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EXPLORING CLIMATE CHANGE IMPACTS AND GROUNDWATER CONTAMINATION DYNAMICS IN A WEST-MEDITERRANEAN COASTAL BASIN

Candidate:

DOMENICO DI MICCO

Thesis advisor:

PROF. TIZIANA ANNA ELISABETTA TOSCO

Co-advisors:

PROF. ALBERT FOLCH
DR. MARC DIEGO FELIU

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ABSTRACT

Groundwater represents approximately 30% of Earth's total freshwater reserves, playing a key role in sustaining ecosystems, supporting agriculture, and providing potable water for millions of people worldwide. However, its long-term availability and utilization are threatened by various natural and anthropogenic factors, including climate change and human-induced contamination. This thesis investigates such impacts in the coastal basin of Garraf (Spain), located in the heart of the Mediterranean climatic hotspot and dotted with detrimental anthropogenic activities that have resulted in significant degradation of groundwater quality, such as agriculture and waste disposal sites. The karstic nature of this basin represents an intriguing and complex setting for the study of underground dynamics due to the numerous subterranean water flows that discharge freshwater into the sea, a phenomenon known as submarine groundwater discharge (SGD). The study employs historical climate data from the Catalan Meteorological Service to assess the impact of climate change on the region, focusing on temperature and precipitation trends over the past seven decades, and evaluating the main adverse effects on groundwater resources in the region. The noticeable increase in temperature and the variability of the precipitation regime are consistent with the projections of the IPCC for the Mediterranean basin. Additionally, a comprehensive analysis of the groundwater hydro-chemical status is conducted using both primary data collected firsthand and secondary data from the Catalan Water Agency. Spatially mapping the contaminant distribution facilitates the identification of critical hotspots and the prediction of groundwater quality in unsampled regions. The basin exhibits high concentrations of nutrients (DIN, DIP, DSi), especially agriculture-derived nitrates in the western sector. On the other hand, seawater intrusion (SWI) affects the eastern portion, as evidenced by the significant presence of chlorides in groundwater samples. Moreover, high concentrations of anthropogenic nitrogenous compounds (NO_3, NO_2, NH_4^+) are found within the SGD fluxes measured on the beach of Sitges, suggesting an impact that extends far beyond local communities, affecting coastal and marine ecosystems. Ultimately, the research explores the interplay between climate change and groundwater contamination, discussing how these factors may interact to exacerbate adverse effects in the target area. This study highlights the urgent need for sustainable groundwater management practices, as the subject under investigation transcends the mere environmental dimension, affecting local communities with significant anthropological, social, and economic repercussions.

1. INTRODUCTION

1.1 OVERVIEW AND RESEARCH JUSTIFICATION

1.2 STUDY OBJECTIVES

Following the aforementioned introductory remarks and research gaps, this section outlines the principal study's objectives with respect to the regional impacts of climate change and groundwater contamination in the coastal basin of Garraf.

1st Objective: climate change impacts
To assess quantitatively and qualitatively the impact of climate change in the region of Catalonia, with specific attention to the coastal basin of Garraf, by means of historical records of temperature and precipitation.

- To understand whether mean surface temperature has increased over the last ~70 years, and how much with respect to the global and Mediterranean average (*is it a global hotspot?*), and what is the consequential impact on the regional coastal areas.

- To understand whether and how the precipitation regime may have changed over the last ~70 years, whether the modification is coherent with respect to the main trends in the Mediterranean basin, and how these shifts in the hydrological regime might possibly affect the aquifer system in Garraf, both in terms of quantity and quality of groundwater.

2nd Objective: groundwater contamination
To analyse quantitatively and qualitatively the main groundwater hydro-chemical trends in Garraf, through the analysis of primary and secondary data of groundwater contaminants and physical-chemical parameters.

- To assess the quality status of groundwater resources in Garraf, with specific respect to nutrient concentrations (nitrates, nitrites, ammonium, phosphates, silicates) and sea water intrusion (chlorides), by comparing the available sampled data with the standard pollution thresholds.

- To evaluate the spatial distribution of the contaminated resources and to highlight hotspot areas by means of creating concentration maps; to predict the contamination in the areas where no data are available through interpolation of samplings; to discuss the most probable causes of contamination by mapping the main anthropic activities in the basin; to spot interesting hydro-chemical patterns and interconnection between different contaminants; to discuss the potential impacts of these compounds on the local ecosystems, and in particular, on the coastal and marine ecology.

- To briefly discuss the interplay of different impacts in the study area, investigating whether climate change and groundwater contamination may interact to further exacerbate their adverse effects.

2. GLOBAL IMPACTS ON GROUNDWATER RESOURCES

Groundwater represents around 30% of the Earth's total fresh water reserves and 99% of total liquid fresh water, playing a pivotal role in the water cycle, sustaining ecosystems and supporting agriculture, while providing drinking water for millions of people worldwide. Globally speaking, it represent ~26% of the total annual water abstraction, accounting for agricultural, industrial and domestic use (IGRAC, 2010). Furthermore, groundwater provides 65% of drinking water and 25% of water for agricultural irrigation in the 27 EU Member States, according to the European Environmental Agency (EEA, 2022). However, the sustainability of groundwater resources is increasingly threatened by several natural and/or anthropogenic factors, leading to significant impacts on both its quantity and quality. Indeed, approximately 24% of the total groundwater body area in EU countries exhibited poor chemical status, while 9% showed poor quantitative status, according to the second river basin management plans of the EU countries (2016).

Several factors are responsible of posing increasing pressure on groundwater, such as population growth, urbanization, unsustainable agricultural practices, and poor water management. Among the numerous global impacts, groundwater depletion stands out as one of the major challenges. Indeed, the overexploitation of subsurface water for agricultural, industrial, and domestic purposes is posing serious concerns to the long-term availability of these resources. Moreover, climate change further exacerbates this scenario by altering the hydrological regime, with modifications in the precipitation patterns and extreme events. For instance, the increasing frequency and intensity of droughts are pushing people to rely more and more on groundwater resources to satisfy their water footprint.

Adding to this challenge is the widespread problem of contamination - mostly of anthropogenic origin - whereby pollutants from diverse sources infiltrate into the aquifers, compromising water quality and posing risks to human health and ecosystems. Agricultural activities, industrial discharge, and urban development are primary contributors to groundwater pollution. Furthermore, the phenomenon of saltwater intrusion poses another serious threat to coastal aquifers, where over-pumping of groundwater induces the infiltration of saline water, exacerbating freshwater scarcity and compromising water usability.

In this context, De Stefano et al. (2012) defined groundwater as the *hidden resource*, given that, unlike surface water, it is virtually invisible, and therefore often overlooked by policy-makers and water practitioners. Hence, effective policy frameworks are urgently needed to address these pressing issues and ensure the long-term sustainability of groundwater. Sustainable groundwater management, coupled with virtuous land-use practices and climate-resilient water policies, will be pivotal in securing the availability of this precious resource for current and future generations, aligning with Sustainable Development Goals (SGDs), such as ensuring clean water access (SDG6), mitigating climate change impacts (SDG13), and supporting terrestrial biodiversity (SDG15).

1.1 CLIMATE CHANGE

Climate change is undoubtedly one of the major challenges of current time. Global surface temperature has increased by 0.99 [0.84 to 1.10] °C from 1850–1900 to the first two decades of the 21st century (2001–2020) and by 1.09 [0.95 to 1.20] °C from 1850–1900 to 2011–2020 (IPCC, 2021). The global warming effect triggered by the escalating concentration of greenhouse gases (GHGs) in the atmosphere is causing numerous and differentiated impacts on planet earth, ranging from the intensification of precipitation events and floods to the melting of ice caps and sea level rise, to the desertification of land and water scarcity – just to mention a few. Indeed, the Intergovernmental Panel on Climate Change (IPCC) has offered extensive evidence on both the changing climate system and its main drivers, assessing that anthropogenic factors are highly likely contributors to climate change, and highlighting the urgent need for global efforts to mitigate and adapt to these changes. In its Sixth Assessment Report (AR6) the IPCC concludes that *it is extremely likely that human influence caused more than half of the observed increase in global mean surface temperature (GMST) from 1951 to 2010.* Moreover, an understanding of the amount of human-induced global warming to date is key to assessing our status with respect to the Paris Agreement goals of holding the increase in global average temperature to well below 2°C above pre-industrial levels and pursuing efforts to limit the temperature increase to 1.5°C (UNFCCC, 2016).

2.1.1 Climate change basics

Climate can be defined as the long-term average of atmospheric conditions - encompassing parameters such as temperature, precipitation, wind, pressure, and humidity - observed in a specific geographic area over an extended period of time. In clear terms *climate is the synthesis of the weather in a particular region,* as stated by Dennis L. Hartmann (2016) in his manual '*Global Physical Climatology*'. Indeed, life and civilization on this planet would not have evolved as they have if the climate were substantially different, but the fundamental importance of climate is occasionally underestimated.

Among the various climatic variables essential for sustaining life on Earth, temperature stands out as the most remarkable. In an unaltered scenario, the global average temperature at the Earth's surface hovers around 15°C, resulting from the intricate global energy balance between solar influx (shortwave radiation) and the Earth's radiative emission outflux (longwave radiation). The gaseous compounds that form the atmosphere, such as water vapor and carbon dioxide (CO_2), are in fact transparent to the solar radiation - allowing it to enter atmosphere and reach the Earth's surface - while absorbent with respect to terrestrial radiation, preserving a warmer condition on the planet. This phenomenon goes by the name of *Greenhouse Effect (GH)*, and is indeed fundamental to support a habitable temperature on Earth. In fact, if no gases were present in the atmosphere, the mean surface temperature of Earth would correspond to its *Emission Temperature (ET)* -namely the temperature that the earth must be emitting at in order to achieve the energy balance with the incoming solar radiation – equal to around -18°C. One way to compute the strength of one planet's GH effect is to make a difference between the ET and the actual temperature given by the GH effect: on the Earth the difference is around 33 degrees (255-288K or -18°C-15°C), while for example on Mars the GH effect is much less relevant (18 degrees), and on Venus is very strong (533 degrees) (D. L. Hartmann, 2016).

Nevertheless, the GH effect has gained attention in recent years for its implication in climate change: although being beneficial when undisturbed, the GH effect can lead to global warming if too many gases enter the atmosphere. Indeed, the so-called GreenHouse Gases (GHGs) resulting from human activities are being released nowadays at an unprecedented rate, posing a considerable threat for the hospitability of planet Earth. Common anthropic GHGs include carbon dioxide (CO2), methane (CH4), chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), nitrous oxide (N2O), and ozone (O3) (IPCC, 2021). While water vapor is indeed the most abundant naturally occurring GHG in the atmosphere, it is noteworthy that CO2 surpasses others as the most emitted one (O. Yoro, O. Daramola, 2020).

Indeed, due to its escalating emissions and persistence in the atmosphere, carbon dioxide is considered the benchmark to measure a GHG's *heat-trapping capacity* and *atmospheric lifetime* through the so-called Global Warming Potential (GWP). Over a 100-year horizon, the GWP of GHGs are remarkably higher than CO2, which is considered the reference value equal to 1 (table 1). Thus, despite CO2 higher concentration and escalating rate from fossil fuel combustion, efforts to mitigate other GHGs should be actively pursued.

GHG	GWP for 100 years
CO_2	1
CH_4	23
N_2O	296
HFC - 23	12 000
HFC – 134a	1 300
SF_6	22 200

Table 1 - Global Warming Potential of different Greenhouse Gases (source: IPCC Third Assessment Report, 2001)

Climate change has become nowadays an obvious fact for the scientific community, with human activity identified as the primary cause since the latter half of the twentieth century, as outlined in the IPCC's Fifth Assessment Report. The main driver of GHGs emissions is the combustion of fossil fuels - such as natural gas, coal and oil - which has been unstoppably increasing since the second half of the 19th century, corresponding to the beginning of the second industrial revolution. On average, per capita CO2 emissions derived from burning fossil fuels and industry worldwidehave increased from less than 1 tonne/year at the end of the 20th century to almost 5 tonnes/year nowadays, with middle-east oil-producing countries leading the chart. However, by taking into account the total annual emissions per country, this scenario is rapidly modified, with China, United States, and India in the top three positions for 2022.

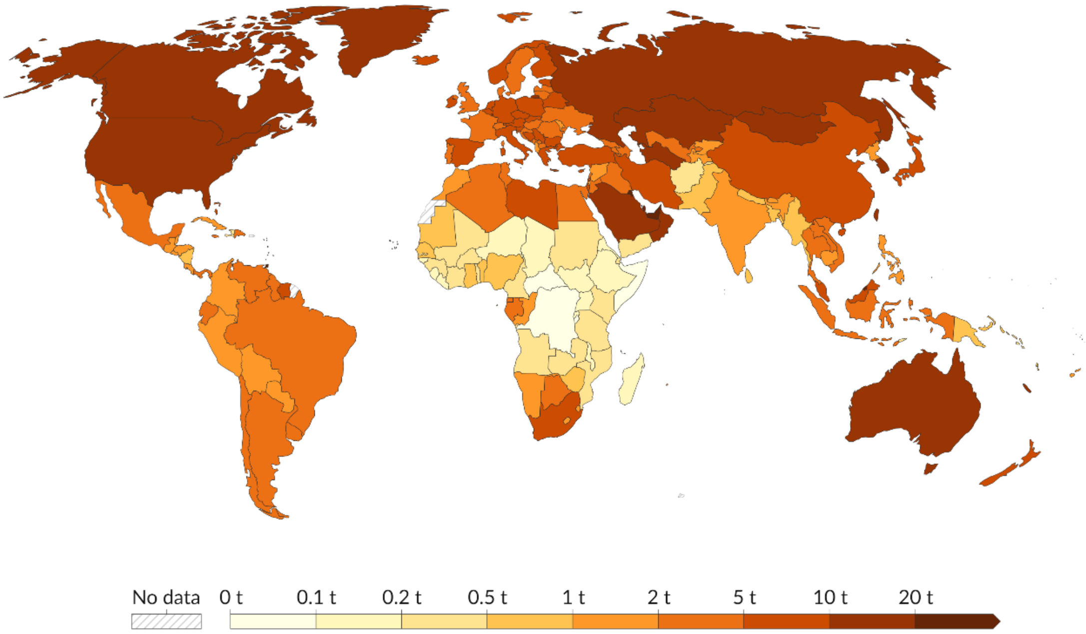

Figure 1 - Per capita CO2 emissions from fossil fuels and industry in 2022 (source: Global Carbon Budget (2023); OurWorldInData.org)

Moreover, what is particularly concerning about GHGs, is that the emissions have not only increased up to the present day but will continue to do so if concrete actions are not taken in the coming years, according to recent climatic projections. As a consequence, atmospheric CO_2 concentration has exceeded 400 parts per million in 2013, a milestone not reached in eight hundred thousand years. As a point of reference, pre-industrial CO_2 levels were around 280 parts per million (ppm) and today, we stand near 420 ppm. Furthermore, in the past ice ages CO_2 levels were about 200 parts per million (ppm), while in warmer periods, they were around 280 ppm, according to paleoclimate scientists. Thus, the term *Anthropocene* has been introduced to describe the current *geological era* in which human action is largely responsible for climate modifications.

Concurrently, the planet's average global surface temperature has surpassed pre-industrial levels by 1°C in 2015, with the 2023 being the warmest year on record so far. More specifically, the first two decades of the 21st century have been the warmest so far: surface temperature has increased by 0.99 [0.84 to 1.10]°C from 1850–1900 to the first two decades of the 21st century (2001–2020) and by 1.09 [0.95 to 1.20] °C from 1850–1900 to 2011–2020 (IPCC, 2021). In its Sixth Assessment Report (AR6) the IPCC concludes that *it is extremely likely that human influence caused more than half of the observed increase in global mean surface temperature (GMST) from 1951 to 2010.*

To understand the magnitude of climate change it is necessary to look at the very short timeframe in which the change is taking place. Indeed, the climate of planet Earth has always undergone large modifications – reaching several degrees above or below the current mean global surface temperature – but these have spanned across millions of years, the so-called geological eras (figure 2). Vice versa, the current rise in temperature associated with anthropogenic climate change has evolved over less than two centuries. Therefore, the carbon stored by fossil fuels through photosynthesis over millions of years - especially during the Carboniferous period which lasted approximately 60 million years - is now being rapidly released into the atmosphere within just a few centuries through their combustion, provoking a major imbalance in the global carbon cycle.

Climate scientists have highlighted the straightforward correlation between mean global surface temperature and CO_2 concentration in the atmosphere during the course of several geological eras and up to present day. Throughout the past 650,000 years, there has been a recurring cycle of fluctuations in temperatures and atmospheric CO2 levels. During glacial periods, commonly referred to as ice ages, extensive ice sheet expansion occurred on terrestrial surfaces, while interglacial intervals brought warmer temperatures. Currently, the Earth has been experiencing an interglacial period for over 11,000 years, and according to IPCC *it is very unlikely that the Earth would naturally enter another ice age for at least 30 thousand years.*

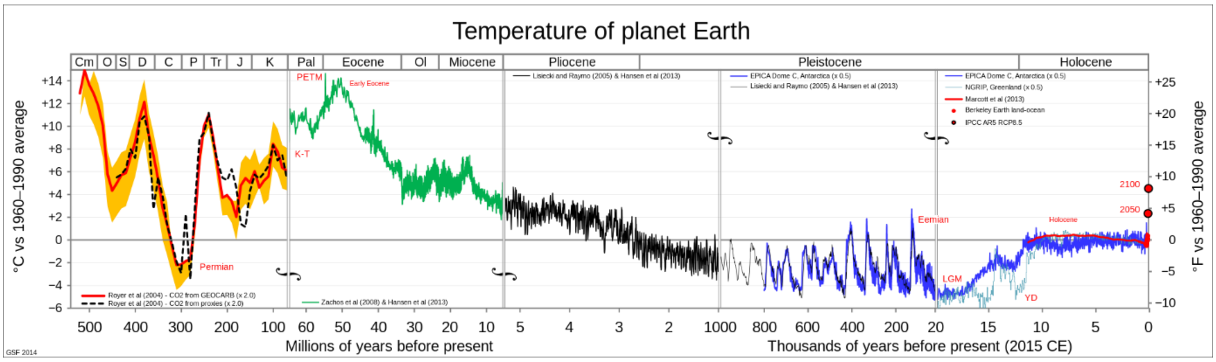

Figure 2 - Estimated global average surface air temperature over the last 540 million years (temperature anomalies, relative to the 1960-1990 average, source: Wikipedia).

Mean global surface temperature is projected to keep increasing in the next coming years if no tangible actions are implemented. The Paris Agreement signed in December 2015, under the United Nations Framework Convention on Climate Change (UNFCCC), established a target to limit the average global temperature increase at 2°C compared to pre-industrial levels, with additional efforts to limit the increase to 1.5°C. All 196 countries that signed the agreement pledged to firmly reduce their GHGs emissions through the implementation of National Determined Contributions (NDCs). Furthermore, they committed to ensuring that human activities would not generate more GHGs than what can be naturally or artificially removed from the atmosphere, employing methods such as carbon sequestration by forests, or artificial CO_2 uptake. Indeed, experts claim that exceeding this 2°C threshold would result in profound social, economic, and environmental repercussions. However, over two-thirds of the admissible carbon emissions contributing to a temperature increase beyond 2°C have already been discharged into the atmosphere. Thus, understanding global warming to date is crucial to assess progress with respect to the Paris Agreement goals of holding the increase in global average temperature to well below 2°C above pre-industrial levels and pursuing efforts to limit the temperature increase to 1.5°C (UNFCCC, 2016).

2.1.2 Climate Change in the Mediterranean

On the light of the previous considerations, it is certain that climate change is a global challenge that affects virtually every country on Earth. However, its effects are not evenly distributed across the globe. In fact, while there is a global trend of rising average temperatures, certain regions are undergoing more rapid warming than others. These are called *Climate Hotspots,* namely areas which are particularly sensitive to the impacts of climate change, due to their peculiar – if not unique – geographical location and/or vulnerability of both natural and anthropic systems. Some examples include the Arctic, the Amazon forest, the Mediterranean basin, Pacific Islands, and sub-Saharan Africa, which all face severe environmental impacts such as ice melting, deforestation and sea-level rise, paving the way for humanitarian crisis such as migration and food insecurity.

According to IPCC, *the Mediterranean region is a hotspot for highly interconnected climate risks due to its particular combination of multiple strong climate hazards and high vulnerability (IPCC, 2021).* Furthermore, *the main risk factor identified is drought, generally expected to increase in the region, significant already at global warming of only 1.5°C* (IPCC, 2021).

Although no univocal scientific explanation is found on the exceptional warming occurring in the Mediterranean, some researchers attribute it to changes in upper atmosphere circulation dynamics and a reduction in the temperature contrast between land and sea. These factors interact to create a high-pressure area over the Mediterranean, resulting in diminished precipitation. In addition, the region could be particularly sensitive to the effects of climate change due to its geographical location and unique environmental characteristics, such as the presence of an enclosed sea surrounded by landmasses. Secondly, the Mediterranean is a densely populated area which is currently home to more than 500 million people, featuring dense urban settlements and industrial infrastructure situated near sea level. In this context, climate change exacerbates existing issues such as urbanization, land use change, overfishing, pollution, biodiversity loss, and degradation of land and marine ecosystems.

In its Sixth Assessment Report (AR6), the IPCC looked for the first time at the regional impacts in the Mediterranean area, drawing conclusion on the main climate modifications that the region is already experiencing (IPCC, 2021):

- The surface temperature in the Mediterranean region has now surpassed the pre-industrial level by 1.5°C, leading to a notable increase in high-temperature extreme events (*high confidence).*

- Trends in precipitation exhibit variability across the basin (*low confidence*), yet droughts have escalated in frequency and intensity, particularly in the northern Mediterranean (*high confidence).*

- The sea surface temperature has risen by 0.29°C–0.44°C per decade since the early 1980s, with more pronounced trends observed in the eastern basin.

- Sea levels have experienced a rise of 1.4±0.2 mm per year throughout the 20th century (2.8±0.1 mm per year over 1993–2018) (*high confidence*). Ocean acidity is increasing (*medium confidence*).

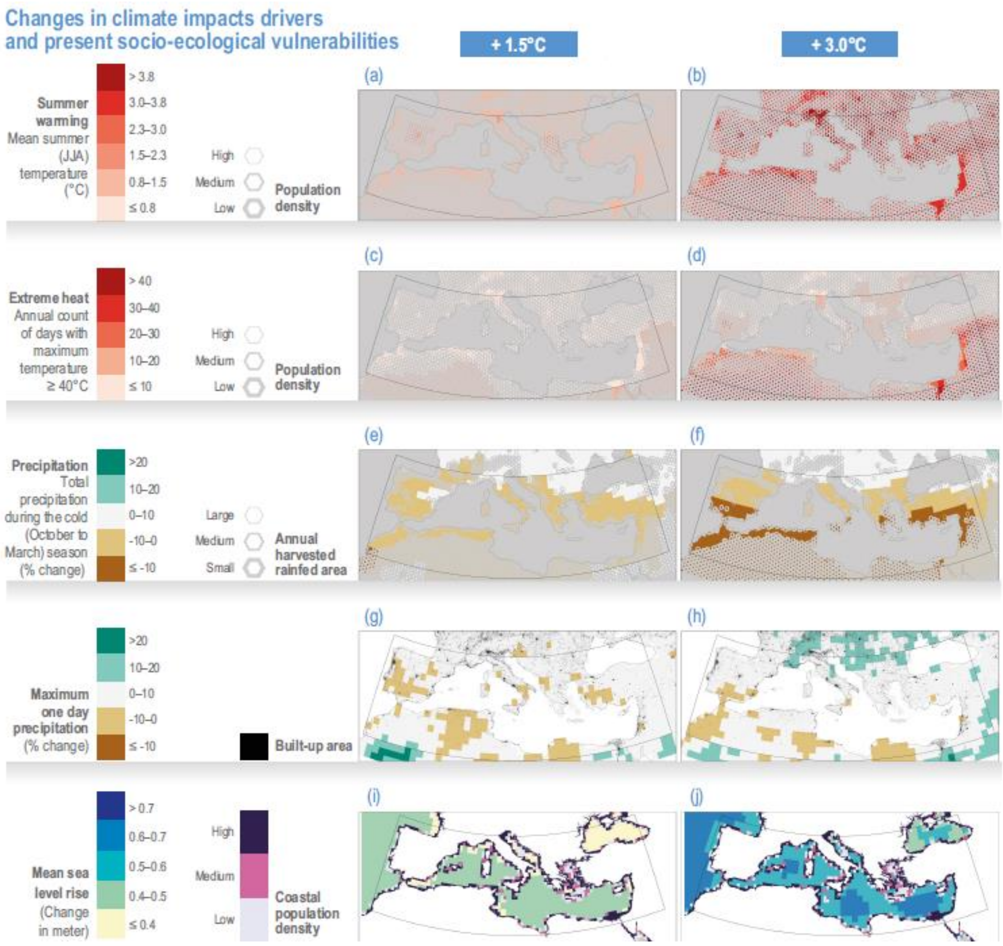

Figure 3 – Changes in climate impact drivers with respect to the 1995-2014 period for 1.5 °C (left column) and 3°C (right column) global warming (source: IPCC, 2021)

In this scenario, the most affected areas seem to be the coastal ones, especially those located in the south part of the Mediterranean basin, due to climate-related risks such as sea level rise, floods, erosion, desertification, plus consequent risks such as saltwater intrusion and agriculture decline (due above all to a reduction in the yield of rainfed crops). In AR6 it is claimed that coastal flood risks is going to increase along 37% of the Mediterranean coastline (currently hosting 42 million people), and that by 2100 the number of people exposed to sea level rise may reach up to 130% compared to present day. Furthermore, all these impacts are expected to grow stronger as the end of the century approaches: both air and sea temperatures, including their extreme events such as heatwaves, are expected to rise at rates exceeding the global average, while most regions are likely to experience a decrease in precipitation ranging from 4–22%, depending on the emission scenario (IPCC, 2021).

2.1.3 Climate Change impacts on Groundwater

As previously stated, climate change is producing – and will continue to produce - widespread impacts on all the different compartments of our planet (e.g. atmosphere, hydrosphere, biosphere etc.). However, the most evident and undeniable impact of rising temperatures is foreseen on the hydrological cycle, affecting the availability, the distribution, and ultimately the quality of water resources, causing alternating patterns of droughts and floods, and increasing the risk of water scarcity in many regions worldwide.

Climate change is expected to affect both groundwater quantity and quality. These impacts include modifications in recharge rates by reducing precipitation and increasing evapotranspiration (Treidel et al., 2012), shifts in aquifer dynamics, and exacerbating contamination risks. However, climate change studies often address surface water, overlooking groundwater resources (Kundzewicz and Döll, 2009; Green et al., 2011).

Impacts On Groundwater Quantity

Speaking about groundwater quantity, it is confident to say that climate change will produce modifications in groundwater recharge rates, affecting the possibility to exploit groundwater resources for human use, since many of them are not renewable over short time scales.

According to Carr & Simpson (2017), the Groundwater Response Time (GRT) *is a measure of the time it takes a groundwater system to re-equilibrate to a change in hydraulic boundary conditions.*

In this regard, it is crucial to make a distinction between different types of aquifer systems. Indeed, unconfined aquifers, being closer to the surface and less constrained, are more likely to contain groundwater that is renewable over human time-scales (less than 100 years), and are more sensitive to climatic variations due to their direct exposure to environmental factors; vice versa, the deeper confined aquifers are more likely to contain non-renewable groundwater volumes (Winter, 1999; Healy and Cook, 2002; Sophocleous, 2002; Lee et al., 2006). In addition, the size of an aquifer can indeed influence its response time to climate change. Smaller aquifers generally exhibit a faster response time compared to larger ones, owing to the quicker flow of water through smaller aquifer dimensions. However, factors such as soil porosity and aquifer permeability also play significant roles in determining the overall response time.

Besides the aquifer type, another factor that influences the groundwater response to climate change is represented by the local climate conditions themselves. According to Bates et al. (2008), an increase in precipitation would enhance groundwater recharge in the semi-arid regions, but would lower the recharge in humid regions due to the conversion of rainfall in surface runoff. Clearly this phenomenon is influenced by topography, soil composition, and land use, which collectively determine the rate at which water can infiltrate the soil and replenish the aquifer.

Cuthbert et al. (2019) provided the first comprehensive assessment of the sensitivity of groundwater recharge to climate change worldwide, determining a global median GRT of almost 6000 years (or 1200 years when excluding hyper-arid regions). Furthermore, they have demonstrated that only the 25% of the total groundwater resources distributed on the Earth's surface are renewable over human time-scales.

In the Mediterranean basin, climate change is expected to decrease groundwater recharge while increasing groundwater withdrawal rates (Treidel et al., 2012). These impacts will be especially dramatic in Southern Europe and North Africa, where groundwater recharge and soil water content will decline especially during summer (Kovats et al., 2014; Niang et al., 2014). In this regard, many studies have analysed the possible outcomes of groundwater recharge rates according to different rainfall conditions. For example, according to Hiscock et al. (2012) there is going to be an intensification of rainfall events during wintertime in North Europe, leading to enhanced groundwater recharge, while limited or zero recharge is expected during summer. An even worse scenario is the one predicted for Southern Europe, featuring the near disappearance of groundwater recharge and increased water stress throughout the year, with Spain being the most affected country.

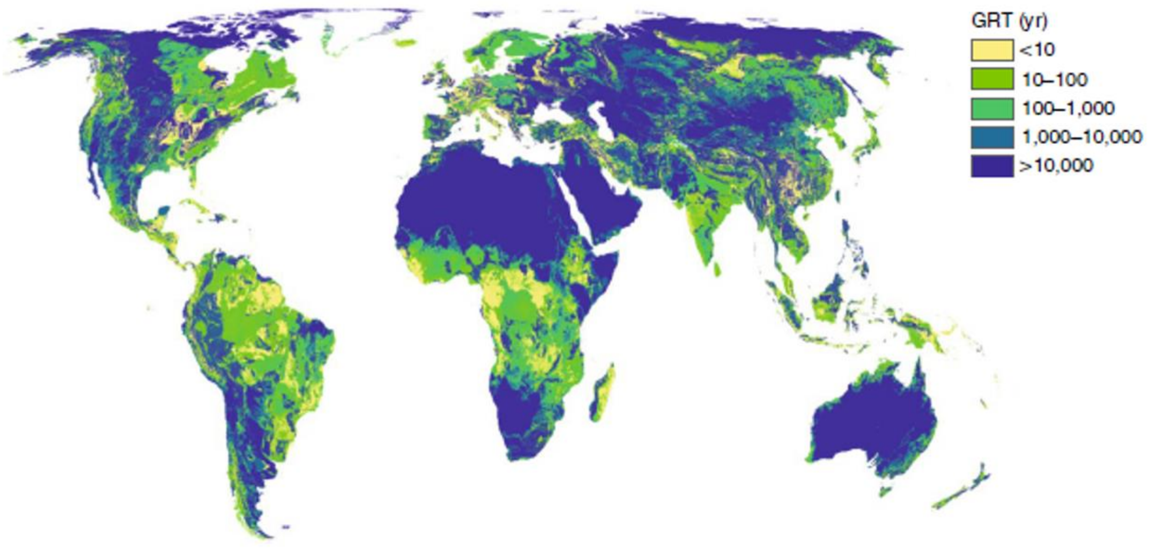

Figure 4 – Global distribution of groundwater response times (log scale) (source: Cuthbert et al., 2019)

Impacts On Groundwater Quality

Groundwater quality plays a critical role in determining its suitability for various purposes, above all drinking and irrigation, and is essential for ensuring the long-term sustainability of global groundwater resources (Gurdak et al., 2012). In this regard, numerous threats are posed by climate change, but the scientific production on this topic is less abundant. Indeed, although climate change has no direct impact on groundwater quality, modifications in the volume of groundwater entering Groundwater-Dependant-Ecosystems (GDEs) may change the quality of the receiving waters (Earman and Dettinger, 2011).

Firstly, the effect of rising temperature and modifications in the hydrological cycle leads to enhanced reliance on groundwater as a primary source of freshwater for agriculture and domestic uses, potentially increasing the risk of contamination. Indeed, both droughts and floods might raise the probability of groundwater to be contaminated. In the first case, reduced groundwater level due to droughts and human over-exploitation increase the risk of contamination from sea water intrusion in coastal aquifers (Werner et al., 2013). Furthermore, according to Okkonen and Kløve (2011), *reduced soil frost result in more recharge and less overland flow*, *increasing groundwater availability but also the risk of leaching of contaminants during winter*. Vice versa, floods due to precipitation extremes might cause higher riverine concentrations of pollutants, potentially impacting groundwater systems that are in direct contact with surface water.

Furthermore, besides from external contaminants, the climatic modifications may also affect the physio-chemical status of groundwater resources and the natural biogeochemical cycles, with negative consequences on the local ecosystems. Thus, it is also fundamental to consider these impacts from an ecological perspective. For instance, Taylor and Stefan (2009) projected a potential increase of up to 4°C in groundwater temperatures in certain climatic regions under a doubling of CO_2 scenarios, which could influence various biogeochemical processes crucial for groundwater quality, such as nitrogen and carbon cycles, contamination, and contaminant transport (Figura et al., 2011).

According to Davidson & Janssens (2006), *climate variables such as temperature and precipitation impact the ecosystems in terms of net primary production and microbial activity, driving the availability of vegetation and its decomposition to Dissolved Organic Carbon (DOC).* Mcdonough et al. (2020) assessed a relevant decrease in DOC concentration during rainfall events in non-arid climates, due to a diluition effect of precipitation: *DOC decreased by 9.5 ± 1.1% for every 10mm increase in precipitation in the driest month of the year and by 2.5 ± 0.8% for every 10mm increase in precipitation in the wettest month of the year.* On the other hand, they discovered a reverse trend for arid climates, where *the precipitation in the wettest month of the year is not enough to cause significant dilution.* An increase in surface temperature and groundwater temperature might also be linked with enhanced biological activity in the soil zone.

2.2 ANTHROPOGENIC IMPACTS

Besides the natural hazards that threaten water resources due to climate change, many anthropogenic impacts add in to the matter, especially for communities that are heavily reliant on groundwater for their water needs. Indeed, current global trends such as population growth and urbanization are leading the increase of water demand for different purposes, primarily domestic, agriculture and industry use. According to the definition given by Bierkens and Wada (2019), domestic demand represents the share of water utilized for basic human needs, such as drinking, cooking and toilet flushing; secondly, agricultural demand refers to water employed for irrigation purposes and livestock-related needs; thirdly, industrial demand includes water used during manufacturing operations such as cooling processes. As a result, the overall volume of water abstracted to satisfy the human demand has increased from 500 to ~4000 km^3/yr over the last 100 years (Oki and Kanae 2006, Hanasaki et al 2008a, 2008b, Wada et al 2014, Hanasaki et al 2018).

Indeed, the scientific community has renamed this trend as the 'silent revolution' of freshwater resources, especially groundwater. Furthermore, while the effect of climate change on groundwater quality is still under study, there is no doubt about the adverse effects of anthropogenic activities. Notably, scientists agrees on the fundamental role that land use and land use change play on the level of contamination of groundwater resources due to landfill leaching, animal waste, fertilizer run-off, and waste (Lapworth et al., 2017).

2.2.1 Agricultural impacts

The Food and Agriculture Organization (FAO) of the United Nations reports that in the next 30 years, it will be necessary to increase agricultural production by 70% compared to current levels to address the pressing global demographic growth and dietary shifts, among other things. In this regard, one of the major concerns is the excessive exploitation of natural resources - such as water and soil - and the use of fertilizers and pesticides that cause degradation of natural ecosystems, such as groundwater (Hasan, 2020) (C. Somerville, 2014). Indeed, the expansion of agricultural systems worldwide demands dramatically high volumes of freshwater for the purpose of irrigation and crop production. Globally speaking, only 17% of agricultural cultivations are irrigated (Abdullah, 2006), yet 70% of freshwater is used for agricultural production and livestock breeding.

Groundwater can act as a supplementary irrigation source during dry seasons when surface water is inadequate. Additionally, in regions with limited access to surface water, groundwater often serves as the primary irrigation source, especially in areas situated above productive aquifers (Wada et al., 2012). Recently there has been a consistent rise in the utilization of non-renewable groundwater, referring to groundwater extracted from aquifers that are unlikely to be replenished within human timescales (Gleeson et al., 2012). Indeed, a total of 70% of global groundwater abstractions are destined to agriculture, and over the last decades some countries have become groundwater-dependent for their crop production in response to growing agricultural demand and climate change. For instance, attempts to boost the domestic agricultural sector have led to the overexploitation of groundwater resources in India and Pakistan, bringing the countries to the brink of a severe groundwater crisis, as reported by FAO. Given the multifaceted impacts of agriculture on groundwater, it is urgent to adopt sustainable agricultural practices and implement effective groundwater management strategies in this sector.

Impacts on groundwater quantity

The most evident impact of agriculture on groundwater is the excessive extraction for irrigation purposes, which ultimately leads to the depletion of aquifers. According to the European Environmental Agency (EEA), the highest abstraction pressures are found in Greece, France, Hungary, southern Italy and Spain. Siebert et al. (2010), report that the current abstraction rate of groundwater for irrigation purposes would be around 545 km^3/year.

Furthermore, Wada et al. (2012) demonstrated that non-renewable groundwater resources accounted for the 20% of total share to the gross irrigation water demand in the year 2000, having more than tripled in comparison to the year 1960. Furthermore, most of these abstractions occurred in arid and semi-arid countries, such as Pakistan, Iran, Saudi Arabia, Libya, UAE and Qatar. The unsustainable use of groundwater for irrigation is a significant concern not only for countries with high groundwater utilization but also for the global community, as international trade connects food production in one country to consumption in another. In this scenario, the stakeholders which are more likely to be negatively affected are the rural communities, as the lowering groundwater levels will require more advanced technology to abstract freshwater in the coming years, something that is not necessarily within reach of small family farmers. Indeed, the escalating phenomenon of *landgrabbing* – namely the large-scale acquisition of land, typically by corporations, and governments – is already reducing access to groundwater resources for small-scale farmers in many parts of the world.

Besides groundwater over-exploitation, the conversion of natural habitats to irrigated agricultural land, can disrupt the natural balance between surface water and groundwater interactions, with severe consequences on groundwater recharge rates and flow patterns. According to Bierkens and Wada (2019), future changes in land use, especially in agriculture, are crucial because areas with intensive irrigation coincide with global hotspots of groundwater depletion.

Finally, intensive groundwater pumping in coastal areas can lead to saltwater intrusion, meaning the movement of saline water into freshwater aquifers, which occurs when the natural balance between freshwater and saltwater is disrupted. This intrusion can have detrimental effects on agriculture, drinking water supplies, and ecosystems, leading to soil salinization, loss of vegetation, and degradation of water quality. Therefore, saltwater intrusion represents a dual anthropogenic impact, both in terms of quantity and quality, primarily resulting from over-pumping, but ultimately degrading the overall quality of underground water resources. When a coastal aquifer undergoes a process of saline intrusion, the primary manifestation is undoubtedly the increase in salinity in extraction wells, establishing a clear cause-and-effect relationship. Given the precise knowledge of the geological and hydrogeological characteristics of a specific aquifer, any approach to studying saline intrusion must be based on prior knowledge of the physicochemical characteristics of the water present in it (Castillo and Morrell, 1988).

Impacts on groundwater quality

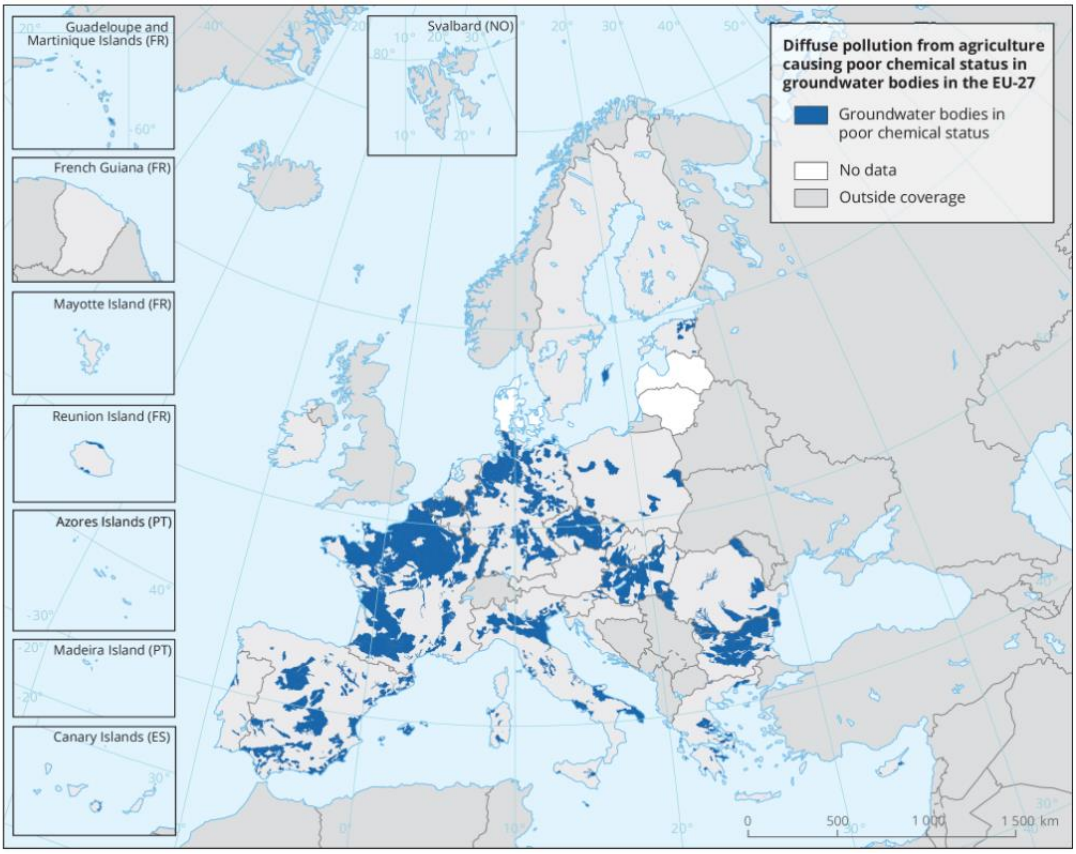

Figure 5 - Groundwater bodies of poor chemical status, affected significantly by diffuse source pollution from agriculture in the EU-27, as reported in national 2016 RBMPs (source: EEA 2020; Psomas, Bariamis, Roy, et al., 2021

2.2.2 Other impacts

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2.2.3 Impacts on groundwater in Spain

According to N. Hernández-Mora et al. (2002), groundwater use in Spain has increased dramatically over the last few decades, going from 2000 Mm3/yr of total pumped volume in 1960, to 6000 Mm3/yr in 2000. Going forward, De Stefano et al. reported that the groundwater demand was estimated to be at 7000 Mm3/yr in 2012. In this regard, the biggest share of abstracted water is requested by the agricultural sector, followed by industry and domestic use, coherently with the global trends. Indeed, almost one third of the Spanish population relies on groundwater as the primary source of drinking water.

Groundwater resources in Spain underwent a long record of overexploitation. In 1985 the Water act declared 'overexploited' 16 aquifers within the country (N. Hernández-Mora et al., 2002). Lately in 1998, the water administration unit labelled as 'overexploited' 77 hydrogeologic units. Nevertheless, not many and comprehensive data are available on the level of exploitation and uses of groundwater in Spain. One reason could be that traditional policies and frameworks have typically centred on surface water management, to the detriment of groundwater. Besides that, groundwater quality has been often overlooked in Spain, in favour of quantitative studies.

Nowadays, some improvements have been achieved thanks to the implementation of the European Water Framework Directive (WFD), which allowed to identify the main priorities in the management of the groundwater bodies (GWBs). According to De Stefano and Llamas (2012), the WFD *has shifted the focus of groundwater management from only satisfying water demands to achieving good chemical and quantitative status of groundwater bodies, as well as protecting the associated aquatic and terrestrial ecosystems.*

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3 DESCRIPTION OF THE STUDY AREA: GARRAF

The target area of the present study is the county of Garraf, one of the 42 administrative division of Catalonia (*comarcas*), which derives its name from the massif overlooking the region. This area belongs to the region of Penedès, in the province of Barcelona, and includes six municipalities: Canyelles, Cubelles, Olivella, Sant Pere de Ribes, Sitges, and Vilanova i la Geltrù, with the last one being the capital of the county. The Garraf Massif spans for approximately 30 kilometers along the Mediterranean coast, and with its Garraf Natural Park, stands out for its distinctive landscape and valuable natural resources, driving both environmental conservation and local economic development.

Besides being an administrative division, this area is also delimited as an independent hydrographic basin by the Catalan Water Agency (Agencia Catalana del Agua – ACA), on the basis of the previous hydrogeological areas defined by the Geological Survey of Catalonia (SGC-ICC, 1992) (figure 5). The analyses performed in this study have been conducted with respect to this very delimitation, comprising mostly the Garraf Range - spanning across the basin in a northeast direction, plus part of the delta of the Llobregat river – in the vicinity of the airport of Barcelona, and part of the Penedés plain in the upper west part of the basin, for a total 233 km².

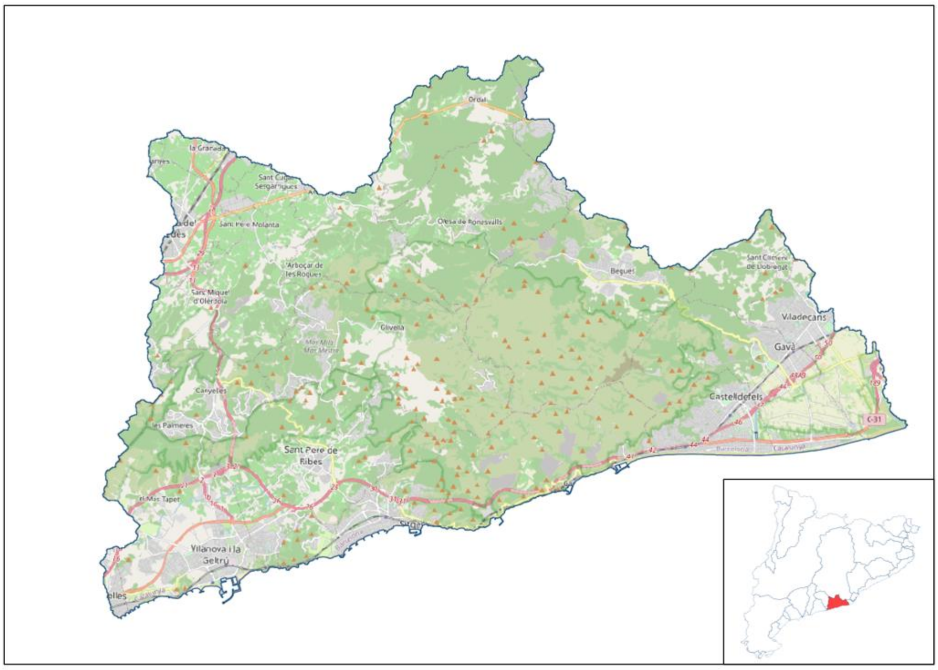

Figure 6 – Delimitation of Garraf hydrographic basin according to the Catalan Water Agency (ACA)

Furthermore, the ACA has identified 37 groundwater bodies (*masas de agua*) within the perimeter of Catalonia, a definition which includes not only the aquifer type and the hydraulic characteristics, but also the hydrochemical status of groundwater, the pressures and the impacts, and the protection levels of the aquifers that have been defined. In these terms, the Garraf basin belongs within the body number 23, identified as karstic formation vulnerable to sea water intrusion, nitrates and sulphates contamination (ACA, 2021).

3.2 REGIONAL HYDROGEOLOGY

The hydrological system of Garraf primarily develops in Jurassic and Cretaceous carbonate units, with thicknesses of up to 1000 m, encompassing both the unsaturated and saturated zones (AMB, 2021). This basin is characterized by its ephemeral streams, earning it the name "Rieres de Garraf." (rieres = ephemeral streams in Catalan). Only the Gaya River and the Foix River flow consistently throughout the year, standing out as exceptions in surface hydrology.

3.2.1 Geology of the massif

The Massif of Garraf is a faulted karstic block which forms part of the Catalonian coastal chain. Starting from the village of Garraf, the massif gradually moves inland, merging with the lower coasts of Penedès to the south. Moreover, detritic materials from the Llobregat delta collect at the base of the cliff. This horst covers an area of 500 square kilometers, forming low mountainous reliefs with a maximum height of 600 meters near the municipality of Begues (*Navarro et al., 2019).* The geology of Garraf has been studied since the early days of geological exploration in Catalonia. As early as 1897, J. Almera published the 1:40,000 scale geological map of the area between the Anoia River and the sea, and the following year, he wrote summaries of scientific excursions made to the Garraf massif.

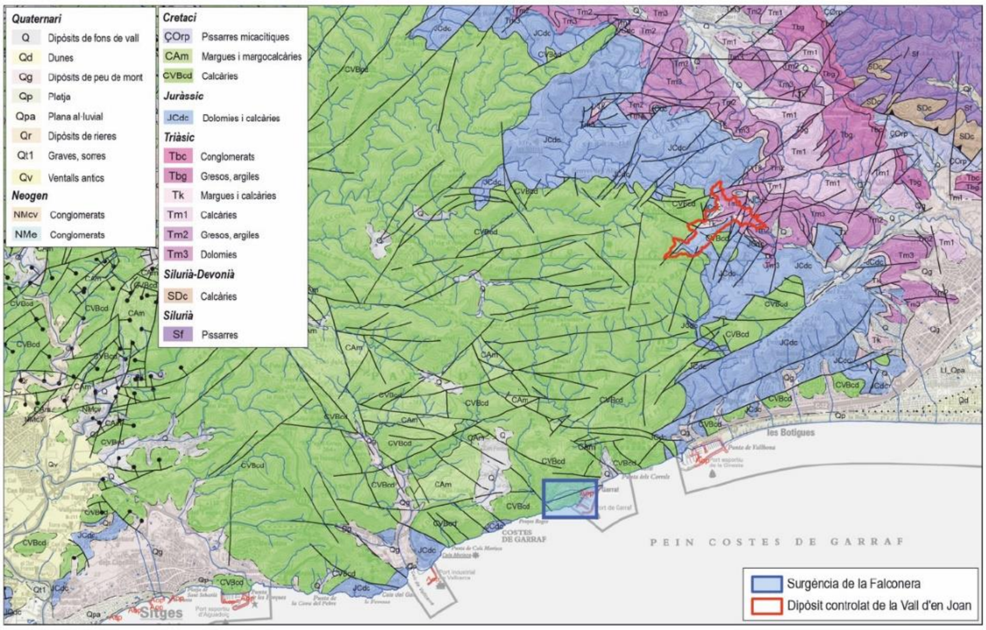

Figure 7 - Regional geological map of the study area 1:50,000 (source: Institut Cartogràfic i Geològic de Catalunya – ICGC)

Overall, the geological history of Garraf is complex, with a sequence of sedimentary rocks deposited over different geological periods, influenced by tectonic activity and environmental changes. Broadly speaking, Garraf is a massif composed of a thick and compact layer of Jurassic and Cretaceous dolomites and limestones, resting on Triassic limestones and sandstones, which in turn overlay Paleozoic materials. The Paleozoic basement consists of micaceous shales, phyllites, quartzites, and carbonates from the Ordovician, Silurian, Devonian, and Carboniferous periods. These rocks exhibit significant fracturing and faulting due to the Hercynian and Alpine orogenies. Paleozoic rocks are mostly exposed in the eastern margin of the Garraf massif, while Quaternary and Tertiary deposits cover much of the area, reappearing in the Collserola Range to the east. The Triassic cover includes conglomerates, sandstones, clays, and dolomites of the Buntsandstein, Muschelkalk, and Keuper formations, which exhibit typical lithological characteristics. The

Jurassic-Cretaceous cover comprises over 1,000 meters of dolomites and limestones, with the upper part belonging to the Cretaceous period, while the lower part is Jurassic. These formations define the Garraf massif and exhibit distinct lithological features, including compact dolomites and limestones. The Jurassic rocks are characterized by dark dolomites, while the Cretaceous rocks consist of extensive layers of light gray limestones with occasional dolomitic intercalations.

The most notable feature of Garraf's landscape is its karst topography, which is typical of limestone regions, where water erosion occurs mainly through surface and underground corrosion of the limestone, resulting in specific landforms and hydrological phenomena. The karst development in Garraf exhibits a polycyclic nature, as three distinct karstification cycles occurred during the Pliocene and Quaternary periods (Navarro et al., 2019).

The karstification process varies depending on the local climate, water abundance, carbon dioxide levels, and the physical and chemical characteristics of the rocks. The primary phenomenon in karstification is the dissolution of limestone rocks, facilitated by the presence of carbon dioxide, which forms carbonic acid when it mixes with water, according to the following reaction:

$$CO2 + H2O \rightarrow H2CO3$$

This carbonic acid dissociates into ions:

$$CO2 + H2O \rightarrow H^{+} + HCO3$$

Simultaneously, limestone can also dissociate into ions:

$$CaCO3 \rightarrow Ca^{+} + HCO3$$

This process is complex, involving reversible and interdependent reactions that can result in limestone corrosion or the formation of new rocks through carbonate precipitation. The dissolution of limestone depends upon factors such as the amount of carbon dioxide, temperature, and pressure. Increased carbon dioxide content enhances limestone corrosion, while temperature influences the solubility of carbon dioxide and, consequently, the dissolution process. Karstification occurs more rapidly in warm and humid climates with high organic matter content, as organic decomposition releases carbon dioxide, increasing water acidity and corrosiveness. The water infiltrated into the ground becomes enriched with carbon dioxide and calcium bicarbonate, leading to limestone dissolution. However, when water reaches areas with lower carbon dioxide pressure, bicarbonates precipitate out of solution. These alternating processes of corrosion and precipitation occur depending on changes in environmental conditions.

Unlike sedimentary aquifers - which typically consist of stratified and homogeneous layers that facilitate the movement of water in a predominant direction through pore spaces – in a karstic system like Garraf the water flow is mainly dictated by the presence of faults and fractures. These structures - which act as conduits for water - determine the socalled secondary permeability. Therefore, while sedimentary aquifers allow for a smoother and more predictable flow, in karstic aquifers the groundwater flow is not trivial to predict. In this regard, a geological map highlighting the underground faults and fractures is fundamental. However, karstic systems are dynamic and ever-changing since the rock formations can be dissolved by water over time, leading to the formation of further karst features such as caves, sinkholes, and underground rivers. Thus, other useful methods to determine the direction of groundwater flow include well monitoring, water tracing tests and spring analysis.

3.2.2 Groundwater hydrology

While the surface hydrology of the area is rather limited, the groundwater hydrology features a fascinating behaviour due to the presence of underground watercourses, which are certainly typical of karstic environments. Indeed, in a highly fractured karst landscape, rainfall quickly infiltrates through the rocks, resulting in minimal or no surface runoff, except immediately after intense downpours, when temporary surface flow occurs and quickly disappears.

According to *Mandel et al. (1972),* two different aquifers lie beneath the mountain range of Garraf: the lower one, being more permeable, would be constituted by basal dolomite and lithographic limestone, while the upper one would feature limestone and marls, making it less permeable.
Indeed, the upper aquifer has been reported to have a lower specific discharge, with boreholes yielding less than 5 m³/hr and local transmissivities in the order of 10 m²/day. Vice versa, some pumping tests performed on the lower aquifer have returned very contrasting results, with the specific discharge being around 5 m³/hr or 150 m³/hr according to the location of the borehole, and with local transmissivities in the order of 10000 m²/day in the second case. These results are coherent with the heterogeneous nature of karstic aquifers, characterised by differences in flow paths, groundwater velocities, and hydraulic conductivity between different locations, and reveal that the lower aquifer has probably reached a more advanced stage of karstification in comparison with the upper one.

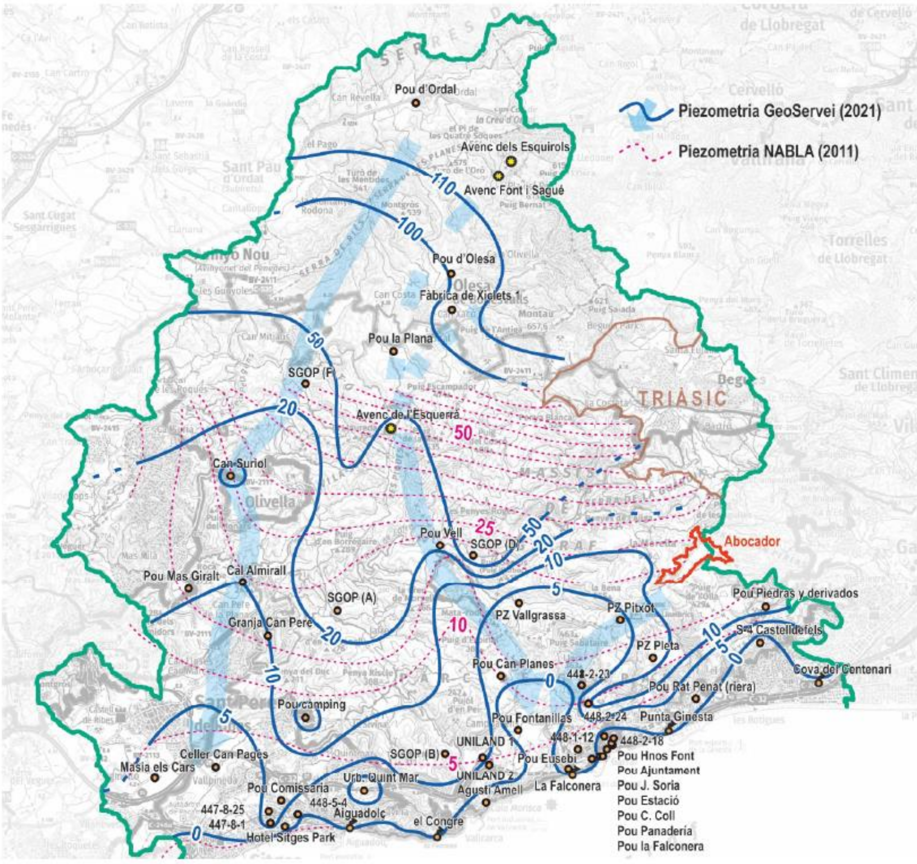

Figure 8 - Approximation of piezometry in Garraf hydrogeological basin (source: GeoServei, 2021)

This difference is also mirrored in the groundwater level of the two aquifers, which does not follow a linear pathway going from the inland area towards the sea, and represent a major challenge in the definition of a precise piezometric map of the groundwater system.

The piezometric level generally remains low relative to sea level, with moderate aquifer permeability influenced by intermingled marls. The Miocene-Quaternary aquifer experiences significant seasonal recharge fluctuations, behaving as both phreatic and confined in different areas. It comprises sand lenticular bodies and paleochannels with higher permeability, surrounded by a lutitic matrix of low permeability (Soler Bartomeus, 1983; Agència Catalana de l'Aigua, 2011c). For what concerns the flow direction, *Mandel et al. (1972)* report that the groundwater follows the main structural lines and faults in the inland part of the basin, while in the coastal part it goes through transverse faults in the seaward direction.

3.2.3 Submarine groundwater discharge

Among the numerous hydrogeological features of the karstic landscape in Garraf, Submarine Groundwater Discharge (SGD) stands out as a critical component of the coastal hydrological system and local ecology. The term submarine groundwater discharge (SGD) refers to the flow of water from the continental margins towards the sea which results in submarine springs.

Moore (1999) defined the mixing zone as the area where groundwater and seawater interacts, leading to several biogeochemical reactions, exchanging nutrients and other elements. Although in many cases this water flow comes straight from the coastal aquifer – generating a freshwater discharge into the ocean – the term SGD refers indeed to any type of submarine flux, regardless of the pathway. In this regard, recirculated seawater and brackish water that has formed in the mixing zone must also be accounted for in the total SGD volume. *Burnett et al. (2003)* probably gave the most inclusive definition of SGD, addressing "*any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force*". On the other side, some uncertainties persist in defining the scale length of the phenomenon, as these water exchanges may occur from meters to kilometres. For instance, *Moore (2010)* excluded from the definition of SGD those phenomena occurring on the scale of less than 1 m, which have been defined with other terms such as porewater exchange or benthic fluxes.

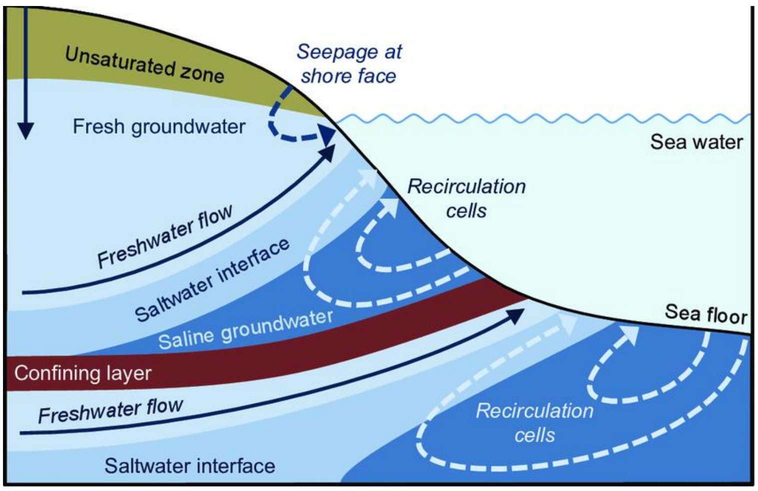

Figure 9 - Principal SGD pathways (source: Valentí Rodellas, 2014)

SGD fluxes take places in many coastal aquifers. In order for these flows to occur, two conditions must be satisfied: a positive hydraulic gradient towards the sea, and permeable rocks or sediments that are hydraulically connected to the sea itself. Due to this, SGD occur both in alluvial and karstic aquifers like Garraf, but in the second case the volumetric contribution of the flux is more relevant with respect to the flow of surface water into the ocean, due to the higher permeability of karstic systems. However, besides the morphology and the lithology of the aquifer, SGD also depends upon tides, waves, and variations of sea levels *(Moore, 1999).*

According to R. *Santos et al. (2021)*, the quantity of freshwater discharged through SGD represents only 1% of the total freshwater influx and less than 1% of overall SGD. However, in karstic carbonate systems like Garraf, fresh groundwater can be the primary component of SGD, often flowing through fractures or preferential paths to reach the ocean, where it emerges as submarine springs or localized seeps. In addition, the shorter travel time of water in karstic aquifers does not allow for many biogeochemical transformations to happen, and an almost direct fresh SDG flow is delivered to the sea.

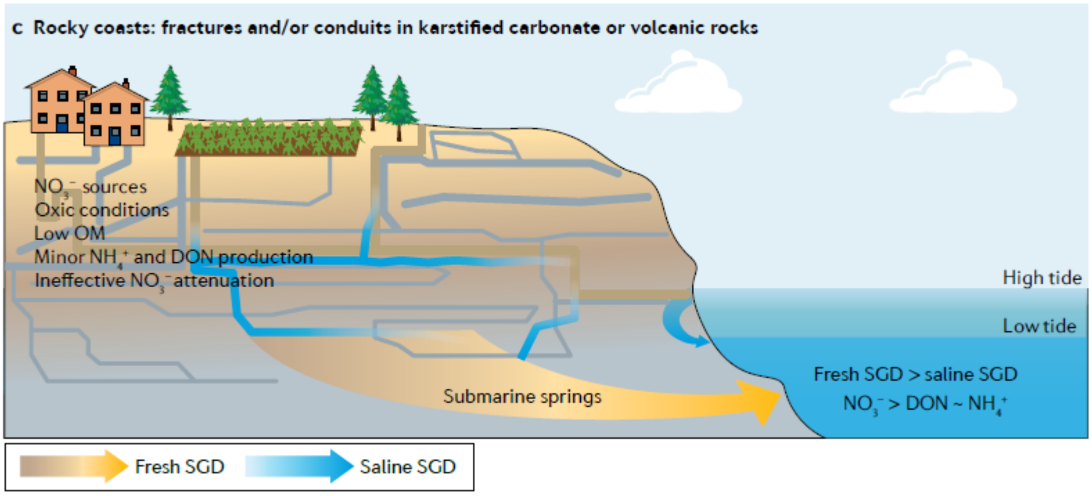

Figure 10 - Typical SGD behaviour in rocky and karstic coastlines (source: R. Santos et al., 2021)

Furthermore, besides the hydrological contribution, SGD fluxes of karstic aquifers represent the major volumetric source of nutrients to coastal areas. Undoubtedly, SGD plays a crucial role in regulating nutrients budget in coastal ecosystems, as groundwater typically has a higher concentration of nutrients, metals and salts than inland water *(Rodellas et al., 2015),* increasing the risk of eutrophication of coastal waters.

Moreover, these fluxes can be a source of anthropogenic elements into the ocean due to potential contamination of groundwater resources, such as pesticides and organic compounds coming from agriculture activities and landfills, posing a serious threat for marine and coastal ecosystems. Therefore, nutrient fluxes from SGD measurements can potentially serve as proxy data for groundwater contamination, although not being easy to quantify. In this respect, reference values have been reported by R. *Santos et al. (2021)* in their SGD review evaluating the fraction of nutrient discharge into the ocean imputable to SGD fluxes in over 200 locations worldwide. According to their analysis, these nutrient fluxes exceed surface water inflows in 60% of study sites, with median total SGD fluxes of 6.0 mmol/m² per day of dissolved inorganic nitrogen (DIN), 0.1 mmol/m² per day of dissolved inorganic phosphorus (DIP), and 6.5 mmol/m² per day of dissolved silicate (DSi). However, it is easy to underestimate the nutrient contribution of SGD to the ocean if the sampling are conducted in baseflow conditions overlooking extreme precipitation events (EPEs).

For example, Diego-Feliu et al. (2022) have estimated that the nutrient inputs after an EPE in a Catalonian coastal basin represented a large fraction of the total annual supply: specifically, 13% for DIN, and 11% for DIP and DSi. Certainly, these considerations are especially relevant when assessing the impact that climate change will exert over coastal and marine ecosystems in the coming years due to the increase of EPEs, both in terms of frequency and intensity.

These fluxes of nutrients are fundamental in the Mediterranean Sea, which is an oligotrophic water body relying on external inputs of nutrients for *primary productivity* (the rate at which organic matter is produced through photosynthesis by autotrophic organisms, such as plants and algae). Indeed, while atmospheric deposition and river runoff have been traditionally acknowledged as key sources, the significance of SGD has been overlooked despite its potential as a major contributor to dissolved compounds in the Mediterranean (Rodellas et al., 2015).

On these premises, the basin of Garraf is a major example, with a total of 17 coastal or submerged springs detected (McDonough et al., 2020). Among these, the Falconera spring has been identified as the largest coastal spring in the area, representing the outlet of a remarkable underground watercourse. In particular, according to the studies of the metropolitan area of Barcelona (AMB), the Falconera spring would have a total length of 600m, and a discharge of 500 l/s on average – which varies between 200 l/s and 10000 l/s according to the precipitation regime.

3.3 REGIONAL CLIMATOLOGY

The Spanish region of Catalonia lies within the temperate Mediterranean climate zone of the Northern Hemisphere, characterized by climatic complexity due to various air masses and irregular terrain. According to the Meteorological Service of Catalonia, the Garraf Massif is geographically located within the southern and central coastal Mediterranean climate zones. Consequently, this type of climate typically exhibits an average annual precipitation ranging between 500 and 700 mm, with a seasonal rainfall peak in autumn, and an average annual temperature between 14.5 and 17ºC. Therefore, the regional climate is temperate, somewhat semi-arid, except for the Begues plateau and nearby areas, where it is slightly more humid. Indeed, the precipitation in the region is irregular, with lower values in the west and southwest areas, and higher total annual amounts in the eastern half, especially in the central and northern regions.

A significant portion of the mountains in the coastal Mediterranean system act as precipitation generators, where moisture-laden winds from the Mediterranean encounter the mountains, forcing their ascent. The Garraf Massif is favourably oriented to both east and southeast winds. Within the framework of atmospheric general circulation, the Mediterranean region is situated to the south of the west general circulation zone. Consequently, this region is exposed to the influences of both the northern Atlantic atmospheric dynamics and the dynamics of the southern subtropical high belt, leading to the natural variability of weather types inherent in the Mediterranean climate. Additionally, these alternating cold and warm air masses from the north and south respectively come into contact with the Mediterranean air mass, characterized by its own temperature and humidity attributes, serving as the trigger for atmospheric instability processes. Thus, interactions between atmospheric conditions at different altitudes and on the surface come into play, potentially leading to the formation of situations of heavy rainfall, often associated with easterly winds or convective rainfall episodes.

In this context, rainfall dynamics play a crucial role in the Garraf's karst system, affecting groundwater discharge along the coast and contaminant transfer. Therefore, understanding rainfall patterns, alongside other factors, helps explain the frequency and intensity of contamination episodes at sites like Falconera and others across the region.
It is worth noting that in the central area of the massif, which is the wettest part of this territory, summer appears as the third season of the year with the highest average accumulated precipitation, due to the significant rainfall brought by summer storms. In the last decade, although they still contribute significantly to the total annual rainfall, the wettest seasons of the year (autumn and

winter) have tended to decrease their seasonal proportions, more noticeably in the case of autumn. The atmospheric mechanisms generating precipitation are the same across the Garraf Massif as a whole, but this mountain range acts as a modifier of rainfall in its spatial distribution, with higher annual precipitation to the east of the massif, exceeding 600 mm, while to the west, average annual values are below 600 mm. Along the strictly coastal strip to the west of the massif, rainfall amounts are lower, falling below 550 mm.

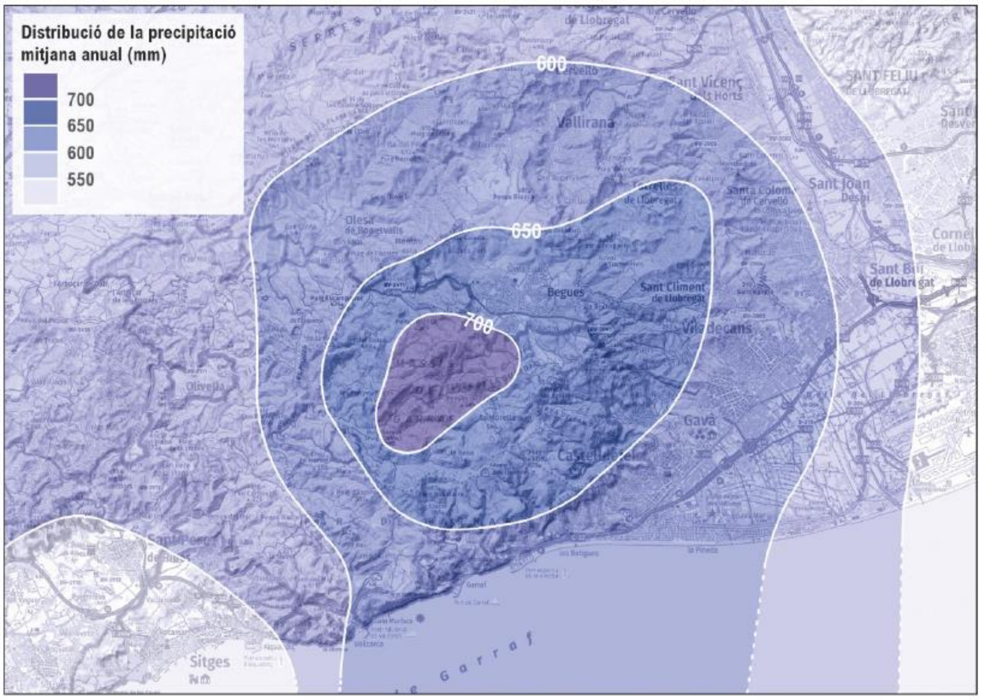

Figure 11 - Spatial distribution of mean annual cumulative rainfall in Garraf (GeoServei, 2021)

The rainiest area of the massif is located in the Vallgrassa valley, with nearly 700 mm annually, followed by Begues. During winter, most precipitation occurs due to the passage of fronts and low-pressure systems, while in spring, the most significant phenomenon is the passage of fronts. In summer, storms and precipitation caused by convective clouds with vertical development are common, and in autumn, easterly winds and fronts occur.

Furthermore, precipitation in the Garraf Massif is characterized by its variable and extreme nature, including modest rainfall, high interannual variability and irregularity, high daily concentration, high hourly intensity, and long dry periods. It is noteworthy that one of the causes of the different distribution of precipitation created by the Garraf Massif can be found in the convergence of air at low levels, given the interaction of relatively cold air descending through the Llobregat valley at night and warm, moist air over the Mediterranean, forming what is singularly referred to as a mesoscale surface front. This facilitates air convection and the formation of intense showers. The streams and torrents of the Garraf and Ordal mountains that flow into the delta and the Llobregat valley contribute to this supply of cool air (Mazón, 2008). When the Mediterranean air mass comes into contact with the cold air, the two air masses converge at the surface, causing the warm and humid air mass to rise over the relatively cold and dry air mass. This leads to the formation of powerful cloud formations, the onset of storms, and the occurrence of intense nocturnal rains, which discharge over the sea and may penetrate inland, affecting the delta area of the Llobregat and the eastern part of the Garraf Massif. This front can become stationary off the central Catalan coast, resulting in significant amounts of rainfall accumulating in a short period, causing flooding along the coastal front.

3.4 GROUNDWATER CONTAMINATION

Garraf constitutes a karstic ecosystem of enormous interest and complexity, but at the same time of high vulnerability. The groundwater resources in the basin have been severely impacted since the latter half of the 20th century from both anthropogenic and natural factors, leading to a deterioration of groundwater quality and damages to the local ecosystems.

The main anthropogenic activities which have negatively affected the basin include urban development, agriculture and farming, open-cast quarries, a cement industry near the coast, ports, and landfill sites such as Vall de Joan *(Navarro et al., 2019)*. These sources of pollution represent a major issue not only for the local communities – which abstract groundwater for domestic and agricultural use – but also for marine ecosystems, due to the fact that SGD fluxes directly discharge these contaminated waters into the sea. On the other hand, the coastal area of the basin is renown to be largely affected by sea water intrusion (SWI), especially the vicinity of the Llobregat river's delta.

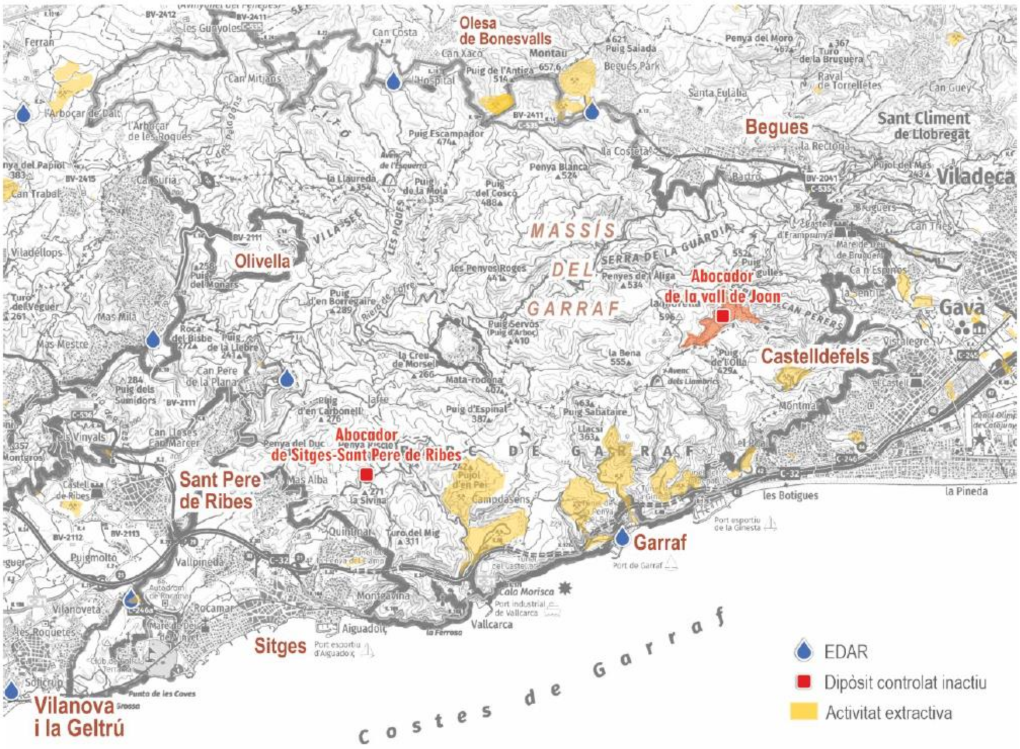

Figure 12 - Industrial activities, landfills, and water treatment facilities in Garraf (source: Metropolitan Area of Barcelona)

Vall de Joan landfill

In the Garraf block, there are various potential anthropogenic sources of groundwater contamination. Firstly, it is important to note the landfill for urban solid waste in the Joan valley or the Terradelles area, which does not comply with the impermeability requirement that should define every urban solid waste landfill.

Additionally, mention should be made of the former landfill for urban solid waste in Sitges, located at Collet de la Fita at the headwaters of the Vallcarca stream, near of the municipalities of Sitges and Sant Pere de Ribes *(AMB, 2021)*.

The Vall de Joan landfill was established in 1970 to accommodate urban waste from Barcelona, resulting in the deposition of nearly twenty-five million tons of diverse waste with heterogeneous properties over thirty years. Despite the favourable topography for landfill purposes, the geological context of the Vall de Joan - characterized by high karstification and fracturing – and poor management practices have posed several challenges. Indeed, the landfill's lack of impermeability has favoured the infiltration of leachate into the underlying carbonate massif, from 0 to 100 m deep (AMB, 2021). De Lapuente et al. (2014) demonstrated that the Vall de Joan landfill’s contaminants cause more embryotoxic damage compared to other Catalan landfills like Can Mata and Montferrer-Castellbó, with harmful effects on both terrestrial mammals and marine fauna and flora *(Navarro et. Al, 2019).*

Nowadays, various measures are being implemented to minimize these impacts, implementing control measures to mitigate the pollution effects. One such measure – prescribed by the Metropolitan Area of Barcelona - involved monitoring an extensive network of wells for both groundwater dissolved contaminants and gaseous compounds. According to the results of the study, the main source of contamination reported within inland groundwater and coastal submarine springs, is indeed the landfill of Vall de Joan itself. This issue not only impacts local ecosystems and the use of groundwater resources, but also the attractiveness and liveability of the area. It represents a multifaceted challenge, primarily of an environmental and ecological nature, but also encompassing social and economic dimensions. For example, according to Navarro et al. (2019), the smells produced by the Falconera submarine spring are so strong that some inhabitants left the area, as reported from the mayor of Sitges.

Figure 13 - Piezometry of Vall de Joan landfill (source: Esolve, 2022)

The analysis of leachates conducted by the Metropolitan Area of Barcelona revealed interesting insights about the main compounds present in the area. A significant quantity of inorganic substances detected in groundwater surpasses potable water quality standards, while some organic microcontaminants should not be present in groundwater et all. Robust markers, such as Total Organic Carbon (TOC) and ammonia, have been found in both leachates and groundwater, plus elevated concentrations of various soluble metals, including tin, aluminum, arsenic, and others, underscoring the toxic nature of the leachates. Moreover, the presence of high levels of chloride, sodium, potassium, bicarbonate, calcium, and magnesium suggested significant mineralization and salinity, while sulfate-reducing processes have been prominently observed in the Falconera spring and, to a lesser extent, in Aiguadolç and Punta Ginesta. Variations in these concentrations are influenced by local hydrodynamic characteristics, hydrological system interactions, and transport mechanisms such as karst drainage or diffusion, among other factors.

As a result, the landfill and its fluid contaminants entail various types of impact: in the hydrogeological environment of Garraf: int the atmospheric environment constituting the unsaturated zone of the karst; in open and underground spaces from gases brought by springs, wells, and piezometers (e.g. the Falconera spring); and in the coastal marine ecosystem due to contaminants and gases brought by SGD fluxes. In addition to the above-mentioned impacts, further threats are posed by the enhanced dissolution or karstification of the overlying carbonates. Indeed, the high production of CO_2 and its incorporation into the underground flow significantly increases the dissolution potential. Moreover, the incorporation of oxygen (O_2), leading to sulfur oxidation and a high supply of hydrogen ions (H^+), can also favour dissolution.

The collective findings conclude that no other potential contamination source in the Garraf massif compares to the Joan valley landfill. The identified contamination at various groundwater points can only originate from a massive contaminant source like the landfill, continually and persistently contributing to contamination.

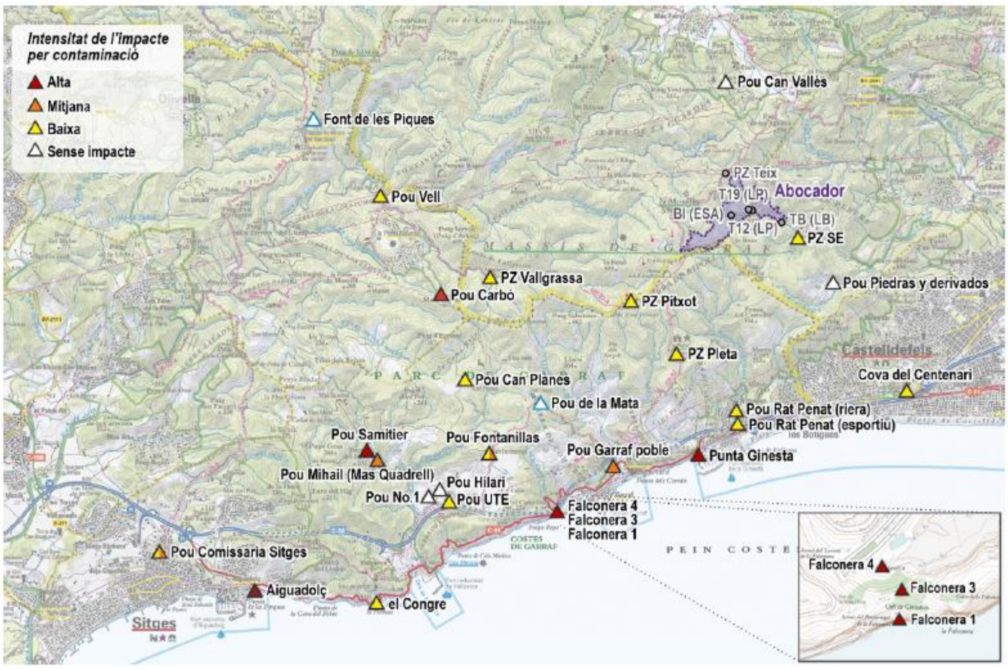

Figure 14 – Intensity of the contamination impact of Vall de Joan landfill across different sampling points in Garraf (source: AMB, 2021)

Agricultural activities

Sea water intrusion

Other anthropic impacts

4 METHODOLOGY

The research methodology employed a comprehensive approach, combining primary data collected directly in the field and secondary data deriving from online public databases, ensuring a robust and multifaceted analysis to address the complexities of the research topic within the scope of the present study.

4.1 DATA COLLECTION

The data collection process posed significant challenges due to the diverse range of data required, both in terms of spatial distribution – referring to the entire Garraf basin - and temporal evolution (historical datasets). The main criticalities included the need to navigate through multiple databases, contend with fragmented data sources, harmonize and manage diverse types of data, and address the absence of prior comprehensive studies on Garraf. These challenges highlighted the need for thorough data management and integration to ensure the research findings were reliable and cohesive. Planning and coordinating the collection of relevant datasets were crucial due to the extensive scope of the study.

First of all, the investigation on groundwater contamination in the Massif of Garraf has been developed through the following sources of data:

- records of groundwater physical-chemical data over the basin of Garraf available on the Catalan Water Agency (ACA) website for the period 1995-2022;

- samplings performed by the Groundwater Hydrology Group (GHS) of the Polytechnic University of Cataluña (UPC), in the context of a research activity on groundwater contamination caused by the Vall de Joan landfill in Garraf, for the period 2019-2022;

- samplings performed firsthand with the GHS on the day 03/10/2023 at the location of Sitges, in the context of a research activity on SGD, and analysed by the Institute of Marine Sciences (ICM) of Barcelona (ICM).

Secondly, for what concerns the climate change impacts analysis in Garraf, the following databases were employed:

- meteorological data, namely temperature and precipitation records, coming from the historical climate datasets of the Catalan Metereological Service (MeteoCat) for the period 1950-2022;

- piezometric data coming from the database of the Catalan Water Agency (ACA) for the period 2007-2022;

- piezometric data coming from the database of the Ministry for Ecological Transition and Demographic Challenge (MiTEco) of Spain for the period 2017-2020;

- piezometric data coming from the database of the Geological and Mining Institute of Spain (IGME) for the period 1969-2001

As a result of the data collection process, a total of 70 monitoring sites was found, each with a different location within or around the study area, and with different types of available data associated (among physical-chemical, nutrients, piezometric and meteorological).
Furthermore, in the case of the field survey conducted in Sitges, several samplings have been performed at different locations within the site, but only one point has been considered here for the purpose of the final distribution of the monitoring sites.

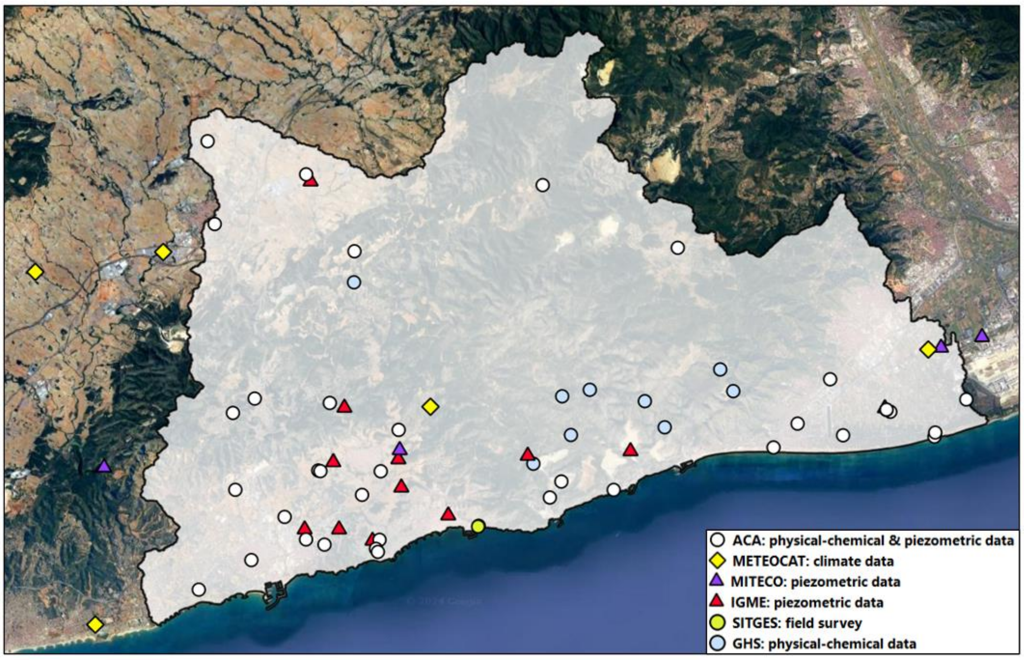

Figure 15 - Distribution of monitoring sites within the study area

In this process, it was observed that a greater cluster of monitoring points is available near the coast, contrasting with the sparser distribution in the inland areas. This may be attributed to the actual difficulty in sampling in rugged mountainous areas. Indeed, the abundance of monitoring stations near the coast proves useful in the analysis of groundwater contamination, which mostly affects these areas.

4.2.1 Metereological stations

Climate series are the main source of monitoring past and present climate, and become the basis for future climate projections. For this reason, it is essential to have series of wide temporal coverage, continuous, of quality, and homogeneous.

The climate data considered in this part of the study have been derived from the Catalan Metereological Service (MeteoCat), on the basis of the CADTEP database (Catalan Daily TEmperature and Precipitation data set). This database has been specifically developed for the region of Catalonia, comprising daily records of minimum temperature (TN), maximum temperature (TX), and precipitation (PPT). It integrates climate records from the State Meteorology Agency of Spain (AEMET) and the Catalan Meteorological Service (MeteoCat), to create homogeneous and uninterrupted time series spanning from 1950 to present day *(Prohom et al., 2023)*. Precipitation data are given in millimeters, while temperature data are presented in degrees Celsius.

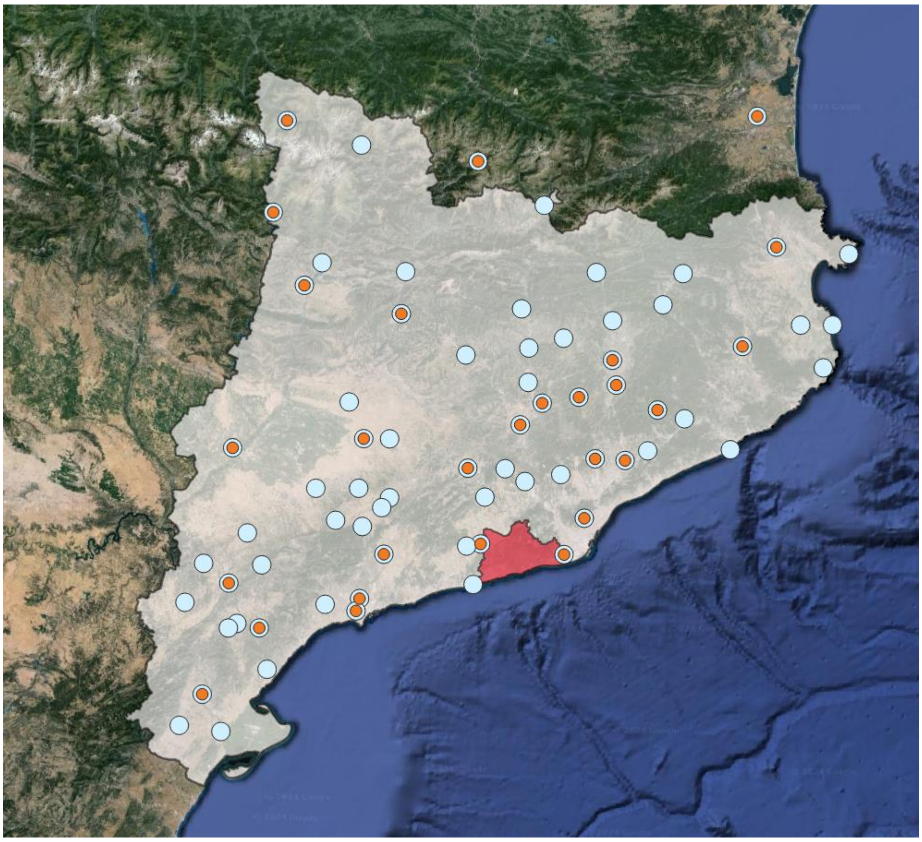

Figure 16 - Historical climate stations in Catalonia: precipitation records as blue dots and temperature records as red dots; Catalonia region in white; Garraf basin in red (source: self-generated image with data provided by the Catalan Metereological Service)

For this study, only daily values sourced from the database were utilized. All aggregations, such as monthly or annual averages and/or cumulative sums, were derived by processing these original daily data independently. Furthermore, the database does not provide a direct measure of daily mean temperature; thus, it was calculated by averaging the daily minimum and maximum temperature values for each day.

Before narrowing the climate change analysis on Garraf, all available stations in Catalonia have been taken into account. This allows for a broader perspective of the main climate impacts in the region, capturing spatial variability and validating the observed changes in Garraf with the general trends in Catalonia. A total of 72 historical climate stations was available in the region, all of them reporting precipitation records, and only 28 providing temperature data.
Among the available stations providing data for the period 1950-2022, only one was found within the study area of Garraf, namely the station located near Barcelona El Prat Airport, close to the coast. Therefore, the majority of the climatic analysis relied on data from this station. However, it was decided to complement the investigation with three additional stations located in the immediate vicinity of the basin: Cubelles, Vilafranca del Penedès, and Castellvì de la Marca. This allowed for a rough comparison of temperature and precipitation trends from different perspectives, including coastal and mountainous areas. Finally, the station of San Pere de Ribes was added, although only recording data from 2007, due to its strategic position within the basin.

Figure 17 - Location of the metereological stations in Garraf (source: Catalan Metereological Service)

Station	Region	X (m)	Y (m)	Z (m)	Data	Timeframe
El Prat Airport	Baix Llobregat	419544	4572631	3	P, T	1950-2022
Cubelles	Garraf	386684	4561776	17	P	1950-2022
Vilafranca del Penedès	Alt Penedès	389362	4576479	176	P, T	1950-2022
Castellví de la Marca	Alt Penedès	384319	4575694	198	P	1950-2022
Sant Pere de Ribes	Garraf	399905	4570375	161	P, T	2007-2022

Table 2 - Metereological stations in Garraf; coordinates are given according to UTM31 (source: Catalan Metereological Service)

4.2.2 Groundwater quality data

Regarding the analysis of groundwater contamination, reference was made to a total of 47 sampling points within the basin, divided as follows: 37 provided by the monitoring system of the Catalan Water Agency (ACA) for the period 2007-2022, and 10 provided by the groundwater hydrology group (GHS) of the Polytechnic University of Barcelona (UPC) for the period 2019-2022.

The water quality data provided by the ACA have been obtained in the framework of the Monitoring and Control Program (PSiC) of the agency, the instrument of hydrological planning that ptovide a detailed overview of the state of water bodies in the River Basin District of Catalonia. The results of this program allow other planning instruments to establish the degree of achievement of environmental objectives for each water body and analyze the necessary measures that must be implemented to achieve them, as well as their evolution over time. The results of the PSiC are then incorporated into the Management Plan of the River Basin District of Catalonia. The PSiC is fully implemented within a period of 6 years, during which different quality elements are measured and analyzed with varying sampling frequencies. Furthermore, the ACA drafted the first PSiC based on the criteria of the Water Framework Directive for the period 2007-2012, and subsequently, its revision was carried out for the period 2013-2018. Prior to this, there were also monitoring and control networks for water quality already in place, although these networks did not adhere to the currently established criteria and were not taken into account for the purpose of the present study.

As for the data provided by the GHS, they have been derived from a monitoring programme on the impact of the Vall de Joan landfill on the quality of groundwater in Garraf, conducted in partnership with the Metropolitan Area of Barcelona (AMB). Hence, these data were meticulously collected by researchers from UPC at the wells situated within the Garraf massif. Indeed, they have been obtained exactly at locations where data from ACA are not available due to the lack of wells in the area, enhancing the overall significance of the analysis.

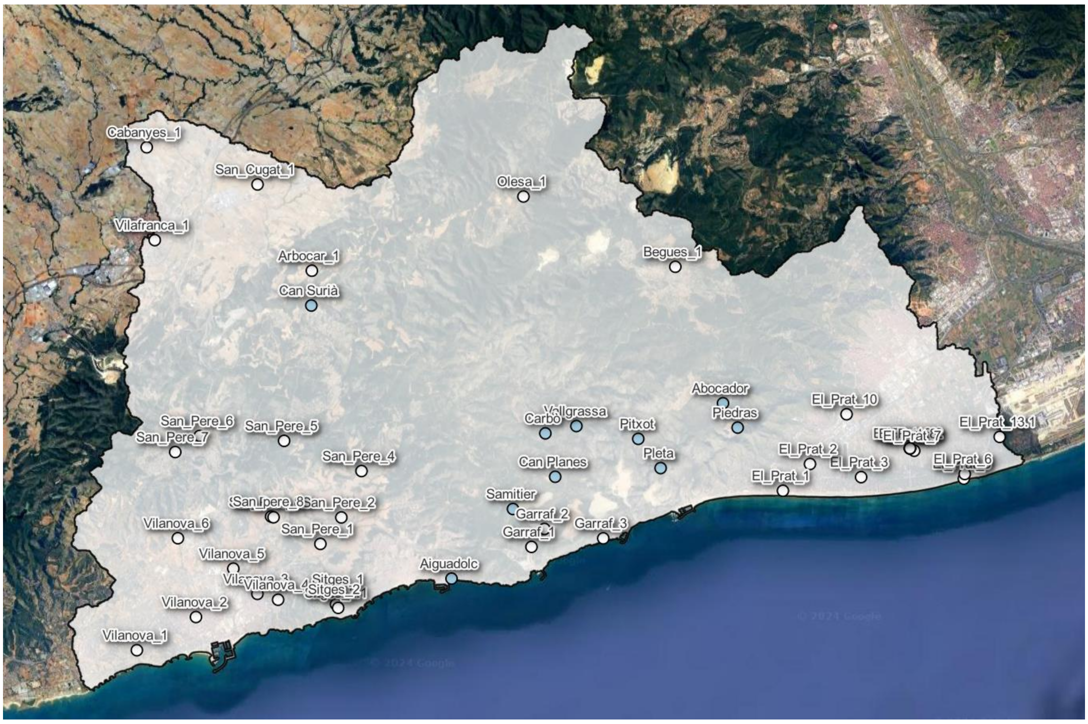

Figure 18 - Location of groundwater quality data in Garraf; monitoring stations from ACA in white, sampling points from GHS in blue.

At this point, the available groundwater quality data provided from both the ACA and the GHS can be divided in the following way:

- Nutrient data to characterize groundwater contamination in Garraf: nitrates, nitrites, ammonium, phosphates, and silicates. Considering both the data obtained from ACA and GHS, the number of sampled points within the basin is: 45 for nitrates, 39 for nitrite and ammonium, 22 for phosphates, and 7 for silicates. Moreover, besides the above-mentioned data, 10 additional coastal and marine samplings have been found available for all nutrients, allowing to compare the level of contamination inland and offshore.

- Physical-chemical water parameters to complement the contamination analysis and spot any potential biogeochemical trend: temperature (T), pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), and electrical conductivity (CE);

- Groundwater salinity - measured through the concentration of chlorides ions (CL^{-}) – to assess the level of seawater intrusion (SWI) in the basin.

Moreover, the available data have been processed and plotted to show different aspects of groundwater contamination according to the following scheme:

- Contaminants concentration maps for nitrates, nitrites, ammonium, phosphates and chlorides, to obtain a first rough interpretation of the contamination levels in the basin, to foresee any contamination hotspot and possibly pinpoint any pollution sources.

- Contamination interpolation maps for nitrates, nitrites, ammonium, phosphates and chlorides, to better visualize the spatial patterns of groundwater contamination in the basin, and possibly determine the groundwater quality status in the areas with no data. However, it must be noted that in a karstic aquifer like Garraf, interpolating nutrient concentrations across various spatial locations is less impactful compared to an alluvial aquifer, mainly due to the unpredictability of groundwater pathways underground. Therefore, the primary benefit lies in obtaining a clear and visually effective presentation of the data.

- Nutrient limitation plot for dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), and dissolved inorganic silicates (DSi). This plot is used to assess the limiting nutrient in an aquatic ecosystem, namely to determine which nutrient is in excess relative to others in a specific sampling location. In the context of contamination studies, a nutrient limitation plot with respect to DIN, DIP, and DSI can be used to assess the impact of nutrient inputs on groundwater.

- Nitrogen speciation plot for nitrogen oxides (NOx) and ammonium (NH_4^+). A nitrogen speciation plot is a graphical tool used to illustrate the different forms of nitrogen present in groundwater, such as nitrate, nitrite, and ammonium. In the context of groundwater contamination, this plot can provide insights into the sources, pathways, and severity of nitrogen contamination.

Looking at the total distribution of the available data in Garraf, there are again some areas where data have not been found, due to the lack of sampling points. However, at the same time, there are numerous points along the coastal area, which is particularly intriguing for the analysis of contamination from seawater intrusion (SWI).

4.1.3 Piezometric data

4.2 Field Survey at Sitges

Sitges is a coastal town located in Catalonia, approximately 35 kilometres southwest of Barcelona along the Mediterranean coast. The field survey was conducted on the 03/10/2023 with the aim of characterizing SGD nutrient fluxes on the beach of Aiguadolç, used in this study as a proxy for groundwater contamination.
Different activities have been performed throughout the day with the purpose of characterize both the water and the nutrient fluxes associated to SGD.

The following instruments and techniques have been used:

- Seepage meters for the quantification of the water flux attributable to SGD. Seepage meters are instruments used to measure the flow of groundwater into surface water bodies like rivers, lakes, or the ocean. They typically consist of a container, such as a bag or chamber, that is placed on the seafloor or riverbed, allowing water to flow into it. The volume of water collected over a specific time period is then measured to determine the rate of seepage. In this case, the volume of water discharged was measured every 2 hours in order to understand the daily pattern of discharge during the day (time-lapse). The quantification of the SGD volumes, although not directly correlated with the target of the current study – namely the contamination of groundwater – is indeed useful in this context to correlate the presence of nutrient fluxes to groundwater itself.

- Geophysical analysis with amphibious Electrical Resistivity Tomography (ERT). ERT works by measuring the electrical resistivity of the subsurface materials using a network of electrodes placed on the ground surface or in boreholes in order to provide valuable information about the geological structures, groundwater presence, contamination plumes, and other subsurface features. Freshwater typically exhibits lower electrical resistivity than saltwater, enabling the identification of zones with freshwater discharge based on the observed resistivity values. In this case, an amphibious analysis was performed, installing 10 on land and 24 at sea.

- On-field detection of physical-chemical parameters from SGD fluxes with multi-parameter probes: temperature, pH, dissolved oxygen, conductivity, oxidation-reduction potential, salinity. The same samples have been sent to the Institute of Marine Sciences (ICM) of Barcelona to estimate the concentration of the main nutrients: nitrate, nitrite, ammonium, phosphorus, and silicates. This was indeed the key step for the purpose of the present analysis, allowing to better understand the level of groundwater contamination of the site.

The volumes of groundwater discharge collected by the seepage meters were calculated and then converted into actual SGD volumes using the following formulas:

where:

- Vf is the final volume of water in the bags at the end of each cycle;
- Vo is the initial volume of water inserted into the bags at the beginning of each cycle, equal to 500 mL;
- A is the discharge area corresponding to each seepage meter, equal to 0.16 m^2;
- t is the duration of each cycle, approximately 120 minutes;
- ΔV is the change in water volume in the bags at the end of each cycle: a positive value indicates groundwater discharge from the aquifer to the sea, and vice versa.

Once the discharge volumes were known, their relative salinity was calculated using the following mass balance equation:

where:

- Sal_o is the initial salinity of the water in the bags at the beginning of each cycle, equal to 34.22 ppt;
- Sal_f is the final salinity of the water collected in the bags at the end of each cycle, measured with a multi-parametric probe;
- Sal_gw is the unknown salinity of the groundwater.

4.3 DATA PROCESSING

5 RESULTS

5.1 CLIMATE CHANGE IMPACTS

5.1.1 Temperature

5.1.2 Precipitation

5.1.3 Indices of extreme events

5.1.4 Piezometric level

5.2 HYDROCHEMICAL ANALYSIS

5.2.1 Ntrates

5.2.2 Nitrites

5.2.3 Ammonium

5.2.4 Phosphates

5.2.5 Silicates

5.2.6 Chlorides

6 DISCUSSION

7 CONCLUSION

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