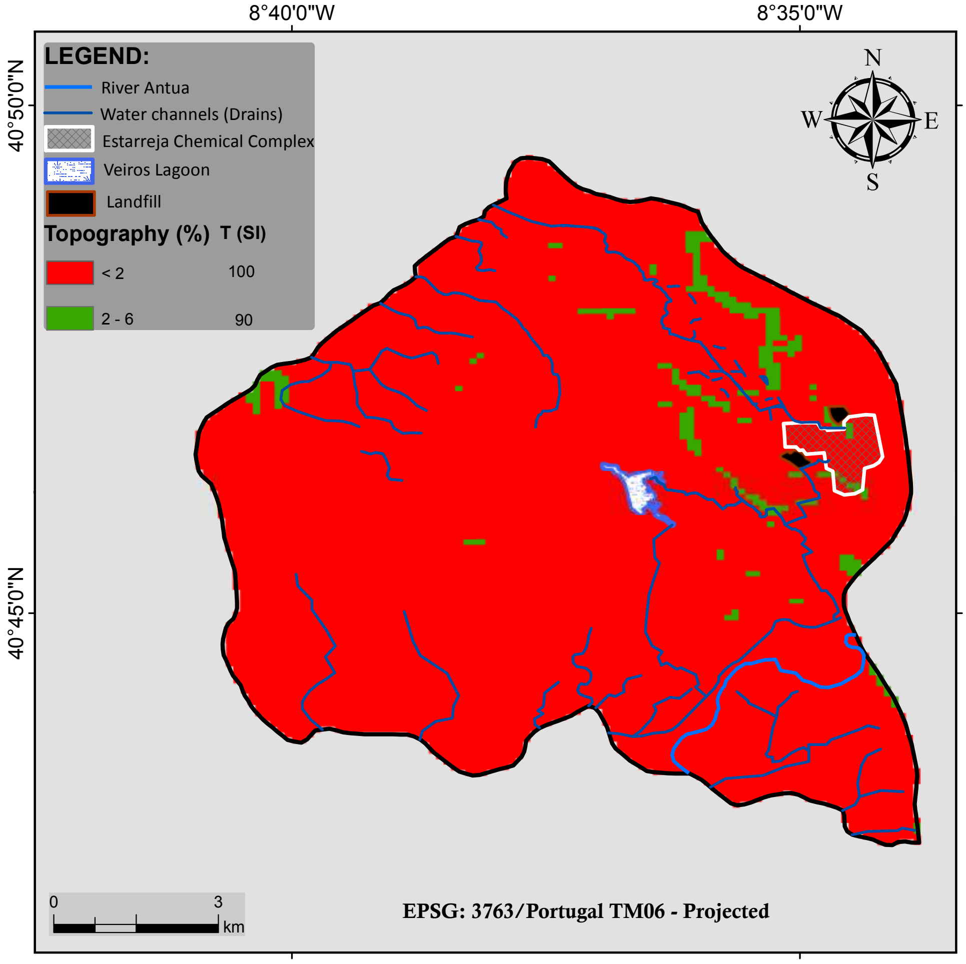


Figure 5.10: *Classified topography ranges and corresponding SI ratings over the study area*

The classified topography SI map (Figure 5.10), shows the area is dominated with high SI rating of 100 (topography relatively flay < 2 %).

5.1.2.5 Land use (LU)

The major parameter introduced to modify the DRASTIC index to SI vulnerability index is the land use pattern of an area. For this study, the land use pattern of the area was gotten from the land use map over the area made by Vale (2014).

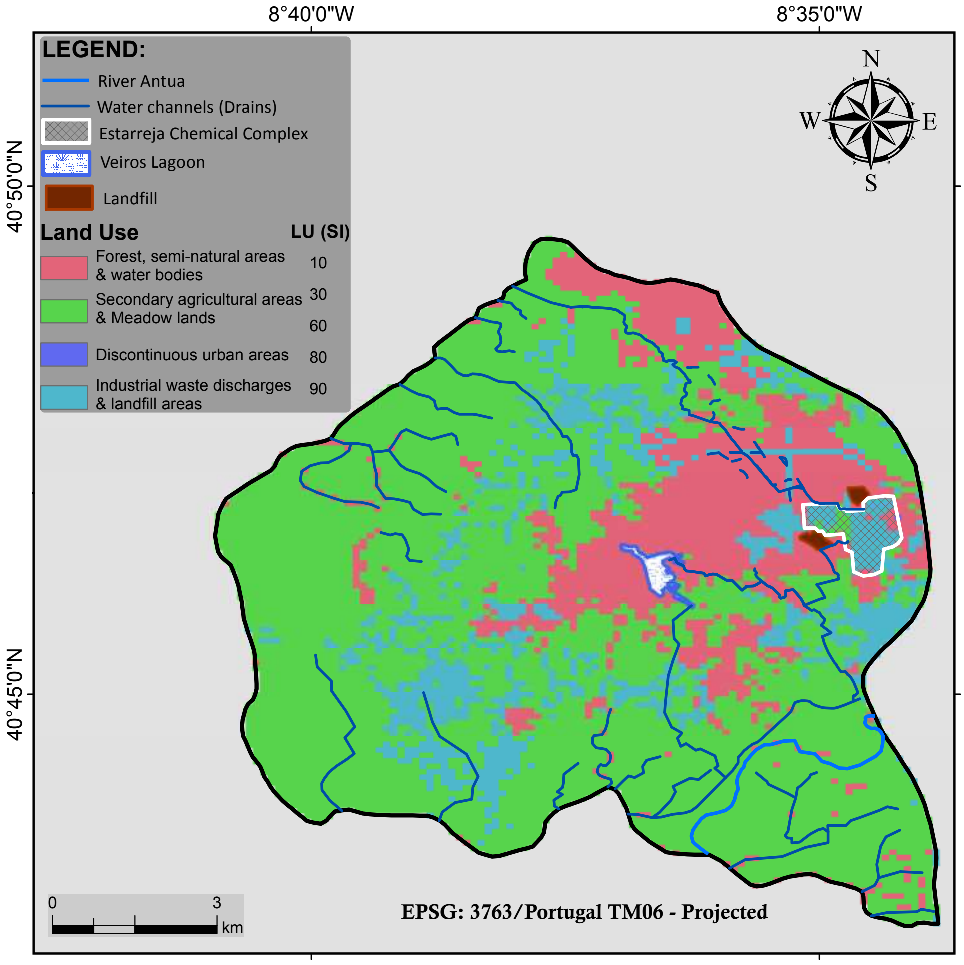


Figure 5.11: *Classified land use patterns and corresponding SI ratings over the study area*

The land use classified map (Figure 5.11), shows the study area is divided amongst four land use type, according to Land use classes for SI method (Table 4.4) (Stigter et al., 2006b). The area around the ECC, was assigned the highest SI rating (90), due to its location in the study area (close to industrial discharges and landfill sites).

A large portion of the area classify under secondary agricultural area with an intermediate SI rating of 30. However, forested areas and water bodies were assigned the lowest SI rating (10), because of their assumed low influence on contamination potential.

5.1.2.6 Computation and mapping of SI index

The Susceptibility (SI) vulnerability map was obtained by overlaying all the individual parameters (maps) into one map. The overlaying of maps was done in ArcGIS with raster calculator. As such, the formula Equation (5.1), was applied to get a single map; which describes the vulnerability to contamination of the area.

$$SI = 0.186 \times D + 0.212 \times R + 0.259 \times A + 0.121 \times T + 0.222 \times LU \tag{5.1}$$

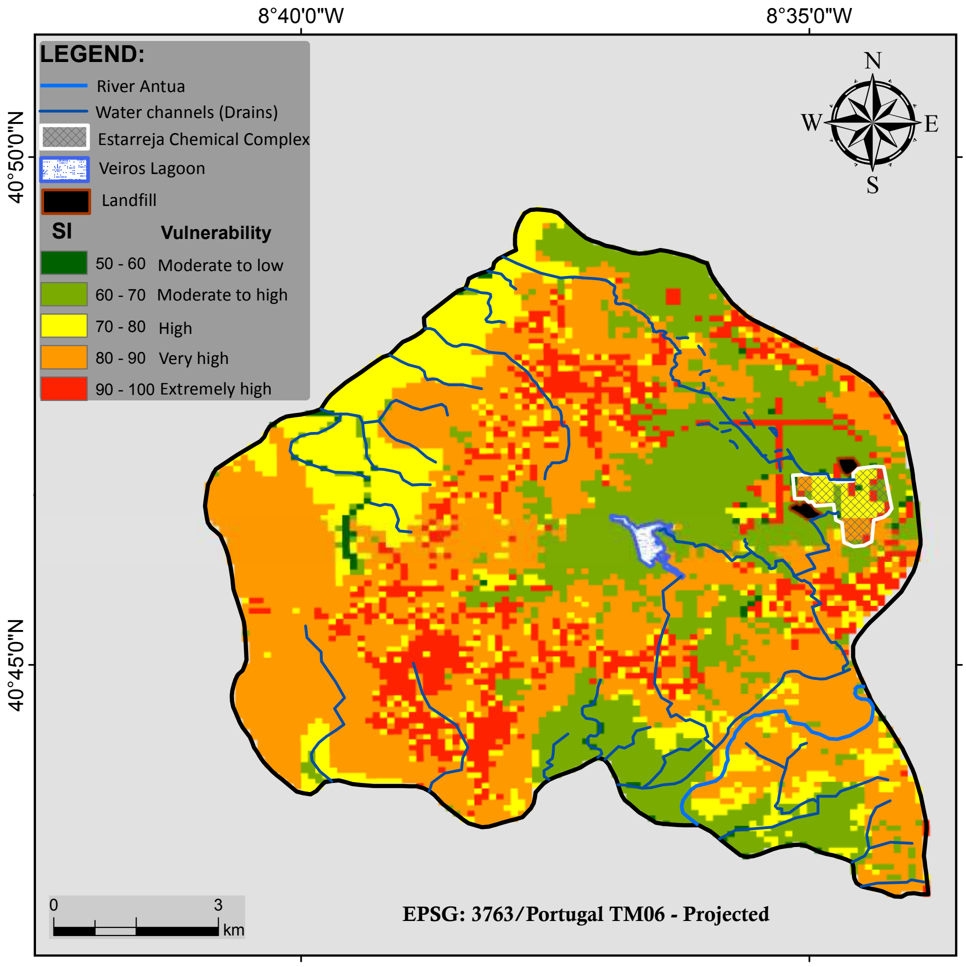


Figure 5.12: *Susceptibility (SI) vulnerability map over the study area*

The SI vulnerability map (Figure 5.12), shows the area is classified between 'moderate to low' and 'extremely high' vulnerability. However, the extremely high vulnerability areas are scattered over different locations in the study area. As such, there is no area that can be clearly defined as 'extremely high vulnerability' as shown on the SI vulnerability map (Figure 5.12). Areas located around the chemical complex (ECC) rank between 'moderate to high' and 'very high' vulnerable. As such, south of the chemical complex and further south-east of the study area is classified as very highly vulnerable, this is a because in these areas groundwater is closer to the surface and the aquifer characteristics (sand aquifer) increases vulnerability.

Also, areas around and close to the chemical complex can be seen as extremely high vulnerable to contamination. The reason being that, these areas have impact of the chemical industry and landfill, coupled with the high permeability of the aquifer material. On the other hand, further away North of the chemical complex; where there is a change in land use (forested areas), and groundwater is further away from the surface. Therefore, with such conditions different from that observed close to the chemical complex; vulnerability decreased to 'moderate to high'.

Furthermore, on the other part of the study area (Western axis); a pattern of vulnerable areas can be clearly seen (Figure 5.12). Thus, South-west of this axis, shows area of extremely high vulnerability. Nevertheless, the reason can be linked to its flat topography, coupled with the fact that its among areas receiving the highest amount of recharge, and located under a sand aquifer.

On the other hand, further west of this axis (close to the lagoon), a patten of very high vulnerable area is observed. This is also connected to the flat slop and the high amount of recharge this area receives.

Overall, the study area can be considered as very highly vulnerable to contamination, due high contribution to contamination by various intrinsic properties SI vulnerability parameters considered in the area.

Chapter 6

HYDROGEOCHEMICAL AND SOCIO-HYDROGEOLOGICAL ANALYSES

This chapter presents detailed analyses of results and discussion of investigations focused at preselected locations in the study area after optimization of the regional field data. The chapter is divided into two major sections, which include analyses of hydrogeochemical data collected from the field. Hydrogeochemical analysis was done by applying specific (graphical and statistical) methods on the hydrogeochemical data to understand the chemistry (interactions) and other processes on-going in the aquifer system in the area. In addition to hydrogeochemical analysis of the groundwater quality data, suitability of the sampled groundwater for use as drinking and irrigation purposes were analysed in accordance with specific standards.

The next section of the chapter, outlines the outcome of socio-hydrogeological study conducted in preselected locations around the study area, where groundwater samples were initially collected for analysis. Socio-hydrological study in the study area, was achieved by interviewing borehole owners (mostly farmers), from which groundwater samples were initially taken for analysis. The interview questions were carefully structured to get idea about the perception of borehole owners concerning the contaminated groundwater resource in the region. Thereafter, qualitative and quantitative analyses (exploratory) were done to understand the responses of the borehole owners (farmers) with respect to the groundwater quality result.

6.1 Hydrogeochemical analysis

The results and discussions presented in this section comprises all methods used to characterize groundwater quality of water samples collected from the study area. Understanding groundwater quality is a key aspect of the present research, as it serves the main indicator justifying suitability of groundwater use in the region for domestic, irrigation and other purposes.

6.1.1 General groundwater chemistry

Groundwater and surface water geochemistry can be influenced by various factors, including the type of rock-mineral, residing time within the host rock, characteristics of water flow path through the rock, and the original groundwater composition (Tóth, 1999).

Thus, quality control check was first conducted on the groundwater chemistry data obtained from the laboratory before proceeding with various analyses. The electro-neutrality (E.N) formula (Equation 6.1) in percentage meq/L was used to check the ion-balance error.

$$E.N\,(\%) \quad = \quad \sum\left[\frac{\left(Na^{+}+K^{+}+Ca^{2+}+Mg^{2+}\right)+\left(Cl^{-}+HCO_{3}^{-}+SO_{4}^{2-}+NO_{3}^{-}\right)}{\left(Na^{+}+K^{+}+Ca^{2+}+Mg^{2+}\right)-\left(Cl^{-}+HCO_{3}^{-}+SO_{4}^{2-}+NO_{3}^{-}\right)}\right] \qquad (6.1)$$

Ion-balance error computed using Equation 6.1, were all within the acceptable range of ±10 %, with the exception of two water samples (SPR04 and SPR05). These water samples (SPR04 and SPR05), showed E.N value of -14 %; which is above the maximum acceptable ±10 % range. Hence, these two samples were critical investigated to determine possible reasons for their relative high E.N values (above ±10 %) recorded. Nevertheless, results of the field chemical parameters monitored during sampling, shows that these two samples were located in highly contaminated areas. Therefore, groundwater collected under this condition, could possibly influence the cation and anion chemistry as observed in the above ±10 % E.N value recorded.

Table 6.1: Descriptive statistical summary of chemical parameters and major ions hydrochemistry of water samples collected at different locations in the study area

Chemical Parameters	**Statistical Parameters**								
	N	**Min.**	**Max.**	**Median**	**Mean**	**5 % TM**	**SD**	**Skewness**	**Kurtosis**
pH	25	4.43	6.92	5.76	5.65	5.65	0.64	-0.20	-0.54
TDS (mg/L)	25	59	1143	237	355	331	273	1	2
TH (mg/L)	25	13.50	236.00	92.54	101.13	98.85	56.38	0.60	0.27
EC ($\mu S/cm$)	25	135	2384	455	699	644	551	2	3
Na^+ (mg/L)	25	12.00	333.00	43.50	81.92	72.59	87.71	1.65	1.92
K^+ (mg/L)	25	0.69	26.60	10.80	12.55	12.44	7.84	0.27	-1.13
Ca^{2+} (mg/L)	25	3.60	67.90	28.70	30.90	30.42	17.94	0.37	-0.60
Mg^{2+} (mg/L)	25	0.54	19.80	4.95	5.73	5.33	3.98	1.94	5.61
$SiO_4{}^{4-}$ (mg/L)	25	3.00	30.30	5.50	6.66	5.76	5.39	3.80	16.57
Cl^- (mg/L)	25	17.20	527.00	67.60	116.61	100.60	139.95	1.83	2.45
$HCO_3{}^-$ (mg/L)	25	0.00	159.11	35.36	42.84	38.88	44.31	1.42	1.65
$SO_4{}^{2-}$ (mg/L)	25	1.19	192.00	49.80	64.93	61.46	46.32	1.53	2.10
$NO_3{}^-$ (mg/L)	25	-0.30	20.50	8.63	7.66	7.39	6.27	0.37	-0.69

N - Sample size; **TM** - Trimmed Mean; **SD** - Standard deviation; **TDS** - Total Dissolved Solids; **TH** - Total Hardness; **EC** - Electrical Conductivity

Water physicochemical properties shows a wide range of variation, as described using basic descriptive statistical measures (Table 6.1). pH values range from 4.43 to 6.92, with an average value of 5.65 (indicating acidic to slightly waters). Also, the 5 % trimmed mean pH of 5.65, and relatively low standard deviation (0.64) suggest that computed statistical measures are stable to extreme outliers (relative high an low value of pH).

EC shows a relative wide range from 135 to 2384 $\mu S/cm$, with a mean value of 699 $\mu S/cm$. The computed 5 % trimmed mean EC of 644 $\mu S/cm$, which is quite different from the mean EC value (699 $\mu S/cm$) suggest that computed statistical measures could be affected by extreme outliers. The presence of extreme EC values, can be linked to groundwater samples located close to the coastal lagoon, and also due to the contamination activities in the study area.

Similarly, TDS shows same pattern as EC values. TDS values range from 59 to 1142.60 mg/L, and a mean value of 355 mg/L. However, the high standard deviations observed for EC (±551) and TDS (±273), suggests a large spatial variability in ionic concentrations in groundwater sampled from the area. The large spatial differences may be attributed to the lithological variations and local impact of agricultural and anthropogenic activities in the region (Tiwari and Singh, 2014).

Generally, Na^+ is the most dominant cation in the groundwater, followed by; Ca^{2+}, K^+ and Mg^{2+} having the lowest concentration amongst the anions. Also, Cl^- is the dominant anion in the groundwater, followed by ${SO_4}^{2-}$, ${HCO_3}^-$, ${NO_3}^-$ and ${SiO_4}^{4-}$ having the lowest concentration amongst the anions (Table 6.1). Overall, Cl^- is the most dominant ion, next is Na^+, ${SO_4}^{2-}$, ${HCO_3}^-$, Ca^{2+}, and K^+, ${NO_3}^-$, ${SiO_4}^{4-}$, Mg^{2+} having a relative lower concentration (below 10 mg/L) compared to other ions constituents in the groundwater.

Chloride (Cl^-) in groundwater may originate from both natural and anthropogenic sources. Also, atmospheric precipitation, dissolution of salt deposits and weathering of halite and evaporite are considered as the major lithogenic source of chloride in the groundwater. In addition, Possible anthropogenic source of chloride are septic, industrial and animal wastes, fertilizers and leachates from landfill and waste dumps (Appelo and Postma, 2004). The Cl^- concentration of groundwater sampled at different locations in the study area, varied between 17.20 and 527.00 mg/L with and average of 116.61 mg/L (contributing 54.23 % of total anions in meq/L). The huge variations and high concentrations of chloride in most sampled groundwater in the area can be traced to local recharge and leaching of saline constituents from anthropogenic contributions in the area (industrial contaminated wastewaters in water channels and some localized agricultural wastes).

On the other hand, concentration of sulphate (${SO_4}^{2-}$) varies from 1.19 to 192.00 meq/L) with an average of 64.93 meq/L (contributing 28.42 % of total anions in meq/L). Sulphate concentration in natural water is usually found between 2 and 80 mg/L, and higher concentration may be attributed to weathering of sulphide minerals or anthropogenic sources like industrial and agricultural effluents (Berner-Kay and Berner, 1987). Therefore, the large concentrations of sulphate observed in some of the sampled groundwater in the area, can be traced to untreated industrial effluents (through contaminated water channels) released into the environment in the past.

6.1.2 Trace element geochemistry

Trace elements are characterized by concentrations lower than 1 mg/L in natural waters. This means that trace elements are not considered when “total dissolved solids” are calculated in rivers, lakes, or groundwaters, because their combined mass is not significant compared to the sum of Na^+, K^+, Ca^{2+}, Mg^{2+}, ${SiO_4}^{4-}$, ${HCO_3}^-$, ${CO_3}^{2-}$, ${SO_4}^{2-}$, Cl^-, and ${NO_3}^-$ (Nielsen, 2003). In addition, Nielsen (2003) opined that, most of the elements, except about ten of them, occur at trace levels in natural waters. However, being trace elements in natural waters does not necessarily qualify them as trace elements in rocks. For example, aluminum, iron, and titanium are major elements in rocks, but they occur as trace elements in waters, due to their low mobility at the Earth’s surface. Conversely, trace elements in rocks such as chlorine and carbon are major elements in waters (Nielsen, 2003).

Table 6.2: Descriptive statistical summary of trace elements hydrochemistry of water samples collected at different locations in the study area compared with WHO and Portuguese drinking water standards

Chemical Parameters	**Statistical Parameters**							
	N	**Min.**	**Max.**	**Median**	**Mean**	**SD**	**Portuguese standard 2007**	**WHO standard 2017**
Copper (Cu)	25	0.1	434.0	1.7	20.8	86.3	2.0	2.0
Zinc (Zn)	25	0.4	4590.0	9.3	240.3	913.2	3.0	3.0
Iron (Fe)	25	7.1	9130.0	20.0	983.2	2224.2	0.3	0.2
Manganese (Mn)	25	0.10	1380.00	77.60	195.50	303.1	0.05	0.05
Lead (Pb)	25	0.10	1.98	0.34	0.45	0.40	0.05	0.01
Arsenic (As)	25	0.02	544.0	0.4	22.6	0.9	0.01	0.01
Cadmium (Cd)	25	0.01	8.20	0.05	0.61	0.30	0.005	0.003
Antimony (Sb)	25	0.01	17.60	0.08	0.99	0.28	0.01	0.01
Barium (Ba)	25	2.4	250.0	31.4	43.3	35.7	NM	1.3
Rubidium (Rb)	25	2.2	58.7	19.9	19.3	18.2	NM	NM
Aluminium (Al)	25	1.41	2000.00	19.00	136.77	125.00	0.20	0.10
Nickel (Ni)	25	0.21	8.20	0.30	1.35	2.85	0.02	0.07
Boron (B)	25	15.0	176.0	84.0	79.3	90.5	NM	2.4
Selenium (Se)	25	0.20	4.10	0.45	0.92	1.53	0.01	0.01
Strontium (Sr)	25	0.03	381.00	90.10	115.49	107.42	NM	NM

Values of trace elements are given in ($\mu g/L$) concentration unit; **N** - Sample size; **NM** - Not Mentioned; **SD** - Standard deviation; **WHO** - World Health Organization

Water analysis performed by Activation laboratories in Ontario, Canada using the inductively coupled plasma mass spectrometry (ICP-MS) method; reported the presence of some trace elements in the groundwater samples. These trace elements include: Copper (Cu), Zinc (Zn), Iron (Fe), Manganese (Mn), Lead (Pb), Arsenic (As), Cadmium (Cd), Antimony (Sb), Barium (Ba), Rubidium (Rb), Aluminium (Al), Strontium (Sr), Nickel (Ni), Boron (B), and others.

Most of the elements reported were below detection limits and therefore not included in subsequent analysis. Summary statistics of the various trace elements concentration shown in Table 6.2, implies that only four of the trace elements (Al, Fe, Zn and Mn) have maximum concentration above 1 mg/L.

But some of these trace elements when injested in small concentrations can be toxic for humans and animals, and could eventually lead to damage of cells and organ dysfunction. Therefore, only trace elements that have been linked to some health conditions (negative) were further analysed, based on World's health organization (WHO) and Portuguese drinking water standards. Result of the comparative analysis of the concentrations of trace elements and other chemical parameters in each groundwater samples are considered in subsequent interpretation (Drinking water quality: section 6.1.5.1).

Comparison of trace elements observed in sampled groundwater in the area with the WHO/Portuguese standards shows, Iron (Fe) and Manganese (Mn) are in excess of 0.69 and 0.15 mg/L respectively. Similarly, Arsenic (As) and Aluminium (Al) are in excess of 0.01 and 0.04 mg/L (negligible amounts) respectively. Therefore, the excess of these four trace elements (Fe, Al, Mn and As), shows that they are being enriched in the sampled groundwater from the area.

Enrichment of Aluminium (Al) can be traced to weathering/alteration of feldspar to clay minerals (kaolin), and dissolution or leaching of Al by infiltrating acidic recharge waters into the shallow aquifer system in the area. Langmuir (1997) stated that natural water having pH values between 4.5 and 7 produces weak carbonic acids and small amount of organic acids such as the fulvic acids.

On the other hand, with the fact that both Fe and Mn occur together in rocks, there is a high chance of them being released and leached into the shallow aquifer in the area, especially under increasing acidic pH as with the case of the measured pH of groundwater in the area.

Overall, the quantity of trace metals present in the sampled groundwater is generally low compared with the WHO/Portuguese standard. As such, may have resulted from the low pH (Table 6.1) where most natural groundwater are mobile and the mass occur as charged metal ion which reach equilibrium with the solid phase usually a metal-hydroxide, metal-carbonate or metal sulphide (Domenico et al., 1998).

6.1.3 Multivariate statistical analyses

Further analysis using two multivariate statistical methods, were applied to determine the relationships that could exist amongst chemical parameters from sampled groundwater in the study area. As such,it can serve as an indicator to further understand different hydrogeochemical processes (natural or anthropogenic), impacting the groundwater chemistry in the area.

6.1.3.1 Correlation of chemical parameters

Correlation analysis can be used to establish relationships that exist between physico-chemical characteristics of water samples, which can reveal the origin of solutes and the process that generated the observed water compositions (Parizi and Samani, 2013).

Correlation analysis (Table 6.3), was implemented using the Pearson's correlation coefficient for Electrical conductivity (EC), pH, Total dissolved solids (TDS), Total hardness (TH), Nitrate NO_3^-, major ions and some selected trace elements (Copper (Cu), Zinc (Zn), Iron (Fe), Manganese (Mn) and Arsenic (As)). The Pearson's relationship coefficient values ranged from +1 to -1. A value close to +1 indicates a perfect correlation, ± 0.75 to ± 1 is a high degree of correlation, ± 0.25 to ± 0.75 is a moderate degree of correlation, and ± 0 to ± 0.25 shows a low degree of correlation. pH shows a moderate degree of correlation (0.48) with K^+, and high degree of correlation (0.83) with HCO_3^-.

TDS shows a high degree of correlation with; EC (0.99), Na^+ (0.96), Cl^- (0.96), and SO_4^{2-} (0.82). Similarly, total hardness (TH) shows a high degree of correlation with; K^+ (0.77), Ca^{2+} (0.97), Mg^{2+} (0.77), but moderate correlation with HCO_3^- (0.53), NO_3^- (0.49), and negatively correlated with Fe (-0.44).

EC shows high positive correlation with; Na^+ (0.98), Cl^- (0.97), and $SO_4{}^{2-}$ (0.83). In addition, other major ions and trace elements shows moderate to strong correlation; for example, Na^+ - Cl^- (0.98), Na^+ - $SO_4{}^{2-}$ (0.79), K^+ - Ca^{2+} (0.98), K^+ - Mg^{2+} (0.79), K^+ - $HCO_3{}^-$ (0.48), K^+ - $NO_3{}^-$ (0.54), Ca^{2+} - Mg^{2+} (0.60), Ca^{2+} - $HCO_3{}^-$ (0.49), Ca^{2+} - $NO_3{}^-$ (0.53), Ca^{2+} - Fe (-0.50), Mg^{2+} - $HCO_3{}^-$ (0.45), $SiO_4{}^{2-}$ - Fe (0.73), Cl^- - $SO_4{}^{2-}$ (0.75), $NO_3{}^-$ - Fe (0.54), and Cu - Zn (0.99).

The high correlation between pH and $HCO_3{}^-$ indicates the possibility of chemical equilibrium between pH and dissolution of carbonates. Hence, it could be a process of CO_2 dissolving to form carbonic acid. Nevertheless, the carbonic acid can later dissociate to form bicarbonate ($HCO_3{}^-$) and hydrogen ion (H^+), depending on the buffering capacity of the groundwater at different locations in the study area. Similarly, EC and TDS, shows same pattern of strong relationship with Na^+, Cl^-, and $SO_4{}^{2-}$. Thus, this strong relationship suggests that, these ions contribute the most to the constituent ions in the groundwater and dominate the driving groundwater chemistry in the study area.

The moderate to high positive correlation observed between Na^+ - Cl^-, K^+ - $HCO_3{}^-$, Mg^{2+} - $HCO_3{}^-$, K^+ - Ca^{2+}, K^+ - Mg^{2+} (Table 6.3), reveals the possibility of predominance weathering and leaching processes in the study area. On the other hand, (Cl^-) shows a good correlation with Na^+ and Mg^{2+}; which could imply the leaching of secondary salts.

Also, a positive correlation of $HCO_3{}^-$ with Mg^{2+}, and K^+ indicates the possibility of chemical weathering process as suggested by Srinivasamoorthy et al. (2011). On the other hand, a good correlation was achieved between Ca^{2+}, Cl^-, $HCO_3{}^-$, Na^+, K^+ and $SO_4{}^{2-}$; signify the possibility of anthropogenic (possibly on-going contamination activities) influence on the aquifer.

According to Li et al. (2013a), it should be noted that chemical reactions that occur in a groundwater system are very complex, and many reactions are involved. As such, correlation analysis, though very useful, can only provide a general insight into water rock interaction. Nevertheless, if one wants to know more about the reactions taking place in a groundwater system, more comprehensive analysis, such as aquifer mineralogy are needed.

Table 6.3: Pearson's correlation matrix and Significant (2-tailed p-value) of groundwater sample chemistry collected from different location in the study area

	pH	**TDS**	**TH**	**EC**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**SiO_4^{4-}**	**Cl^-**	**HCO_3^-**	**SO_4^{2-}**	**NO_3^-**	**Cu**	**Zn**	**Fe**	**Mn**	**As**
pH	1.00																	
TDS	0.27	1.00																
TH	0.36	0.09	1.00															
EC	0.23	__0.99**__	0.02	1.00														
Na^+	0.12	__0.96**__	-0.13	__0.98**__	1.00													
K^+	__0.48*__	0.12	__0.77**__	0.06	-0.03	1.00												
Ca^{2+}	0.33	0.09	__0.97**__	0.03	-0.12	__0.67**__	1.00											
Mg^{2+}	0.34	0.05	__0.77**__	-0.03	-0.11	__0.79**__	__0.60**__	1.00										
SiO_4^{4-}	0.23	-0.15	-0.05	-0.17	-0.15	-0.14	-0.09	0.07	1.00									
Cl^-	0.13	__0.96**__	-0.15	__0.97**__	__0.98**__	-0.07	-0.13	-0.15	-0.14	1.00								
HCO_3^-	__0.83**__	0.31	__0.53**__	0.24	0.09	__0.48*__	__0.49*__	__0.47*__	0.09	0.11	1.00							
SO_4^{2-}	-0.07	__0.82**__	0.14	__0.83**__	__0.79**__	0.03	0.14	0.07	-0.22	__0.75**__	0.04	1.00						
NO_3^-	0.03	-0.10	__0.49*__	-0.08	-0.11	__0.54**__	__0.53**__	0.21	-0.16	-0.16	-0.12	-0.10	1.00					
Cu	-0.32	-0.07	-0.17	-0.08	-0.04	-0.28	-0.17	-0.12	-0.01	-0.05	-0.17	0.10	-0.26	1.00				
Zn	-0.36	-0.04	-0.17	-0.04	0.01	-0.27	-0.16	-0.13	-0.01	-0.01	-0.22	0.14	-0.24	__0.99**__	1.00			
Fe	0.08	-0.04	__-0.44*__	-0.05	0.02	-0.35	__-0.50*__	-0.14	__0.73**__	0.05	-0.06	-0.10	__-0.54**__	0.24	0.24	1.00		
Mn	-0.16	0.02	0.09	0.01	0.02	-0.09	0.10	0.03	-0.19	0.03	-0.09	0.07	-0.07	0.21	0.23	-0.07	1.00	
As	0.08	-0.09	-0.04	-0.08	-0.10	-0.14	-0.03	-0.08	-0.11	-0.11	0.08	-0.03	-0.23	-0.00	-0.03	-0.01	-0.07	1.00

Values of variables are given in mg/L except for EC (Electrical conductivity, $\mu S/cm$), pH (-)
TDS - Total Dissolved Solids; **TH** - Total Hardness; **EC** - Electrical Conductivity
* Correlation is significant at the 0.05 level (2-tailed)
** Correlation is significant at the 0.01 level (2-tailed)

6.1.3.2 Principal Component Analysis (PCA)

The correlation amongst chemical parameters using the pearson's correlation matrix (Table 6.3) showed that, a number of parameters were strongly correlated with more that one chemical constituents analysed. PCA, the correlations amongst variables are used to estimate principal components (PCs) with common associations and associated constituent loadings on the principal component axis (Lucas and Jauzein, 2008). Also, PCA can be used to reduce observations into principal components (PCs), through which relationships between hydrochemical variables can be identified. These components can be used to understand the dominant mechanisms controlling groundwater chemistry (Salifu et al., 2012).

Table 6.4: Summary of principal component loadings (-), eigen values (-), and explained variances of hydrochemical parameters for five principal components with varimax normalized rotation (VNR)

Chemical Parameters	**Principal components (PCs)**				
	PC1	**PC2**	**PC3**	**PC4**	**PC5**
pH	-	**0.565**	-0.394	0.399	0.365
TDS (mg/L)	**0.988**	-	-	-	-
TH (mg/L)	-	**0.941**	-	-	-
EC ($\mu S/cm$)	**0.944**	-	-	-	-
Na^+ (mg/L)	**0.981**	-	-	-	-
K^+ (mg/L)	-	**0.855**	-	-	-
Ca^{2+} (mg/L)	-	**0.873**	-	-0.276	-
Mg^{2+} (mg/L)	-	**0.839**	-	-	-
${SiO_4}^{4-}$ (mg/L)	-	-	-	**0.866**	-
Cl^- (mg/L)	**0.977**	-	-	-	-
${HCO_3}^-$ (mg/L)	-	**0.693**	-	0.269	0.469
${SO_4}^{2-}$ (mg/L)	**0.853**	-	-	-	-
${NO_3}^-$ (mg/L)	-	0.401	-	-0.434	**-0.558**
Copper (Cu)	-	-	**0.968**	-	-
Zinc (Zn)	-	-	**0.974**	-	-
Iron (Fe)	-	-0.294	-	**0.876**	-
Arsenic (As)	-	-	-	-	**0.811**
Total eigenvalues	4.868	4.537	2.185	1.902	1.260
Explained variance (%)	26.634	26.688	12.854	11.186	7.413
Cumulative variance (%)	28.634	55.323	68.177	79.364	86.776

Values of trace elements are given in **mg/L**; the highlighted and underlined values are loadings that are significant (> 0.5); **(-)** - indicate values of loadings below ±0.15 (suppressed during PCA computation in SPSS); **PC** - Principal component; **TDS** - Total Dissolved Solids; **TH** - Total Hardness; **EC** - Electrical Conductivity

Hence, the PCA technique was applied to 18 parameters; pH, total dissolved solids (TDS), total hardness (TH), electrical conductivity (EC), all major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, $SiO_4{}^{4-}$, Cl^-, $HCO_3{}^-$, $SO_4{}^{2-}$, $NO_3{}^-$) and some selected trace elements (Copper (Cu), Zinc (Zn), Iron (Fe), Manganese (Mn), and Arsenic (As)).

Factor analysis using the principal component analysis (PCA) as the extraction method, was implemented using SPSS 25.0 statistical software. Principal component analysis in SPSS is done in two major steps; first a check is done to determine which of the parameters can be used for the next step. The first check output of SPSS, uses the condition that a parameter can only be used only if the value of communalities is greater than 0.5. As such, after this test, manganese (Mn) value (0.258) was below the expected value (0.5).

Therefore, manganese was not included in the next step of the principal component analysis using varimax normalized rotation (VNR). Moreover, after the second step of PCA using the selected parameters (extraction value grater than 0.5), five uncorrelated principal components with eigen value grater than 1; explaining 87 % of the total variance in the hydrochemical parameters (Table 6.4).

The first two principal components explain 28.6 and 26.7 % of the variance, respectively, accounting for most of the variance explained. Also, principal component three (PC3), (PC4) and (PC5) explain the least, 12.9 %, 11.2 %, and 7.4 % respectively of the total variance. Principal component one (PC1) shows significantly high positive PCA loadings for TDS, EC, Na^+, Cl^-, and $SO_4{}^{2-}$. Therefore, the dominance of Na^+, Cl^-, and $SO_4{}^{2-}$ is indicative of anthropogenic contribution (contamination) of groundwater in the area, whereas the significant presence of TDS and EC indicates that these ions are the major contributors to the ions in the groundwater.

Contamination activities in the area can be linked to infiltration of contaminated water in unlined channels used to discharge industrial effluents in the past. The second principal component (PC2) shows significantly high positive PCA loadings for pH, TH, K^+, Ca^{2+}, Mg^{2+}, and $HCO_3{}^-$. As such, the dominance of pH and $HCO_3{}^-$ is indicative of the ongoing acidifying processes in groundwater chemistry; which could be among the cause of acidic groundwater in the area as explained in section 6.1.1.

In addition, significant dominance of K^+, Ca^{2+}, and Mg^{2+}; indicates one of the trends influencing groundwater chemistry in the area, most likely the dominance by dissolution of carbonates and silicates minerals. Also, this dissolution process could be followed by strong cation exchange processes as explained in section 6.1.4.3. Therefore, principal component two (PC2) is indicative of ongoing acidifying process, followed by dissolution processes (of carbonates and silicates), and then cation exchange processes in the groundwater.

Principal components three, four and five (PC3, PC4 and PC5), explained the least variance of 12.9 %, 11.2 % and 7.4 % respectively, compared to other principal components. Therefore, the significant dominance of Copper (Cu) and Zinc (Zn) in PC3 is indicative of trace elements influence on the groundwater chemistry. Similarly, the significant dominance of $SO_4{}^{2-}$ and Iron (Fe) in PC4 is indicative of chemical rock weathering of these minerals. Moreover PC5 with negative and positive loading factors for NO_3^- and Arsenic (As) respectively; indicates the low influence agricultural activities (major source of nitrate) in groundwater sampled from the area.

Generally, the most common acid generation processes in groundwater include acid rain recharge, nitrification following wastewater infiltration and oxidation of organic matter or sulphide minerals such as pyrite FeS_2 (Appelo and Postma, 2004). Therefore, the PCA analysis indicates that; anthropogenic contamination from infiltration of industrial effluents discharged in the past, and groundwater acidification processes are the dominant processes affecting groundwater chemistry in the area.

6.1.4 Hydrochemical facies and processes

Chemical processes on-going in the aquifer as groundwater interacts with the environment can further be understood by making diagrams such as piper and Durov plots of chemistry data. Piper's diagram illustrates the scatter plots of the cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) and anions (HCO_3^-, Cl^-, and SO_4^{2-}) classifying the hydrochemical characteristics (Piper, 1944).

A large portion of groundwater samples collected from different locations in the study area are mostly dominated by; Cl^-, followed by SO_4^{2-}, and HCO_3^- having the lowest abundance ($Cl^- > SO_4^{2-} > HCO_3^-$). However, cation in the sampled groundwater is dominated by; Na^+, followed by Ca^{2+}, K^+, and then Mg^{2+} ($Na^+ > Ca^{2+} > K^+ > Mg^{2+}$).

Five main water types can be clearly identified from the piper scatter plot (Figure 6.1), which are; Ca^{2+}-HCO_3^- ($Ca(HCO_3)_2$ water type), Mixed Ca^{2+}-Mg^{2+}-Cl^- ($CaCl_2$ and $MgCl_2$ water types), Ca^{2+}-Cl^- ($CaCl_2$ water type), Na^+-Cl^--SO_4^{2-} (NaCl and Na_2SO_4 water types) and Ca^{2+}-Na^+-HCO_3^- ($Ca(HCO_3)_2$ and $NaHCO_3$ water types).

In addition, the central diamond-shaped field (Figure 6.1) suggests that, strong acids exceed weak acids water types in most of the groundwater samples plotted on the piper diagram. As such, it is in line with the measured pH values for most of the groundwater samples (slightly acidic to acidic waters) in the study area. Therefore, it shows that acidic waters in different water channels located in the study area have significant influence on the groundwater chemistry (acidic water contamination).

The observed dominant hydrochemical facies of sampled groundwater in the area; with Na^+-Cl^--SO_4^{2-} accounting for 60 %, mixed Ca^{2+}-Mg^{2+}-Cl^- - 28 %, and 4 % for Ca^{2+}-HCO_3^- and Ca^{2+}-Cl^-. Hence, it can be inferred that, groundwater chemistry in the area is greatly influenced by Na^+ and Cl^- ions; which can be linked to sea water intrusion (a major source of Cl^- ions). Also, Li et al. (2013a) suggested that, the dissolution of halite is probably one of the most important sources of Na^+.

The Concentration of Na^+ in proportion to Cl^- ions, suggest the influence of other factors contributing to Na^+ concentration in the groundwater. As such, Na^+ can be influenced by cation exchange processes between Ca^{2+} or Mg^{2+} (most likely from industrial effluents discharged into the environment over the years). In addition, Ria de Aveiro lagoon is the closest source of salt water that can influence groundwater chemistry in the area. But only four out of the 24 sampled groundwater (Appendix F) are closest to the lagoon (possible influence on the groundwater chemistry). On the other hand, the remaining groundwater samples are quite distant from the lagoon, suggesting the influence of other contamination sources. As such, (Appendix F) shows that, most of the sampled groundwater are located close to one or more water channels (contaminated) in the area. In addition, since all groundwater samples were collected from the shallow aquifer in the area; therefore the contribution of surface water to groundwater chemistry is certain and vice-versa.

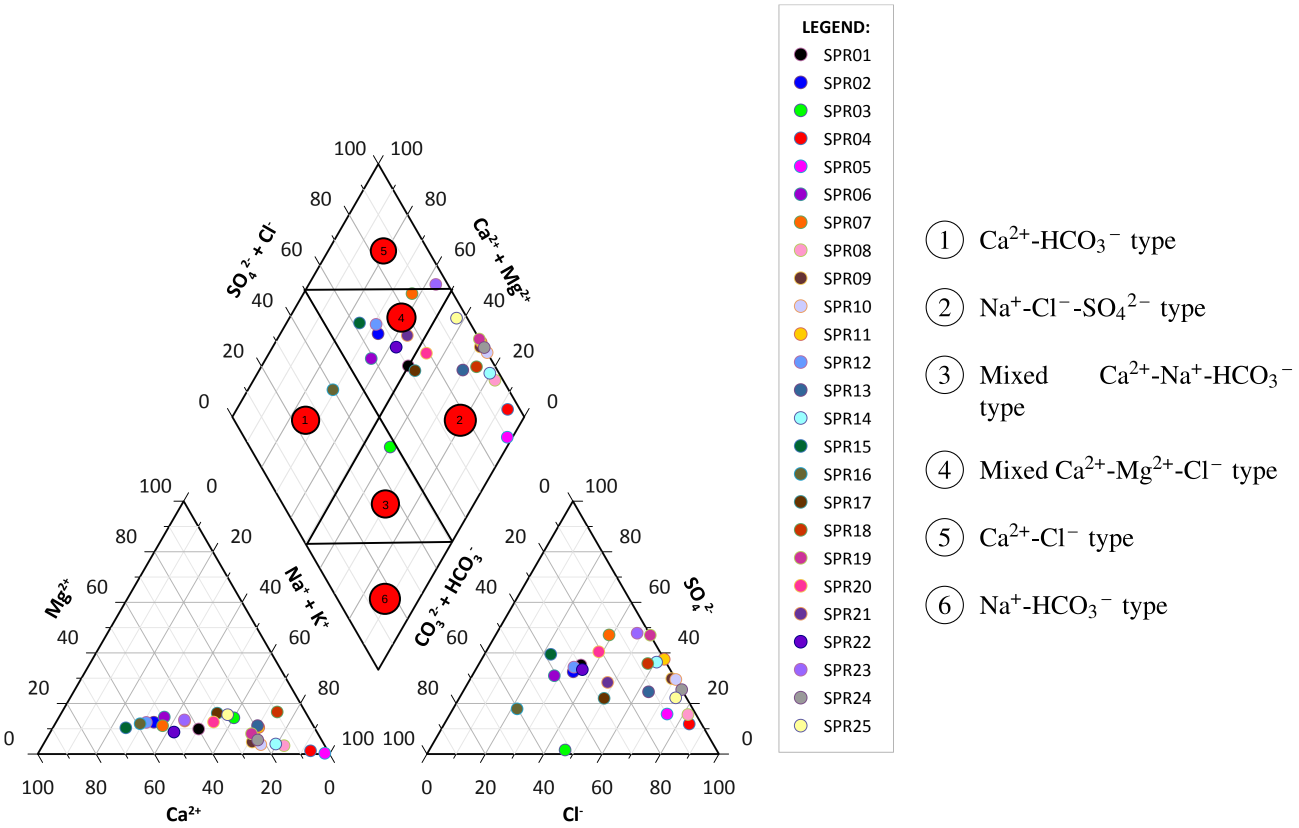


Figure 6.1: *Piper plot of major ions hydrochemistry and corresponding piper classifications of water sampled from the study area*

Likewise, Durov plot (Figure 6.2), further explains possible chemical processes on-going in the aquifer. The fact that ion exchange and simple dissolution or mixing water types dominates in the study area, can be seen as 88 % of sampled groundwater are plotted in region of fields 4 and 5 (Figure 6.2).

According to Lloyd and Heathcode (1985) classification, the pattern of chemistry can be attributed to recharged water of gypsiferous deposits, otherwise mixed or exhibiting simple dissolution. In addition, three (12 %) of the groundwater samples plots on the region of field 2; indicating water type dominated by Ca^{2+} and HCO_3^- ions. This can be associated with dolomite for those samples which Mg^{2+} is significant. However, since most groundwater samples are dominated by Na^+ ion, an important ion exchange is presumed.

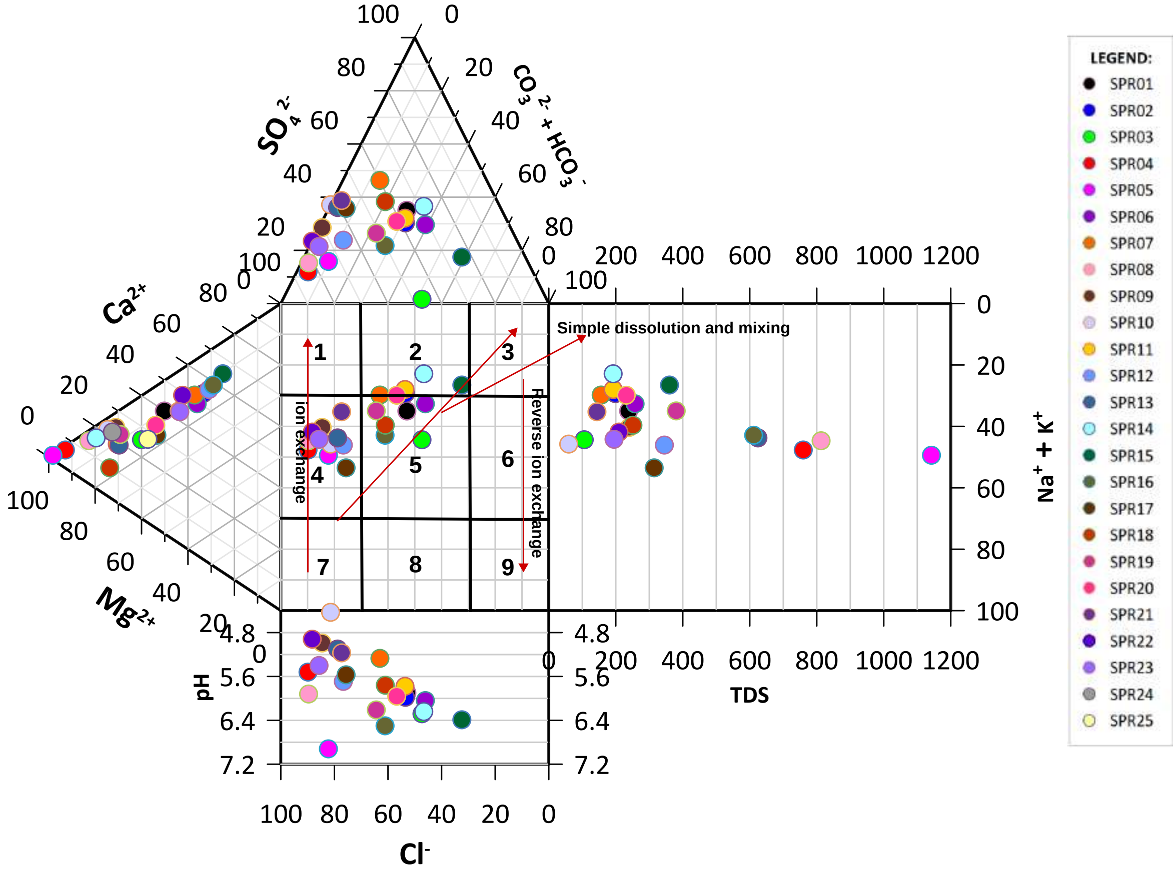


Figure 6.2: *Durov plot explaining the major hydrochemical processes controlling the chemistry of water sampled from the study area (Lloyd and Heathcode, 1985)*

6.1.4.1 Chloro-alkaline Indices (CAI)

Ion exchange occurring between groundwater and the host environment, either during residence or movement processes poses as influential controlling factors towards water chemistry (Shamsuddin et al., 2019). Ion exchange is of great significance in the evolution of hydrochemical compositions (Peiyue et al., 2011).

Ion exchange can be studied through chloro-alkaline indices proposed by Schoeller (Li et al., 2013b; Marghade et al., 2012). The Schoeller indices, such as CAI-I and CAI-II (Equations 6.2 and 6.3) respectively were calculated (all ions expressed in meq/L) to determine the ion exchange processes occurring in the sampled groundwater. Interpretation of the Schoeller indices follows that; if negative values for the Schoeller indices (Equations 6.2 and 6.3) are obtained, Ca^{2+} and Mg^{2+} have been removed from solution, and Na^+ and/or K^+ have taken their place in the solution. However, if the calculated indices are positive, then the reverse reaction have taken place.

$$CAI-I \quad = \quad \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \tag{6.2}$$

Table 6.5: Summary of schoeller (chloro-alkaline) indices values of water sampled from different locations in the study area

Sample ID	CAI-I	CAI-II	Sample ID	CAI-I	CAI-II	Sample ID	CAI-I	CAI-II
SPR01	-0.52	-0.38	SPR10	0.02	0.07	SPR19	-0.29	-0.65
SPR02	-0.51	-0.30	SPR11	-0.11	-0.34	SPR20	-0.94	-0.78
SPR03	-0.21	-0.18	SPR12	-0.44	-0.25	SPR21	-0.32	-0.33
SPR04	0.17	1.40	SPR13	-0.40	-0.93	SPR22	-0.86	-0.57
SPR05	0.02	0.07	SPR14	-0.31	-0.86	SPR23	-1.04	-0.97
SPR06	-0.82	-0.38	SPR15	-0.78	-0.27	SPR24	-0.63	-2.22
SPR07	-0.14	-0.14	SPR16	-0.76	-0.23	SPR25	-0.03	-0.14
SPR08	-0.21	-1.35	SPR17	-0.26	-0.32			
SPR09	-0.39	-1.30	SPR18	-0.51	-1.21			

CAI-I - chloro-alkaline index I; **CAI-II** - chloro-alkaline index II

$$CAI-II = \frac{Cl^- - (Na^+ + K^+)}{HCO_3^- + SO_4^{2-} + CO_3^{2-} + NO_3^-} \tag{6.3}$$

Furthermore, 88 % of groundwater samples collected from different locations in the study area, showed negative CAI-I and CAI-II values (Table 6.5). The obtained negative values for CAI-I and CAI-II, suggests chloro-alkaline disequilibrium and cation-anion exchange reactions in the groundwater. On the contrary, only three (12 %) out of the 25 collected groundwater samples from the study area, had positive CAI-I and CAI-II values. Therefore, these three groundwater samples (SPR04, SPR05, SPR10) suggest a base-exchange reaction.

6.1.4.2 Enrichment of ions

The possible sources of ions explaining groundwater interaction with rocks found in the study area, can be explained by computing ratios in mmol/L for different ions found in the sampled groundwater. Hence, explanation regarding the source of ions and rocks influencing groundwater chemistry as given in (Appendix E) are as follows:

(a) Ratio showing relationship between Na^+ and $Na^+ + Cl^-$ ($Na^+/(Na^+ + Cl^-)$), can be indicative of possible contribution of sea water. As such, ratios higher than 0.5 are indicative of sea water contribution and lower ratios suggest otherwise. In this regard, twenty-two (88 %) of the sampled groundwater from the area showed ratio higher than 0.5; signifying the influence of sea water in the aquifer. However, it was earlier stated that, only four of the sampled groundwater can be strongly linked to the influence of salt water from the lagoon, and the remaining samples to other sources (anthropogenic influence from contaminated surface water in channels) in the area.

(b) According to Shamsuddin et al. (2019), ratio values of $Mg^{2+}/(Ca^{2+}+SO_4{}^{2-})$ found to be less than 0.5 are indicative of more contributory influence of calcite and gypsum compared to dolomite, and ratios above 0.5 suggest otherwise. Therefore, since 90 % of computed ratios showed values lower than 0.5, it further affirms the fact that, sea water is not the major source (only source) of salt water controlling groundwater chemistry in the aquifer, but other sources (anthropogenic contribution from contaminated surface water in channels located at different part of the study area) exist as clearly described by the Durov plot shown in Figure 6.2.

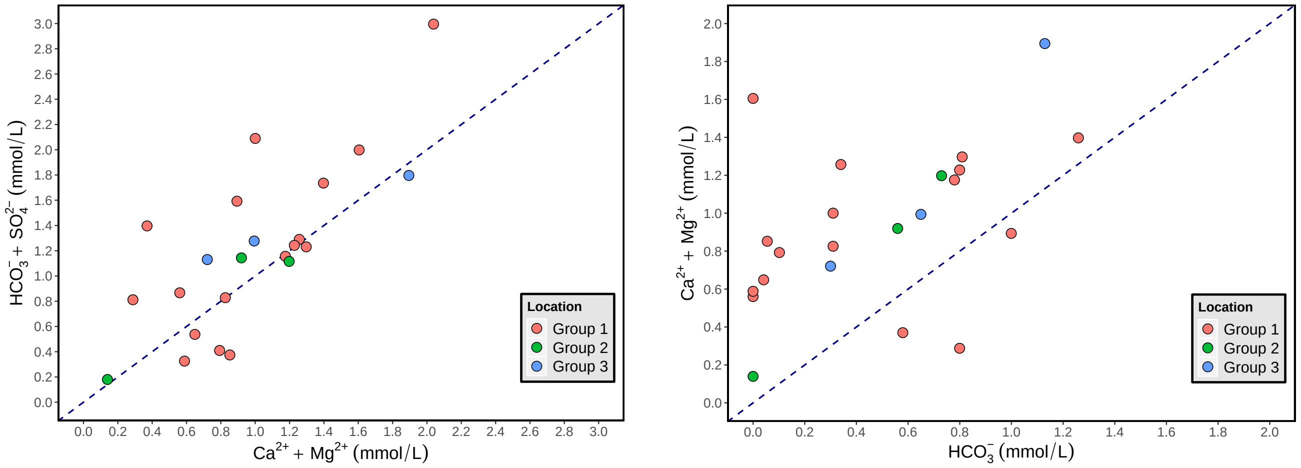
(c) Ratio values of $Mg^{2+}/(Ca^{2+}+Mg^{2+})$ that is bigger than 0.5 are indicative of dolomite dissolution and calcite precipitation, whereas a value less than 0.5 is indicative of limestone–dolomite weathering (Shamsuddin et al., 2019). The result of computed ratio shows that 96 % of groundwater samples have values less than 0.5; indicating limestone-dolomite weathering process in the area.

(d) According to Shamsuddin et al. (2019), ratio values of $Cl^{-}/\sum$anions less than 0.8 is indicative of rock weathering. Therefore, since all (80 %) except five of the groundwater sample showed ratio less than 0.8; suggesting rock weathering as the dominant process in the aquifer found in the area.

(e) Ratio value of $HCO_3^{-}/\sum$anions less than 0.8 is suggestive of seawater and brine, and ratio above 0.8 suggest otherwise. Therefore, since all groundwater sample showed ratio less than 0.8; suggesting that groundwater in the area have chemistry similar to seawater.

6.1.4.3 Processes controlling groundwater chemistry

Processes influencing groundwater chemistry in the area can be further understood by analysing relationship between various ions in sampled groundwater. Also, these relationships can further give insight into possible rock-groundwater interactions on-going in the aquifer system.



(a) $(Ca^{2+}+Mg^{2+})$ versus $(HCO_3{}^{-}+SO_4{}^{2-})$

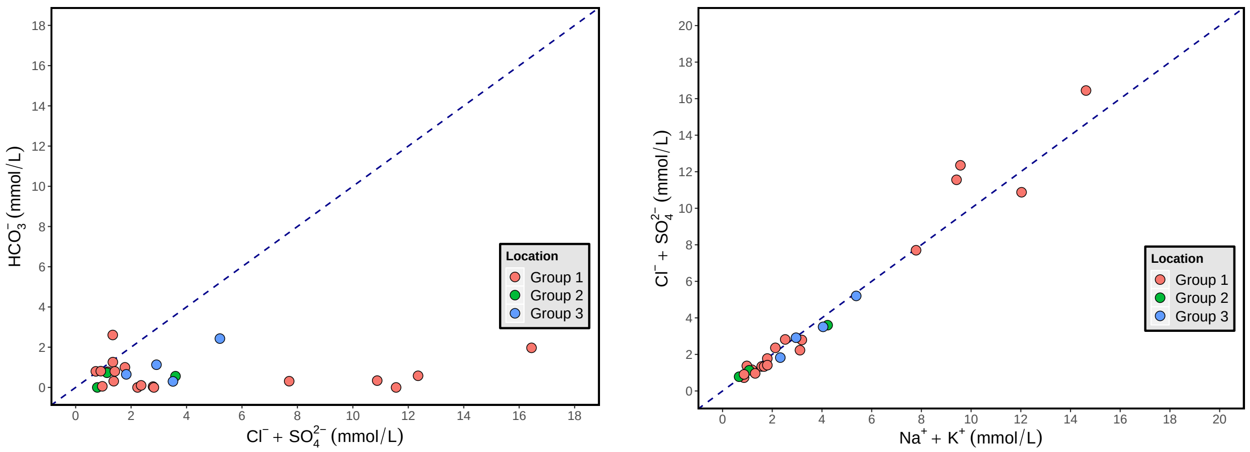
(b) $HCO_3{}^{-}$ versus $(Ca^{2+}+Mg^{2+})$

Figure 6.3: *Scatter plots of 1:1 equiline: (a) $(Ca^{2+}+Mg^{2+})$ versus $(HCO_3{}^{-}+SO_4{}^{2-})$; and (b) $HCO_3{}^{-}$ versus $(Ca^{2+}+Mg^{2+})$ explaining processes controlling groundwater chemistry in the area (**Group 1:** close to one of the official water channels, **Group 2:** close to the Ria Aveiro lagoon , **Group 3:** close to water channel South of Veiros lagoon)*

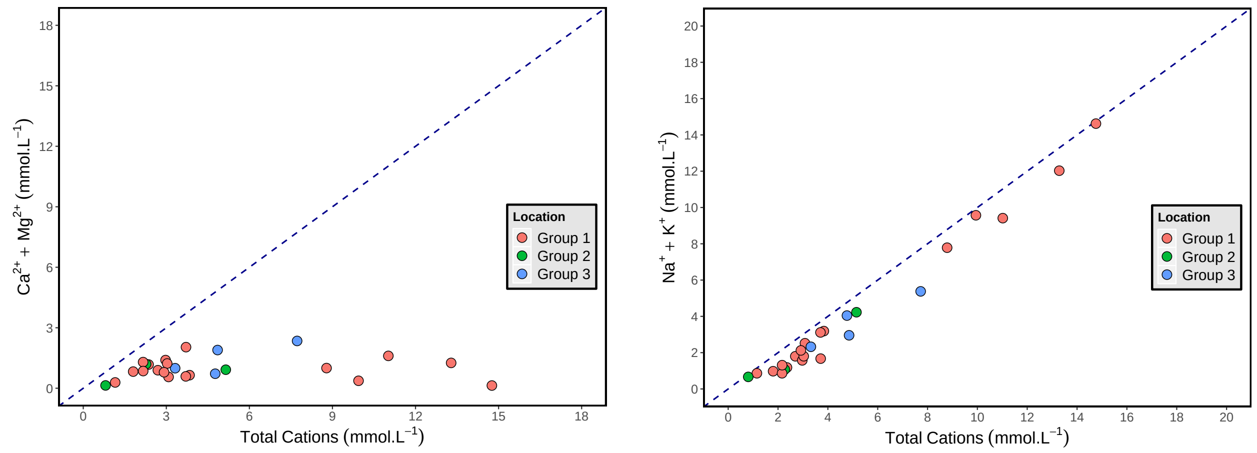
Lakshmanan et al. (2003); Barzegar et al. (2016), suggested that silicate weathering is demonstrated by the predominance of ($HCO_3{}^-$+$SO_4{}^{2-}$) over (Ca^{2+}+Mg^{2+}); whereas, reversed ion exchange can be suggested by the dominance of (Ca^{2+}+Mg^{2+}). Therefore, as shown in Figure 6.3a; there is dominance of ($HCO_3{}^-$+$SO_4{}^{2-}$) over (Ca^{2+}+Mg^{2+}) in most of the groundwater samples. As such, indicating silicate weathering process as one of the reactions affecting the groundwater chemistry in the area.

Fisher and Mullican III (1997) stated that, the plot of (Ca^{2+}+Mg^{2+}) versus ($HCO_3{}^-$+$SO_4{}^{2-}$) can be employed to distinguish the ion exchange processes that occur. Hence, in the case of a dominant ion exchange, the points will show a left-sided shift due to excessive ($HCO_3{}^-$+$SO_4{}^{2-}$), where as a reverse ion exchange occurring will result in a right-sided shift due to excessive (Ca^{2+}+Mg^{2+}) over ($HCO_3{}^-$+$SO_4{}^{2-}$). However, from the plot of (Ca^{2+}+Mg^{2+}) versus ($HCO_3{}^-$+$SO_4{}^{2-}$) (Figure 6.3a); a larger percentage of the samples fall below the equiline, suggesting a reverse ion exchange process dominating normal ion exchange process in the aquifer system.

Similarly, the plot of Ca^{2+}+Mg^{2+} versus $HCO_3{}^-$ (Figure 6.3b), shows all except two of the groundwater samples from group 1, fall above the 1:1 equiline. This indicates dominance of alkaline earth elements (Ca^{2+}+Mg^{2+}) over $HCO_3{}^-$, whereby the excess Ca^{2+} and Mg^{2+} ions are balanced by Cl^- and $SO_4{}^{2-}$ and/or supplied by silicate weathering (Zhang et al., 1995). On the other hand, two of the samples from group 1, plotted below the 1:1 equiline (Figure 6.3b), indicating that feldspar minerals react with carbonic acid in the presence of water to release $HCO_3{}^-$ (Lakshmanan et al., 2003). Overall, the plot for (Ca^{2+}+Mg^{2+}) versus $HCO_3{}^-$ of the groundwater samples shows that greater percentage fall below the equiline, indicating that, excessive $SO_4{}^{2-}$ should be balanced by (Ca^{2+}+Mg^{2+}) (Shamsuddin et al., 2019).



(a) $(Cl^-+SO_4{}^{2-})$ versus $HCO_3{}^-$ **(b)** (Na^++K^+) versus $(Cl^-+SO_4{}^{2-})$



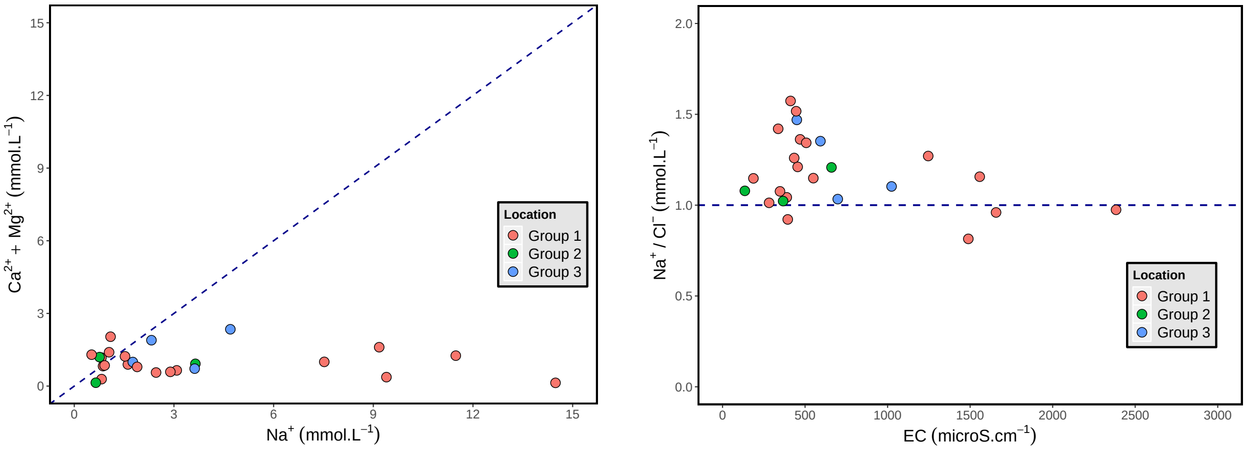
(c) Total cations versus $(Ca^{2+}+Mg^{2+})$ **(d)** Total cations versus (Na^++K^+)

Figure 6.4: *Scatter plots of 1:1 equiline: (a) $(Cl^-+SO_4{}^{2-})$ versus $HCO_3{}^-$; (b) (Na^++K^+) versus $(Cl^-+SO_4{}^{2-})$; (c) Total cations versus $(Ca^{2+}+Mg^{2+})$; and (d) Total cations versus (Na^++K^+); explaining processes controlling groundwater chemistry in the area (**Group 1:** close to one of the official water channels, **Group 2:** close to the Ria Aveiro lagoon , **Group 3:** close to water channel South of Veiros lagoon)*

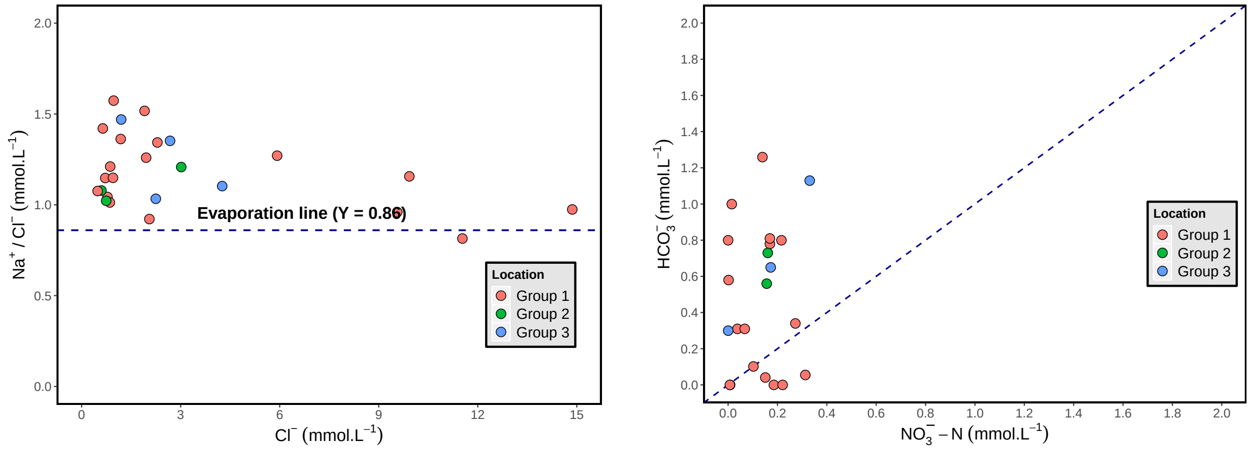
Plot of $HCO_3{}^-$ against $(Cl^-+SO_4{}^{2-})$, shows a dominance of $(Cl^-+SO_4{}^{2-})$ over $HCO_3{}^-$ at higher concentrations (Figure 6.4a) for all groups of groundwater samples plotted. Similarly, the plot of $(Cl^-+SO_4{}^{2-})$ against (Na^++K^+) shows most of the groundwater samples from all groups (Group 1, 2, and 3), plot close to and immediately above the 1:1 equiline (Figure 6.4b). This further confirms the dominance of (Na^++K^+) in the groundwater chemistry.

The plot of $(Ca^{2+}+Mg^{2+})$ against total cations (Figure 6.4c), shows all groundwater samples plotted below the 1:1 equiline, with more deviation away from the equiline at highet concentrations (Figure 6.4c). As such, it is indicative of increasing significant contribution of (Na^++K^+) with more dissolved solids (Shamsuddin et al., 2019). Also, increased alkaline influences can result in greater $(Cl^-+SO_4{}^{2-})$, elucidating its soil sources as $Na^+SO_4{}^{2-}$ and $K^+SO_4{}^{2-}$ (Shamsuddin et al., 2019). Additionally, higher Na^+ concentration found in the groundwater may also be due to silicate weathering (Singh and Hasnain, 1999).

The plot of (Na^++K^+) against total cation (Figure 6.4d), further confirms the fact that; there are higher ratios of cation present in the sampled groundwater, which is mainly due to silicate weathering, alkaline/saline soils, and residence time (Stallard and Edmond, 1987). According to Rocha (1993), the study area is dominated by fine sand with low clay components. He further stated that, quartz, plagioclase, potassium feldspar, calcite and dolomite are the principal minerals found in the study area. Therefore, with the reported mineralogical constituents of rocks and soils found in the area, coupled with the acidic nature of surface water and groundwater chemical weathering of silicate minerals dominating the groundwater chemistry is expected as observed in the sampled groundwater.



(a) Na^+ versus $(Ca^{2+}+Mg^{2+})$ **(b)** EC versus (Na^+/Cl^-)



(c) Cl^- versus (Na^+/Cl^-) **(d)** NO_3^--N versus HCO_3^-

Figure 6.5: *Scatter plots of 1:1 equiline: (a) Na^+ versus $(Ca^{2+}+Mg^{2+})$; (b) EC versus (Na^+/Cl^-); (c) Cl^- versus (Na^+/Cl^-); and (d) NO_3^--N versus HCO_3^-; explaining processes controlling groundwater chemistry in the area (**Group 1:** close to one of the official water channels, **Group 2:** close to the Ria Aveiro lagoon , **Group 3:** close to water channel South of Veiros lagoon)*

The plot of Na^+ against $(Ca^{2+}+Mg^{2+})$ (Figure 6.5a), further explains the influence of ion exchange on the groundwater chemistry. As such, values plotting above the 1:1 equiline indicates reverse ion exchange, whereas below suggests normal ion exchange process. (Figure 6.5a) shows most of group 1, 2 and 3 water samples plot below the 1:1 equiline, therefore indicating dominance of normal ion exchange over reverse ion exchange. In addition, (Figure 6.5b) further confirms dissolution as another primary source of salinazation that is ongoing in the groundwater. However, Barzegar et al. (2016) suggested that, should evaporation emerges as the major process in the water, EC versus (Na^+/Cl^-) plot will yield a horizontal line. Similarly, in the case of sodium being a product of halite dissolution, it will result in Na^+/Cl^- molar ratio that is approximately equal to 1, whereas a ratio greater than 1 is reflective of the ions produced from silicate mineral weathering (Meybeck, 1987). The EC versus (Na^+/Cl^-) plot (Figure 6.5b), shows most of the water samples plotted above the 1.0; therefore confirming silicate weathering as the major process contributing to Na^+ to the groundwater.

The plot of sodium against chloride will further give more insight about ongoing hydrogeochemical processes in the aquifer. However, Appelo and Postma (2004) stated that, the Na^+/Cl^- ratio for rain mainly derived from seawater is 0.86. On the other hand, a deviation from this value (0.86); which is the case shown in (Figure 6.5c), is an indication of a continental source of sodium. Moreover, ratios greater than 1 at low Cl^- (Figure 6.5c) concentrations suggests additional source of Na^+ in the groundwater. As such, the most probable source of Na^+ could be rock weathering of silicate minerals that are sodic.

Redox reactions is one of the reactions that can influence groundwater chemistry. As such, having some idea about the redox condition in groundwater can influence other chemical reactions and activities (pollution processes) in groundwater. Nevertheless, some part of the study area is under high agricultural activities (cropping of lands and rearing of livestocks). As such, this could serve as a source of localized contamination (nitrate) into the groundwater system in the area. However, since the upper aquifer in the area is a shallow unconfined alluvial aquifer; therefore a reasonable amount of nitrate would be expected in groundwater sampled from the area.

The plot of $NO_3{}^-$-N versus $HCO_3{}^-$ (Figure 6.5d), shows this is not always the condition as higher number of the water sample have a relative low nitrates at higher $HCO_3{}^-$ concentrations. Therefore, nitrate reduction plays an important role in reducing nitrate contamination in the groundwater system; as observed in the groundwater chemistry of water sampled from the area having low nitrate concentrations. Which is justified by the low values of dissolved oxygen (DO) and redox potential E_h values.

6.1.5 Water quality assessment

Groundwater resource in the area is used by the locals for different purposes, but major of them are for domestic (sometimes drinking) and irrigation purposes. Hence, the need to assess the groundwater quality (of constituents chemical) in the area for drinking and irrigation purposes. As such, hydrochemical constituents of each sampled groundwater from different locations in the area were compared with World Health Organization (WHO) and Portuguese guidelines for drinking-water quality standard (WHO, 2017; DECREE NO. 306/2007, 2007). Also, standard methods for assessing irrigation water quality were applied to assess suitability of the groundwater for irrigation purpose.

6.1.5.1 Drinking water quality

Groundwater sampled at different locations in the study area, were assessed to confirm their suitability for drinking and other domestic purposes. Thus, groundwater quality data for each water sample were compared with the standard guideline values recommended by the World Health Organization (WHO, 2017) and Portuguese drinking-water standard (DECREE NO. 306/2007, 2007).
pH of all groundwater samples (96 %), exceeded both WHO and Portuguese drinking-water standards

Table 6.6: Comparison of groundwater quality of each water sample with guidelines of WHO and Portuguese drinking-water standards

Chemical parameter	Portuguese standard	WHO Drinking water Quality standard	Samples exceeding permissible limits	Number of samples	% of samples
pH	$\geqslant 6.5$ & $\leqslant 9.0$	8.2 - 8.8	All except SPR05	23	96 %
TDS	NM	500	SPR04, SPR05, SPR08, SPR10, SPR13, SPR17	6	25 %
TH	NM	500	None	0	0 %
Na^+	200	200	SPR04, SPR05, SPR08, SPR10	4	17 %
K^+	NM	NM	NM	NM	NM
Ca^{2+}	100	200	None	0	0 %
Mg^{2+}	50	30	None	0	0 %
$HCO_3{}^-$	NM	NM	NM	NM	NM
Cl^-	200	250	SPR04, 05, 08, 10, 14	5	21 %
$SO_4{}^{2-}$	250	250	None	0	0 %
$NO_3{}^-$-N	11.3	11.3	SPR08, 10, 21, 22, 23, 24	6	25 %
Antimony (Sb)	0.005	0.02	SPR05	1	4 %
Arsenic (As)	0.01	0.05	SPR01	1	4 %
Cadmium (Cd)	0.005	0.003	None	0	0 %
Copper (Cu)	2	2.00	None	0	0 %
Chromium (Cr)	0.05	0.05	None	0	0 %
Lead (Pb)	0.05	0.01	None	0	0 %
Aluminium (Al)	0.20	0.10	SPR07, 11, 23	3	13 %
Manganese (Mn)	0.05	0.05	All except SPR02, 09, 11, 15, 17, 20, 21, 23, 24	15	63 %
Iron (Fe)	0.2	0.3	SPR01, 03, 04, 05, 14, 18	6	25 %
Zinc (Zn)	3	3	None	0	0 %

Values of drinking-water standards for all water quality parameters are given in mg/L except for pH (-)
TDS - Total Dissolved Solids; **TH** - Total Hardness; **WHO** - World Health Organization; **NM** - Not Mentioned

(Table 6.6), with the exception of only one sample (SPR05). Therefore, the groundwater is unsafe for drinking, except some measures are taken to adjust the pH by concerned authorities or individuals in the area. Also, as regards total hardness (TH), all samples were within the specified limits. As regards, total dissolved solids (TDS); six samples (25 %) exceeded the specified limits.

Amongst the cations, sodium plays a vital role in human health. As such, a higher sodium intake may cause hypertension, congenial heart diseases, nervous disorder and kidney problems (WHO, 2017). Therefore, the recommended limit for sodium concentration in drinking water is 200 mg/L (WHO, 2017;

DECREE NO. 306/2007, 2007). Moreover, four (17 %) out of the groundwater samples (Table 6.6) exceeded the recommended limit for sodium. Nevertheless, calcium and magnesium are two important elements needed for proper bone, nervous system and cell development (WHO, 2017). One possible adverse effect from ingesting high concentration of calcium for long periods may be an increased risk of kidney stones (MARANGELLA et al., 1996). All sampled groundwater from the area (Table 6.6), were within the specified limits of magnesium and calcium concentrations in drinking water (WHO, 2017; DECREE NO. 306/2007, 2007).

Concentrations above certain threshold value for HCO_3^- and Cl^-, have no known adverse health effects. However concentrations should not exceed the safe limits of 300 and 200 mg/L respectively in drinking water (WHO, 2017; DECREE NO. 306/2007, 2007). Comparison of measured Cl^- concentrations showed that, five samples (21 %) exceed the specified standards for drinking water. However, all sampled groundwater are within the recommended SO_4^{2-} limit for drinking water (Table 6.6). Meanwhile, NO_3^--N specified concentration limit for drinking water was exceeded in 6 (25 %) of total number of sampled groundwater in the area.

On the other hand, five (Cd, Cu, Cr, Pb and Zn) out of the total trace elements analysed in the sampled groundwater are within the specified limits (Table 6.6). Meanwhile, only one sample (4 %) exceeded specified limits for antimony (Sb) and Arsenic (As) in the sampled groundwater. Also, three (13 %) of groundwater samples exceeded the specified aluminium standard for drinking water; whereas 25 % of groundwater samples exceeded iron (Fe) specified limit.

All the trace elements, manganese concentration was exceeded in 15 (63 %) of the groundwater samples; making manganese the trace element found in more than half (50 %) of the sampled groundwater in the area. Overall, all sampled groundwater exceed one or more of the drinking-water standards (WHO, 2017; DECREE NO. 306/2007, 2007).

The major quality parameter most exceeded by groundwater sampled in the area is the pH. Therefore, the use of water samples that only failed the pH standard limits; whereas based on Portuguese maximum permissible standards only 5 % of the sampled groundwater were below the limits..

6.1.5.2 Irrigation water quality

There are many indices that can be used to assess the suitability of water for irrigation (Kumar et al., 2007). However, in this study only selected indices were applied to assess the suitability of sampled groundwater for irrigation purpose. The selected indices are; electrical conductivity (EC), chloride concentration, percent sodium (% Na^+), sodium absorption ratio (SAR), magnesium absorption ratio (MAR) and kelly's ratio.

Electrical conductivity (EC) classification (Wilcox, 1955), shows that 8 % of the groundwater samples are excellent, 67 % are good but probable, 21 % permissible and only 4 % doubtful for irrigation purpose (Table 6.7). Meanwhile, according to chloride classification, 75 % of the samples are suitable for irrigation, 8 % good, 13 % are permissible, and only 1 sample (4 %) is doubtful for irrigation purpose (Table 6.7).

Magnesium hazard (MH) ratio is a parameter calculated using Equation (6.4), proposed by Szabolcs and Darab (1964);

$$MH = \left[\frac{Mg^{2+}}{(Ca^{2+}+Mg^{2+})}\right] \times 100 \tag{6.4}$$

According to Szabolcs and Darab (1964), MH ratio less than 50 meq/L is suitable for irrigation purpose, whereas exceeding 50 meq/L is indicative of water unsuitable for irrigation. Hence, MH ratio of all groundwater samples (96 %) except one fall under 50 meq/L. Therefore, indicating that most of the sampled groundwater are suitable for irrigation based on magnesium hazard ratio.

Kelly (1964), defined the kelly's index (KI) calculated using Equation (6.5) for assessing suitability of water for irrigation purpose. As such, water having KI greater or equal to 1 (one) is suggestive of excess sodium level, and therefore not suitable for irrigation purpose. Whereas, KI less than 1 (one) is considered suitable for irrigation.

$$KI = \left[\frac{Na^{+}}{(Ca^{2+}+Mg^{2+})}\right] \tag{6.5}$$

Thus, groundwater samples show almost equal number partition between the KI categories; of which 11 groundwater samples (46 %), and 13 (54 %) suitability and unsuitability (Table 6.7) respectively for irrigation purpose.

Furthermore, sodium Na^+ above a certain limit can reduce soil fertility. Also, sodium is an important cation in water used for irrigation; as such, high concentrations of Na^+ can impact negatively upon plant growth (Shamsuddin et al., 2019). Therefore percent sodium (% Na^+) is calculated using Equation (6.6) (Wilcox, 1955).

$$(\%Na^{+}) = \left[\frac{(Na^{+}+K^{+})}{(Ca^{2+}+Mg^{2+}+Na^{+}+K^{+})}\right] \times 100 \tag{6.6}$$

Hence, 25 % of groundwater samples are certified good, 29 % permissible, 33 % doubtful, and 13 %

Table 6.7: Classification of groundwater quality based on the suitability for irrigation purposes based on some selected indices

Method of classification	**Classification classes**	**Classification limits**	**Number of samples within limits**	**% of samples within limit**
Electrical conductivity (Wilcox, 1955)	Excellent	< 250	2	8 %
	Good	250 - 750	16	67 %
	Permissible	750 - 2250	5	21 %
	Doubtful	2250 - 5000	1	4 %
	Unsuitable	> 5000	None	0 %
Chloride (meq/L)	Excellent	< 4	18	75 %
	Good	4 - 7	2	8 %
	Permissible	7 - 12	3	13 %
	Doubtful	12 - 20	1	4 %
	Unsuitable	> 20	None	0 %
Percent Sodium (Wilcox, 1955)	Excellent	0 - 20	None	0 %
	Good	20 - 40	6	25 %
	Permissible	40 - 60	7	29 %
	Doubtful	60 - 80	8	33 %
	Unsuitable	> 80	3	13 %
Sodium Absorption Ratio (SAR) (Richards, 1954)	Very low	< 2	13	54 %
	Low	2 - 12	9	38 %
	Medium	12 - 22	1	4 %
	High	22 - 32	None	0 %
	Very high	> 32	1	4 %
Magnesium Absorption Ratio (MAR) (Szabolcs and Darab, 1964)	Suitable	< 50	23	96 %
	Unsuitable	> 50	1	4 %
Kelly's ratio (Kelly, 1964)	Suitable	< 1	11	46 %
	Unsuitable	≥ 1	13	54 %

Values of classification standards are given in meq/L except EC ($\mu S/cm$)

unsuitable for irrigation purpose (Table 6.7). Overall, 75 % of groundwater samples were considered doubtful for irrigation purpose based on percent sodium (% Na^+).

In addition, another index used to classify suitability of water for irrigation is the sodium absorption ratio (SAR). SAR can be used to assess the degree to which irrigation water tends to participate in cation exchange reaction in soil. As such, excess sodium will be adsorbed into soil particles and subsequently alter their properties, thereby reducing permeability (Ayers and Bronson, 1975). According to Richards

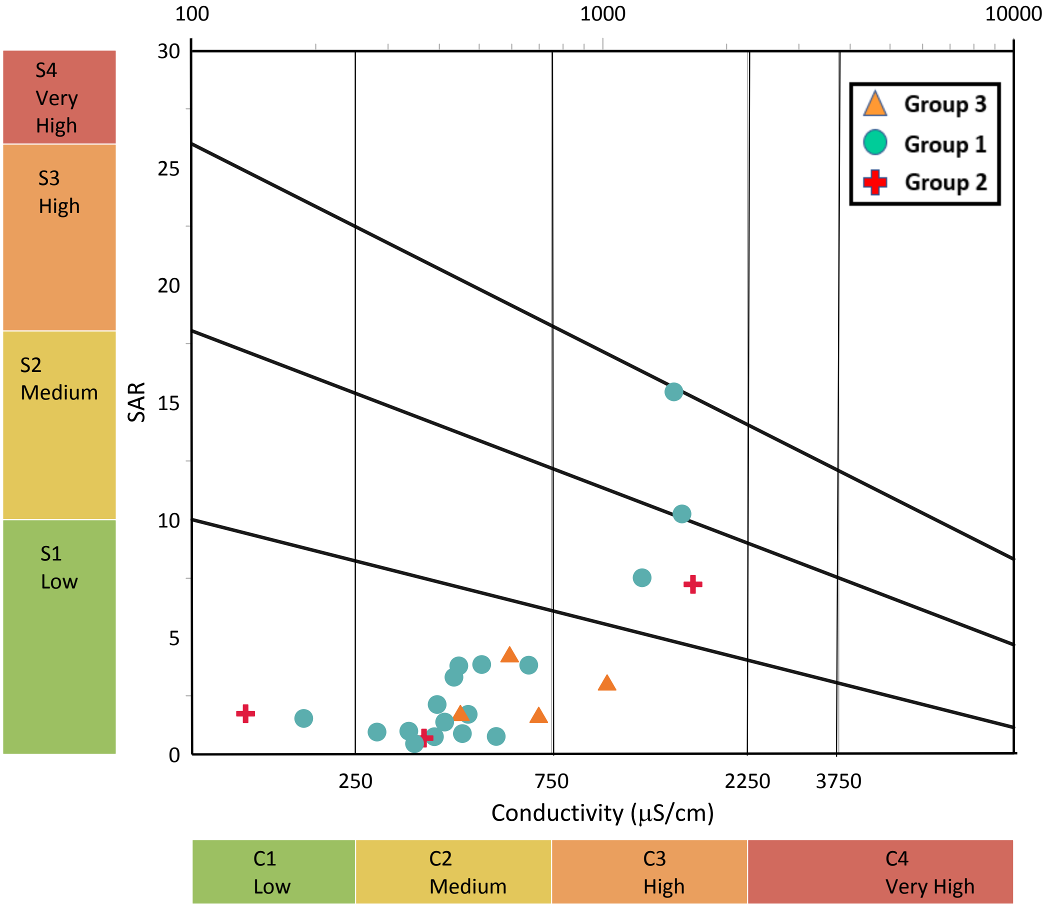


Figure 6.6: *United States salinity diagram (USSL) for classifying the suitability of water for irrigation purpose*

(1954), SAR ratio is an important parameter in determining groundwater suitability for irrigation purposes as it measures the extent of alkali/sodium hazard towards crops. As such, can be calculated using Equation (6.7). SAR ratios calculated, shows that 92 % of sampled groundwater fall within very low and low SAR ratio (Table 6.7).

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}} \tag{6.7}$$

As such, can be considered for irrigation purpose. However, 1 groundwater sample group under medium and very high SAR ratio respectively. As such, indicating unsuitability for irrigation purpose.

Furthermore, groundwater samples were plotted on the united States salinity diagram; on which the electrical conductivity (EC) is assumed as salinity hazard, and SAR as alkalinity hazard (USSL, 1954). Thus, the USSL diagram (Figure 6.6) shows that, most of the groundwater samples plot under the C2S1 group, whereas two samples plot under the C3S2, C3S3, and C1S1 group each. AS such, with higher number of groundwater samples plotting within the C2S1 and C1S1 group; therefore indicating good to moderate quality of water for irrigation.

Overall, only five (25 %) out of the 24 sampled groundwater from the area is certified suitable based on assessment with the selected irrigation quality parameters. Therefore, suitability of the sampled groundwater for irrigation purpose is probable, and should be used with caution.

6.2 Socio-Hydrogeological analyses

The results and discussion presented in this section, comprises outcomes and interpretation of socio-hydrogeological study (in form of social interview), carried out in the study area to understand the perception of locals concerning contamination of groundwater resource in the region. Hence, given the fact that majority of information retrieved from interviewed respondents were normative (categorical variables) in nature; and also coupled with one the primary goal of the thesis which is to understand the perception amongst different respondents.

A total of 24 respondents, cutting across different social and personal status were interviewed in the area. Data gotten from the interview were treated and interpreted more qualitatively rather than quantitatively. Similarly, descriptive statistics was utilized rather than inferential statistics (which could lead to misleading interpretation due to quality and quantity of data available).

Interpretation of the data was done with cautions, reason being that many social and human factors (personal beliefs, culture, behavioural patterns, and many others) are connected to each response. Hence, the interview question can be better viewed from a cognitive perspective. As such, the cognitive process should be taken into consideration; which could influence most of the responses given by each respondents to various interview questions.

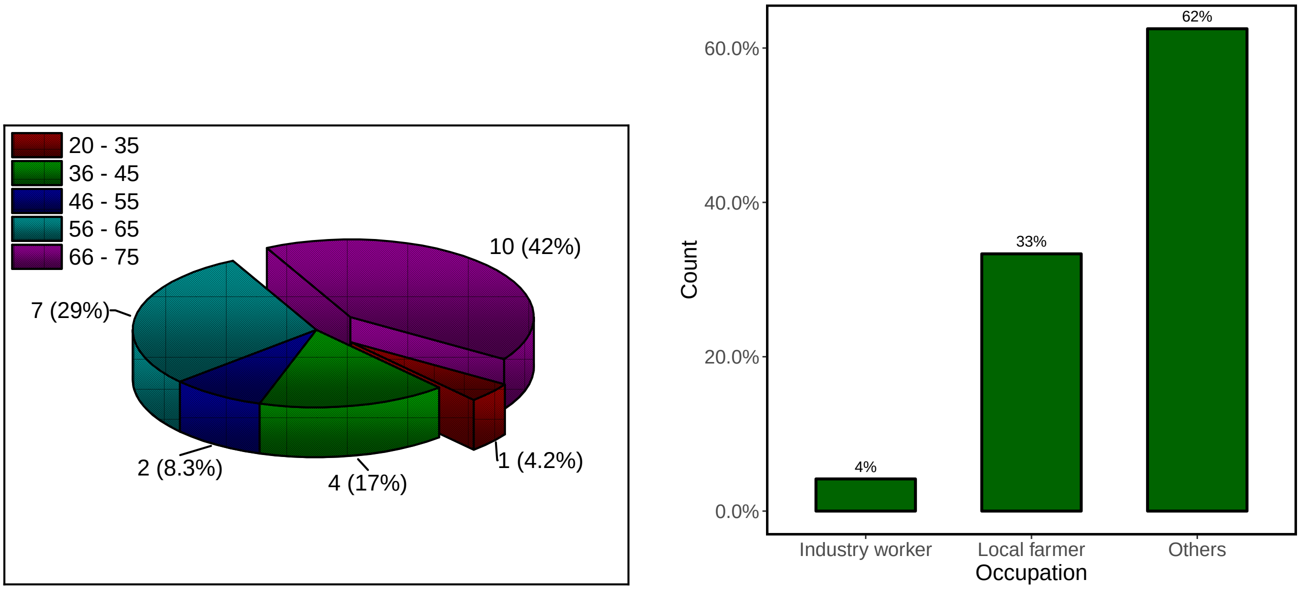
Outcome of the interview were not taken literally to come up with a final conclusion about perception of locals about the issue (contamination of groundwater resource). On the contrary, responses were analysed in the light of many factors which could influence each responses given, and therefore suggesting possible hypothesis that could be deduced from such response.

6.2.1 Findings and discussion

The major research findings and discussion deducted from retrieved information (qualitative interview) conducted in the study area are presented in seven different sub-headings. These sub-headings were coined from major themes that constitute interview questions administered on each respondent: Personal and social characteristics, Groundwater use, perception about contamination status of groundwater resources, personal stewardship practices, role of municipality, health challenges, and personal suggestion/actions.

6.2.1.1 Personal and social characteristics of respondents

Interview questionnaires were administered to locals that cut across different works of life and social status in the area (Figure 6.7). Moreover, respondents were not preselected, but guided based on groundwater sampling location scattered over the study area of Estarreja and Murtosa region. As such, each water analysis results can be matched with information provided by respondents.
The age bracket of respondent interview (Figure 6.7a), shows 42 % are from the oldest group (60 - 75 years) in the area, followed by 56 - 65 age range (29 %), and the lowest percentage of 4 % for the youngest group in the area (20 - 35 year). Therefore, it implies that there is an uneven distribution of age amidst respondents in the area, as the age range decreases from the oldest to the youngest in the



(a) Age range of respondents interviewed

(b) classification of major occupations of respondents interviewed

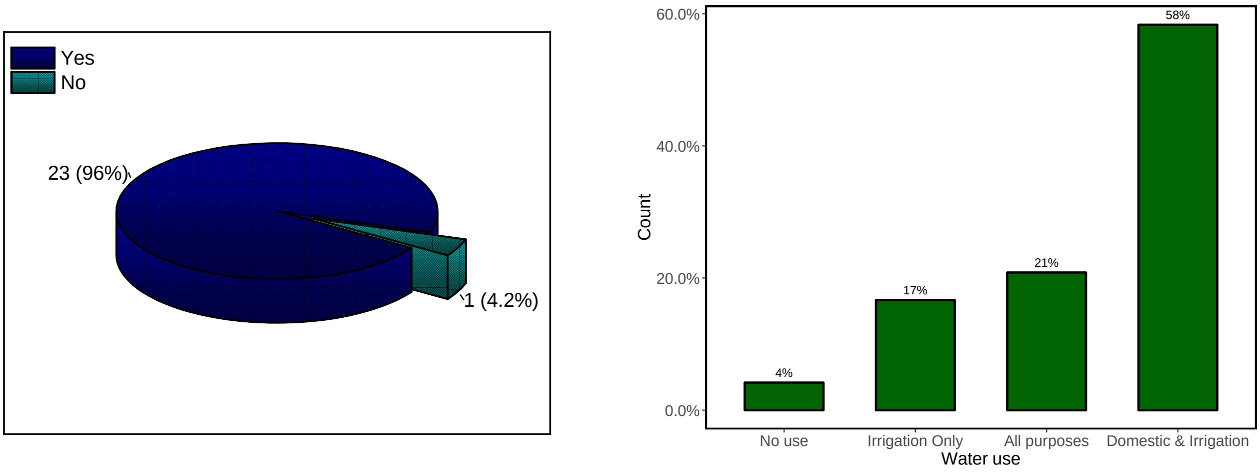
Figure 6.7: *Distribution of personal and social characteristics showing: (a) Age range; and (b) classes of major occupations, of respondents interviewed in the study area*

area (Figure 6.7a). On the other hand, 80 % of respondents interview were males, and the remaining consist of females living in the area. Similarly, a measure of the social status of respondents in the area as seen in their occupation (Figure 6.7b); shows a major percentage of respondents interviewed (62 %), are involved in other occupations different from typical occupations (local farmers and industry worker) in the area. However, local farmers in the area constituted the next group of respondents (33 %), and the smallest percentage (4 %) work in one of the chemical industries in the area. As such, the spread of the occupation of respondents, suggests that outcomes from respondents interviewed were not biased towards people working in the chemical complex.

6.2.1.2 Groundwater use

Groundwater use theme under the interview questionnaires, focuses on two key questions concerning if each interviewed respondents well is currently in use and what purpose(s). The response given to both questions indicate that, all (96 %) with the exception of only one respondent (4 %) use their wells, and mostly for domestic and irrigation purposes (Figure 6.8).

However, by further examining the response on use of groundwater in the area (Figure 6.8a), suggests locals mostly rely on groundwater resources (personal wells) to met their daily water needs. As such, potential risk of having health challenges related to use of the groundwater (untreated) will be high in the area. Meanwhile, the uses are diverse (Figure 6.8b), but water from wells are mostly used from domestic and irrigation purposes (58 %), followed by all purposes (drinking, irrigation and domestic)-21 %, next for irrigation purpose only-17 %, and only one respondent does not use his well-4 %. As such, it can be hypothesised that, decision to use water from wells can be strongly linked to individual assessment (incomplete knowledge) of the risk involved, and not based on pre-informed knowledge (backed by scientific proofs and figures) of potential risks. Also, examining the reason given by the respondent that



(a) Interviewed respondents well usage

(b) Classification of water uses by respondents

Figure 6.8: *Distribution groundwater use pattern showing: (a) well usage; and (b) classes of water uses, of respondents interviewed in the study area*

does not use his well, because the water smells terribly and burns his crops. Therefore, his decision not to use water from his well is solely based on the immediate reactions and physical judgement of the water, and not from pre-informed knowledge (backed by scientific proofs and figures).

On the other hand, respondents having different experiences (with nature of their wells), feel the water can be used for other purposes aside drinking, as this is still acceptable (possibly poses no risk). According to Simon (1957), in his work on decision making and human behaviour, which he highlighted two key factors that could influence human decisions. First, he noted that human make decisions with incomplete and imperfect knowledge - that is, they do not consider many information available for decision-making, therefore some of their beliefs are imperfect or incorrect (Summers, 2010). The second issue Simon (1957) raised is that, humans have limited cognitive capacity (limited brain power) and as such cannot fully consider all aspects of all decisions (but moved mainly by their pressing needs).

Furthermore, based on the current water quality status of sampled groundwater in the area (suitability for drinking and irrigation purposes); using World Health Organization (WHO) and Portuguese guidelines for drinking-water quality standard (WHO, 2017; DECREE NO. 306/2007, 2007). The result showed that three quarters (75 %) and all (100 %) of sampled groundwater in the area are unsuitable for irrigation and drinking purposes. As such, examining this result (water quality) with the responses given by each respondents, suggests the level of irrationality (action taken from inadequate use of reason, or through emotional distress or cognitive deficiency) in their decisions on groundwater use and purpose of use. However, rationality or irrationality can not be fully justified from their responses; but it can be hypothesised that, assessment of perception to possible risk of using the water by respondents is quite poor (not measured appropriately).

6.2.1.3 Perception about contamination status of groundwater

This theme question focuses on the knowledge of each respondents, as regards the contamination of groundwater in the area. Therefore, questions asked during interview under this theme include;

assessing each respondents knowledge about the contamination of groundwater and the likely source(s) of contamination in the area.

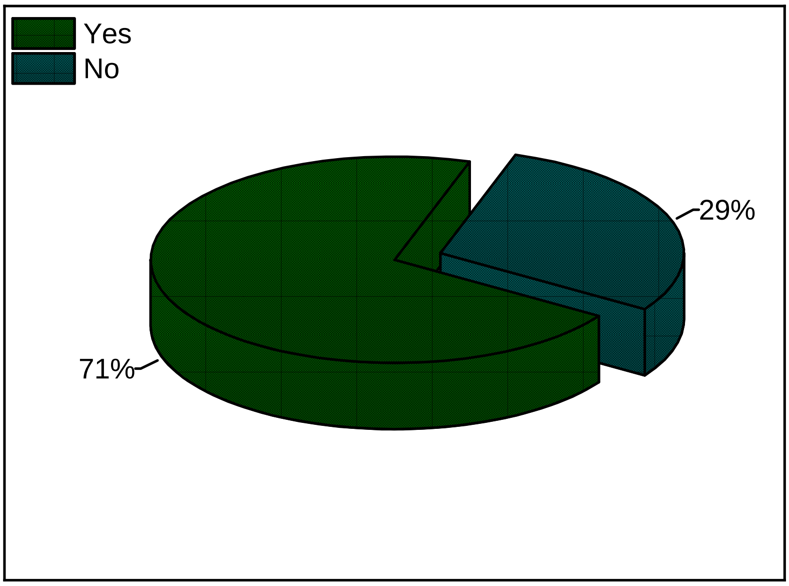


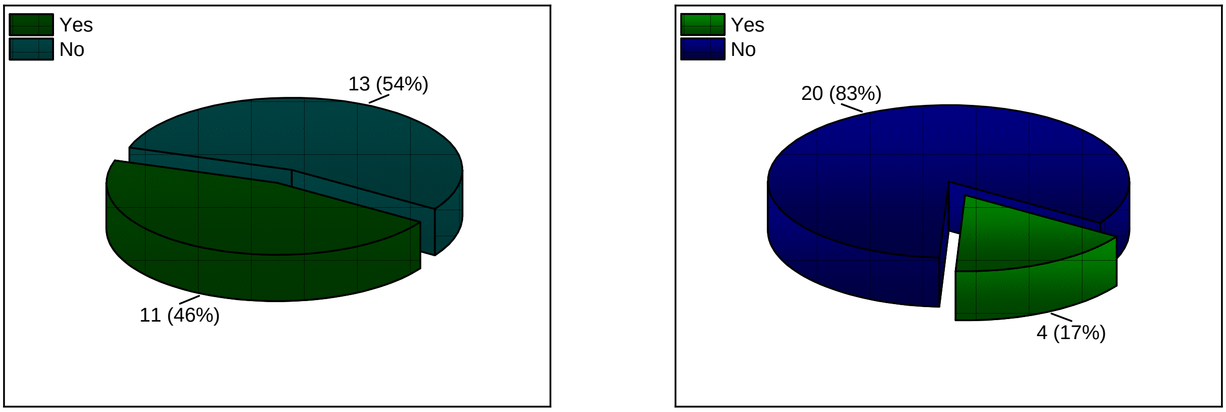
Figure 6.9: *Distribution of interviewed respondents perception of groundwater contamination in the area*

The knowledge of respondents (Figure 6.9), shows a vast majority (71 %) are aware of the contamination issue existing in the area. However, the main source of their knowledge can not be ascertain from responses provided by each respondent; but it could be based on their contact with the water over the years (basic instinct). In addition, some of the respondents (32 %) were uncertain about the possible source of contamination in the area. Whereas, a vast majority of respondents (68 %), had different opinions about possible sources of contamination that could affect the groundwater resource in the area. Major of their response was linking the source of contamination to the industrial activities in the area, and just two respondents highlighted the agricultural activities in the area (livestock rearing and use of fertilizers). As such, it can be hypothesised that, majority of respondents views suggests their personal opinions about contamination of their wells, that originates mainly from their basic instincts and beliefs over the years. Moreover, not from a coherent well-informed idea about the issue of contaminated groundwater resource in the area by any authority.

6.2.1.4 Personal stewardship practices

This theme question focuses on the practices by each respondents in response to contamination of the groundwater resource in the area (Figure 6.10). Questions in this theme include; if respondent perform water analysis, if water usually undergo any treatment and what they do in case of any accident. Out of 24 respondents interviewed, 13 (54 %) do not conduct any water analysis and others (46 %) perform water analysis on their water (Figure 6.10a). There is an observed vast majority of respondents that do not apply any treatment to their well (83 %) whereas, only four respondent (17 %) do apply some form of treatment to their water (Figure 6.10b).

Respondents replies about what to do in case of emergency shows all except two respondents, who were sure of the next line of action in case of emergency. Hence, the responses to this thematic question (personal stewardship practices) suggests that a vast majority are aware of the contamination. However,



(a) Interviewed respondents well usage

(b) Classification of water uses by respondents

Figure 6.10: *Distribution of groundwater use pattern showing: (a) well usage; and (b) classes of water uses, of respondents interviewed in the study area*

they are not taking so much concrete efforts to personally deal with the issue. This still sums up to the fact that behavioural patterns are no same and could trigger different decision in events of challenges.

6.2.1.5 Role of municipality

The questions under this theme include; who pays for their water, any relative working in one of the industries and if they have any form of contact with associations in the area. Response to if their water is being paid for py the industries reveals, only one out of the 24 respondents water is being paid for by the industries.

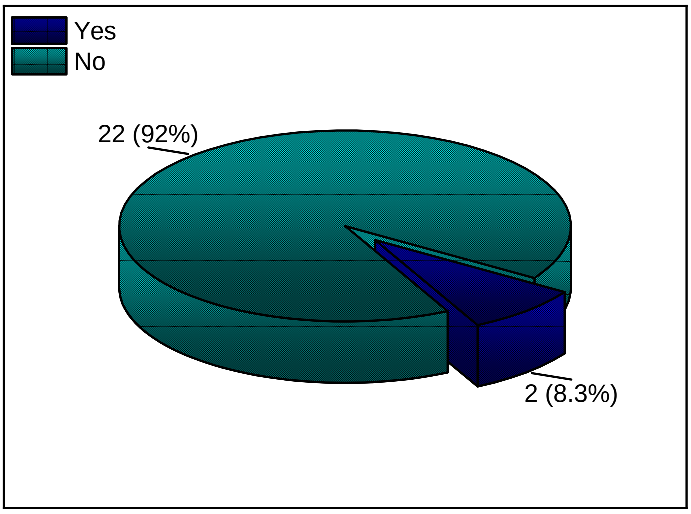


Figure 6.11: *Distribution of respondents in contact with associations in the area*

Moreover, by critically analysing comment by the respondent whose water is being paid for raises some level of suspicion if it is true or not. This further reveals that respondents are not comfortable with some issues. As such the process may not be very transparent (the level of transparency is questionable).

Question about if respondents have any relative working in one of the complex reveals only 6 (25 %) out of the 24 respondents responded in the affirmative. Whereas, the remaining 16 (75 %) have no relative working in one of the industries. The responses given by respondents on whether they are in connection with any association shows a vast majority (92 %) are not in contact with any association and only two respondents have a connection with associations in the area. Hence, this theme question proposes that there is a missing link between the municipality, and locals, or enough is not being done in this aspect (sensitization and awareness campaigns).

6.2.1.6 Health challenges

This theme question is mainly about having idea of any health challenges being faced in the area. The question directed to each respondent was if any family member connected to them is having any health challenges.

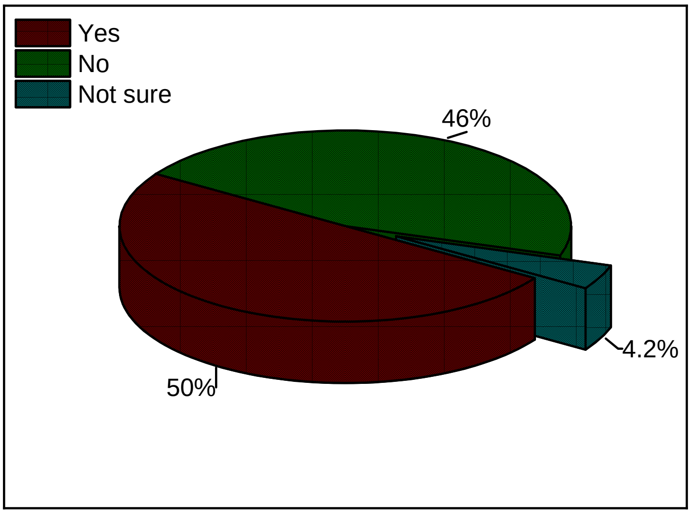


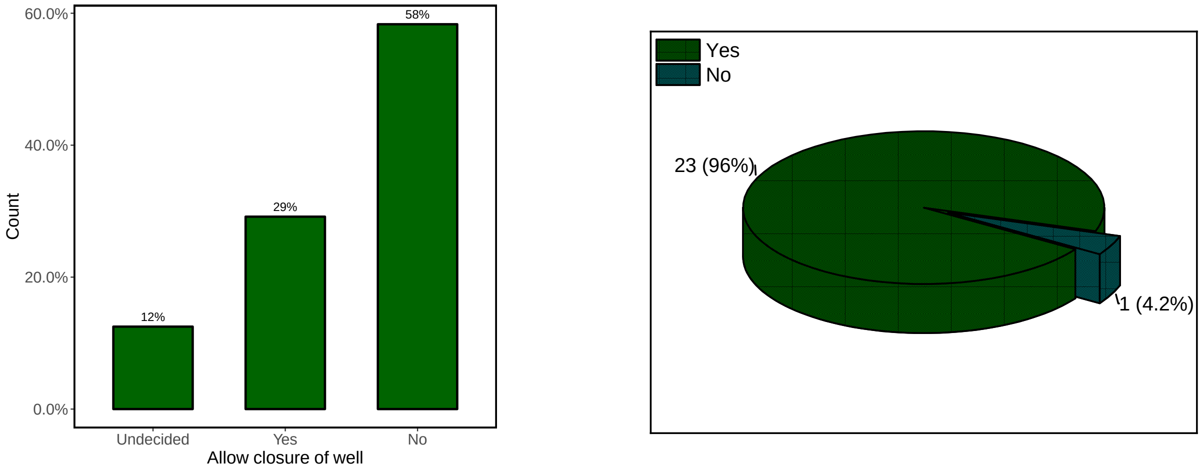
Figure 6.12: *Distribution of health challenges responses from interviewed respondents in the area*

The outcome of responses by respondents shows 50 % were sure of a health challenge, 46 % said no and 2 % not sure (Figure 6.12). Hence, from responses it can be hypothesised that the possibility of being down with a health challenge is likely in the area.

6.2.1.7 Personal suggestions and actions

This theme question focuses on retrieving information as regards possible suggestions by respondents that could be employed to deal with the issue. Questions asked under this theme are; if they would allow closure of the wells and would like to receive outcome of the study (Figure 6.13).

A vast majority (58 %) of respondents interviewed said no to closure of their wells, only 7 (29 %) agreed for their wells to be closed and 12 % were undecided (Figure 6.13a). However, conclusions can not be made based on responses of respondents (Yes, No and not sure) on this question (closure of wells) because, it would require more in-depth conversation with each respondents. But, it can be hypothesised from respondents comments that they do not clearly see the contamination, possible risk on health and



(a) Responses to closure of wells by interviewed respondents

(b) Responses of interviewed respondents who like to receive result

Figure 6.13: *Distribution of personal suggestions/actions about: (a) closure of wells; and (b) who like to receive result, of respondents interviewed in the study area*

the link between major water uses (drinking and irrigation) in the area. Also, it can be observed that may be they are not rational or current about the issue.

Chapter 7

CONCLUSIONS & RECOMMENDATIONS

7.1 Conclusions

The study reflects a complex reality of integrating for the first time hydrogeological and social data (perception) to improve the understanding of environmental and societal challenges from different perspectives. In this study, both the hydrogeological and human perception data were explored to understand the impact of long-term contamination activities in the area towards improving the population resilience.

The Aveiro Quaternary aquifer is a poor qualitative status according to the reports of the River Management Plans and the region around Estarreja is one of the areas selected by APA to implement mitigation measures. However, these are measures aim at improving environmental resilience and completely forget the need to increase public perception of the contamination risks in order to improve the resilience of local populations.

Vulnerability assessment of the aquifer using the susceptibility index (SI) method reveals the aquifer is highly vulnerable in some parts of the study area. Areas around the Estarreja Chemical Complex (ECC) showed high to very high intrinsic vulnerability with the land use occupied by chemical industry and landfills also contributing to susceptibility. The geology of the area which is made up of mostly alluvial deposits, coupled with the shallow depth of the groundwater table are the major factors influencing the vulnerability in the area. Areas of very high to extremely high vulnerability were identified along the main water channels which are in connection with groundwater levels and dependent ecosystems.

A high-resolution investigation method was used to map surface water bodies in the area, which include Veiros lagoon reveal various contamination levels. Overall, the water channels scattered across the investigated area have low pH (acidic to slightly acidic waters) and relatively high electrical conductivities confirming contamination. Therefore, these surface water bodies may still have a strong impact on the groundwater quality due to the surface-groundwater interaction processes.

Based on the regional high-resolution results (mostly pH and EC), pre-defined wells were selected for further sampling and analyses of major, minor and trace elements. The results were analyzed using different statistical and graphical methods. Multivariate analysis using principal component analysis (PCA) reveals principal component 1 (PC1) showing the dominance of Na^+, Cl^-, and $SO_4{}^{2-}$ was indicative of anthropogenic contribution (contamination) of groundwater in the area, whereas the significant presence of EC indicated that these ions are the major contributors for the total dissolved ions in the groundwater. PC2 indicated ongoing acidifying process, followed by dissolution processes (of carbonates and silicates), and then cation exchange processes in the groundwater. PCs 3, 4 and 5 indicated low influence of agricultural activities (major source of nitrate) in groundwater sampled from the area and a natural capacity of the aquifer to attenuate redox sensitive species.

The major geochemical processes controlling the natural groundwater chemistry are mixing and cation exchange and their impact is clearly observed in the dominating ions, which are chloride (Cl^-) and sodium (Na^+) ions. The sodium chloride (NaCl) type water results from the infiltration of rainwater with seawater signatures but in some areas close to the Aveiro coastal lagoon processes of local salinization were also identified and coincide with EC values higher than 500 µS/cm and corresponding fractions of seawater greater than 1 %.

Ionic ratios were used to confirm mixing and cation exchange processes and to further infer other geochemical processes, such as silicate and carbonate minerals' weathering. The signature of coastal areas is observed from the water types as the ratio of Na^+ and NaCl is dominant but diluted compared to that of sea water (contributions from precipitation). Also, the presence of some $CaCl_2$ and Na_2SO_4 water types further confirms cation exchange processes ongoing in the aquifer which can be linked to interactions between the surface and groundwater system in the area. However, only four of the samples collected close to the lagoon (Ria de Aveiro) were linked to the mixing process occurring with contribution from sea water.

Redox processes also play an important geochemical role in the aquifer. The presence of organic layers that semi-confine the aquifer contribute to reduce in some parts the content of dissolved oxygen (DO) and the corresponding redox potential E_h values. the groundwater chemistry of the waters sampled in the area showed that nitrate reduction contributes to reduce concentration (median values of 8.6 mg/L $NO_3{}^-$-N) in a highly impacted aquifer from agricultural practices.

The most important contaminants found in the groundwater are: Na^+, Cl^-, $SO_4{}^{2-}$ and trace elements (Aluminium (Al), Zinc (Zn), Iron (Fe), Manganese (Mn)). The current groundwater quality as compared with the WHO and Portuguese standards reveals all of the sampled groundwater were above the recommended limits for drinking water standards. But just considering the Portuguese maximum permissible standards there were 5 % of the sampled groundwaters below the limits. For irrigation water quality assessed based on standard methods only 75 % were suitable for irrigation purpose. Therefore, caution should be observed and adequate measures taken before using the water for any purpose.

The perception of the population interviewed reveals that there is a poor interaction between responsible authorities, industry and the population. This could be a result of the lack of practical public policies in the area as their responses showed they are not well informed about the risks involved in using the contaminated groundwater resources. Also, with the current status of groundwater quality which reveals the groundwater resource is not suitable for the purposes most of the population are already using it for. As such, these results implies that the population decisions and risk perception are quite low (mainly due to their residual knowledge and belief system over the years).

Finally, by relating the hydrogeological and social data (perceptions and other related data) constituted very complex realities (not following a logical line of thought). Therefore posing further challenges for investigating and understanding them (locals) decisions as regards the issue of the contaminated groundwater resources in the area.

7.2 Recommendations

The following recommendations are suggested towards improving the environmental and population resilience in the area:

(1) Installation of more monitoring wells should be done in strategic areas especially identified contaminated hotspots areas close to the water channels and lagoons. Also, decontamination of the water channels located at different places in the study area should be done.

(2) Further studies should be done on understanding the attenuation capacity of the aquifer by considering all available contaminants (inorganic and organic) towards planning an effective remediation procedure in the area.

(3) Law should be promulgated by established authorities restricting the use of water by inhabitants for drinking and irrigation purposes. Also, defining a protection perimeter around the chemical complex (groundwater protection zone).

(4) There should be incorporation of programs of public awareness and sensitization of the population (locals) towards changing their beliefs and well informed with facts and figures of the implications of using the water. Also, in this line, stewardship practices of their wells (carrying out water analysis, being very observant of their wells) should be emphasized.

(5) Participatory approach should be improved upon as it showed from interviews that locals are ready to incorporate new ideas but there is almost any effective communication link with them. As such, encouraging public participation can go a long way in improving their well-being.

(6) Inter-stakeholders dialogue is needed to incorporate more information and also, training for resilience should be a priority for concerned institutions in the area.

(7) A more comprehensive social campaign incorporating many factors will go a long way in better understanding the issue.

Since the aquifer belongs to the Hydrographic region RH4 (Vouga, Mondego and Lis rivers) (APA, 2016). It is recommended to implement strictly the planned measures for the Quaternary aquifer:

(a) Implementation of a specific programme of action in the nitrate vulnerable areas of Estarreja-Murtosa e Litoral Centro;

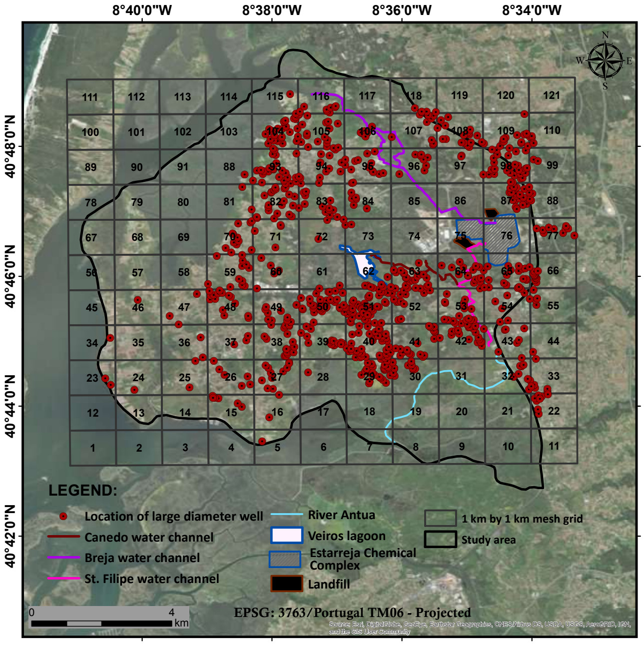
(b) Decontamination of the aquifer surrounding ECC;

(c) Preserve the groundwater dependent ecosystems (aquatic and terrestrial)

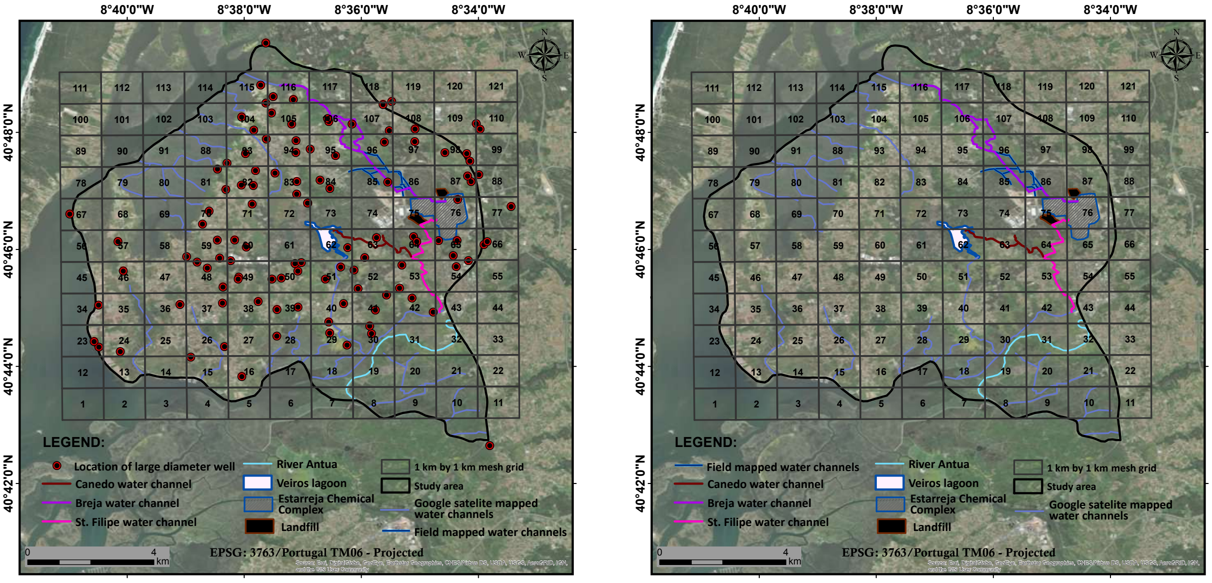
Appendices

Appendix A

High Density (Field) Sampling Maps



(a) *Inventories of all large diameter wells (Source: from Barreiras (2019))*



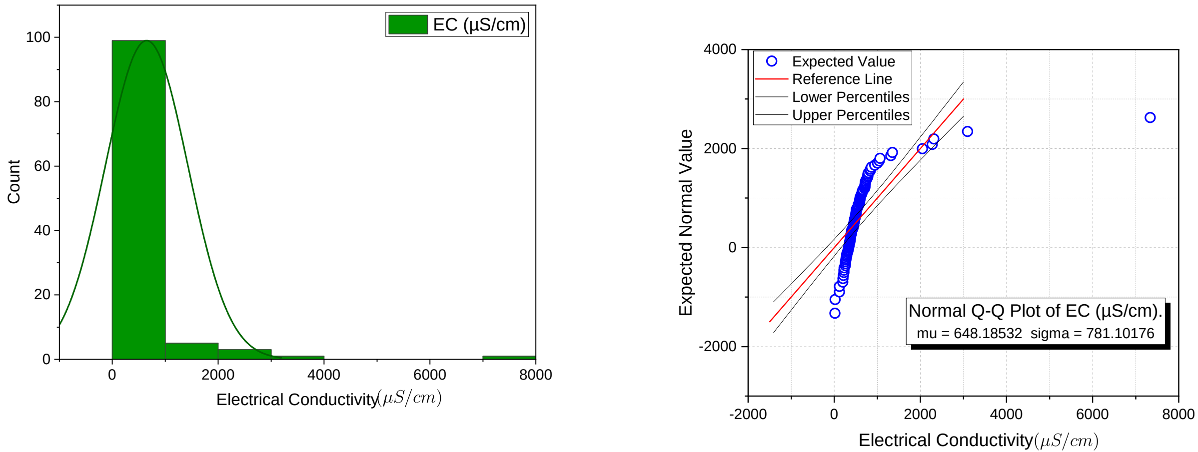
(b) Actual number of large diameter wells mapped

(c) All Water channels and Veiros lagoon

Figure A.1: (a) Inventories of all large diameter wells; (b) Actual number of large diameter wells mapped (c) All Water channels and Veiros lagoon in the study area

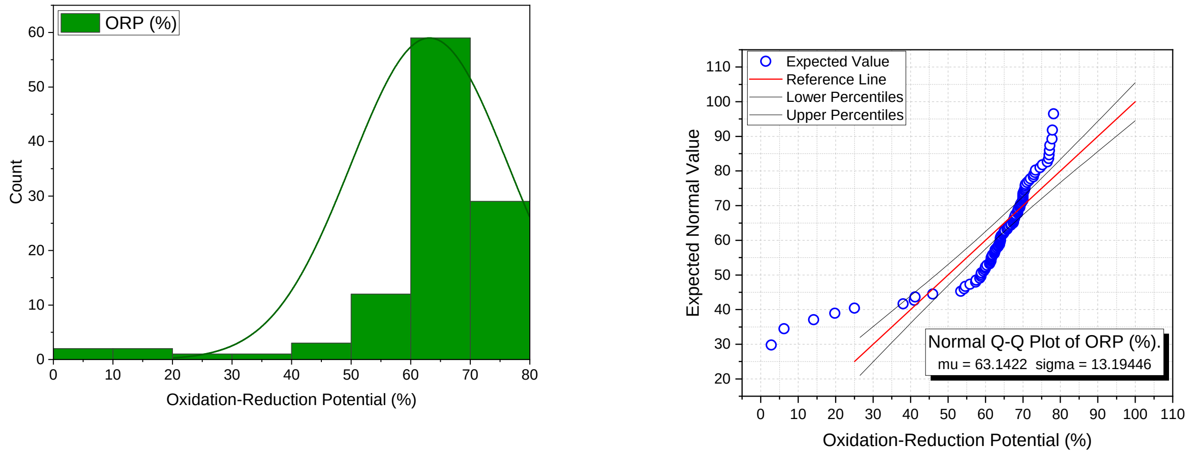
Appendix B

Supplementary Test of Normality Plots



(a) Histogram and cumulative plots showing distribution of measured EC

(b) Q-Q plot of EC



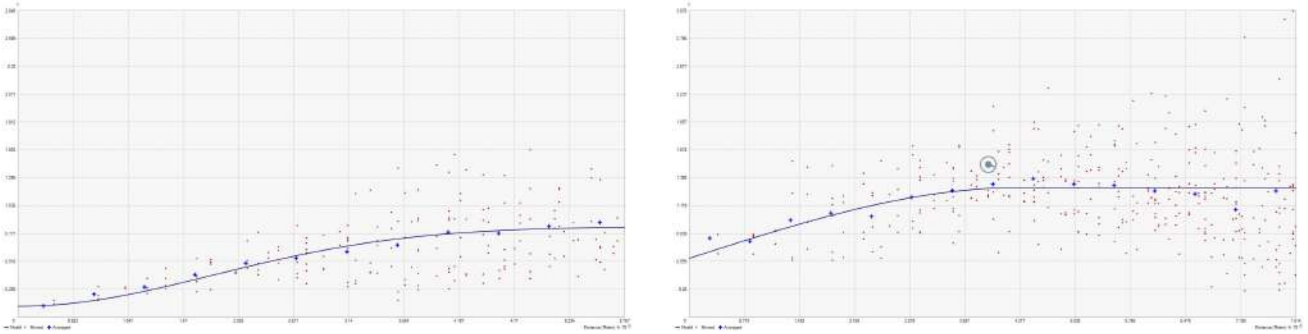
(c) Histogram and cumulative plots showing distribution of ORP

(d) Q-Q plot of measured ORP

Figure B.1: *Plots to check normality of measured field data using Histogram and cumulative plots showing distribution of: (a) Electrical conductivity (EC) (b) Q-Q plot of EC (c) Histogram and cumulative plot of ORP, and (d) Q-Q plot of measured ORP in the study area*

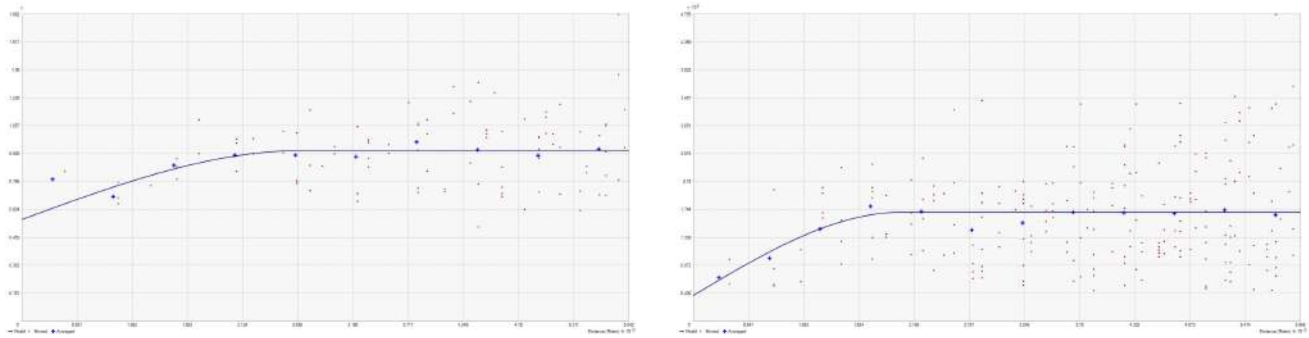
Appendix C

Geostatistics (Semi-variogram) Plots



(a) Semivariogram plot for groundwater level (exponential)

(b) Semivariogram plot for pH (spherical)



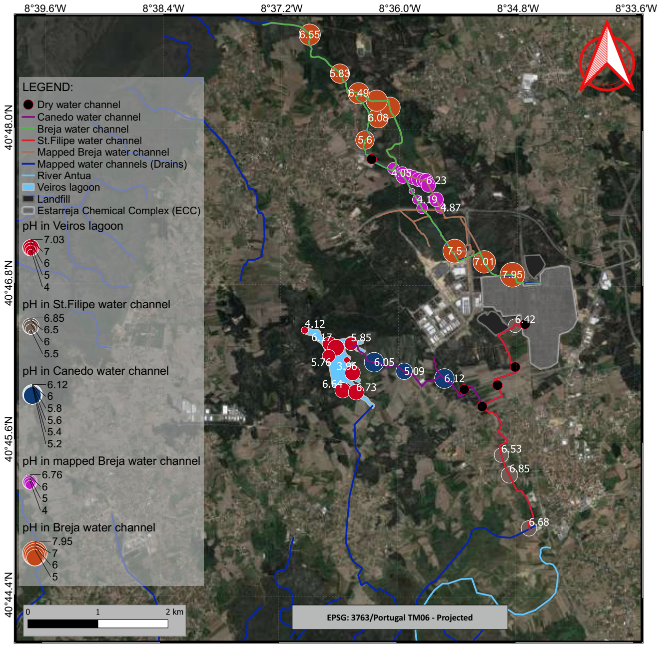
(c) Semivariogram plot for EC (spherical)

(d) Semivariogram plot for ORP (spherical)

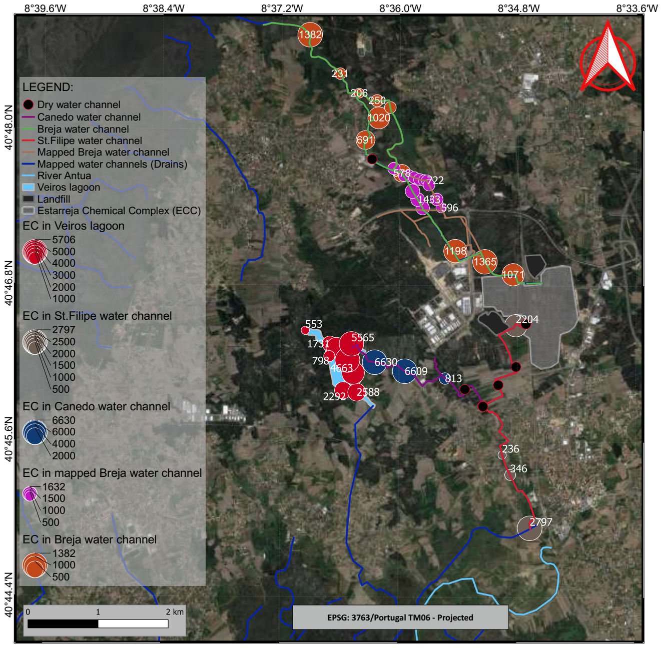
Figure C.1: Geostatistical plots of variogram models for (a) Groundwater level (exponential); (b) pH (spherical) (c) EC (spherical) (d) ORP (spherical)

Appendix D

Field Chemical Measurements in Surface water



(a) pH mapped along water channels and Verios lagoon



(b) EC mapped along water channels and Verios lagoon

Figure D.1: *Distribution of chemical parameters in surface water bodies: (a) mapped pH values; and (b) mapped EC values in the study area*

Appendix E

Enrichment of Ions

Table E.1: Summary of schoeller (chloro-alkaline) indices values of water sampled from different locations in the study area

Sample ID	$\frac{Na^+}{(Na^+ + Cl^-)}$	$\frac{Mg^{2+}}{\left(Ca^{2+} + SO_4^{2-}\right)}$	$\frac{Mg^{2+}}{\left(Ca^{2+} + Mg^{2+}\right)}$	$\frac{Cl^-}{(\sum anions)}$	$\frac{HCO_3^-}{(\sum anions)}$
SPR01	0.58	0.14	0.20	0.42	0.36
SPR02	0.51	0.17	0.19	0.37	0.37
SPR03	0.53	0.52	0.36	0.47	0.52
SPR04	0.45	0.06	0.18	0.89	0.04
SPR05	0.49	0.01	0.16	0.81	0.11
SPR06	0.55	0.21	0.23	0.32	0.46
SPR07	0.50	0.12	0.18	0.50	0.18
SPR08	0.54	0.12	0.19	0.86	0.03
SPR09	0.57	0.10	0.17	0.77	0.01
SPR10	0.50	0.07	0.15	0.81	0.00
SPR11	0.52	0.18	0.36	0.76	0.00
SPR12	0.51	0.16	0.18	0.37	0.36
SPR13	0.55	0.29	0.37	0.70	0.13
SPR14	0.56	0.08	0.19	0.73	0.04
SPR15	0.52	0.12	0.14	0.26	0.42
SPR16	0.53	0.17	0.70	0.23	0.64
SPR17	0.52	0.33	0.35	0.55	0.31
SPR18	0.57	0.42	0.63	0.70	0.08
SPR19	0.56	0.11	0.26	0.69	0.00
SPR20	0.60	0.20	0.27	0.45	0.25
SPR21	0.51	0.21	0.23	0.51	0.26
SPR22	0.61	0.12	0.15	0.40	0.33
SPR23	0.59	0.21	0.24	0.48	0.04
SPR24	0.60	0.15	0.20	0.78	0.00
SPR25	0.48	0.36	0.36	0.80	0.04

CAI-I - chloro-alkaline index I; **CAI-II** - chloro-alkaline index II

Appendix F

Possible local salinization of samples

Table F.1: Summary of sampled groundwater and corresponding distance from the lagoon to explain the process of possible salinization

ID	Water sample	Classification of water sample (water type)	pH	EC	Description of water sample location in study area
SPR01	Groundwater	NaCl and Na_2SO_4	5.90	470	close to St.Filipe water channel
SPR02	Groundwater	Mixed $CaCl_2$ and $MgCl_2$	5.98	389	close to St.Filipe water channel
SPR03	Groundwater	Mixed $Ca(HCO_3)_2$ and $NaHCO_3$	6.88	187	close to Canedo water channel
SPR04	Groundwater	NaCl and Na_2SO_4	5.52	1489	close to Canedo water channel
SPR05	Groundwater	NaCl and Na_2SO_4	6.92	2384	close to St.Filipe water channel
SPR06	Groundwater	Mixed $CaCl_2$ and $MgCl_2$	6.04	455	close to Breja water channel
SPR07	Groundwater	Mixed $CaCl_2$ and $MgCl_2$	5.27	282	close to St.Filipe water channel
SPR08	Groundwater	NaCl and Na_2SO_4	5.92	1558	close to Canedo water channel
SPR09	Groundwater	NaCl and Na_2SO_4	4.99	507	close to Canedo water channel
SPR10	Groundwater	NaCl and Na_2SO_4	4.63	1657	close to Canedo water channel
SPR11	Groundwater	NaCl and Na_2SO_4	4.43	135	close to a water channel South of (Veiros lagoon)
SPR12	Groundwater	Mixed $CaCl_2$ and $MgCl_2$	5.78	367	close to a water channel South of (Veiros lagoon)
SPR13	Groundwater	NaCl and Na_2SO_4	5.69	660	close to a water channel South of (Veiros lagoon)
SPR14	Groundwater	NaCl and Na_2SO_4	5.10	1246	close to St.Filipe water channel
SPR15	Groundwater	Mixed $CaCl_2$ and $MgCl_2$	6.24	348	close to St.Filipe water channel
SPR16	Groundwater	$Ca(HCO_3)_2$	6.39	550	close to St.Filipe water channel
SPR17	Groundwater	NaCl and Na_2SO_4	6.50	1024	1.3 km away from Ria Aveiro lagoon
SPR18	Groundwater	NaCl and Na_2SO_4	5.57	593	2.5 km away from Ria Aveiro lagoon
SPR19	Surface water	NaCl and Na_2SO_4	4.58	434	close to Breja water channel
SPR20	Groundwater	NaCl and Na_2SO_4	5.76	450	2.5 km away from Ria Aveiro lagoon
SPR21	Groundwater	Mixed $CaCl_2$ and $MgCl_2$	6.21	698	3.0 km away from Ria Aveiro lagoon
SPR22	Groundwater	Mixed $CaCl_2$ and $MgCl_2$	5.96	412	close to Breja water channel
SPR23	Groundwater	$CaCl_2$	5.17	337	close to Breja water channel
SPR24	Groundwater	NaCl and Na_2SO_4	4.92	446	close to Breja water channel
SPR25	Groundwater	NaCl and Na_2SO_4	5.40	395	North of the Chemical Complex

Appendix G

Supplementary appendices

Clickable link to supplementary appendices Appendices

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