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Submarine groundwater discharge feedbacks on ecosystem services

Aaron Alorda Kleinglass

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1. **Alorda-Kleinglass, A.**, Garcia-Orellana, J., Rodellas, V., Cerdà-Domènech, M., Tovar-Sánchez, A., Diego-Feliu, M., Trezzi, G., Sánchez-Quilez, D., Sanchez-Vidal, A. and Canals, M., (2019): Remobilization of dissolved metals from a coastal mine tailing deposit driven by groundwater discharge and porewater exchange, Sci. Total Environ. *Chapter 4*
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4. Diego-Feliu, M., Rodellas, V., **Alorda-Kleinglass, A.**, Saaltink, M., Folch, A. and Garcia-Orellana, J., (2022): Extreme precipitation events induce high fluxes of groundwater and associated nutrients to coastal ocean, Hydrol. Earth Syst. Sci.
5. Diego-Feliu, M., Rodellas, V., Saaltink, M. W., **Alorda-Kleinglass, A.**, Goyetche, T., Martínez-Pérez, L., Folch, A. and Garcia-Orellana, J., (2021): New perspectives on the use of 224Ra/228Ra and 222Rn/226Ra activity ratios in groundwater studies, J. Hydrol.
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7. Olid, C., Rodellas, V., Rocher-Ros, G., Garcia-Orellana, J., Diego-Feliu, M., **Alorda-Kleinglass, A.**, Bastviken, D. and Karlsson, J., (2022): Groundwater discharge as a driver of methane emissions from Arctic lakes, Nat. Commun.
8. Garcia-Orellana, J., Rodellas, V., Tamborski, J. J., Diego-Feliu, M., van Beek, P., Weinstein, Y., Charette, M. A., **Alorda-Kleinglass, A.**, Michael, H. A., Stieglitz, T. and Scholten, J., (2021): Radium isotopes as submarine groundwater discharge (SGD) tracers: Review and recommendations, Earth-Science Rev.

List of abbreviations

DIN	Dissolved inorganic nitrogen
DIP	Dissolved inorganic phosphorus
DSi	Dissolved Silica
ES	Ecosystem Service
FIB	Fecal indicator bateria
GDE	Groundwater dependent ecosystem
HAB	Harmful algal bloom
MEA	Millennium ecosystem assessment
PEX	Porewater exchange
Ra	Radium
Rn	Radon
SGD	Submarine Groundwater Discharge
SGD-ES	Submarine groundwater discharge derived ecosystem service
WoS	Web of Science
WWTP	Wastewater treatment plant

Abstract

Humans have a notable ability to modify their surrounding environment for their own benefit. Nonetheless, some anthropogenic changes have led to global-scale consequences, causing the degradation of Earth's ecosystems. To analyze these human-nature interactions, the Ecosystem Services framework poses four categories of services referred to the benefits to society of using and modifying ecosystems toward their well-being (i.e., Supporting, Provisioning, Regulating and Cultural). Coastal areas are a crucial source of ecosystem services for humans, being both productive and sensitive. Coastal ecosystems, renowned for their diversity and productivity, depend on hydrological land-ocean connectivity regulated by processes such as rivers, streams, and Submarine Groundwater Discharge (SGD). Among them, SGD is recognized as a fundamental hydrological process that supports many coastal biogeochemical cycles and social-ecological systems. However, very little has been investigated about how SGD affects society and human well-being. To bridge this gap of knowledge, this thesis aims to advance the understanding of the social dimension of Submarine Groundwater Discharge, contributing to address the existing disconnection between the natural and social sciences in this field. To this aim, this thesis assesses both the impacts of highly polluting anthropogenic activities on SGD and the societal implications of this process by developing and applying the Ecosystem Services framework (a socio-ecological system approach) to SGD research. The results of this thesis demonstrate how polluting anthropogenic activities can induce large fluxes of dissolved metals and nutrients into the coastal ocean, having a significant impact on coastal marine ecosystems. In addition, the diversity of pathways of SGD plays a relevant role in controlling the solutes fluxes supplied into the coastal ocean. The findings of this thesis also show that the high pressure exerted on coastal areas by tourism activities can lead to alterations in SGD fluxes, thereby endangering coastal ecosystems and the services they provide.

To advance the understanding of the social implications of SGD, this thesis develops the first framework for identifying and classifying the Ecosystem Services provided by SGD and their effects on the well-being of local societies. Results show that SGD, from its use as a water resource to its cultural influence, is deeply rooted in many coastal societies at a global scale, and SGD-dependent ecosystems have a significant impact on the local communities. Additionally, results from the local perceptions of two Mediterranean societies (Mallorca and Salento) towards SGD, including its uses and its role in coastal communities, highlight the necessity of integrating data from the scientific literature, together with the information available in the grey literature and local knowledge for a complete understanding of the cultural dimension of SGD. Findings also show that the limited historical documentation on SGD causes bias in reporting present ecosystem services compared to the past in the two studied areas. The interdisciplinary approach followed in this thesis represents a novelty and brings new knowledge and evidence to guide policy and management strategies regarding SGD. In sum, this thesis is a walkthrough of the strong bounds between SGD and coastal societies' well-being, which provides both solid scientific evidence and robust methodological guidance on the influence of SGD on coastal societies from a social-ecological approach.

Resumen

Los seres humanos tienen una importante capacidad para modificar su entorno en beneficio propio. No obstante, algunos cambios antropogénicos han tenido consecuencias a escala global, provocando la degradación de los ecosistemas del planeta. Con el fin de analizar estas interacciones entre personas y la naturaleza, el marco de Servicios Ecosistémicos propone cuatro categorías de servicios (Apoyo, Abastecimiento, Regulación y Culturales), que hacen referencia a los beneficios que la sociedad obtiene del uso y modificación de los ecosistemas para su bienestar. Las zonas costeras son una fuente crucial de servicios ecosistémicos para las personas, caracterizadas por ser de las más productivas y sensibles que podemos encontrar. Los ecosistemas costeros, reconocidos por su diversidad y productividad, dependen de la conectividad hidrológica entre la tierra y el océano regulada por procesos como los ríos, arroyos y la Descarga Submarina de Agua subterránea (SGD de sus siglas en inglés). Entre ellos, la SGD se reconoce como un proceso hidrológico fundamental que sostiene muchos ciclos biogeoquímicos costeros y sistemas socio-ecológicos. Sin embargo, se ha investigado muy poco sobre cómo la SGD afecta a la sociedad y el bienestar humano. Para llenar este vacío, esta tesis tiene como objetivo avanzar en el entendimiento de la dimensión social de la SGD, contribuyendo a abordar la desconexión existente entre las ciencias naturales y sociales en este campo. Con este fin, esta tesis evalúa tanto los impactos de actividades antropogénicas altamente contaminantes en la SGD como las implicaciones sociales de este proceso mediante el desarrollo y la aplicación del marco conceptual de Servicios Ecosistémicos (marco conceptual para el análisis de sistemas socio-ecológicos) a la investigación de la SGD. Los resultados de esta tesis demuestran cómo las actividades antropogénicas altamente contaminantes pueden inducir grandes flujos de metales y nutrientes disueltos en el océano costero, teniendo un impacto significativo en los ecosistemas marinos.

Además, la diversidad de subprocesos que componen la SGD juegan un papel fundamental en el control de los flujos de solutos suministrados al océano costero. Los hallazgos de esta tesis también muestran que la alta presión ejercida sobre las zonas costeras por las actividades turísticas puede provocar alteraciones en los flujos de SGD, poniendo en peligro los ecosistemas costeros y los servicios que proporcionan. Para poder avanzar en el conocimiento de las implicaciones sociales de la SGD, esta tesis desarrolla el primer marco teórico para identificar y clasificar los Servicios Ecosistémicos proporcionados por la SGD y sus efectos en el bienestar de las sociedades locales. Los resultados muestran que la SGD, desde su uso como recurso hídrico hasta su influencia cultural, está profundamente arraigada en muchas sociedades costeras a escala global, y los ecosistemas dependientes de la SGD tienen un impacto significativo en las comunidades locales. De acuerdo con los resultados obtenidos de la percepción local de dos sociedades mediterráneas (Mallorca y Salento) sobre su uso y papel en las comunidades costeras, se evidencia la necesidad de integrar datos de la literatura científica, información disponible en la literatura gris y conocimiento local para obtener una comprensión completa de la dimensión cultural de la SGD. Los hallazgos de esta tesis también muestran que la limitada documentación histórica sobre el SGD provoca sesgos en la recopilación de datos de los servicios ecosistémicos actuales en comparación con el pasado en las dos zonas estudiadas. El enfoque interdisciplinario seguido en esta tesis representa un avance en el conocimiento de la SGD y aporta nuevos conocimientos y evidencias para guiar las estrategias políticas y de gestión con relación a la SGD. En conclusión, esta tesis ofrece un análisis detallado de la estrecha relación entre el SGD y el bienestar de las comunidades costeras, proporcionando evidencia científica sólida y una metodología robusta para comprender la influencia del SGD en estas sociedades desde un enfoque socioecológico.

Resum

Els éssers humans tenen una important capacitat per modificar el seu entorn en benefici propi. No obstant això, alguns canvis antropogènics han tingut conseqüències a escala global, provocant la degradació dels ecosistemes del planeta. Amb la finalitat d'analitzar aquestes interaccions entre persones i la natura, el marc de Serveis Ecosistèmics proposa quatre categories de serveis (Suport, Proveïment, Regulació i Culturals), que fan referència als beneficis que la societat obté de l'ús i modificació dels ecosistemes per al seu benestar. Les zones costaneres són una font fonamental de serveis ecosistèmics per a les persones, caracteritzades per ser de les zones més productives i sensibles que podem trobar. Els ecosistemes costaners, reconeguts per la seva diversitat i productivitat, depenen de la connexió hidrològica entre la terra i l'oceà regulada per processos com els rius, rierols i la Descàrrega Submarina d'Aigua subterrània (SGD de les seves sigles en anglès). Entre ells, la SGD està reconeguda com un procés hidrològic fonamental que sosté molts cicles biogeoquímics costaners i sistemes soci-ecològics. No obstant això, s'ha investigat molt poc sobre com la SGD afecta a la societat i el benestar humà. Per a omplir aquest buit, aquesta tesi té com a objectiu avançar en el coneixement de la dimensió social de la SGD, contribuint a abordar la desconnexió existent entre les ciències naturals i socials en aquest camp. Amb aquesta finalitat, aquesta tesi avalua tant els impactes d'activitats antropogèniques altament contaminants en la SGD, com les implicacions socials d'aquest procés mitjançant el desenvolupament i l'aplicació del marc conceptual de Serveis Ecosistèmics (marc conceptual per a l'anàlisi de sistemes soci-ecològics). Els resultats d'aquesta tesi demostren com les activitats antropogèniques altament contaminants poden induir grans fluxos de metalls i nutrients dissolts en l'oceà costaner, tenint un impacte significatiu en els ecosistemes marins. Així mateix, la diversitat de subprocessos que componen la SGD juguen un paper fonamental en el control dels fluxos de soluts

subministrats a l'oceà costaner. Les troballes d'aquesta tesi també mostren que l'alta pressió exercida sobre les zones costaneres per les activitats turístiques pot provocar alteracions en els fluxos de SGD, posant en perill els ecosistemes costaners i els serveis que proporcionen. Per poder avançar en la coneixement de les implicacions socials de la SGD, aquesta tesi desenvolupa el primer marc teòric per identificar i classificar els Serveis Ecosistèmics proporcionats per la SGD i els seus efectes en el benestar de les societats locals. Els resultats mostren que la SGD, des del seu ús com a recurs hídric fins a la seva influència cultural, està profundament arrelada en moltes societats costaneres a escala global, i els ecosistemes dependents de la SGD tenen un impacte significatiu en les comunitats locals. D'acord amb els resultats obtinguts de la percepció local de dues societats mediterrànies (Mallorca i Salento) sobre el seu ús i paper en les comunitats costaneres, s'evidencia la necessitat d'integrar dades de la literatura científica, informació disponible en la literatura grisa i coneixement local per a obtenir una comprensió completa de la dimensió cultural de la SGD. Les troballes d'aquesta tesi també mostren que la limitada documentació històrica sobre el SGD provoca biaixos en la recopilació de dades dels serveis ecosistèmics actuals en comparació amb el passat en les dues zones estudiades. La perspectiva interdisciplinària seguida en aquesta tesi representa un avanç en el coneixement de la SGD i aporta nous coneixements i evidències per a guiar les estratègies polítiques i de gestió en relació amb la SGD. En conclusió, aquesta tesi ofereix una anàlisi detallada de l'estreta relació entre el SGD i el benestar de les comunitats costaneres, proporcionant evidència científica sòlida i una metodologia robusta per a comprendre la influència de la SGD en aquestes societats des d'un enfocament socioecològic.

Chapter 1 Introduction

1.1. Humans and nature interactions

Humans have interacted with nature since their bare existence. During almost all of human history, this interaction has been on a local scale, where human activities hardly modified the biophysical environment, except for large-scale migrations, trade-comers, or wars (Liu et al., 2007b). However, since the industrial revolution important changes started to scrape nature, whose consequences started to land on people's well-being on a regional and global scale (Vitousek et al., 1997). Humans have increasingly intervened and modified nature to fulfill the demand of their necessities by increasing livestock and intense agriculture, changing coastlines, modifying element cycles, or enhancing climate change, which has led to Global Change (Grübler, 2003). The present trend towards greater economic and demographic growth, along with rising demands for natural resources such as water and energy, is putting greater pressure on already degraded ecosystems. This, in turn, is having a significant impact on social systems, as the unequal distribution of reliable and beneficial ecosystem services is aggravating the gap between the rich and poor.

These global changes led scholars from different disciplines to question to what extent humans and natural systems, as different entities, are interrelated and how each impacts the other (Ma and Wang, 1984; National Research Council, 1999; Odum, 1971; Pickett and McDonnell, 1993; Thomas, 1970; Turner et al., 1993). However, natural and social sciences have often worked independently since the late XIX century. On one hand, studies related to human or social systems, which have been explored since the ancient Greeks (Apostle, 1952), have focused on people or communities interaction, human knowledge, technology or culture (Berkes and Folke, 1998; Liu et al., 2007a; Scholz and Binder, 2004). On the other hand, investigations on ecological or environmental systems were born under the name of "*oecologie*" by Ernst Heinrich Haeckel in 1866 and began as "the economy of nature" which included a human dimension into the term. However, the following research lines regarding this term shifted from an interest in animal populations (Andrewartha and Birch, 1954) to a broader focus on "the structure and function of ecosystems" (Odum and Barrett, 1971).

To bridge the gap between natural and social sciences, during the '70s and '80s, natural scientists made important efforts to incorporate social sciences into their research (e.g., Holling and Walters, 1978; McIntosh, 1985; Meadows et al., 1972; Odum, 1971). During the same decades, social scientists and economists moved towards incorporating natural sciences in their research (e.g., Ayres, 1978; Boulding, 1981; Dunlap, 1980; Hardesty, 1977; Harris, 1979). During the '90s, multiple approaches and definitions came into the academic field to provide a multidisciplinary vision where social and natural sciences were combined (e.g., Berkes and Folke, 1998; Costanza, 1996; Costanza et al., 1997; Daily, 1997; Ostrom, 1990; Redman, 1999; Vitousek et al., 1997). For example, Redman (1999) followed up on the initial assessment of "Human Domination of Earth's Ecosystems" (Vitousek et al., 1997) and explored the "Human Dimensions of Ecosystem Studies." This study examines human ecosystems by integrating social and natural systems and analyzing them across four domains, spanning from nature to culture and from biotic to abiotic. Other authors such as Ostrom (1990) published the first framework where natural resources, property rights and management are discussed, and set the base for the social-ecological systems framework that was later emphasized by Berkes and Folke (1998) as a needed approach to fully understand stability and change and develop adaptive and flexible management systems. Costanza (1996) published the basis on which ecological economics will grow in the next decades. Daily (1997) and

Costanza et al. (1997) presented the bases for the Ecosystem Services Framework (see section 1.2), from a natural science and economics science point of view, respectively. Relying on this research, Funtowicz and Ravetz (2003) argued that complex management issues should be approached through a new framework for an integrated view of human and nature systems that dealt with uncertainty and supported participatory decision-making, which they called post-normal science. Finally, in the 2000s, numerous authors established different interdisciplinary frameworks from which social and ecological systems are analyzed from different perspectives and where social and natural sciences are no longer considered independent disciplines (e.g., Folke, 2006; Liu et al., 2007b; MEA, 2005; Newell et al., 2005; Ostrom, 2009, 2007; Scholz and Binder, 2004; Young et al., 2006). This, in turn, has led to the emergence of an interdisciplinary research field under the concept of social-ecological systems (SES) (Berkes and Folke, 1998). There is a multitude of methodological approaches, definitions, and frameworks created to assess SES. According to Binder et al. (2013), the following ten frameworks (Table 1.1) can be considered the most important conceptualizations of SES and the interactions between the social and ecological system.

Table 1.1: Most relevant frameworks for Social-Ecological Systems: goals, social scale (refers to the social system affected), interaction type (social; refers to the interactions between social hierarchies), spatial scale (refers to the extent or size of the analyzed system), interaction type (ecological; refers to the interactions between ecologic hierarchies), interaction between social and ecological systems (refers to the direction on which activities and consequences are perceived from), point of view between social and ecological systems (describes the lens through which the system is perceived) and main references. Table based on Binder et al. (2013).

Framework	**Acronym**	**Goal**	**Social scale**	**Interaction type (social)**	**Spatial scale**	**Interaction type (ecological)**	**Social Ecological Interactions**	**Point of view between social and ecological systems**	**References**
Driver, Pressure, State, Impact, Response	DPSIR	Develop an improved understanding of indicators for appropriate responses to impacts of human activities on the environment along the causal chain-drivers-pressure-state-impact-responses.	Decision makers	Macro	Any	Interaction between scales not considered.	Human activities affect the ecological system.	Anthropocentric	(Carr et al., 2007; Eurostat, 1999; Svarstad et al., 2008)
Earth System Analysis	ESA	Understand the global interactions and dynamics of the earth system as well as its sustainable evolutions.	Society	Macro	Global	Interaction between spatial scales not considered. Interaction between	Human activities affect the ecological system.	Ecocentric	(Schellnhuber, 1998, 1999; Schellnhuber et al., 2005)

						subsystems considered.			
Ecosystem Services	ES	Analyze the integral, dynamic, and complex interactions of biotic and abiotic components of an ecosystem in relation to the supply of services this system provides to support life on Earth.	Society	Macro and micro relation	Any	Interaction between scales not considered.	Human activities affect the ecological system.	Ecocentric	(Costanza et al., 1997; Daily, 1997; de Groot et al., 2002; Limburg et al., 2002; MEA, 2005)
Human Environment Systems Framework	HES	Provide a methodological guide or template for analyzing the structure of social-ecological systems and understanding the processes and dynamics between the social and ecological systems as well as within different scales of the social system.	All hierarchical levels.	Macro	Any	Interaction between scales can be considered if necessary.	Reciprocity between the social and the ecological systems.	Anthropocentric	(Scholz and Binder, 2011, 2004)

Material and Energy Flow Analysis	MEFA	Analyze the metabolic profiles of societies. Analyze the material and energy flows as they represent the metabolism of a society, region, or nation.	Society	Macro and micro relation	Any	Interaction between scales not considered.	Human activities affect the ecological system.	Ecocentric	(Ayres, 1978; Baccini and Bader, 1996; Brunner and Rechberger, 2005; Haberl et al., 2004)
Management and Transition Framework	MTF	Support the understanding of water systems, management regimes, and transition processes toward more adaptive management; enable comparative analyses of a wide range of diverse case studies; and facilitate the development of simulation models based on empirical evidence.	All hierarchical levels	Macro and micro relation	Any	Interaction between special scales considered.	Reciprocity between the social and the ecological systems.	Anthropocentric	(Knieper et al., 2010; Pahl-Wostl, 2009; Pahl-Wostl et al., 2010)

Social-Ecological Systems Framework	SESF	Provide a common language for case comparison for organizing the many variables relevant in the analysis of SES into a multitier hierarchy that can be unfolded when needed, and for facilitating the selection of variables in a case study.	All hierarchical levels	Macro and micro relation	Local and Regional	The ecological system can be addressed at any scale. Scales are named but not conceptualized.	Reciprocity between the social and the ecological systems.	Anthropocentric and ecocentric	(Ostrom, 2009, 2007, 1990)
Sustainable Livelihood Approach	SLA	Analyze which combination of livelihood assets enable the following of what combination of livelihood strategies with sustainable outcomes.	Local stakeholders	Macro to micro	Local and Regional	Interaction between spatial scales not considered.	Ecological activities affect the human system.	Anthropocentric	(Ashley and Carney, 1999; Scoones, 1998)
The Natural Step	TNS	Provide a framework for planning toward sustainability based on constitutional principles (how the system is constituted),	Business or regions	Macro to micro	Business or regions	Interaction between business and other systems	Human activities affect the ecological system.	Ecocentric	(Burns and Katz, 1997; Missimer et al., 2010; Robèrt,

		outcome (principles for sustainability), and process to reach this outcome (principles for sustainable development).				not considered.			2000; Upham, 2000)
Vulnerability Framework	TVUL	Analyze who and what are vulnerable to multiple environmental and human changes, and what can be done to reduce these vulnerabilities.	Local communities	Macro to micro	Local scale	Interactions between the spatial scales are not explicitly considered.	Ecological activities affect the human system.	Anthropocentric	(Turner et al., 2003a, 2003b)

These SES frameworks differ from each other significantly. Due to their different goals, disciplinary backgrounds, specific temporal and spatial scales, the conceptualization of the social and ecological systems or interaction types, these different frameworks produce outputs almost impossible to be compared (Binder et al., 2013). Each framework indeed focuses on different criteria (Table 1.1). Regarding the *social scale,* the ES framework focuses on the society that gains well-being from the ecosystem service, TVUL concentrates only on the local community that is vulnerable to environmental and human changes. Alongside, depending on the depth of analysis of this *social system*, some frameworks explore the *interactions* between the different hierarchical levels. ESA, ES, or MEFA focus on the “Macro” scale, where the focus is only focused on the society or governance system but does not transcend to the “Micro” scale (i.e., the individual), whilst other frameworks like TVUL, TNS or SLA consider the relation vice-versa, from Macro to Micro scales. Also, frameworks such as HES, MTF, or SESF consider the relation between Macro and Micro, or in other words how the duality between these two hierarchies influences each other. Regarding the *spatial scale*, ES, HES, or MEFA consider any scale, whereas frameworks like SESF or SLA are focused on the regional to the local scale. Each framework is also conceived to understand the system on a different scale. The *interaction* between hierarchies in the *ecological* system is also analyzed differently by each framework. Although most frameworks investigate the interactions between subsystems, most of them do not consider the interaction concerning all dimensions. For instance, ESA investigates the interaction between subsystems (i.e., cell, tissue, organ, animal, population) but not across these subunits; SESF names the interactions between scales but does not conceptualize those connections; or ES directly does not consider the interaction between scales. Finally, almost all frameworks are partially scored toward the science there were born from. Therefore, the *point of view* from where the framework is positioned can be anthropocentric (i.e., born from the social sciences and looks at how humans interact with nature) or ecocentric (i.e., born from the natural sciences and looks at how the ecosystem interacts with humans). The SESF framework can be considered the most equilibrated framework because it looks into the ecological and social systems in the most equilibrated way (although it is formally considered anthropocentric).

Among the different approaches, the Ecosystem Services Framework has emerged as the most prolific and applied approach to evaluate SES (Norgaard, 2010). Since the definition of the term Ecosystem Service by Costanza et al., (1997) and Daily (1997), the number of publications applying this approach has evolved exponentially, including the establishment of a specific high-impact international journal "Ecosystem Services" (Costanza et al., 2017). Given its ecosystem-centered approach and incorporation of common and transversal terminology (see section 1.2), this framework has succeeded in establishing itself as a universal language for connecting SES.

1.2. Ecosystem Services Framework

Among the numerous challenges and burdens that Global Change presents, the *Millennium Ecosystem Assessment* (MEA) was established in 2000 under the United Nations General Assembly to create a new transversal and multiscale assessment framework "to provide an integrated assessment of the consequences of ecosystem change for human well-being and to analyze options available to enhance the conservation of ecosystems and their contributions to meeting human needs" (MEA, 2005). To do so, 1400 scientists from social and natural sciences backgrounds, governments, the private sector and non-governmental organizations, gathered to provide the Ecosystem Services Framework.

1.2.1. The Millennium Ecosystem Assessment

The *conceptual framework* of the Millennium Ecosystem Assessment (MEA, 2005) focuses on human well-being as the central concept on which the framework develops. Similar to all other living organisms on our planet, humans also interact with diverse ecosystem functions. Ecosystems can enhance human well-being and offer numerous benefits. The benefits obtained from ecosystems that directly or indirectly support the survival and quality of life can be defined as *Ecosystem Services* (Costanza et al., 2017, 1997; Daily, 1997; de Groot et al., 2002; Harrington et al., 2010). Ecosystem services include products such as water or food, regulating services such as biological control, and nonmaterial benefits such as religious or aesthetic values.

The MEA framework can be divided into four main blocks (Figure 1.1): (i) *the ecosystem services*; (ii) *the well-being*; (iii) *indirect dynamic interventions*; and (iv) *direct dynamic interventions*. All of those are related to each other through *strategies and interventions*. In addition, those interactions occur on a framework that considers a *multiscale on space and time*, where changes and relations can occur from local to global and from immediate responses to long-term.

This framework considers the ecosystem as the analysis unit, which is already defined by a determined temporal and spatial scale. An ecosystem is understood as "a dynamic complex of plant, animal, and microorganism communities and the nonliving environment interacting as a functional unit" (MEA, 2005). Thus, such definition includes all kinds of ecosystems, from systems completely unalerted by humans (e.g., unalerted forests) to human-created ecosystems (e.g., urban areas). To take into account all interactions between ecosystems and humans, this framework establishes a spatial and temporal multiscale evaluation. Thus, ecosystems always depend on mid and long-term spatial and temporal fluctuations. For instance, although a coastal fishery may be localized, annual changes in the regional processes (e.g., rivers, coastal lagoons, submarine groundwater discharge) affecting this area, or global changes in climate or precipitation regimes during decades may have important impacts on the coastal ocean affecting the ecosystem stability. Ecosystems and their services are grouped by MEA into marine, coastal, inland water, forest, dryland, island, mountain, polar, cultivated, and urban regions, which in turn are allocated along regions and the ecosystems in different areas are influenced by short and long-time changes.

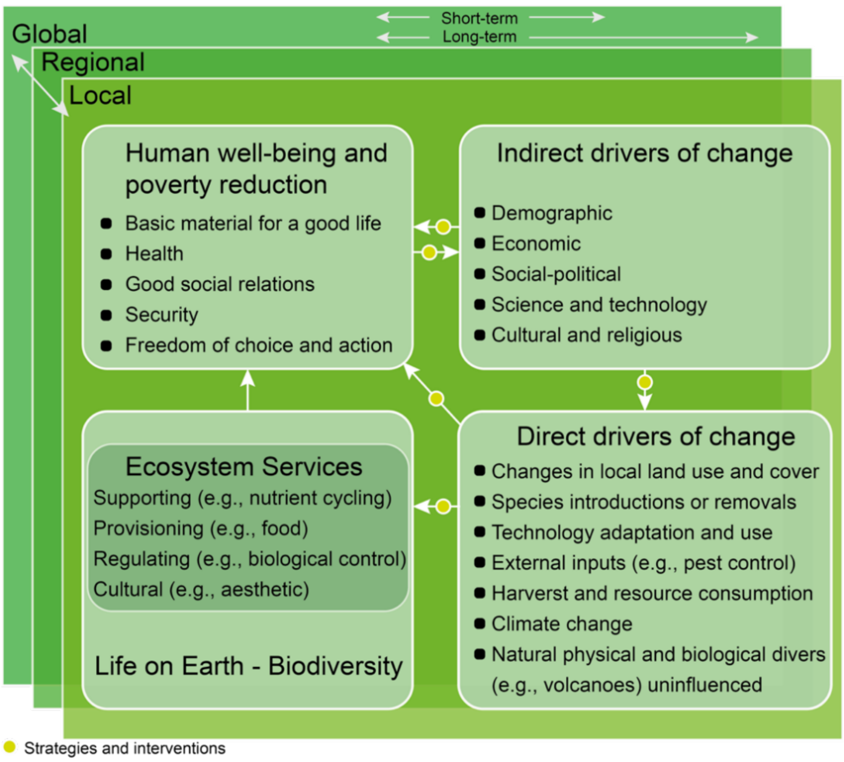

Figure 1.1. Diagram of the Ecosystem Service Framework. In this order, ecosystem services, which are part of the biosphere, provide services that benefit humans' well-being. This well-being is in synergy with indirect drivers of change, which in turn depend on direct drivers of change to modify human well-being. Analogously, direct drivers also can directly change the ecosystem services and human well-being. All those changes must be ruled by strategies or interventions that are represented by yellow balls. This framework works on a temporal and special multiscale. Adapted from MEA, (2005).

The MEA (2005) especially focuses on the connections between ecosystem services and human well-being (Figure 1.2). The ecosystem services are divided into four different categories; Provisioning, Regulating and Cultural, which are directly perceived by humans, and Supporting, which is necessary for the existence of the other three, but it is not perceived.

- *Provisioning services* are defined as products that can be directly obtained from an ecosystem. These services can be divided into: Food and fiber; Fuel; Generic resources; Biochemicals; Ornamental resources; and Freshwater.
- *Regulating services* are defined as those that control crucial processes for habitats and ecosystems. These services can be divided into: Air quality and maintenance; Climate regulation; Water regulation; Erosion control; Water purification and waste treatment; Regulation of human diseases; Pollination; and Storm protection.
- *Cultural services* are defined as the non-material benefits provided by ecosystems that contribute to human values and influence behavior. The perception of those ES can vary across stakeholders or communities, due to the subjectivity of the observer. These services can be divided into: Cultural diversity; Spiritual and religious values; Knowledge systems; Educational values; Inspiration; Aesthetic values; Social relations; Sense of place; Cultural heritage values; Recreation and ecotourism.
- *Supporting services* are those that are necessary for the existence of all other ecosystem services. Their impacts on people are either indirect or occurring over a very long time. These services can be divided into: Soil formation and retention; Nutrient cycling; Primary production; Water cycle; Production of atmospheric oxygen; Provisioning of habitat.

These subcategories were the first ones established by this framework but considering that each ecosystem can be completely different from one to another, these subcategories can be changed, or new ones can be added. Therefore, this framework is not restrictive, but flexible to the uncountable different ecosystems that exist.

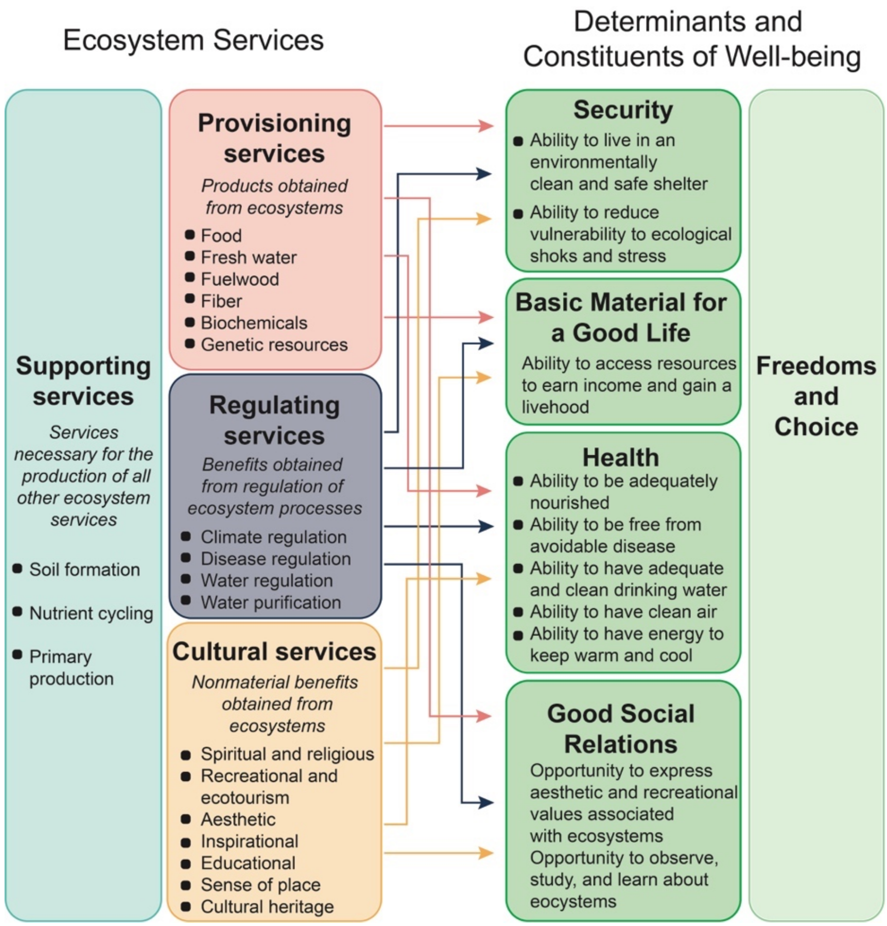

Figure 1.2. Ecosystem Services and their categories relating to the Determinants and Constituents of well-being. Each ES category is divided into different subcategories. Arrows represent how any change in an ES will have an influence on any Determinant and Constituent of well-being. Adapted from MEA (2005).

1.2.2. Ecosystem Services and well-being

Changes in Provisioning, Regulating and Cultural services directly influence the *well-being of humans*, as each service can impact all *determinants and constituents* of well-being (Figure 1.2). Furthermore, the sum of all determinants and constituents of well-being significantly influences the *freedoms and choices* available to a social system. These determinants and constituents of well-being can be categorized into:

- *Security:* Ability to live in an environmentally clean and safe shelter and to reduce vulnerability to ecological shocks and stress.
- *Basic Material for a Good Life:* Ability to access resources to earn income and gain a livelihood.
- *Health:* Ability to be adequately nourished, to be free from avoidable disease, and to have adequate basic supplies of water, air and energy.
- *Good Social Relations:* Opportunity to express aesthetic, recreational, cultural, spiritual, study and learn values associated with ecosystems.

The gaining of freedoms and choices ultimately determines the well-being of individuals, which has consequences for any social system. However, the willingness of gaining freedoms and choices is not fixed and static because they indirectly influence any social system by attempting to modify the ecosystems to obtain improved conditions. This willingness to improve the well-being of societies is considered an *Indirect Driver of Change*, which can be divided into different categories: demographic, economic, sociopolitical, scientific and technological, cultural and religious (Figure 1.1). These indirect drivers of change must be related to a *Direct Driver of Change*, since the willingness to change by a social system cannot imply a passive action over natural systems (Figure 1.1). Direct drivers are those that imply changes in ecosystem services by direct actions conducted by societies. For instance, when the availability of a provisioning service allows obtaining access to fresh water to a social system, human well-being will be increased. Such change can trigger an Indirect Driver of change like the increase in population due to higher access to water. However, such change implies at the same time a Direct Driver of Change related to higher resource consumption and generation of residues, which will inevitably impact the well-being. Real social-ecological systems have however multiple interacting drivers and more complex interactions, with synergies between drivers. Additionally, this complex interaction net translates also into trade-offs between ecosystem services and drivers of change, which led to social decisions among stakeholders or different societies to achieve the desired well-being.

All the interactions between drivers, well-being and ecosystem services are regulated through *strategies and interventions*, including laws, regulations, and enforcement schemes; partnerships and collaborations; the sharing of information and knowledge; and public and private action. However, those are strongly conditioned to the spatial and temporal scales, the cultural context of the interveners, political orientation, and implications for equity and trade-offs. In this line, most times those strategies and interventions imply different stakeholders holding counterposed positions. In this sense, an intervention to enhance an ecosystem service that benefits a group of stakeholders (e.g., increase fertilization in agriculture) may have an ecosystem "disservice" to another party (e.g., pollution of an aquifer). An academic debate exists about what to call "negative" effects provided by ecosystems. Some authors define harmful effects as Ecosystem Dis-services, being "the ecological processes that affect human well-being in negative ways, causing harm or costs" (Barnaud et al., 2018; W. Zhang et al., 2007). On the other hand, other researchers argue that such dichotomy is a matter of perception as some people can be damaged while others can benefit from them, highlighting that such an approach does not reflect reality (Saunders and Luck, 2016). Following this second line of thinking, in this dissertation, I consider that both positive and negative ecosystem services impact human well-being. This facilitates detecting and discussing potential trade-offs and synergies between organisms, ecosystems and human activities that cannot be related to a single ES (Norberg, 1999; Saunders and Luck, 2016).

The examination of the ecosystems that impact human well-being becomes highly relevant when analyzing complex socio-ecological systems with a myriad of human-nature interactions. This is the case of coastal areas, which are a crucial source of ecosystem services for humans. Coastal ecosystems are characterized by their diversity and productivity. They are highly influenced by the hydrological land-ocean connectivity, mainly regulated by processes such as riverine inputs, stream flows and Submarine Groundwater Discharge (SGD). Besides the well-known effects of rivers, SGD is also recognized as a fundamental hydrological process that supports many coastal biogeochemical cycles and social-ecological systems.

1.3. Submarine Groundwater Discharge

Coastal areas host some of the most dynamic, diverse, and productive ecosystems on Earth, where almost half of the world's population civilizations are established. Those coastal ecosystems are known to be among the most productive locations on earth, which in turn provide a combination of the most distinct and rich ecosystem services for the well-being of the societies that there live in (Alder et al., 2006). These ecosystems rely on their hydrological land-ocean connectivity which is governed by processes such as riverine inputs, ephemeral streams, or submarine groundwater discharge (SGD). For decades, the importance of surface water discharge from rivers to coastal ecosystems has been extensively studied and documented. However, it is only in recent times that the groundwater component of this hydrological connectivity (SGD) has been recognized as a significant contributor to the hydrological and biogeochemical budgets of coastal ecosystems.

1.3.1. Historical perspective and definitions

Although the scientific field of "Submarine Groundwater Discharge" is relatively young (~30 years old), the knowledge concerning this process has existed for centuries. Several studies documented the use of the freshwater component of SGD since the Phoenician times along the Mediterranean coasts (Kohout, 1966). Aristotle in his treatise "Meteorology" (ca. 350 BC), explains how karstic streams sink into the subsurface and travel short distances to discharge into sea (Clendenon, 2009). Strabo (63 BC – 21 AD), a geographer from the Roman empire, reported how fresh water for the citizens of Latakia, Syria, was extracted using a lead funnel and leather tube from a submarine spring 2.5 miles offshore (Kohout, 1966). The Greek geographer from the II century AC Pausanias (8:VII) described how the people of Argos used to make offerings to Poseidon at the site of a SGD spring, now known as the Kiveri spring (Leake, 1830; Moosdorf and Oehler, 2017). The knowledge and cultural understanding of this phenomenon is not limited to the Mediterranean region but are extended globally. The Aboriginal community of Kaurna in Australia honors the story of the ancient creator Tjilbruke, who wept for his nephew and created freshwater springs on the beach from his tears (Amery, 2016; Moosdorf and Oehler, 2017). In Bali (Indonesia) the Hindu temple Tanah Lot was built to protect a spring that was magically moved from inland to the sea (Lubis and Bakti, 2013; Moosdorf and Oehler, 2017). In Rapa Nui (Easter Island), it is believed that the original civilization survived thanks to the construction of wells and "punas" (dams) taking advantage of the fresh SGD (Brosnan et al., 2018).

Moving on to the 19th and 20th centuries, one of the first assessments describing the magnitude of a submarine spring was done by Shaler (1894). Other authors such as Matson and Sanford (1913), Roques (1953), Burdon and Papakis, (1961), Pous (1961), or Newport and Haddor (1963) also reported important submarine springs. Parallel to these earliest observations, hydrogeologists had taken the lead in acknowledging this process as part of the hydrological cycle, focusing on the saltwater-freshwater interface in coastal aquifers (Baydon-Ghyben, 1889; Herzberg, 1901; Hubbert, 1940; Manheim, 1967). During the second half of the 20th century, other disciplines started to look into this phenomenon. For instance, biologists defined anchialine habitats as those caves where fresh SGD created a unique environment where new species could be found (Sket, 1996; Stock, 1986). Oceanographers, after authors such as Kohout (1966), Fairbridge (1966), Zektser et al. (1973) Stringfield and LeGrand (1971, 1969), or Valiela et al. (1992, 1990) started to investigate SGD as a relevant contributor to the biochemical cycles of the coastal ocean (Cable et al., 1996; Church, 1996; Rama and Moore, 1996). Since different disciplines became interested in the study of SGD, the common definition established by hydrogeologists that only focused on the fresh component of the groundwater flow started to shift towards a more inclusive and transversal definition. Pioneer works such as those from Bokuniewicz (1992), Church (1996), or Moore (1996) demonstrated that the process of SGD not only involved meteoric fresh groundwater but also the circulation of seawater through the coastal aquifer, a process that was shown to contribute large amounts of dissolved compounds to the ocean.

As a result of the discoveries made during the final decade of the 20th century, Burnett et al. (2003) created one of the most inclusive definitions of SGD; "any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force". During the same years that this definition was born, SGD was gathering such attention among the international oceanographic community that the SCOR Working group 112 was established to investigate the "Magnitude of Submarine Groundwater Discharge and Its Influence on Coastal Oceanographic Processes". This international effort resulted in the UNESCO (2004) special report focused exclusively on SGD, where the importance and magnitude of this process were established, alongside the future challenges in the field. In the last two decades, there has been a significant advancement in methodologies for measuring the water and solute fluxes derived from SGD, resulting in a better understanding of the magnitude of SGD and the implications SGD-driven fluxes have on ecosystems and society (Taniguchi et al., 2019). Slightly different definitions of SGD have also been proposed over the last years. Moore (2010) introduced a more restrictive definition, where only long-scale processes (from meter to kilometers) defined SGD, excluding short-scale processes such as porewater exchange. In contrast, Taniguchi et al. (2019) updated the initial definition proposed by Burnett et al. (2003) to encompass the release of water through insular margins, as these areas may exhibit higher discharge rates than continuous margins (Moosdorf et al., 2015). The choice to use either the comprehensive or narrow definition of SGD is a matter of discretion and is dependent on the specific research objectives and intended audience. Overall, SGD today is understood as a fundamental process of land-ocean interaction, which has an essential role in sustaining many coastal SES (Erostate et al., 2020; Lecher and Mackey, 2018; Moosdorf and Oehler, 2017; Santos et al., 2021; Taniguchi et al., 2019). Consequently, SGD research has become a common ground where oceanographers, hydrogeologists, geochemists, biologists and, lately, social scientists can collaborate in order to continue understanding the magnitude and consequences of land-ocean interaction for the coastal environment and societies.

1.3.2. Pathways of SGD and driving forces

Submarine Groundwater Discharge is composed of a combination of pathways and driving forces (Garcia-Orellana et al., 2021). Each pathway possesses unique temporal and spatial characteristics and groundwater origin, resulting in varying levels of enrichment of the diverse solutes present in the geological matrix (Michael et al., 2011; Robinson et al., 2018; Santos et al., 2012). Consequently, the environmental impacts of these pathways can be distinct from one another. The pathways of SGD can be divided into five different categories (Garcia-Orellana et al., 2021): (i) Terrestrial groundwater discharge (usually fresh groundwater); (ii) Density-driven seawater circulation; (iii) Seasonal exchange of seawater; (iv) Shoreface seawater circulation; and (v) cm-scale porewater exchange (PEX) (Figure 1.3).

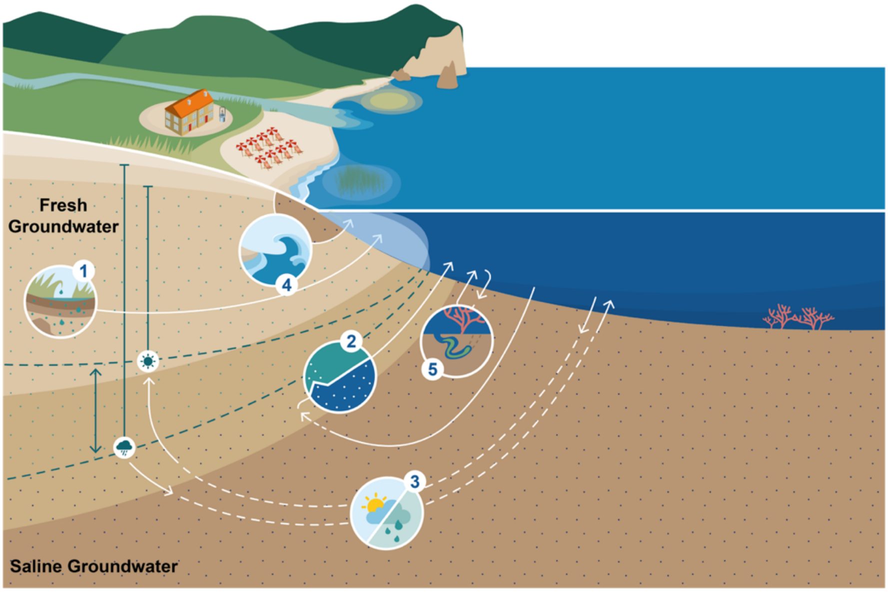

Figure 1.3. Submarine Groundwater Discharge pathways: 1) Terrestrial groundwater discharge (usually fresh groundwater); 2) Density-driven seawater circulation; 3) Seasonal exchange of seawater; 4) Shoreface seawater circulation; and 5) cm-scale porewater exchange (PEX). Pathways 1, 2 and 3 could be extended farther offshore in systems with confined units (adapted from Garcia-Orellana et al., 2021).

i. Terrestrial groundwater discharge

The flow of meteoric groundwater driven by terrestrial hydraulic gradients.

This pathway can take place either as submarine springs from karstic (Bakalowicz, 2015; Fleury et al., 2007; Mijatović, 2006; Stieglitz et al., 2013) or volcanic formations (Jeong et al., 2012; Kim and Kim, 2017; Knee et al., 2010b) or diffusive seepage at the beachfront with high permeabilities and pressure gradients (Santos et al., 2012). Whether the discharge is diffuse or point-sourced, the terrestrial groundwater discharge are particularly significant as they are the only pathway representing a net input introducing freshwater to the coastal ocean (Luijendijk et al., 2020).

ii. Density-driven seawater circulation

The flow of seawater driven by density gradients originated due to the mixing of fresh and saline groundwater in the saltwater wedge of coastal aquifers.

The discharge is driven by a combination of forced convection and free or natural convection resulting of fluid density variations (Smith, 2004), which depends on the geological properties of the coastal aquifer and its hydraulic properties (Kiro et al., 2014; Smith, 2004; Tamborski et al., 2017).

iii. Seasonal exchange of seawater

The flow derived by the movement of the freshwater-saltwater interface caused by changes in aquifer recharge or sea level fluctuations over time.

The changes in the water table due to seasonal changes on the recharge of the aquifer or changes in the sea-level will induce movements in the mixing zone (Michael et al., 2005). In addition, those changes can also be supported by episodic extreme precipitation events (e.g., Adyasari et al., 2021; Diego-Feliu et al., 2022; Palacios et al., 2020).

iv. Shoreface seawater circulation

The flow of recirculated seawater or intertidal circulation at the beach faces, mangroves or salt marshes driven by tidal inundation or wave setup.

The seawater infiltrates through the frontline of the coastal aquifer, which is filled and then discharges into the sea creating a recirculation cell (Palacios et al., 2020; Robinson et al., 2018). This first cell or upper saline plume (Robinson et al., 2006) sits on the fresh groundwater that discharges into the sea, that at the same time is limited by the saline wedge (Robinson et al., 2007). The temporal and spatial scales of this process rely on the driving mechanism of recirculation. Consequently, while waves primarily affect superficial distances of centimeters with rapid flushing times (seconds to minutes), tidal pumping affects deeper distances of meters with slower flushing times (hours to days) (Santos et al., 2012).

v. cm-scale porewater exchange (PEX)

The flow of centimeter-scale exchange of groundwater through the water-sediment interface. This pathway is governed by eight different driving forces (Santos et al., 2012): (i) Wave pumping driven by hydrostatic pressure oscillations; (ii) Flow- and topography induced pressure gradients; (iii) Ripple migration or any resuspension/deposition dynamic; (iv) Shear-induced groundwater flow formed by water column currents that extend into the bed; (v) Convection driven by thermohaline gradients; (vi) Bioirrigation and bioturbation; (vii) Upwelling of gas bubbles generated in the sediment; (viii) Compaction of sediment due to deposition of new sediment.

Whilst they are often treated in isolation, the pathways and driving forces of SGD are often occurring at the same time in natural systems. In addition, this classification does not list all the components of SGD but the most common ones in coastal areas. Other mechanisms must be considered depending on the formations of the coastal area, for instance, permeable sand barriers in coastal lagoons can have an advective flow induced by a hydraulic gradient between water levels (sea and interior of the lagoon) (Tamborski et al., 2017).

1.3.3. Methods and approaches to detect SGD

Given the complexity and variety of pathways composing SGD, different techniques have been developed in order to identify the occurrence of SGD and estimate its water flow. The different techniques and approaches commonly used to detect and quantify SGD can be grouped into four groups: (i) direct measurements; (ii) hydrological methods; (iii) geophysical methods; and (iv) geochemical methods.

- Direct measurements

Direct visualization of the SGD process was the earliest method of detection. This technique has been in use since records of the process exist (Kohout, 1966). For instance, according to Taniguchi (2002), Pliny the Elder (ca 1st century AD) described the continuous bubbling of freshwater from springs in the Black Sea. Many of those locations described during ancient history were freshwater resources, and in some cases, different instruments were created to capture the groundwater. A device that was used in the past consisted of a lead funnel fixed to the seabed on top of the spring. This funnel collected the water that was discharged and channeled it through a leather hose to a boatman. (Kohout, 1966; Rosenberry et al., 2020). A very similar design to this device would become one of the most common techniques to directly quantify SGD that is seeping from permeable sediments (Duque et al., 2020; Rosenberry et al., 2020). This method, *seepage meters*, which basic design by Lee (1972) has barely changed in 50 years, was the first device to locally quantify the terrestrial groundwater discharge and seepage flow at the same time in lakes (Lee, 1972) and estuaries (Lee, 1977). The device consists of a head-opened cylinder (drum) with a sealed connection on the closed end which connects the drum to a reservoir container (plastic bag). The drum is installed onto the sediment by burring the walls until the sediment almost reaches the drum's sealed end, then the plastic bag is filled with a known volume of water and attached to the sealed connection. Therefore, the water flow can be calculated as the volume gained or lost in the plastic bag during a certain amount of time through the surface of the device. The device creates a sealed benthic chamber where under a known surface (drum circumference) the water flow can be calculated although the flow is positive (inflow of water into the chamber and filling the bag) or negative (outflow of water out of the chamber and empty the bag).

This simple and effective method has evolved over the decades and has been adapted to different environments such as coastal areas to quantify SGD (Duque et al., 2020; Rosenberry et al., 2020). Some improvements have been added to the method by adding vent tubes to evacuate gasses (Lee and Cherry, 1978), adding water quality sensors (Krupa et al., 1998), automized continuous head flowmeters (Taniguchi et al., 2003) or nailing down the error of the measurement (Belanger and Montgomery, 1992). Therefore, the introduction of the seepage meter allowed easily locating and quantifying the SGD that discharged either from a point source location or from diffusive inputs along a permeable substrate. However, this technique is limited to relatively small areas. Several seepage meters need to be deployed to cover the spatial and temporal variability inherent to SGD, even at a beach or bay scale (Taniguchi et al., 2003). Regional direct estimates cannot be achieved with this method.

- Hydrological methods

Hydrological methods are based on the techniques to study and quantify the movement and distribution of water on Earth. The most used methods can be divided into water balances and hydrologic models.

Water balances aim to measure both the inflows (e.g., precipitation, water injected into aquifers, and desalination) and outflows (e.g., evapotranspiration, rivers, glaciers, streams and groundwater discharge) of the water cycle. By accurately determining all the inputs and outputs into the coastal aquifer (except for the discharge of fresh groundwater into the ocean) the amount of fresh submarine groundwater discharge can be estimated by calculating the difference between the known variables (Knee and Paytan, 2011). This method has been applied on a regional scale (e.g., Gwak et al., 2014; Sekulic, 1996) and it is dependent on the precision of quantifying all inputs and outputs. As fresh submarine groundwater discharge typically constitutes only a minor fraction of the aquifer water budget (Moore, 2010a), uncertainties associated with other processes may lead to uncertainty in fresh groundwater discharge that might be as large as the estimated water flow (Burnett et al., 2006).

Hydrologic models are based on analytical and numerical simulations which need representative data from the field in order to accurately estimate the water flows (Knee and Paytan, 2011). The data fed into the model has to be broad and accurate enough to represent the large special and temporal variability of the process (Burnett et al., 2006). Those models have been applied to quantify the global fresh groundwater discharge (Luijendijk et al., 2020), quantify SGD under rainfall events (Guo et al., 2012; Yu et al., 2017), estimate the SGD flow under tidal pumping conditions (Li et al., 2016;

Robinson et al., 2007), or wave set up (Anwar et al., 2014). These hydrologic models often depend on Darcy's Law, which states that the water flow is directly proportional to the cross-sectional area, hydraulic gradient, and hydraulic conductivity of the medium (Prakash et al., 2018). Models thus require reliable inputs of the hydraulic conductivity of the aquifer and need a proper characterization of the fluctuation in seepage rates arising from the heterogeneity in the geology of the aquifer. (Burnett et al., 2006). Moreover, this method only allows accurately quantifying the terrestrial (fresh) groundwater discharge in relatively homogeneous or well characterized aquifers, since hydraulic conductivity may vary by orders of magnitude along the aquifer and depending on the flow direction (Knee and Paytan, 2011; Shackelford, 2013).

- Geophysical methods

Geophysical methods are based on variations in salinity, temperature and variations on geology along the hydrological continuum. Those have received increasing attention during the last years as a complementary method to connect the gap between regional- and local-scale studies (Taniguchi et al., 2019). The different methods allow a better location of groundwater discharge but not its quantification. Those can be divided into bathymetry and seismic profiling, geoelectrical methods, eddy correlation and thermal infrared sensing.

Bathymetry and seismic profiling, although it is a descriptive geological tool, allows identifying geological formations that are related to preferential pathways for groundwater flows, such as fractures or paleochannels (e.g., George et al., 2020; Goff, 2019).

Geoelectrical methods are based on the conductivity (or resistivity) of the subsurface which depends on the groundwater conductivity and porosity of the geological matrix (Hoefel and Evans, 2001; Palacios et al., 2020). Those methods allow an accurate location of the preferential groundwater discharge locations and seawater-groundwater interference (Stieglitz et al., 2008; Swarzenski et al., 2006). To determine conductivity, multiple electrodes are positioned on the medium under evaluation. These electrodes release an electrical pulse which is then detected by other electrodes that are also installed (Costall et al., 2018). The electrodes can be installed only the ground, on the ground and the sea sediment, or towed by a boat (e.g., Palacios et al., 2020; Su et al., 2014; Swarzenski et al., 2006).

The Eddy correlation method involves continuously measuring the vertical velocity fluctuations above the sediment-water interference using acoustic Doppler velocimeters and concurrently the changes in temperature and/or salinity to estimate groundwater discharge (Crusius et al., 2008, 2005; Ganju, 2011; Hu and Hemond, 2020). When the salinity or temperature of the SGD differs from that of the water column, the specific flow SGD can be estimated through a temperature or salt balance analysis (Crusius et al., 2008).

Thermal infrared sensing (TIR) is an image-based technique that allows to accurately find the location and extension of superficial SGD. Thus, a TIR sensor can detect a contrast on the sea surface whenever there is a temperature difference between the groundwater discharge and the seawater at spatial scales from meters to kilometers (Johnson et al., 2008; Tamborski et al., 2015). TIR technology can thus be attached to different devices such as satellites (Jou-Claus et al., 2021; Wilson and Rocha, 2012), aircrafts (Bejannin et al., 2017; Lee et al., 2016; Mejías et al., 2012; Miller and Ullman, 2004), automated vehicles (Lee et al., 2016; Young and Pradhanang, 2021) or handheld (Röper et al., 2014).

Notice that all these techniques are powerful tools to precisely locate SGD at any spatial scale but is necessary to combine them with other methodologies in order to be able to estimate the SGD water flow, except for Eddy correlation.

- Geochemical methods

Geochemical methods are the most common and extended procedure to quantify SGD and its derived fluxes into the coastal ocean. These methods depend on a naturally occurring or artificially added tracer that is more concentrated in coastal groundwaters than in coastal seawater, and which presents a conservative behavior in the coastal ocean (Moore, 2010a). In addition, the natural tracers that enter the system through groundwater pathways present an integrative signal on the coastal water column. This allows the attenuation of small-scale spatial and temporal variations that are intrinsic to SGD (Burnett et al., 2001). The most common method for estimating SGD flows using tracers involves developing a mass balance. This requires precise determination of inputs and outputs of the tracer other than SGD, as well as the system's volume, the residence time of coastal waters, and the endmember concentration of the chosen tracer in the discharging groundwater (Burnett et al., 2006).

On the contrary of most *naturally occurring tracers*, salinity presents an inverse pattern than other tracers, where the inflow of SGD reduces the concentration of the tracer in the coastal water column. Despite its limitations, this tracer has been utilized in numerous studies to estimate fresh groundwater discharge, particularly in situations where no other freshwater inputs are present (e.g., Crusius et al., 2005; Tamborski et al., 2020). Moreover, other naturally occurring tracers are used such as helium (Top et al., 2001), silica (Oehler et al., 2019; Tamborski et al., 2020), barium (Moore, 1997), methane (Cable et al., 1996; Dulaiova et al., 2010), $\partial^{18}O$ and $\partial^{2}H$ (Godoy et al., 2013; Rocha et al., 2016), dissolved organic matter (Nelson et al., 2015) and naturally-occurring radionuclides (Burnett et al., 2006; Garcia-Orellana et al., 2021; Moore, 2010a; Taniguchi et al., 2019).

Among all of those, *naturally-occurring radionuclides* (Ra isotopes and Rn) are the most used technique among all to estimate SGD water flows and its derived solute fluxes (Garcia-Orellana et al., 2021; Taniguchi et al., 2019). Ra isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) and Rn are reliable tracers for quantifying SGD mainly because i) Ra isotopes and Rn are enriched in both groundwater and porewater relative to the coastal ocean, ii) have a conservative behavior, iii) the coastal ocean integrates their inputs via different pathways and enables the smoothing of small scale space and temporal variations, and iv) Ra isotopes have different half-lives that allow differentiating pathways (Burnett et al., 2001). Ra isotopes can also be used combined in order to differentiate the origins and pathways of the SGD (Rodellas et al., 2017). In addition, combining ^{224}Ra:^{228}Th can be used to distinguish water flows of fresh terrestrial groundwater discharge and PEX (Cai et al., 2014; Hong et al., 2018).

Alternatively, *artificial tracers* (e.g., fluorescent dye, SF_6, ^{32}P and ^{131}I) can be injected into the sediment or the coastal aquifer and then monitored in order to trace SGD and quantify its water flow (Cable and Martin, 2008; Corbett et al., 2000; Knee and Paytan, 2011; Santos et al., 2012).

1.3.4. Significance and extent

The important academic and technological advances in SGD during the last 30 years have proven that this process plays a relevant role in the water cycle in numerous areas around the globe, and actively participates as a major pathway of solutes to the coastal oceans which supports numerous and diverse ecosystems along the world. In addition, small but important first steps are being made by the scientific community to start to introduce the social perspective into the field. Thus, the importance of SGD in terms of its significance and extent can be structured in four domains; (i) hydrological; (ii) biochemical; (iii) ecological; and (iv) social.

- Hydrological

Submarine Groundwater Discharge is a ubiquitous phenomenon that occurs on varied spatial (cm to km) and temporal scales (seconds to years) around the globe (Knee and Paytan, 2011; Moore, 2010a; Taniguchi et al., 2019). Although SGD has numerous pathways and driving forces (see section 1.3.2.), those can also be divided depending on their origin into two main categories, fresh SGD (as terrestrial groundwater discharge) and saline or recirculated SGD (as the sum of all the other pathways and driving forces). Although it is a simplistic approach, this classification helps to understand the magnitude of SGD from a hydrological perspective.

Focusing on the fresh fraction of SGD, since the 60s different attempts have been done to quantify its contribution to the water cycle (Burdon and

Papakis, 1961; Isbister, 1966; Muir, 1968; Newport and Haddor, 1963). Nace (1967) was able to calculate that fresh SGD would represent 5% of the surface runoff on a global scale. During the 70s and following decades, different estimates were published, where the calculated global flow varied by orders of magnitude, ranging from 0.01 to 10 % of the total runoff (e.g., Church, 1996; Nace, 1970; Sawyer et al., 2016; Taniguchi et al., 2007; Zektser and Loaiciga, 1993). Moving on to the last decade, important advancements have been done to improve those estimations by introducing better-constrained water balances (Zhou et al., 2019) and hydrological models (Luijendijk et al., 2020). These recent estimates suggest that fresh SGD contribution is estimated to be between 1.3% and 0.6% of the total water inputs into the global ocean, respectively. Thus, fresh SGD only has a small contribution to the total water budget of the ocean and it usually represents only <10% of the total SGD (Burnett et al., 2003b; Li et al., 1999; Taniguchi et al., 2006). However, in specific areas such as volcanic or karstic geologies, or those areas where permanent streams are not present, fresh SGD can play a major role in the water budget of these localities (e.g., Garcia-Solsona et al., 2010; Knee et al., 2010).

Whilst not representing a net water source, the recirculated or saline portion of submarine groundwater discharge (SGD) represents a large component of the global ocean budget, accounting for between 80% and 160% of the freshwater that enters the Atlantic Ocean from rivers (Moore et al., 2008), up to 4 times that amount when also considering the Indo-Pacific Oceans (Kwon et al., 2014), or as much as 16 times that amount for the Mediterranean Sea (Rodellas et al., 2015a).

- Geochemical

Besides the water volume that SGD delivers into the coastal oceans, both fresh and saline SGD are considered to be an important carrier of solutes from land to the coastal seas (Johannes, 1980; Knee and Paytan, 2011; Moore, 2010a; Santos et al., 2021; Valiela et al., 1992). Submarine Groundwater Discharge driven solutes have been quantified in numerous coastal environments such as estuaries (Charette and Buesseler, 2004), coral reefs (Dadhich et al., 2017; Oehler et al., 2019), coastal lagoons (Lee et al., 2009; Rodellas et al., 2018), mine beaches (Trezzi et al., 2016b), mangroves (Tait et al., 2017) or saltmarshes (Moore, 2006; Wilson and Rocha, 2012). Fresh SGD provides a net source of solutes into the sea, delivering the nutrients, metals and pollutants that are present in the coastal aquifers. Additionally, the saline SGD, despite having no net water flow towards the sea, facilitates the remobilization of solutes that were previously removed from the water column and may transport many that were not moved by the fresh component due to physicochemical factors. Thus, the saline fraction of SGD enables a continuous and slow release of recycled and new nutrients along all the permeable coasts along the globe (Beck et al., 2017; Cho et al., 2018; George et al., 2020).

Among the solutes that SGD delivers into the oceans, inorganic nutrients and their biogeochemical cycles have had increasing attention since the 80s (Johannes, 1980; Santos et al., 2021). SGD-driven inputs of dissolved inorganic nitrogen (DIN), phosphorus (DIP) and silica (DSi) have been assessed at a global (Cho et al., 2018) and basin or regional scale at the Mediterranean Sea (Rodellas et al., 2015a) or the coast of China (Zhang et al., 2020). At a local scale, Santos et al. (2021) states in their extensive review that ~50% of the local studies that report nutrient fluxes derived from SGD indicate larger values compared to those derived from river discharge. In specific areas absent of permanent streams with karstic (e.g., Garcia-Solsona et al., 2010a; Montiel et al., 2018; Tovar-Sánchez et al., 2014) or volcanic geologies (e.g., Cho et al., 2019; Hwang et al., 2005; Knee et al., 2010), SGD is the major source of nutrients to the coastal ecosystems. Even some studies next to rivers have reported that the main pathway for nutrients is SGD (e.g., Charette et al., 2013; Liu et al., 2012). Important work has also been done regarding fluxes of carbon, where significant fluxes of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) are supplied into the coastal oceans by SGD. Fluxes of DIC driven by SGD can be up to 50% of major rivers (Pearl River, China; Liu et al., 2012). SGD can also account to be 10-70 times more important in riverine-dominated areas (Southwest Florida Shelf; Liu et al., 2014), or be the major contributor (55-77%) in basin-scale areas acting as a buffering mechanism (Bohai Sea; Zhang et al., 2022). DOC inputs delivered by SGD into the coastal ocean predominantly comes from the decomposition of accumulated organic matter on coastal shores (Goñi and Gardner, 2003). SGD has proven to account as a major component of coastal carbon budgets and provide better accuracy for mangrove blue carbon budgets (Chen et al., 2018b). At Masan Bay on the southern coast of Korea, SGD accounts for as much as 65% of the overall DOC fluxes (Oh et al., 2017), while in Sydney Harbor, Australia, the DOC fluxes driven by SGD are twice as high as those delivered by riverine fluxes (Correa et al., 2020). Moreover, SGD-driven DOC plays an important role in the subterranean estuary and coastal waters fueling biological activity and regulating the release of trace metals into the environment (Knee and Paytan, 2011).

Coastal groundwaters can also get naturally enriched on trace metals (e.g., Ag, As, Cd, Co, Cu, Fe, Hg, Ni, Mo, Pb, V, or Zn) during its transit through metal-rich substrates of the aquifer or as a consequence of pollution by anthropogenic activities (e.g., mining or urban development) (Beck et al., 2009; Knee and Paytan, 2011; Trezzi et al., 2016b). Trace metals are highly reactive to any physicochemical changes in the mixing zone (or subterranean estuary; Moore, 1999) and therefore those may be released or removed from the solution. Therefore, trace metals are conditioned in the subterranean estuary by changes in the pH, oxidation-reduction potential, salinity and abundance of colloids and humic substances (Beck et al., 2010, 2007; Charette and Sholkovitz, 2006). In addition, on sites where groundwaters carry large amounts of dissolved iron, or the geological matrix is rich in this element, when those waters reach the mixing zone, they can create an "iron curtain" (Charette and Sholkovitz, 2002). When this phenomenon occurs, a large amount of precipitation of Fe-oxides takes place in the mixing zone, the resulting area filled with these oxides can serve as a barrier or filter that traps metals and other compounds transported by SGD. (Charette and Sholkovitz, 2006, 2002; Trezzi et al., 2016b).

At a regional scale, SGD contributes as a major pathway of trace metals in Bohai Bay (Wang et al., 2019), western Mediterranean (Trezzi et al., 2016a) or the southern coastline of Brazil (Windom et al., 2006). Likewise, at a local scale, trace metal fluxes driven by SGD have been estimated as a main source in urban beaches (Rodellas et al., 2014), mine beaches (Trezzi et al., 2016b), bays (Beck et al., 2009; Jeong et al., 2012) or mangrove environments (Sadat-Noori and Glamore, 2019). Trace metals considered micronutrients such as Fe (Sanders et al., 2015), Cu (Charette and Buesseler, 2004), Mn (Gonneea et al., 2014), Mo (O'Connor et al., 2015), Ni (Pavlidou et al., 2011) or Zn (Trezzi et al., 2016b) have been measured as SGD-driven fluxes in different parts of the globe. Likewise, soluble contaminants such as Hg (e.g., Szymczycha et al., 2013), Pb (e.g., Trezzi et al., 2016b), As (Coomar et al., 2023), radionuclides from nuclear power plant accidents (Fukushima, Japan) (Sanial et al., 2017) or from high naturally occurring radioactive areas (Garcia-Orellana et al., 2013) have been reported. Other studies have quantified that SGD can also supply pharmaceutical and caffeine residues (Knee et al., 2010a; Szymczycha et al., 2020), pesticides and persistent organic pollutants (Dzierzbicka-Głowacka et al., 2019; Pavlidou et al., 2014) to the coastal ocean.

- Ecological

SGD supplies large amounts of water and solutes to coastal waters that can significantly impact the physicochemical and solute concentrations of coastal ecosystems (see previous sections). These changes in the environment confer an area of influence where the ecosystems benefit and drawback by this pathway (Lecher and Mackey, 2018). At the microscopic level, SGD creates a continuous and varied habitat that enables numerous microbial communities to thrive. These communities, in turn, play a crucial role in the various biochemical processes that occur within subterranean estuaries and coastal groundwaters (Ruiz-González et al., 2021). Cyanobacteria or blue-green algae, classified as primary producers, have been observed to blossom in response to nutrients from submarine groundwater discharge (SGD). Studies in Japan (Blanco et al., 2008) and the Gulf of Mexico (Blanco et al., 2011) have reported such phenomena. Other primary producers such as diatoms tend to bloom with ease under SGD inputs of DIP, DIN and DSi (Lomas and Glibert, 2000). Thus, those blooms can be sustained in time thanks to the non-seasonality of SGD (Lecher et al., 2016, 2015). Some genera like Pseudo-nitzschia, which thrives in high-salinity environments, may show a more favorable response to nutrients derived from SGD (saline or brackish fraction) rather than those from rivers (Liefer et al., 2009; McCabe et al., 2016; Trainer et al., 2012). However, this same genus will produce a neurotoxin under stress after a bloom where DSi or DIP are limiting (Liefer et al., 2009; McCabe et al., 2016). In this direction, the proliferation of phytoplankton can progress into blooms of dinoflagellates, which may ultimately result in the formation of harmful brown or red tides, causing adverse impacts on higher trophic levels (Gobler and Sañudo-Wilhelmy, 2001; Hu et al., 2006; Laroche et al., 1997a).

Macrophytes have also been shown to be highly sensitive to SGD nutrient inputs. Thus, under large inputs of nutrients, microalgae and macroalgae can bloom into green tides which derive environments into eutrophication or even anoxia (Cho et al., 2019; Hwang et al., 2005; Kwon et al., 2017). An example of macroalgae is *Ulva spp.,* which absorbs nutrients through its blades and exhibits a strong affinity towards high concentrations of DIN (dissolved inorganic nitrogen), which can be sourced from SGD (Foley, 2018; Kwon et al., 2017; Teichberg et al., 2010). Other macrophytes such as marine plants can react negatively to large amounts of nutrients or changes in salinity due to SGD. *Zostera marina* may experience patchiness due to excessive nutrient loads caused by SGD, as well as light limitation resulting from phytoplankton blooms and epiphytes derived from those nutrients (Short and Burdick, 1996; Valiela et al., 1992).

Excessive nutrient inputs from SGD can lead to macroalgal blooms that have a detrimental impact on coral reefs by reducing the amount of light available for photosynthesis. In severe cases, these blooms may even displace the corals from their habitat (Knee and Paytan, 2011). Fresh SGD, in addition, can lead to a reduction in the diversity of coral reefs by decreasing the number of species that can tolerate low salinities. This can also reduce their growth and directly affect their calcium structure when exposed to water flows with lower pH levels (Amato et al., 2016; Crook et al., 2012; Lirman et al., 2003). Segmented worms, nematodes, or other meiofauna were found in

Portugal to have higher richness and diversity in SGD-influenced zones rather than in other areas that were not influenced (Encarnação et al., 2013). However, in Portugal and France, on the contrary, in those areas influenced by SGD, due to their lower salinity, meiofauna was less rich and diverse (Kotwicki et al., 2014; Migné et al., 2011). Moreover, other animal genera such as isopods, crabs, snails, or different species of fish (e.g., *Lateolabrax japonicas*, *Acanthopagrus schlegelii,* or *Pseudopleuronectes yokohamae*) are more abundant and dominant around influenced SGD areas because of their temperature, salinity and nutrient stable conditions (Andrisoa et al., 2019a; Encarnação et al., 2015; Honda et al., 2018; Piló et al., 2018; Utsunomiya et al., 2017; Waska and Kim, 2010).

- Social

Researchers have investigated the impact of SGD on the water cycle, coastal chemistry, and marine ecosystems (see previous sections). Additionally, human-induced activities can significantly affect SGD, and vice versa, SGD can also have implications for the resources and activities of societies. Indeed, hydrogeologists started their research on SGD as a freshwater resource for coastal populations (UNESCO, 2004). Fresh SGD might thus ensure water resources for people’s livelihoods, particularly in arid or semi-arid coastal regions where freshwater resources are limited (Erostate et al., 2020; Moosdorf and Oehler, 2017). From the oldest records of extraction of SGD (e.g., Romans; Zektser, 1996) to today's latest attempts (Bakalowicz, 2018), this water pathway continues to be key for the sustainability and survival of many coastal societies around the globe. Around the Mediterranean (Gilli, 2015; Mijatović, 2006; Moullard et al., 1967; Stefanon, 1972), Florida (USA) (Dimova et al., 2011), Queensland (Australia) (Stieglitz, 2005) or Fiji (Moosdorf and Oehler, 2017; Wiese, 2009) different attempts have been made to extract this resource during the last five decades.

However, this precious resource faces numerous threats that Michael et al. (2017) define as the "coastal groundwater squeeze". This term can be understood as the sum of nine factors that threaten and regulate the quality of coastal groundwaters. Among them, those can be summarized in three concepts; (i) the overexploitation of groundwaters reduces fresh SGD enhancing seawater intrusion into the coastal aquifers, (ii) anthropogenic activities (e.g., agriculture, mining, or construction) pollute coastal aquifers, and (iii) sea-level rise and flooding salinize coastal aquifers (Foster et al., 2004; Liu et al., 2008). Therefore, although fresh SGD continues to be a fundamental or potential freshwater resource for many societies, it faces a combination of challenges that compromise its sustainability in the next future.

SGD supplies solutes to the coastal ocean (e.g., Cho et al., 2018; Johannes, 1980; Moore, 2008; Rodellas et al., 2015), which directly impacts the productivity of coastal ecosystems on which humans rely on (e.g., Erostate et al., 2020; Johannes, 1980; Johannes and Hearn, 1985; Lecher, 2018; Taniguchi et al., 2019; Valiela et al., 1990). Submarine Groundwater Discharge can also supply dissolved contaminants to the coastal ocean derived from natural and anthropogenic sources (e.g., agriculture, industrial, mining activities, domestic wastewater) (e.g., Pavlidou et al., 2014; Rodellas et al., 2014; Sternal et al., 2017; Szymczycha et al., 2020; Trezzi et al., 2016b), which can also pollute the freshwater resource or endanger the coastal ecosystems. In this regard, the introduction of substantial amounts of nutrients into the coastal ocean through SGD, whether caused naturally or by human activities, can trigger the development of harmful algal blooms (HABs) that can pose a risk to human health or food resources (Hu et al., 2006; Knee and Paytan, 2011; McCabe et al., 2016). Furthermore, the contamination of coastal aquifers by sewage can be carried through SGD into coastal bathing zones, thereby introducing fecal bacteria that may be a risk to human health (Boehm et al., 2004; Knee et al., 2008; Paytan et al., 2004).

Humans take direct advantage of SGD-influenced sites. For instance, the abundance of certain species in SGD-influenced sites is a source of food to catch fish in Australia (Stieglitz, 2005), or create aquaculture in Japan (Hosono et al., 2012; Utsunomiya et al., 2017). These sites contain food resources for human coastal societies that can be threatened when environmental changes occur (Cardellicchio et al., 2016; Duarte et al., 2010; Pongkijvorasin et al., 2010). When polluted SGD enters those waters, fisheries can be endangered due to the harmful effects of some pollutants. In two cases in Japan (Burnett et al., 2018, 2015) and Hawaii (Duarte et al., 2010; Pongkijvorasin et al., 2010), exists a tradeoff between the usage of SGD as a freshwater resource or as a nutrient driver to sustain marine food resources. In these cases, there were direct linkages between the use of groundwater as a freshwater resource and the exploitation of nearshore biomass productivity fueled by SGD, where a gain of one goes to the detriment of the other. Hence, in such situations, various monetary evaluations have been conducted to identify the optimal management approach that addresses the trade-off between the benefits of providing fresh water and the benefits of supplying food resources.

Although there has been dispersed work attending SGD and its relations with humans, only one study before this thesis has partially addressed the social implications of SGD. Moosdorf and Oehler (2017) asses an overview of the societal implications of the fresh fraction of SGD, highlighting the usage by different societies around the globe on this fraction. These authors divided their examples into six categories: (i) drinking, (ii) hygiene, (iii) agriculture, (iv) fishing/diving, (v) cultural, and (vi) ship navigation. The most reported examples refer to drinking and fishing/diving, thus referring to the obtention of resources derived directly or indirectly from fresh SGD. Cultural examples are divided into sites named after SGD, such as Olhos del Agua (Portugal), religious sites such as the Hindu temple Tanah Lot in Bali (Indonesia) and mythical as the use of water to heal wounds in Fiji.

Political conflicts have already erupted in Hawaii (USA) due to the significant anthropogenic impacts on nearshore environments from land-based activities. The consequences of these impacts can also affect algae aquaculture, which may intensify social conflicts as the cultural values of algae aquaculture have strong roots in the Hawaiian community (McDermid et al., 2019). One side of the political sphere acknowledges that groundwater extraction reduces SGD and can harm coastal marine ecosystems, while the other side argues that the trade-off between reducing SGD and obtaining fresh water is insignificant. Regarding this matter, the US Supreme Court has recently issued its first-ever ruling in favor of safeguarding the link between the coastal aquifer and the coastal ocean (SGD) (Cornwall, 2020). This establishes a new base to assess the social conflicts arising from SGD (Santos et al., 2021).

Chapter 2 Objectives and thesis structure

2.1. Objectives

The general objective of this thesis is to advance the understanding of the social dimension of Submarine Groundwater Discharge (SGD), contributing to address the existing disconnection between the natural and social sciences in this field. This is achieved by both i) evaluating the impacts of anthropogenic activities on SGD fluxes and consequently in the quality of coastal waters and ii) assessing the societal implications of SGD by applying the Ecosystem Services framework (a socio-ecological system approach) to SGD research. The development of a comprehensive approach for achieving a complete understanding of the effects of human activities on SGD and the impacts of SGD on coastal communities are relevant and necessary in the current context of global environmental change and to address the current socio-ecological challenges.

The objective of this thesis is divided into four specific objectives, which constitute the main 4 chapters of this thesis:

i. Determine the role of SGD as a source of dissolved metals into the coastal waters in a historical mining area.

ii. Evaluate the potential transference of nutrients injected into a karstic aquifer from a wastewater treatment plant (WWTP) to the coastal sea via SGD and the impacts of this process on the quality of coastal waters.

iii. Develop a new framework based on the scientific literature to analyze the ecosystem services associated with SGD for the evaluation of the social implications of SGD.

iv. Achieve a comprehensive understanding of the social dimension of SGD at the regional scale through the integration of academic literature and local knowledge on the social implications of SGD.

The first two specific objectives examine the impacts of human activities in SGD, focusing in areas where anthropogenic activities have considerably impacted the environment. Whilst these first objectives do not directly include the social perspective of SGD (i.e., not evaluating the impacts of SGD on coastal communities), they are used to highlight the effects of human activities on SGD. In contrast, the remaining two objectives aim to conceptualize and analyze the diverse social implications of SGD by using an Ecosystem Services perspective.

2.2. Thesis structure

i. Chapter 1 introduces the social-ecological systems and submarine groundwater discharge, setting the stage for a comprehensive exploration of the interaction between human society, the environment, and this process.

ii. Chapter 2 presents the general aim of the thesis, along with its specific objectives. The structure of the thesis is outlined, accompanied by a brief summary of each chapter.

iii. Chapter 3 provides a concise description of the analytical techniques used to measure Ra isotopes, which were used as tracers to quantify SGD in Chapters 4 and 5. The methods used for analyzing dissolved inorganic nutrients, dissolved metals, Chl-*a*, and $\partial^{15}N$ are also presented. Additionally, this chapter outlines the conceptual and methodological foundations for conducting a systematic literature review on the social implications of SGD in

Chapter 6. The methods followed for conducting semi-structured interviews and the use of grey literature applied in Chapter 7 are also described in this chapter. Finally, this chapter elucidates the ethical considerations adhered to in this thesis.

iv. Chapter 4 investigates the impacts of mining on coastal areas on the fluxes of metals supplied by SGD to the sea. Currently, knowledge regarding the specific physical processes responsible for the release of dissolved metals from mining waste into the ocean is scarce. This study is conducted in Portman Bay (Spain), a highly polluted coastal environment due to mining activities that took place for 40 years and ceased three decades ago. The objective of this chapter is to determine the concentration and distribution of dissolved metals in the coastal waters and evaluate the role of SGD (and porewater exchange) as a mechanism for releasing dissolved metals from mine tailings to the water column.

v. Chapter 5 evaluates the impact of SGD discharging from an aquifer polluted by a wastewater treatment plant (WWTP) on a touristic coastal bay. The hypothesis put forward is that heavily fractured systems, such as karstic aquifers located along the coastline, provide preferential conduits that can facilitate the rapid transfer of solutes injected into the aquifer from WWTP to the coastal sea. The aim of this chapter is to assess the potential transference of nutrients introduced into a karstic aquifer from a WWTP to the coastal sea through SGD and to evaluate the resultant impact of this process on the quality of coastal waters. The study is conducted in Deià (Mallorca), a popular tourist destination where the effluent from the WWTP is injected into a coastal karst aquifer that is linked to a cove (Cala of Deià).

vi. Chapter 6 introduces a new framework to evaluate social-ecological systems through the scope of the Ecosystem Services approach associated with SGD. To this end, a systematic review of the existing scientific literature is conducted to collect information on the social implications of SGD on a global scale. Specifically, this chapter is focused on analyzing the coastal ecosystem services provided by SGD as a social-ecological system, which encompasses both positive and negative impacts on human well-being and quality of life. The information obtained is then classified using the Millennium Ecosystem Assessment as a framework baseline. Additionally, this chapter reviews the direct social impacts of SGD, including synergies and trade-offs toward well-being, as well as research gaps and opportunities for further studies.

vii. Chapter 7 aim is to obtain a comprehensive understanding of the social dimension of SGD at a regional scale by examining both academic literature and local knowledge on SGD. Two regions in the Mediterranean are studied in this chapter, the island of Mallorca and the peninsula of Salento. An evaluation of the ecosystem services provided by SGD in these sites enabled an exploration of the links between coastal societies and SGD, a comparison of the similarities and differences of each Mediterranean society concerning the ES provided by SGD, and an identification of the historical evolution of the perception of SGD and the services it provides.

viii. Chapter 8 presents a summary of the key findings and conclusions obtained in this thesis and offers a glimpse into the future directions that SGD research should take regarding its social implications.

Chapter 3 Methodological approaches

Given the interdisciplinary character of this thesis and its objectives, it combines natural and social sciences methodological approaches. Regarding natural sciences approaches, Ra isotopes are used in Chapters 4 and 5 (described in section 3.1) in order to quantify the fluxes of water and solutes supplied by SGD. Solutes supplied by SGD analyzed in this thesis include dissolved metals and nutrients are measured in Chapters 4 and 5, respectively (described in section 3.2). Additionally, in Chapter 5, Chl-*a*, and $\partial^{15}N$ in waters and Possidonia oceanica leaves measured to evaluate the environmental state of the coastal waters (described in section 3.2). Regarding social sciences approaches, a systematic review of the academic literature is developed in Chapter 6 following the guidelines of section 3.3. To complement the academic literature in Chapter 7, semi-structured interviews and grey literature are used to provide an overall view of the social perspective of SGD (see section 3.4). Additionally, the ethical considerations of the thesis are presented in section 3.5.

These methodologies have been applied over the course of five years (Figure 3.1). However, some samples for Ra isotopes and dissolved metals from Chapter 4 had been already collected and analyzed before the start of this thesis.

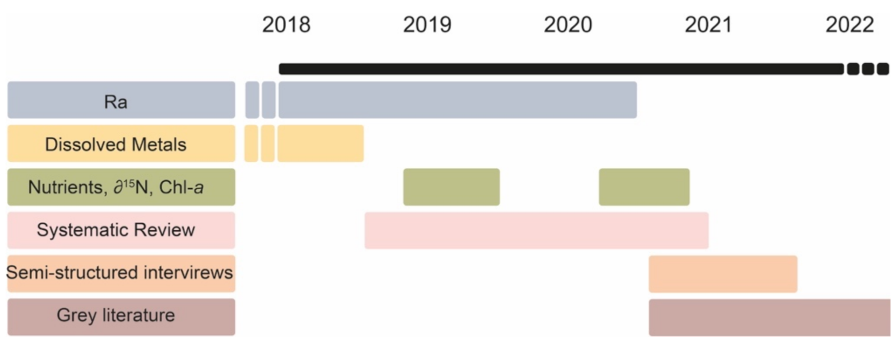

Figure 3.1. Schematic temporal evolution of the methodology used over the course of the thesis.

3.1. Radium isotopes

Radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) are naturally-occurring radionuclides that are commonly used as tracers to quantify Submarine Groundwater Discharge (SGD). Measuring the concentration of Ra isotopes in natural water samples requires pre-concentrating the dissolved isotopes from the water samples. The most common method is based on filtering water through manganese oxide acrylic fibers (MnO_2 fibers) which adsorb quantitatively the Ra isotopes present in the water sample (Moore, 1976; Moore and Reid, 1973). Before filtering MnO_2 fibers are fluffed into PVC cartridges with a top filter of raw acrylic fiber to reduce the amount of suspended particles reaching the MnO_2 fiber (see Figure 3.2). Then, large water volumes (1 to 50L for groundwaters and 50 to >200 L for seawater samples) are slowly filtered (< 1L min^{-1}) through 20 to 25 g of MnO_2 fibers loaded into the cartridge. After filtration, MnO_2 fibers are rinsed with Ra-free water to remove particles or salt that could interfere during measurement. To achieve optimal efficiency in detecting short-lived Ra isotopes (^{223}Ra and ^{224}Ra) using the RaDeCC system, the MnO_2 fibers, are dried until their water content is adjusted to 1:1 to their dry weight (40 to 50 g) (Moore, 2008; Sun and Torgersen, 1998).

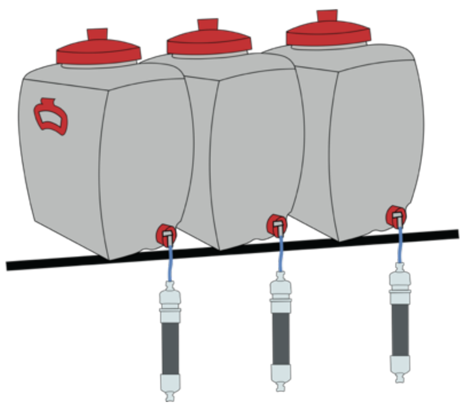

Figure 3.2. Water samples filtered through MnO_2 fiber cartridges. Adapted from Diego-Feliu (2022).

3.1.1. Short-lived Ra isotopes: Radium Coincidence Counter (RaDeCC).

Short-lived Ra isotopes (^{223}Ra and ^{224}Ra) were counted with a Radium Delayed Coincidence Counter (RaDeCC; Moore and Arnold, 1996). The dried MnO_2 fiber is allocated into a PVC cartridge which is connected to a He closed gas circuit moved by a gas pump. When a ^{224}Ra or ^{223}Ra adsorbed to the fiber decays, a ^{220}Rn or ^{219}Rn are produced, respectively, and are mobilized from the fiber following the He circuit (see Figure 3.3). This Rn reaches a ZnS coated 1.1 L scintillation cell (Lucas cell) where eventually a ^{220}Rn or ^{219}Rn alpha decay might be produced. When the alpha particle hits the scintillation cell wall, light is emitted, which is captured by the photomultiplier connected to the cell. Then the photomultiplier converts the light signal into an electric pulse which is then amplified and captured by the Decay Coincidence Circuit (DCC). This electronic device enables distinguishing the different events produced by each isotope opening or closing three electronic circuits which depend on consecutive events.

When a first event is recorded the three circuits (219 Channel, 220 Chanel and Total Chanel, which refer to the ^{219}Rn, ^{220}Rn and total decays, respectively) are activated. The Total Chanel will record all electric pulses received by the DCC. The 219 and 220 Channels however will only record those pulses if a consecutive decay is recorded inside a time widow that this device opens. Following a delay of 0.01 ms (t_{D-219}) from the first pulse, the 219 Chanel remains open for 5.6 ms (t_{G-219}) ($\sim 3 \cdot T_{1/2}$ of ^{215}Po, ^{219}Rn daughter) to detect subsequent events in the 219 Channel. Concurrently, the 220 Chanel is opened for 600 ms (t_{G-220}) ($\sim 4 \cdot T_{1/2}$ of ^{216}Po, ^{220}Rn daughter) after a delay of 5.61 ms (t_{D-220}) to lower the chances of a ^{215}Po decay from ^{219}Rn during this time interval and then record any pulse inside the 600 ms time window. However, not all events recorded in the 219 Chanel and 220 Chanel will correspond to the ^{223}Ra and ^{224}Ra, respectively. A number of corrections and adjustments must be made to those counts in order to account for the background, the efficiency of each detector, avoid cross-talk between the 219 and 220 Channels, counts derived by ^{222}Rn produced by ^{226}Ra, ^{224}Ra supported by ^{228}Th, or random counts. In order to do so, Ra-224 and Ra-223 were quantified in this thesis following the criteria and recommendations described by Moore and Arnold (1996), Moore (2008) and Diego-Feliu et al. (2020) with uncertainties calculated according to Garcia-Solsona et al. (2008).

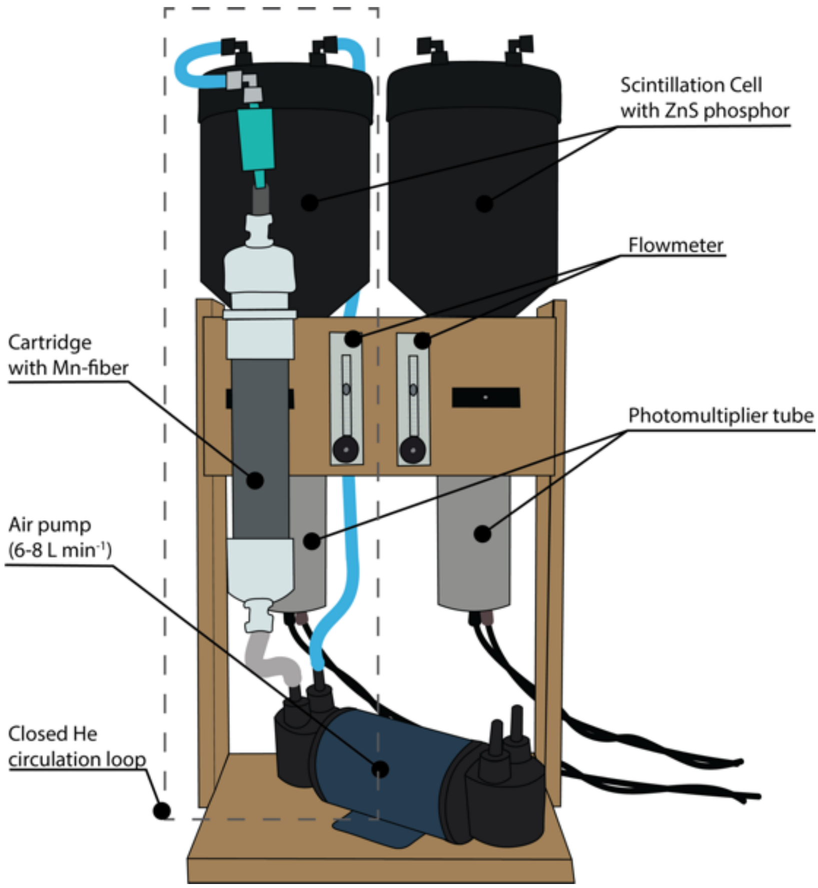

Figure 3.3. Pair of Radium Delayed Coincidence Counter detectors (RaDeCC). Adapted from Diego-Feliu (2022).

3.1.2. Long-lived Ra isotopes: Gamma spectrometry

Long-lived Ra isotopes (^{226}Ra and ^{228}Ra) were measured with gamma spectrometry. Once the short-lived Ra isotopes were measured, the MnO_2 fibers were placed into 250 mL porcelain containers and incinerated at 820 °C for 16 h. Then the remaining ashes were ground into a fine powder, introduced into a cylindrical counting vial of 5.6 cm^3 and then sealed with parafilm. The vials are sealed to avoid ^{222}Rn to exit and are stored at least for 21 days to guarantee equilibrium between ^{226}Ra and its daughters. After this time the samples were placed for 1 to 4 days (depending on their long-lived Ra activities) for counting into a well-type (14.5 mm diameter, 40 mm length), low-background, high resolution and high-purity germanium detector (HPGe) from CANBERRA. The detector consists of a high-purity germanium crystal housed in a cryostat, which is further shielded by iron, copper, and lead. To achieve the necessary temperature of -196 ºC, liquid nitrogen (N_2) is used as cooling method. When photons are emitted, a pulse is generated, which is then electronically recorded by the multichannel analyzer (MCA) (see Figure 3.4). The MCA comprises 8192 channels and is capable of detecting emission lines within the energy range of 40 to 3000 keV. ^{228}Ra and ^{226}Ra activities were determined through the photopeak of their daughters. Notice that, ^{226}Ra is not calculated through its direct photopeak (185.7 keV) because of its lower quantum yield (q_γ = 3.6%) and higher background in comparison to its daughter ^{214}Pb (Dulaiova and Burnett, 2004; Scholten et al., 2013). Ra-226 is calculated through the ^{214}Pb ($T_{1/2} = 1.64 \cdot 10^{-4}$ s; q_γ = 37.2%) photopeak 352 keV and ^{228}Ra through the ^{228}Ac ($T_{1/2}$ = 6.1 h; q_γ = 27.7%) at 911 keV. The gamma spectrometry software Genie 2000 from CANBERRA was used to calculate the long-lived Ra activities, accounting for detector efficiencies, background and peak area computation and correction.

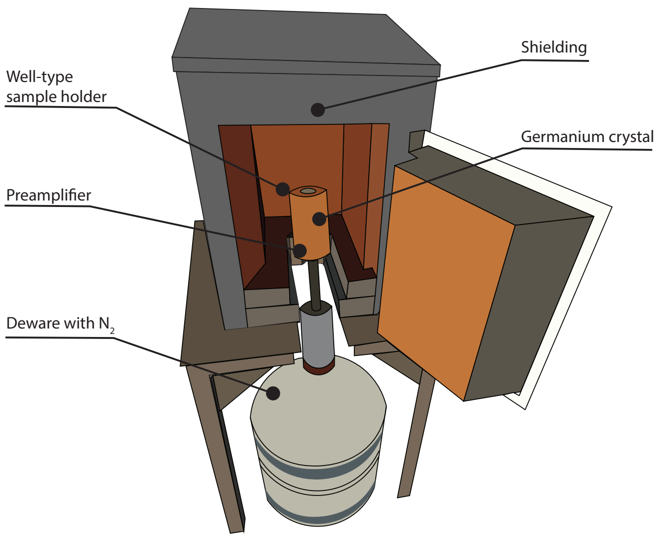

Figure 3.4. Well-type, high purity germanium detector and its components. Adapted from Diego-Feliu (2022).

3.1.3. Estimating SGD using Ra isotopes

Radium isotopes are used in this thesis to estimate SGD water flow. To do so, we utilize the most common approach developed by Moore (1996) where a mass balance of Ra is applied. This approach is based on assuming that, inputs of Ra into a system should be balanced by outputs if the system is in steady-state. If all inputs and outputs of Ra are accurately constrained except for SGD, the imbalance of Ra fluxes between inputs and outputs can be attributed to SGD. This implies that before sampling there must be a proper characterization of the study site, from which a conceptual model can be built to accurately select the Ra isotopes that will be used for the mass balance (Garcia-Orellana et al., 2021; Figure 3.5).

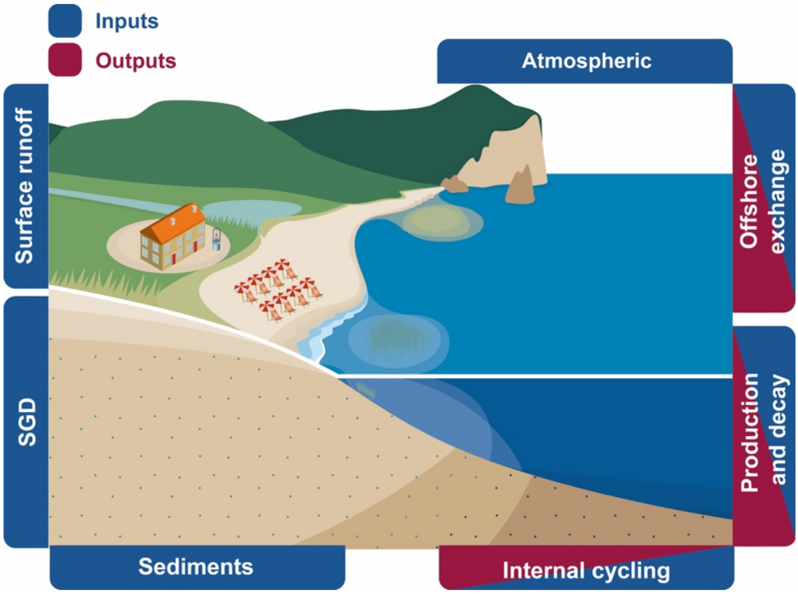

Figure 3.5. Mass balance on a coastal System for Ra isotopes. Blue boxes represent potential inputs into the System. Red boxes represent the potential outputs of the system. Adapted from (Garcia-Orellana et al., 2021).

In this direction, since short-lived and long-lived Ra isotopes have different half-lives, different isotopes can be used to differentiate or integrate the different pathways of SGD (Rodellas et al., 2017). Thus, once all the different potential sources and sinks of SGD have been properly sampled, and Ra has been quantified (see previous section), the mass balance can be conceptualized. Depending on the study site, Ra inputs can be attributed to surface inputs, sediments, internal cycling, production, offshore exchange, atmospheric deposition, and SGD. Radium outputs will be attributed to precipitation or uptake of this element, decay, and water exchange with the open ocean. However, atmospheric deposition and Ra precipitation and uptake are minor fluxes in comparison to other terms and can be often neglected. Thus, the Ra mass balance can be presented as in Equation 3.1:

$$F_{{}^{x}Ra-SGD} + F_{sed} + F_{atm} + F_{stream} = \frac{({}^{x}Ra_{cw-ex}) \cdot V}{\tau_r} + [\lambda \cdot {}^{X}Ra_{cw} \cdot V] \qquad \text{Eq. 3.1}$$

Where the terms found on the left represent the inputs of Ra into the system and those on the right account for the outputs. Notice that *x* refers to the specific isotope used. On the left, $F_{{}^{x}Ra-SGD}$ is the ^{x}Ra flux from SGD (dpm $\cdot d^{-1}$), which is the unknown and target term, F_{sed} is the ^{x}Ra flux from the sediments (dpm $\cdot d^{-1}$), F_{atm} is the ^{x}Ra flux from atmospheric deposition (dpm $\cdot d^{-1}$), and F_{stream} the ^{x}Ra flux from superficial waters (dpm $\cdot d^{-1}$). On the right, the term ($\frac{({}^{x}Ra_{cw-ex}) \cdot V}{\tau_r}$) represents Ra outputs due to exchange with the open ocean (or export offshore), which depend on the ^{x}Ra excess in the system relative to offshore concentrations (${}^{x}Ra_{cw-ex}$; dpm m^{-3}), the volume of the system (V; m^3) and the flushing time of solutes in coastal waters (τ_r; d^{-}); and the term $[\lambda \cdot {}^{x}Ra_{cw} \cdot V]$ represents Ra losses due to radioactive decay, which depends on the decay constant of ^{x}Ra (λ; d^{-1}), the activity of ^{x}Ra in the system (${}^{x}Ra_{cw}$; dpm m^{-3}) and the volume of the system (V; m^3). The SGD water flow (F_{SGD}; $m^3 \cdot d^{-1}$) can be obtained by dividing the $F_{{}^{x}Ra-SGD}$ by the ^{x}Ra activity in the discharging groundwater endmember (${}^{x}Ra_{SGD}$; dpm m^{-3}) (Equation 3.2).

$$F_{SGD} = \frac{F_{{}^{x}Ra-SGD}}{{}^{x}Ra_{SGD}} \qquad \text{Eq. 3.2}$$

3.2. Dissolved metals, nutrients, ∂^{15}N and Chl-a

Dissolved metal samples were analyzed at the CSIC-ICMAN (Cadiz, Spain) following the methodology described by Tovar-Sánchez (2012). Briefly, dissolved metal samples were acidified to pH < 2 with ultrapure grade HCl (Merck) in a class-100 HEPA laminar flow hood and stored for at least 1 month before extraction. Dissolved (<0.22 μm) metals (Fe, Zn, Pb) were pre-concentrated in a clean lab by the APDC/DDDC organic extraction method and analyzed by ICP-MS (PerkinElmer ELAN DRC-e). The accuracy of the analysis was established using Coastal Seawater Reference Material for trace metals (NASS-7, NRC- CNRC; recoveries obtained ranging from 92% to 106% for Zn). Silver, for fixed piezometer samples and for manual piezometer samples was below the detection limit 0.02 nM.

Dissolved NO_3^-, NO_2^-, NH_4^+ (DIN), PO_4^{3-} (DIP), SiO_2 (DSi), TN and TP were determined with an Autoanalyzer AA3 HR (Seal Analytica) using colorimetric techniques (Grasshoff, 1983) at the ICM-CSIC (Barcelona, Spain). The detection limits for NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, TN and TP in the lowest range (MDL) of the analysis were 0.006, 0.003, 0.003, 0.010, 0.071 and 0.032 μM, respectively.

Water samples for $\partial^{15}N$ were defrosted and analyzed following the hypobromite method by (L. Zhang et al., 2007) in a Thermo Finnigan PreCon (Thermo Scientific) couplet to an isotope-ratio mass spectrometer IRMS (Finnigan MAT-253) at the MAiMA-UB (Barcelona, Spain). Analytical reproducibility of the reported ∂ values, based on sample replicates, was better than ±0.3‰ for $\partial^{15}N$.

Dried *P. oceanica* leaves were grounded (Fourqurean et al., 2007) and $\partial^{15}N$ was analyzed using a standard elemental analyzer isotope ratio mass spectrometer (EA-IRMS) at the Universidad de la Coruña (Spain). The EA-IRMS was used to combust the organic material and to reduce the formed gases into N_2, which was measured on a Finnigan MAT Delta C IRMS in a continuous flow mode. Analytical reproducibility of the reported ∂ values for seagrass leaves, based on sample replicates, was better than ±0.2‰ for ∂^{15}N.

The sample isotopic ratios (R) are reported in the standard delta notion (‰; Equation 3.3):

$$\partial^{15}N\ (‰) = \left[\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right] \cdot 1000 \qquad \text{Eq. 3.3}$$

where R_{sample} and $R_{standard}$ refer to the isotopic ratio of the sample and the standard, respectively. These R are presented with respect to the international standards of atmospheric nitrogen (AIR, N_2).

Fluorometric analysis (Parsons et al., 1984) was used to determine the Chl-*a* concentration in water samples at the ICM-CSIC. The filters were left to extract in 90% acetone overnight, and the resulting fluorescence was measured on a Turner Designs fluorometer, which had been calibrated with pure Chl-*a* from Sigma Co.

3.3. Systematic literature review

Literature reviews serve a broader purpose than merely condensing the concepts of a given subject. They can also provide guidance for future research, systematically analyze various perspectives from studies on the same or opposite topics, or examine past and present theories to generate new frameworks or proposals for interventions (Petticrew and Roberts, 2006). Traditional reviews consist of summarizing a certain topic from a particular number of publications where one expert or group of them, which are recognized in the field, discuss and summarize the aimed topic. Although there are many very well-written and objective traditional reviews, those are always under the suspicion of the partiality of the author/s, which may induce into the vision of those instead of what is the broad picture. The lack of a detailed procedure on how the information is gathered, classified and selected, introduces a bias that depends on the authors' subjectivity to correctly select the literature and ideas from which the review will be made (Mulrow, 1994). On the contrary, systematic reviews are a type of literature review that follows a rigorous set of scientific methods with the aim of minimizing systematic error or bias. The main objective of a systematic review is to identify, evaluate, and integrate all relevant studies to address a specific research question. To accomplish this goal, systematic reviews predefine their methods with detailed protocols similar to those employed in social research (Petticrew and Roberts, 2006).

In this thesis, in order to develop a correct systematical review, we have followed the criteria highlighted by Petticrew and Roberts (2006) for systematical review in social sciences.

i. A clear objective of the study was clearly stated before the research was conducted, specifying the boundaries in time and space, alongside the social context.

ii. Different experts reviewed the aim, selection criteria and selected information to develop the review.

iii. A detailed procedure was designed, specifying the information that will be reviewed, the sources that will be searched, the methods that will be used to include or reject studies, the information that will be extracted and the final classification.

iv. Once the research question was established and the protocol was approved, the different keywords and topics were searched in the defined databases (Web of Science and Scopus).

v. The different selection filters were applied according to the protocol to narrow down the number of studies suitable of interest for the review.

vi. A selection of studies was screened in more detail and abstracts were analyzed for the final selection.

vii. Each study from the final selection was examined in detail looking for the desired information. Then the selected information was tabulated and classified according to the protocol previously designed.

viii. The results were synthesized into a comprehensive summary, figures and tables where the different criteria that were selected to achieve the objective were represented.

ix. The results, criteria, and protocol were reviewed to find any biases and limitations in order to correctly report those in the final step.

x. The final report of the study where all steps are presented and transcribed was produced.

3.4. Grey literature and Semi-structured interviews

Local ecological knowledge is not all printed or published in academic publications. To obtain a comprehensive characterization of this knowledge, in this thesis we also considered grey literature (see below) and local knowledge. Local ecological knowledge is defined as a cumulative body of knowledge, practices and beliefs about local ecosystems and their management that is handed down through generations by cultural transmission and supported by customary institutions (Berkes et al., 2000; Molnár and Babai, 2021; Olsson and Folke, 2001; Ostrom, 1990). The most antique and non-structured method to obtain this information are personal communications, where different individuals from a society provide their own knowledge to the researcher. However, there are different tools to deep-in societies' perspectives such as semi-structured interviews or grey literature.

Semi-structured interviews are a methodological tool that develops predetermined interviews which permit open questions that encourage the discussion and argumentation of the interviewees' responses (Newing, 2011). This type of interview promotes open responses to the questions which are complemented by the interviewee's experiences, perceptions and insights. This methodology permits the interviewer to deep into the objectives of their research, obtaining rich and in-depth responses that can then be systematically analyzed according to the research objectives. Semi-structured interviews are constructed in different blocks or sections, where each one of those addresses a different specific objective of the interview. Questions must be formulated clearly and suggest the interviewee develop their answers from their perspective or point of view. The order of the questions can be altered depending on the answers, therefore those must have a certain independence from each other and not be repetitive. Overall, the interview must be a guide for the interviewer but at the same time offer the opportunity for personal and elaborate responses.

Grey literature can be defined as "all documents except journal articles that appear in widely known, easily accessible electronic databases will be considered grey literature" (Rothstein and Hopewell, 2009). Gathering all the available information is challenging both because local and regional documents are not easily accessible and because this research requires involving people proficient with those local languages. However, those provide a diverse and rich second source of information that focuses on other perspectives different from the academia. Although grey literature has been criticized due to the lack of peer-reviewed, permanent accessibility, and quality, it has become a fundamental source of information for academic research thanks to its wider pool of participants, diversity of ideas, and different perspectives or easy access formats (Mahood et al., 2014; Seymour, 2010).

3.5. Ethical considerations

Special attention must be given to the host communities and organizations participating in research that involves human subjects. The researcher has a responsibility to the communities where the research is conducted, as well as specific groups within that communities (Newing, 2011). Based on that, prior informed consents were obtained from those local people participating in the interviews in the different case studies of this thesis: Portmán and Deià at the local scale, and Mallorca and Salento at the regional level.

In order to obtain prior informed consent from the local people selected for the purpose of interviews, I introduced myself and provided an explanation of my research, including its objectives and anticipated results. I then requested verbal consent to proceed with the research. During the interviews, I took notes and never noted any sensitive information that the interviewee requested or personal information. Alongside, all data were processed anonymously and under rigorous ethical standards. Moreover, although interviews are not reported in chapters 4 and 5, those were made as previously unpublished work which was key to correctly addressing and understanding the natural system. Following the principle of beneficence Newing (2011) I shared my research with the "Liga de Vecinos de Portmán" and compromised to provide a report to the politicians of Deià and the Fundació Iniciatives del Mediterrani on the findings reported in Chapter 5.

Chapter 4 *Remobilization of dissolved metals from a coastal mine tailing deposit driven by groundwater discharge and porewater exchange*

4.1. Introduction

Coastal environments have been largely modified by human activities over time on a global scale (Glavovic et al., 2015). Just as continental waters are contaminated by anthropogenic activities, coastal environments are also impacted by those, which may have important implications for biogeochemical cycles in coastal ecosystems, such as estuaries or coral reefs (Valiela et al., 1990; Amato et al., 2016). One of the activities that have a significant impact on the marine environment is ore mining, which leads to the disposal of tailings and effluents in the coastal zone and beyond either through river systems (Wang et al., 2019) or directly into lagoons, beaches, and shallow and deep water environments (Ramirez-Llodra et al., 2015). Some examples of significant mining impacts on coastal environments are El Salvador Cu mine in Chile (Ramirez et al., 2005), the Fe mining area next to the Mãe-Bá coastal lagoon in Brazil (Pereira et al., 2008), the mining district in Tinto River basin in Spain (Olías et al., 2006), or and the numerous sulfide mines along mainland Norway leading to waste dumping into fjords (Kvassnes and Iversen, 2013).

Another world-class prominent example is Portmán Bay, located in the province of Murcia, SE Spain (Figure 4.1). From 1957 to 1990, the open-pit mining of a massive Pb-Zn sulfide deposit resulted in a large volume of tailings, estimated at 60 million tons, which were pumped through a pipeline directly into the sea. This caused the almost complete infill of the bay's 750,000 m^2, which was accompanied by a seaward shoreline shift of 500 - 600 m (Oyarzun et al., 2013). Tailings consist of two main facies: "black sands", a sandy material with a high concentration of magnetite, and "yellow crusts", mainly made of clays and sulfates. Tailings are metal-rich, with reported mean contents of 40% Fe, 0.70% Zn, 0.30% Pb, 0.56% As, 0.10% Cu, 0.07%

Cd and 0.04% Hg (Manteca et al., 2014). Precious studies conducted in Portmán Bay evaluated the impacts of the waste accumulation on the marine environment and the potential ecotoxicological effects that resuspension of these tailings could cause (Mestre et al., 2017, and references therein). Toxicological effects on mussels (*Mytilus galloprovincialis*), red mullets (*Mullus barbatus*) and seabreams (*Sparus aurata L.*) have been shown in other studies (Fernandez et al., 2010; Martinez-Gomez et al., 2012; Benhamed et al., 2016, 2017; Mestre et al., 2017). However, red mullet and red porgy (*Pagrus pagrus*) specimens collected in 2014 had mean mercury concentrations of 0.17 mg $\cdot$kg^{-1} ww and 0.24 mg $\cdot$kg^{-1} ww, respectively, which are below the EU allowed maximum level (Llull et al., 2017). Other studies have also demonstrated that bulk atmospheric deposition fluxes of dust from the mine tailings were over the legal threshold for atmospheric concentrations of Zn (Sánchez Bisquert et al., 2016). Finally, the effectiveness of an immobilization technique for sediments contaminated by heavy metals has also been evaluated in the framework of the environmental remediation project (Martínez-Sánchez et al., 2014).

Despite the previously mentioned studies, the understanding of the actual physical processes that can release dissolved metals from the tailings into the sea is still limited. The aim of this work is to determine the concentration and distribution of dissolved metals in the coastal waters of Portmán Bay and to understand the role of SGD and PEX as release mechanisms for dissolved metals, about 30 years after the end of mining waste disposal.

4.2. Methods

4.2.1. Study site

Portmán Bay is located in the Cartagena - La Unión mining district, also known as Sierra Minera (literally *Mining Sierra*) because of the abundance of valuable minerals, which have been exploited at least since Carthaginian times, in the 3rd Century BC (Oyarzun et al., 2013) (Figure 4.1). The Sierra hosts one of the largest and richest polymetallic massive sulfide deposits in SE Spain (García-Lorenzo et al., 2014). The ores are of hydrothermal and epigenetic origin and are composed of galena, sphalerite, marcasite, chalcopyrite, greenalite, chalcopyrite and secondary minerals (Navarro-Hervás et al., 2012; Oen et al., 1975). Those ores have been exploited for Ag, Fe, Pb and Zn, especially during the 19^{th} and 20^{th} centuries (Pérez de Perceval et al., 2013; Oyarzun et al., 2013). The company "Sociedad Minero Metalúrgica Peñarroya España" exploited the ores at an unprecedented scale through open pit mining, which lasted from 1953 until 1991. Large volumes of ore minerals were transported to the treatment plant in the bay, known as "Lavadero Roberto", where the main target metals at that time, Pb and Zn, but also Ag, Fe and S, were concentrated by froth flotation (Oen et al., 1975; Manteca and Ovejero 1992; Pérez de Perceval et al., 2013; Manteca et al., 2014). The waste generated by this process started being pumped directly into the sea by a pipeline in 1957, leading to the infill of the bay, from west to east, by about 60 Mt (Manteca et al., 2014) due to the sea currents (Pauc and Thibault, 1976). Regarding its tremendous environmental consequences, dumping into the bay was stopped by the authorities in 1990. Since the metal extraction process at "Lavadero Roberto" was not of high efficiency, the materials released into the bay, which have grain sizes between 100 and 500 µm (Martínez-Sánchez et al., 2008), are metal-rich (Gómez-García et al., 2015; Manteca et al., 2014). Actually, because of the high metal concentrations, the tailings are considered a secondary ore, at least for Fe. A study by MINEMET (1974) found the following mineralogical composition of the tailings: carbonates (mainly siderite), 35.9%; phyllosilicates (greenalite, chlorite, clays), 25.7%; silica (quartz, opal, chalcedony), 20.0 %; Fe oxides (magnetite, hematite, goethite), 15.6 %; and sulfides (mainly pyrite), 2.7 % (Manteca et al., 2014). Also, these tailings have a noticeable content of heavy metals such as Pb and Zn (about 0.20 % of Pb and 0.60 % of Zn) (Oyarzun et al., 2013). In turn, samples from the artificial beach atop the deposits consist of 17% quartz, 35% magnetite, 35% siderite and 12% hematite (Manteca et al., 2014).

Open-pit mining activities and tailings generation have led to complex hydrogeochemical processes, starting with the oxidation of the pyrite and other sulphides in the tailings deposit, thus triggering the release of protons and metal ions into groundwaters and their consequent acidification (Balci et al., 2012; Robles-Arenas and Candela, 2010). These acid waters run through the local hydrological system causing the dissolution of minerals such as galena and sphalerite, and the release of Pb, Zn and other metals. They also react with carbonates and silicates, which dissolution generates a buffer solution that lowers the acidification of porewaters in the tailings (Robles-Arenas et al., 2006). Additionally, porewaters are oxygenated when they interact with seawater, thus inducing the precipitation of most of the dissolved metals (Trezzi et al., 2016a). In 2015, the Spanish ministry in charge of environmental issues started a restoration project where 2 Mm^3 of tailings are planned to be removed from the partially emerged, landward part of the waste deposit (BOE, 2011; 2015).

4.2.2. Sampling

On March 2015 a first campaign onboard the oceanographic vessel Ángeles Alvariño, from the Spanish Oceanographic Institute (IEO), was conducted. Three transects were established perpendicular to the shore: Western (W), Central (C), and Eastern (E) transects, each of them composed of 8 stations (Figure 4.1). In each station, 500 mL and 60 L samples were collected to determine dissolved metals (Ag, Cd, Co, Fe, Pb, and Zn) and Ra isotopes, respectively, together with vertical profiles of temperature and salinity. All samples were taken directly from surface waters (~50 cm below the water surface) using a submersible pump for Ra samples and a peristaltic pump with acid-clean tubing for metal samples. On stations C4, C6 and C8 two additional samples were taken at 7 m depth (intermediate depth in the water column) and at ~1 m above the seafloor (to avoid contamination of resuspended sediments), to obtain a vertical representation of the parameters analyzed. On January 2016, a second campaign was performed, to collect coastal seawater samples for Ra and dissolved metals in three different sites within the bay: nearshore station at W, C and E transects. Additional porewater samples at 1 m depth were also collected by means of a manual piezometer at different points along a transect perpendicular to the shoreline in the western part of the bay, where the lowest salinities were measured (PW1, PW2, PW3, PW4, PW5 and PW6 from north to south, respectively; Figure 4.1). In both campaigns, temperature and conductivity of seawater and porewater samples were measured directly with a YSI 650 multiparameter probe. Between March and September 2016, conductivity, temperature and groundwater table temporal oscillations were measured with a CTD-Diver© installed at piezometers PZ01 and PZ04. In July 2016 a third campaign was performed to collect samples from porewaters for Ra isotopes and dissolved metals from four 2.2 m deep slotted piezometers that had been installed along the bay at ~50 - 100 m from the shoreline during the second campaign (PZ01, PZ02, PZ03, and PZ04, from west to east). In each piezometer, water samples for Ra isotopes (20 L) were obtained. In addition, temperature, salinity, pH, O_2, and conductivity were measured. Water from the piezometers was pumped through a flux cell in order to measure pH, and O_2 with a multiparametric HACH® HQ40d. In November 2017, a fourth and last campaign was performed. Porewater samples for Ra isotopes and dissolved metals were collected from two locations (PW7 and PW8) at 6 different depths (5, 15, 30, 50, 75 and 100 cm below the sediment surface) using manual piezometers (5 L samples for Ra; 1 L for dissolved metals). All piezometer and seawater samples were also measured for temperature, salinity, pH, O_2 and conductivity with a multiparametric HACH® HQ40d.

Seawater and porewater samples collected for Ra isotopes were filtered (<1 L $\cdot$min^{-1}) through 25 g of acrylic fibers impregnated with MnO_2 to adsorb Ra isotopes (Moore, 1976). Samples for dissolved metals were collected in 0.5 L acid-cleaned low-density polyethylene plastic bottles by using a peristaltic pump connected to an acid-cleaned rubber tube and filtered through an acid-cleaned polypropylene cartridge filter (0.22 μm; MSI, Calyx®). Clean trace metal procedures were followed in order to prevent metal contamination (Tovar-Sánchez, 2012). After sampling, dissolved metal samples were acidified to a very low pH (<2) with 4 mL HCl trace metal grade (TMG) and stored for at least one month before analysis.

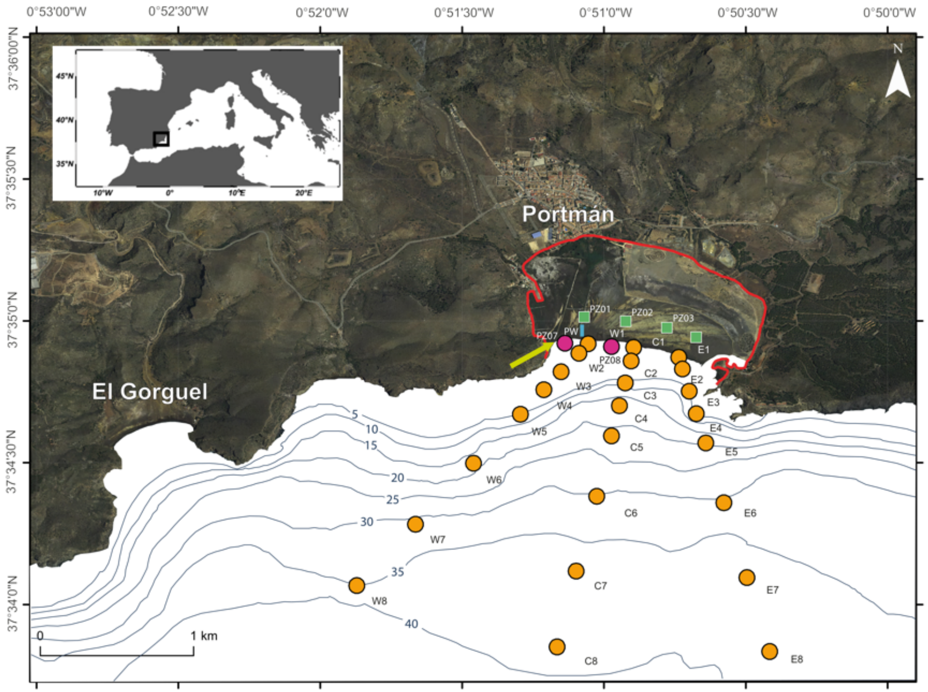

Figure 4.1. Location and bathymetry map of Portmán Bay. Orthophotomap from Instituto Geográfico Nacional (IGN). Bathymetry, in meters, adapted from Cabo de Palos map of Instituto Español de Oceanografía. The red line represents the shoreline in 1929, according to aerial photographs from IGN. Seawater sampling stations are indicated by orange circles, porewater piezometers PZ01 to PZ04 by green squares, manual piezometer by pink circles and the porewater sampling transect (PW) by the blue rectangle. W, C and E in sampling station codes stand for western, central and eastern seawater sampling transects. The arrow shows the location of the picture in Figure 4.6.

4.3. Results and Discussion

4.3.1. Hydrology

Porewater samples collected from both installed (PZ) and manual piezometers (PW) showed a heterogenous distribution of physicochemical parameters as shown in Table 4.1.

Porewater temperatures ranged from 16 ºC to 26 ºC, describing an ascendant gradient from west to east, and from 18 ºC to 24 ºC downwards in the depth profiles (PW7 and PW8). Salinities had a temperature-like pattern ranging from 10 to 29 from west to east. Such difference is evidenced by the presence of a fresher groundwater plume, located in the western part of the bay where PZ01 was located. The influence of this low-salinity groundwater in the western porewater transect showed a salinity gradient seaward, ranging from 8 to 35 (nearshore coastal seawater salinities of ~37). All porewaters had very low to low O_2 concentrations, ranging from 1.7 to 5.5 mg·L^{-1}, thus indicating anoxic conditions inside the tailings deposit. Most porewater samples had neutral to slightly acidy pH, ranging from 5.1 to 7.4, with the lowest values in the central part of the bay (PZ03).

Results from the groundwater table and salinity monitoring from March to May 2016 in PZ01 and PZ04 are shown in Figure 4.2, with the daily precipitation (AEMET, 2017) and the significant wave height (H_0) records (Puertos del Estado, 2017). Salinities in the groundwater-influenced piezometer (PZ01) showed significant fluctuations (from 10 to 26), whereas only minor variations (ranging from 34 to 35) were observed in the easternmost piezometer (PZ04). Salinity fluctuations in PZ01 coincided with the increase of the significant wave height (H_0 in Figure 4.2), associated with the characteristic Western Mediterranean storms occurring in spring and autumn seasons. Such changes modify the equilibrium of the hydraulic gradient, which displaces the salinity interface inland, thus resulting in an increase of salinity in PZ01. During sporadic rainfall episodes (e.g., April 22nd, 2016) the recharge of the aquifer counteracts the inland displacement of the salinity interface. Unlike other coastal aquifers in the Western Mediterranean, which are mainly dominated by the rainfall regime (e.g., Cerdà-Domènech et al. 2017), the increase of frequency and height of waves appears to be the main driver controlling the salinity interface position in Portmán Bay.

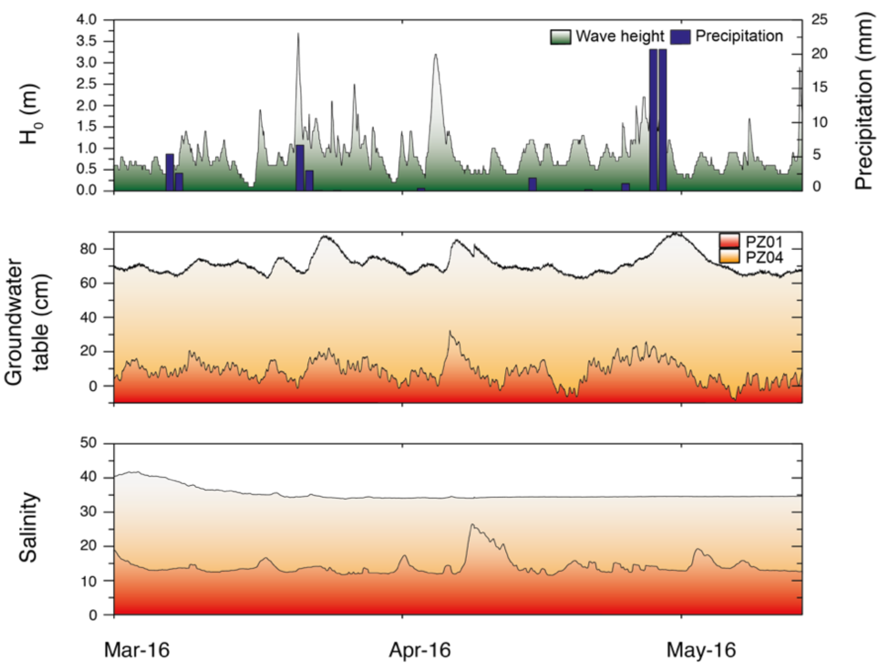

Figure 4.2. Temporal evolution of hydrogeological parameters in PZ01: time variation of groundwater table in PZ01 and PZ04, salinity, and significant wave height at point SIMAR-2074090 (37.50°N–0.83°W). The precipitation record corresponds to Cartagena, 12 km from Portmán Bay.

Table 4.1. Physicochemical parameters of Portmán Bay porewaters.

Station	Date	Temperature °C	Salinity	pH	O_2 mg·L^{-1}	^{223}Ra			^{224}Ra dpm·100L^{-1}			^{226}Ra			^{228}Ra		
PZ01	11/7/16	22	10	6.1	5.5	156	±	17	733	±	67	145	±	15	133	±	10
PZ02	12/7/16	26	16	5.7	4.4	246	±	25	993	±	91	227	±	15	493	±	9
PZ03	11/7/16	26	15	5.1	4.3	1.27	±	0.63	57	±	7	31	±	5		< 21*	
PZ04	11/7/16	25	29	5.8	4.3	103	±	12	2100	±	200	123	±	17	378	±	7
PW1	26/1/16	16	9	7.0	n.m	41	±	4	123	±	12	99	±	9	50	±	16
PW2	26/1/16	18	8	6.6	n.m	17	±	2	70	±	7	25	±	3	23	±	5
PW3	26/1/16	19	15	6.3	n.m	28	±	3	136	±	13	23	±	1	18	±	2
PW4	26/1/16	17	19	6.5	n.m	26	±	3	108	±	11	19	±	2	22	±	4
PW5	26/1/16	14	35	6.9	n.m	52	±	6	242	±	22	58	±	3	32	±	3
PW6	26/1/16	16	33	6.6	n.m	71	±	7	322	±	28	101	±	6	33	±	4
PW7_5	7/11/17	21	37	7.4	3.1	15	±	2	105	±	10		< 42**			< 106***	
PW7_15	7/11/17	20	36	7.3	2.7	22	±	3	146	±	13		< 42**			< 106***	
PW7_30	7/11/17	21	36	7.3	3.0	302	±	45	1329	±	124	233	±	36		< 106***	
PW7_50	7/11/17	21	37	7.2	2.8	380	±	54	1963	±	182	223	±	76		< 106***	
PW7_75	7/11/17	23	18	7.0	2.3	220	±	28	1010	±	95	481	±	43	285	±	41
PW7_100	7/11/17	24	14	7.1	1.9	168	±	24	616	±	63	187	±	37	265	±	47
PW8_5	7/11/17	20	36	7.4	2.2	5	±	1	61	±	7	98	±	36		< 106***	

PW8_15	7/11/17	19	35	7.3	2.7	9	±	2	85	±	8	< 42**			< 106***
PW8_30	7/11/17	19	36	7.3	2.9	17	±	4	138	±	14	< 42**			< 106***
PW8_50	7/11/17	18	35	7.3	2.5	16	±	3	180	±	18	< 42**			< 106***
PW8_75	7/11/17	19	35	7.3	1.7	14	±	4	172	±	19	184	±	62	< 106***
W8_100	7/11/17	19	36	7.3	1.7	39	±	7	344	±	32	< 42**			< 106***

n.m: Not measured

*^{228}Ra MDA$_{PZ}$(4L): 21 dpm ·100L^{-1}

**^{226}Ra MDA$_{PW}$(1L): 42 dpm ·100L^{-1}

***^{228}Ra MDA$_{PW}$(1L): 106 dpm ·100L^{-1}

4.3.2. Distribution of dissolved metals

- Porewater

Dissolved metal concentrations in porewaters ranged from 1 to 88 nM for Ag, 2 to 1200 nM for Cd, 2 to 530 for Co, 140 to 152000 nM for Fe, 2 to 23 nM for Pb and 1920 to 9060 nM for Zn. 2 to 910 nM for Cd, 16 to 530 nM for Co, 128000 to 733000 nM for Fe, 200 to 7700 nM for Pb and 610 to 103900 nM for Zn (Table 4.2). Iron, Cd, and Pb concentrations were higher in the acid conditions of PZ03, whereas Co and Zn concentrations were significantly higher in PZ02. The lowest values for dissolved metal concentrations were measured in the eastern part of the bay (PZ04) in coincidence with the reduced influence of fresh groundwaters. Relatively high dissolved concentrations of Fe, Pb, and Zn were found in the western part of the bay (PZ01), where porewaters have anoxic and low salinity conditions. Samples collected along the western transect evidenced an increase in dissolved metal concentrations along the three northernmost stations. Porewaters flowing seawards from these stations experienced a decrease in the concentrations of Co, Fe and Pb in PW5 and PW6, probably due to dilution with seawater and/or removal by iron hydroxides precipitation (Table 4.2). The same pattern was observed in porewaters collected at different depth profiles in piezometers PW7 and PW8. Deep, brackish and low ($< 2\ mg \cdot L^{-1}$) oxygen porewaters (100 cm) had generally low concentrations of dissolved metals.

The dissolved metal concentrations measured in Portmán Bay porewaters are amongst the highest reported in groundwaters from Mediterranean coastal aquifers and subterranean estuaries (Martinez-Soto et al., 2016; Rodellas et al., 2014; Tovar-Sánchez et al., 2014; Trezzi et al., 2016a, 2016b). Dissolved metal concentrations are similar to those in porewater samples from severely polluted areas around the world, such as polluted estuaries in New York for Cd, Co, Fe, Pb and Zn (Beck et al., 2009, 2010), contaminated rivers in China for Cd (Wang et al., 2012), a polluted coastal aquifer in India for Fe and Zn (Samantara et al., 2017), or a polluted ship breaking area in Bangladesh for Cd, Fe, Pb and Zn (Hasan et al., 2013).

Table 4.2. Dissolved trace metals in Portmán Bay porewater (nM)

Sample	Ag	Cd	Co	Fe	Pb	Zn
PZ01	BDL	3	49	178000	200	1800
PZ02	BDL	619	533	128000	590	103900
PZ03	BDL	914	72	733000	7700	12800
PZ04	BDL	2	16	165000	562	610
PW1	BDL	62	55	11000	149	20300
PW2	BDL	200	141	166000	360	24800
PW3	BDL	500	100	175000	6500	6300
PW4	BDL	440	51	170000	1100	16600
PW5	BDL	980	70	152000	1600	24300
PW6	BDL	1200	79	146000	1200	27800
PW7_5	15	79	8	1500	3	5400
PW7_15	78	78	3	200	BDL	7900
PW7_30	88	92	15	8500	2	3300
PW7_50	34	98	12	42000	8	2200
PW7_75	6	42	32	151000	24	3000
PW7_100	BDL	15	24	83000	19	1900
PW8_5	BDL	29	2	140	9	4900
PW8_15	8	36	3	750	16	8800
PW8_30	6	35	3	850	14	8800
PW8_50	1	33	4	730	15	9100
PW8_75	n.m	n.m	n.m	n.m	n.m	n.m
PW8_100	n.m	n.m	n.m	n.m	n.m	n.m

n.m: Not measured
BDL: Below detection limit

- Seawater

Concentrations of dissolved metals in offshore seawaters are shown in Figure 4.3 (also in Appendix A.1). They range from 0.01 to 0.46 nM for Ag, 0.2 to 17 nM for Cd, 0.15 to 0.86 nM for Co, 4 to 4350 nM for Fe, 0.9 to 9.4 nM for Pb, and 4 to 1300 nM for Zn. The highest concentrations are found on the western part of the bay, coincident with the lowest salinities in the bay. The inshore-offshore gradients shown by Ag, Cd, Co, Pb and Zn suggest an export of dissolved metals from the shoreline and a terrestrial metal source. Concentrations of dissolved Ag, Cd and Zn measured in Portmán Bay seawater are in the upper range of concentrations found in other Mediterranean sites (Table 4.3). Dissolved lead concentrations are higher than those measured in seawaters from other coastal sites, with the exceptions of the industrial port of Algeciras (Spain) (Morillo and Usero, 2008) and Iyidere (Turkey) (Baltas et al., 2017). Dissolved Fe concentrations in coastal seawaters are unexpectedly lower considering the extremely high concentrations measured in porewater samples from beach piezometers. Dissolved Fe concentrations in Portmán Bay waters are indeed lower than those measured in other less anthropogenically impacted sites in the Mediterranean, such as Palma beach (Spain) (Rodellas et al., 2014), Mallorca (Spain) (Tovar-Sánchez et al., 2014), Toulon (France) (Coclet et al., 2017) or Maó (Spain) (Martinez-Soto et al., 2016). Dissolved metal concentrations are similar to other polluted sites in the world, such as the Bing Bong coast (Australia) for Co and Fe (Munksgaard and Parry, 2001), or the Dakar coast (Senegal) for Zn (Diop et al., 2014).

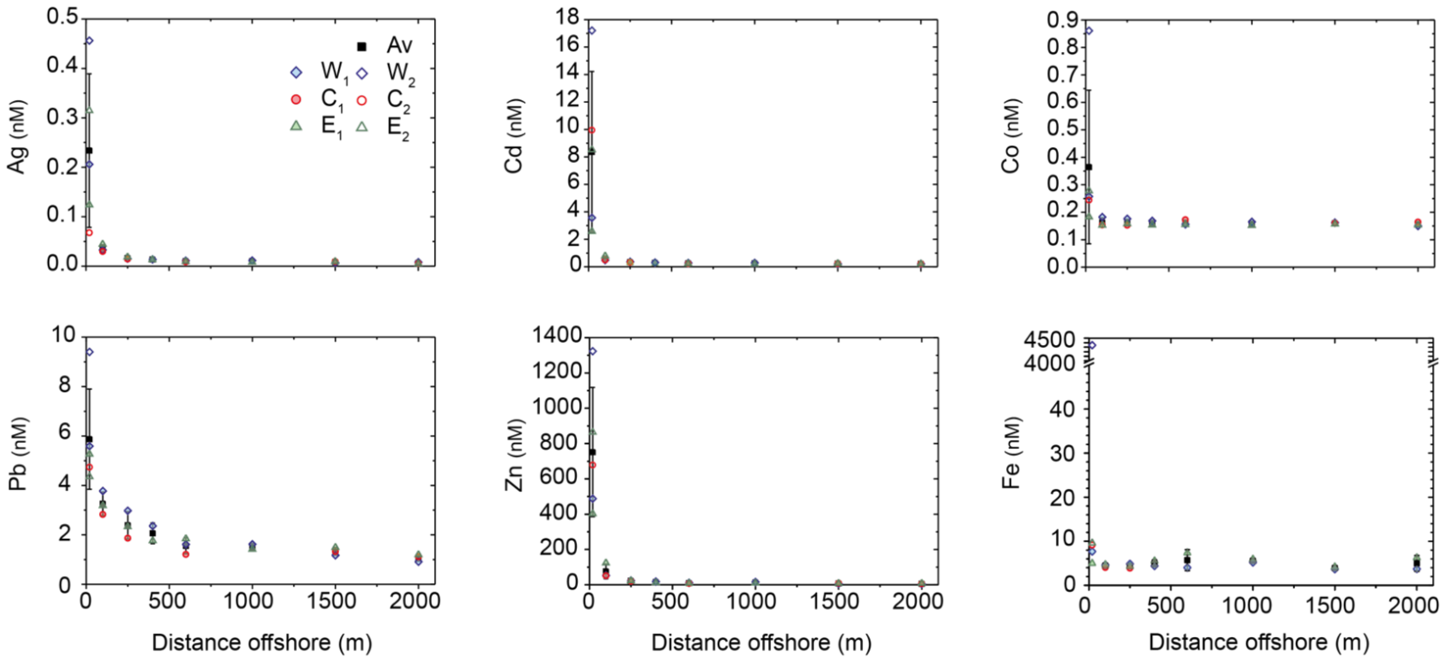

Figure 4.3. Offshore concentrations of dissolved metals. Blue diamonds correspond to the western transect, red circles to the central transect, green triangles to the eastern transect and black squares to average values. Filled figures correspond to samples obtained in November 2015 and empty correspond to samples obtained in January 2016.

Table 4.3. Dissolved metal concentrations in seawater (nM).

Site	Ag	Cd	Co	Fe	Pb	Zn
Portmán	0.005 - 2	0.18 - 4	0.14 - 0.26	4 - 8	0.38 - 6	3 - 488
[a]Gorguel	n.m	< 0.08	n.m	n.m	0.65 - 2.4	n.m
[b]Vigo	n.m	0.02 - 0.10	0.30 - 1.6	n.m	0.08 - 0.25	7 - 19
[c]Palma	n.m	n.m	n.m	3 - 6	0.28 - 0.40	3 - 10
[d]Algeciras	n.m	0.1 - 0.3	n.m	n.m	12 - 16	70 - 190
[e]Mallorca	n.m	0.20 - 0.37	0.12 - 0.29	2 - 15	0.07 - 0.24	2 - 12
[f]Toulon	n.m	0.06 - 0.36	n.m	n.m	0.10 - 5.3	7 - 208
[g]Maó	n.m	0.1 - 0.4	0.1 - 0.6	1 - 35	0.2 -2 .4	2 - 59
[h]Algeria	0.0045	0.004	1.3	390	0.3	56
[i]Iyidere	n.m	8.9	17	90	63	1300
[j]Dakar coast	n.m	1.6	3.1	n.m	4.5	610
[k]Bing Bong coast	n.m	n.m	0.5	6.9	n.m	n.m

n.m: Not measured
[a]Trezzi et al., 2016a; [b]Santos-Echeandía et al., 2009; [c]Rodellas et al., 2014; [d]Cánovas et al., 2007; [e]Morillo and Usero 2008; [f]Coclet et al., 2017; [g]Martinez-Soto et al., 2016; [h]Tovar-Sánchez et al., 2016; [i]Baltas et al., 2017; [j]Diop et al., 2014; [k]Munksgaard and Parry 2001.

4.3.3. Estimation of SGD and PEX water flows

In order to assess the magnitude of dissolved metals inputs into the sea from the mine tailings deposit, it is necessary to firstly identify the potential mechanisms and pathways conveying these metals into the coastal sea. Inputs of dissolved metals driven by runoff water discharge can be neglected given the low precipitation in the study area (< 300 mm·y^{-1}), where there are no permanent streams. Atmospheric deposition can also be discarded taking into account its direct relation to rain events and wind regime in the area (Sánchez Bisquert et al., 2016). Diffusion from the deposit of submerged sediments may also be a relevant pathway for dissolved metals, particularly considering the high dissolved metal concentrations in the sediments (Cheevaporn et al., 1995). However, the submerged section of the mine tailings deposit is mostly made of sands with coarse grains that have high permeabilities that facilitate the exchange of water across the sediment-water interface (Martínez-Sánchez et al., 2008). In these systems, porewater fluxes generally exert a bigger control than molecular diffusion on the exchange of solutes (Anschutz et al., 2009; Santos et al., 2012). Considering the influence of low salinity groundwaters in the western part of the bay, the discharge of groundwater to the sea could also represent an important pathway for dissolved metals to reach the coastal sea. Consequently, submarine groundwater discharge (SGD) and porewater exchange (PEX) are considered the main conveyors of dissolved metals from the mine tailings deposit to coastal waters. It should be noticed that we are evaluating the system in relatively calm and stable conditions and that other processes (e.g., storm-driven sediment resuspension) may also play an important role during sporadic extreme events. In order to estimate the water flows supplied by SGD and PEX into Portmán Bay, Ra isotopes are used as tracers (Rodellas et al., 2017).

- Ra concentrations

Concentrations of Ra isotopes in porewater samples ranged from 1 to 250 dpm ·100L^{-1} for ^{223}Ra, from 60 to 2090 dpm ·100L^{-1} for ^{224}Ra, from 19 to 480 dpm ·100L^{-1} for ^{226}Ra and from 18 to 490 dpm ·100L^{-1} for ^{228}Ra, with the lowest values in the central part of the bay (PZ03). Short-lived Ra isotopes clearly decreased landward in the westernmost side of the bay. Depth profile samples showed increasing gradients for ^{223}Ra, ^{224}Ra and ^{226}Ra in PW7 and only for short-lived isotopes in PW8. However, ^{228}Ra concentrations were below the detection limit, except for those samples collected at the deepest sections of PW7, ranging from 265 to 285 dpm ·100L^{-1}. In PW8 no relationships were observed between Ra isotopes and salinities either along or across the bay, likely as a consequence of mineral heterogeneity within the mine tailings (García-Lorenzo et al., 2014).

Radium isotopes concentrations in seawater are depicted in Figure 4.4. Short-lived Ra isotopes showed an exponential decrease offshore (from 0.1 to 2.1 dpm ·100L^{-1} for ^{223}Ra, and from 1.6 to 16.4 dpm ·100L^{-1} for ^{224}Ra), with the highest concentrations in nearshore samples, suggesting the presence of an important source of these isotopes at the shoreline or nearshore area. Long-lived Ra isotopes did not show any gradient along all the offshore transects, with relatively constant values (9.2 - 13.8 dpm ·100L^{-1} for ^{226}Ra, and 2.7 - 5.7 dpm ·100L^{-1} for ^{228}Ra) indicating the lack of significant inputs of these isotopes from the shoreline. However, the highest concentrations of ^{228}Ra were detected in the western zone (groundwater-influenced area).

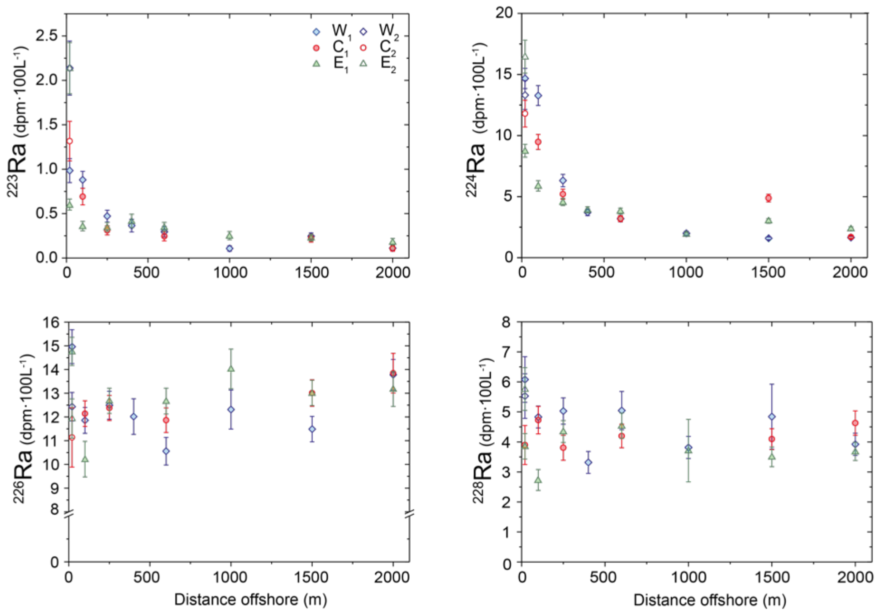

Figure 4.4. Offshore concentrations of Ra isotopes. Blue diamonds correspond to the western transect, red circles to the central transect and green triangles to the eastern transect. Filled figures correspond to samples obtained in November 2015 and empty correspond to samples obtained in January 2016.

Several mechanisms have been identified as driving forces for PEX (Santos et al., 2012), but it is likely that wave pumping is one of the major forces in this system considering that tides play a minor role. The noticeable offshore gradients of short-lived Ra isotopes (^{223}Ra and ^{224}Ra), combined with the lack of significant enrichments of long-lived Ra isotopes (^{226}Ra and ^{228}Ra) in nearshore waters, suggests that the main mechanism delivering Ra isotopes to the water column involves water in contact with the geological matrix (i.e., sediments or mine tailings) for only a relatively short time (hours to days). This short temporal scale is long enough to allow for a significant enrichment of short-lived Ra isotopes from the sediments, while preventing the regeneration of ^{226}Ra and ^{228}Ra (Rodellas et al., 2017). This observation suggests that most inputs of Ra isotopes to the water column are driven by shallow and rapid flushing, i.e. by porewater exchange (PEX), of the materials in the deposit since this process is an important source of short-lived Ra isotopes but not of long-lived ones (Rodellas et al., 2017). In addition, the low salinities measured in coastal porewaters from the western side of the bay and the slight ^{228}Ra enrichment in nearshore seawater samples from the westernmost transect, suggest that SGD may also occur.

- Mass balance

Adapting the methodology described in Chapter 3 a mass balance was constructed for different Ra isotopes to quantify concurrently SGD and PEX, since combining different isotopes with different half-lives allows assessing different water flow pathways (Rodellas et al., 2017). Indeed, concentrations of Ra isotopes in porewaters were much higher than those measured in coastal waters, which indicates that SGD and PEX are the main sources for increased Ra isotope concentrations in coastal waters. Assuming steady-state conditions, water flows ($m^3 \cdot d^{-1}$) from SGD and PEX can be estimated as follows (Equation 4.1 modified from Moore, 1996 and Rodellas et al., 2017):

$$F_{SGD} \cdot {}^{x}Ra_{SGD} + F_{PEX} \cdot {}^{x}Ra_{PEX} = \frac{({}^{x}Ra_{cw-ex}) \cdot V}{\tau_r} + [\lambda \cdot {}^{x}Ra_{cw-ex} \cdot V] - [F_{sed} \cdot A_{sed}] - [F_{stream} \cdot {}^{x}Ra_{stream}] \quad \text{Eq. 4.1}$$

All the terms in Equation 4.1 are defined in Table 4.4. A volume V of 6.7 10^6 m^3 was considered by creating a triangular polygon, where a depth and width of 20 m and 1000 m were used. Fluxes of Ra from surface streams (F_{stream}) were neglected due to their total absence during the period of study. Inputs of Ra from sediment diffusion (F_{sed}) were also discarded due to the presence of coarse-grain sands (Martínez-Sánchez et al., 2008), which are considered to have low U/Th content (Luek and Beck, 2014). In addition, several studies have suggested that Ra diffusion rates usually do not represent more than a 10% of the total Ra inputs (Beck et al., 2007; Garcia-Orellana et al., 2014; Rodellas et al., 2015b).

Table 4.4. Water flow and Eq. 4.1 parameters

Term	Definition		Value			Unit
F_{SGD}	Water flow from SGD		10	±	4	$m^3 \cdot d^{-1}$
F_{PEX}	Water flow from PEX		66	±	33	$m^3 \cdot d^{-1}$
F_{sed}	Water diffusion rate in sediments					$m^3 \cdot d^{-1} \cdot m^{-2}$
F_{stream}	Water flux from streams			-		$m^3 \cdot d^{-1}$
		Isotope				
${}^{x}Ra_{cw-ex}$	Area-weighted activity excess of Ra in coastal waters	^{224}Ra	18	±	4	$dpm \cdot 100L^{-1}$
		^{228}Ra	0.33	±	0.07	
${}^{x}Ra_{SGD}$	Ra isotope concentration in the SGD endmember	^{224}Ra	600	-	1000	$dpm \cdot 100L^{-1}$
		^{228}Ra	190	-	480	
${}^{x}Ra_{PEX}$	Ra isotope concentration in the PEX endmember	^{224}Ra	85	-	140	$dpm \cdot 100L^{-1}$
		^{228}Ra	BDL	-	BDL	
λ	Decay constant of the Ra isotope used as endmember	^{224}Ra		0.191		s^{-1}
		^{228}Ra		0.121		y^{-1}
τ_r	Apparent age of seawater in Portmán Bay			1.2		d
A_{sed}	Area covered by sediments			$6 \cdot 10^5$		m^2
V	Volume of the bay			$6.7\ 10^6$		m^3

BDL: Below detection limit

Equation 4.1 was solved using ^{228}Ra and ^{224}Ra concentrations to assess the magnitude of the two unknown terms: F_{SGD} and F_{PEX}. Given that ^{224}Ra and ^{223}Ra are well correlated ($R^2 = 0.93$), the use of ^{223}Ra as a tracer would produce similar results but with higher uncertainties. On the other hand, ^{228}Ra was used as SGD tracer due to its long half-life (5.75 y), which allows tracing SGD while having a minor influence of PEX inputs.

- Ra endmembers of SGD and PEX

The lack of relevant ^{228}Ra inputs in the eastern part of the bay (where PEX is also expected to occur), suggests that most of ^{228}Ra inputs to the system are supplied via SGD. Thus, the ^{228}Ra concentration in the PEX endmember ($^{228}Ra_{PEX}$) is considered negligible. In order to constrain the ^{224}Ra activities in the PEX endmember ($^{224}Ra_{PEX}$), the $^{224}Ra/^{223}Ra$ activity ratios ($AR_{224/223}$) in nearshore coastal waters can be used (Moore, 2000a). Assuming that PEX inputs are the main source of short-lived Ra isotopes to coastal waters and that there is no significant decay in nearshore samples, the $AR_{224/223}$ in those samples should be the same as the $AR_{224/223}$ in the PEX endmember. Among all porewater samples collected, only PW8 at 15 and 30 cm have $AR_{224/223}$ comparable to those measured in nearshore bay waters ($AR_{224/223}$ ~ 12). We, therefore, use the average of concentrations measured in these samples as the ^{224}Ra endmember for PEX. It should be noticed that, since PEX does not represent a net water flow mechanism, concentrations of Ra isotopes in nearshore waters need to be subtracted to estimate the endmember (Cook et al., 2018a). Analogously, the ^{228}Ra concentration in these samples is below the detection limit, which is consistent with the previous assumption of negligible concentrations of ^{228}Ra in the PEX endmember.

For the ^{228}Ra and ^{224}Ra concentrations in the SGD endmember, we selected those samples collected in PW7 at 75 and 100 cm. These samples were selected because they are located at the western part of the bay, where physicochemical conditions (low salinities and O_2 concentrations) indicate that these porewaters are influenced by low salinity groundwaters. In addition, the selected samples have a relatively high concentration of ^{228}Ra, which allows explaining the excess ^{228}Ra in the western coastal waters.

- Residence time of coastal waters

To calculate the residence time of seawater in the bay τ_r, we used the Ra isotopes method described by Moore (2000a), which is the most commonly applied approach. We used ^{224}Ra and ^{223}Ra because their short half-life are suited for the expected short residence times. Both Ra isotopes were clearly enriched in porewaters relative to seawater. However, the almost constant $AR_{224/223}$ in coastal seawaters point to an extremely low residence time, which prevents applying this methodology. Thus, in order to obtain a conservative value of the SGD flux, a maximum water residence time (τ_r) of 1.2 days is calculated by means of Equation 4.2 (modified from Knee et al. (2010)).

$$\tau_r = \frac{\ln\left(1-\sqrt{(d^{223}Ra)^2+(d^{224}Ra)^2}\right)}{-\lambda_{224}} \qquad \text{Eq. 4.2}$$

where $d^{223}Ra$ and $d^{224}Ra$ are the relative average errors associated with ^{223}Ra and ^{224}Ra in the coastal stations (19% and 7%, respectively) and λ_{224} is the decay constant of ^{224}Ra.

- SGD- and PEX-driven water flows

Solving the mass balance in Equation 4.1 for ^{224}Ra and ^{228}Ra allows estimating the total PEX and SGD water flows into the Portmán Bay, which are $180 \pm 90 \cdot 10^3$ and $27 \pm 11 \cdot 10^3$ $m^3 \cdot d^{-1}$, respectively. A total annual shore-normalized water flow of 76 ± 33 $hm^3 \cdot km^{-1} \cdot y^{-1}$ is subsequently calculated by adding up the total annual SGD (10 ± 4 $hm^3 \cdot km^{-1} \cdot y^{-1}$) and PEX ($66 \pm 34$ $hm^3 \cdot km^{-1} \cdot y^{-1}$) after considering a shoreline of 1000 m. The flushing of shallow sediment via PEX is, volumetrically, up to seven times higher than the estimated flow of SGD. The obtained total annual shore-normalized water flow into Portmán Bay is 3 - 4 times greater than that of El Gorguel, a small pocket beach adjacent to the study site, also affected by mining activities (Trezzi et al., 2016a). Similar SGD flows have been reported from other sites in the Mediterranean Sea, ranging from 3 to 11 $hm^3 \cdot km^{-1} \cdot y^{-1}$ (Taniguchi et al., 2006; El-Gamal et al., 2012; Mejías et al., 2012; Pavlidou et al., 2014; Rodellas et al., 2018).

4.3.4. Estimation of SGD- and PEX-driven dissolved metal fluxes

The most common method used to estimate SGD- and PEX-driven dissolved metal fluxes is multiplying the previously estimated water flows by the groundwater and porewater endmember dissolved metal concentrations (Santos et al., 2011). In our study, metal fluxes are calculated separately for each pathway: SGD and PEX. Accordingly, the endmembers for each process have to be directly related to the specific transport mechanism, and thus the same samples used for the Ra mass balance are used as endmembers for dissolved metal concentrations: PW8 at 15 and 30 cm is used for PEX and PW7 at 75 and 100 cm is used for SGD.

The estimated shore-normalized maximum fluxes of dissolved metals are, respectively, for PEX and SGD, 1.3 ± 0.7 and 0.2 ± 0.1 $mol \cdot d^{-1} \cdot km^{-1}$ for Ag, 6.5 ± 3.2 and 0.8 ± 0.6 $mol \cdot d^{-1} \cdot km^{-1}$ for Cd, 0.6 ± 0.3 and 0.7 ± 0.3 $mol \cdot d^{-1} \cdot km^{-1}$ for Co, 2.7 ± 1.4 and 0.6 ± 0.3 for $mol \cdot d^{-1} \cdot km^{-1}$ for Pb, 1600 ± 790 and 67 ± 34 $mol \cdot d^{-1} \cdot km^{-1}$ for Zn, 145 ± 73 and 3200 ± 1800 $mol \cdot d^{-1} \cdot km^{-1}$ for Fe. These results highlight that i) the rapid small-scale recirculation of seawater through the tailings (i.e., PEX) remobilizes large amounts of dissolved metals from the tailings to the water column, and ii) SGD represents the main conveyor of dissolved Fe into seawater.

The significance of these fluxes as sources of dissolved metals in the coastal waters of Portmán Bay can be assessed by comparing the inventory of dissolved metals driven by these processes with the dissolved metal inventory in coastal waters (Trezzi et al., 2016a). The total inventories derived from SGD and PEX were calculated by multiplying the dissolved metal flux by the water age of bay waters and then adding up both inventories. The excess inventory of dissolved metal in coastal waters was calculated by multiplying the area-weighted excess dissolved metal concentration by the volume of the study site. The estimated dissolved metal inventories supplied by SGD and PEX are much higher (> 100%) than the inventories obtained from the dissolved metal concentrations in coastal waters (Table 4.5).

Table 4.5. Metal inventories in Portmán Bay (mol).

	Ag	Cd	Co	Pb	Zn	Fe
PEX	1.5 ± 0.8	7.7 ± 3.8	0.7 ± 0.3	3.2 ± 1.6	1900 ± 950	170 ± 87
SGD	0.2 ± 0.1	0.92 ± 0.73	0.9 ± 0.4	0.7 ± 0.3	80 ± 41	3800 ± 2200
Excess Inventory	0.01	0.15	0.01	1.6	20	1.3

This qualitative comparison indicates the potential relevance of both mechanisms, as well as the existence of a significant removal mechanism for dissolved metals. We hypothesize that there could be a significant removal of dissolved metals both i) in mine tailings preventing the metals to reach the sea and ii) in the water column. i) In mine tailings, an "iron curtain" might be formed in the surface beach when large amounts of soluble Fe^{2+} oxidates into insoluble Fe^{3+} (Charette and Sholkovitz 2002; Windom et al., 2006; Beck et al., 2009; Trezzi et al., 2016a). Samples above 75 cm in PW7 presented reduced concentrations of dissolved Fe (Figure 4.5), indicating the removal of iron from the dissolved phase and the precipitation into iron hydroxides due to the mixture with oxygenated waters (Santana-Casiano et al., 2005).

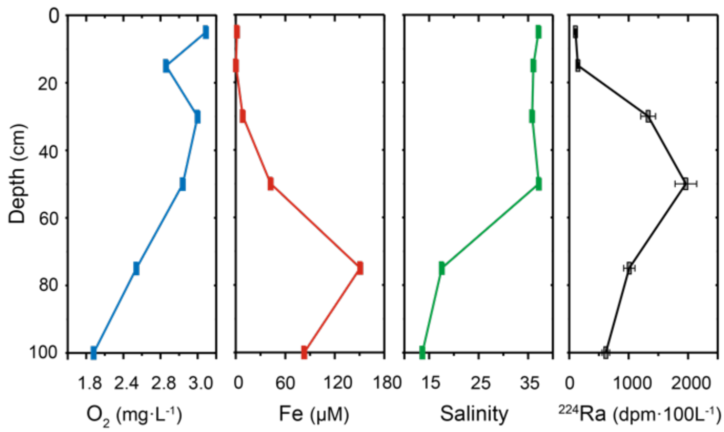

Figure 4.5. O_2, Fe, salinity and ^{224}Ra depth profiles at PW7.

Unfortunately, the fact that Portmán Bay mine tailings are enriched in Fe compared to other dissolved metals, prevents visually identifying an enriched Fe layer from the piezometers. Contrarily, the deepest 25 cm waters of PW7, which are influenced by fresh anoxic porewaters (according to their pH, salinity and O_2 concentration) present extremely high dissolved Fe concentrations (see Table 4.2). The precipitation of iron hydroxides in mine tailings forming the "iron curtain" could act as a geochemical barrier, and retain other dissolved metals (Charette and Sholkovitz, 2002). ii) In the water column, the discharge of low-salinity groundwater to the coastal sea (i.e., SGD) drives large inputs of dissolved Fe into coastal waters, producing a plume of iron hydroxides that can be visually identified (Figure 4.6). Such SGD-driven inputs of Fe could contribute to the removal of large amounts of dissolved metals from the water column, due to the co-precipitation of different metal species with iron hydroxides (Lee et al., 2002), reducing the concentrations of dissolved metal in the coastal water column.

Figure 4.6. Picture showing iron hydroxide plumes in coastal waters adjacent to the shoreline in Portmán Bay. Photograph during November 2017.

The estimated total fluxes of dissolved metals in Portmán Bay are higher than other SGD- and PEX-driven dissolved metal fluxes reported worldwide (Table 4.6). The nearest reported site, El Gorguel, which is also affected by mining activities, has a Fe flux that is three orders of magnitude lower, a Zn flux that is one order of magnitude lower, and a maximum Pb flux that is 6 times lower than those reported in the current study. In Mallorca, a site not affected by mining activities (Rodellas et al., 2014; Tovar-Sánchez et al., 2014), Zn the measured fluxes of Pb, and Fe are two to four orders of magnitude lower than those reported in Portmán Bay. All dissolved metal fluxes in Portmán Bay are one to three orders of magnitude higher than in Bangdu, Korea (Jeong et al., 2012). Even one of the highest Fe SGD-driven fluxes reported until now, in Patos Lagoon (Windom et al., 2006), is almost half of the minimum Fe flux reported in this study. This comparison of dissolved metal fluxes with other studies demonstrates the relevance of SGD and PEX as sources of dissolved metals in Portmán Bay, as well as potentially in other highly polluted coastal sites. However, it should be noted that the removal of dissolved metals from the water column to the sediments through co-precipitation with SGD-driven iron hydroxides, could minimize the export of dissolved metals to offshore waters.

Table 4.6. Driven metal fluxes (mol d^{-1} km^{-1}).

Site	Ag	Cd	Co	Pb	Zn	Fe
Portmán	1.4 ± 0.7	7.2 ± 3.3	1.3 ± 0.4	3.3 ± 1.4	1660 ± 790	3330 ± 1800
[a]El Gorguel	n.m	n.m	n.m	0.20 - 0.60	47 - 180	4 - 32
[b]Palma Bay	n.m	n.m	n.m	0 - 0.01	0.1 - 1.4	0.4 - 20
[c]Santanyí cove	n.m	n.m	n.m	n.m	2.9	0.25
[d]Romàntica cove	n.m	n.m	n.m	n.m	0.24	0.61
[e]Sa Nau cove	n.m	n.m	n.m	n.m	1.6	0.5
[f]Bangdu Bay	n.m	n.m	0.01 - 0.24	n.m	n.m	4 - 160
[g]Patos lagoon	n.m	n.m	n.m	n.m	n.m	1333

n.m: Not measured

[a]Trezzi et al., 2016a; [b]Rodellas et al., 2014; [c,d,e]Tovar-Sánchez et al., 2014; [f]Jeong et al., 2012; [g]Windom et al., 2006. Where Portmán are the total dissolved metal fluxes reported.

4.3.5. Implications on the environmental status of Portmán Bay

The results of this study confirm that more than 25 years after the cessation of dumping mine waste, there is still a continuous flux of dissolved metals to the coastal ocean from the tailings deposits in Portmán Bay. The main process governing the release of dissolved metals into the water column is the flushing of shallow beach sediments (PEX). Whereas most dissolved metals (Ag, Cd, Pb and Zn) in coastal waters would result from the circulation of seawater through the top centimeters of the tailings deposit, the main source of Fe to the sea appears to be SGD. These inputs of dissolved Fe from anoxic porewaters may indeed contribute to more efficient removal of the dissolved metals from the water column to the sediments, because of co-precipitation of dissolved metals with Fe hydroxides (Figure 4.7a).

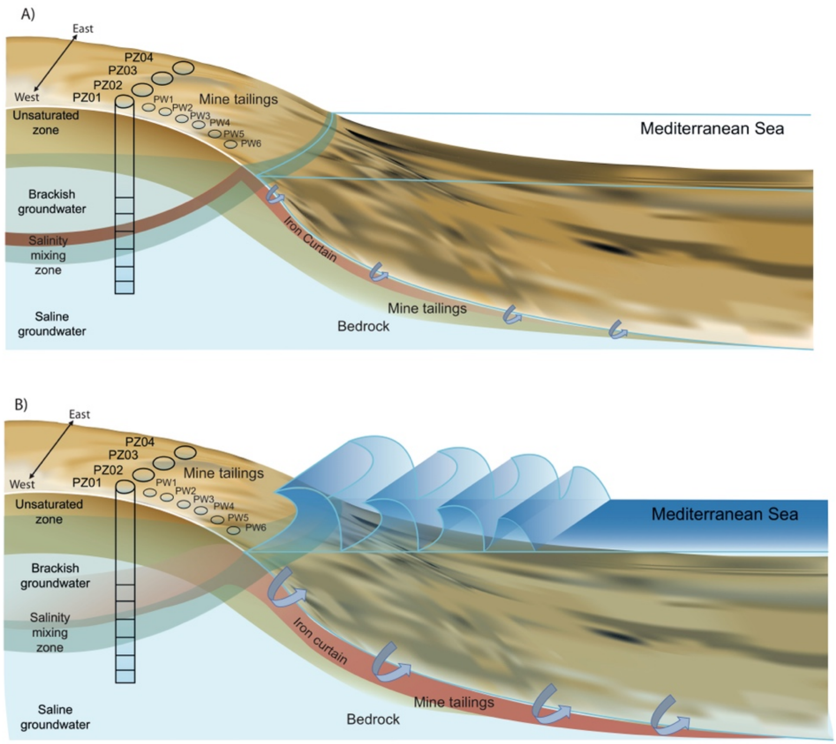

Figure 4.7. Sketch showing the two different recirculation situations in Portmán Bay under A) stable environmental conditions, and B) stormy conditions. For location of piezometer and porewater sampling stations the reader is referred to Figure 4.1. Curved arrows represent PEX.

Considering that samples were collected in relatively calm and stable weather conditions, the SGD- and PEX-driven dissolved metal fluxes estimated in this study could be significantly enhanced as a consequence of sporadic intense events, such as heavy rainfalls or sea wave storms. Indeed, our CTD piezometer records showed that precipitation events often occur at the same time as sea storms, subsequently rising the underground water table and increasing porewater salinities. This evidence the major role of marine processes on the landward section of the tailings deposit. During such events, seawater circulates through the deposits changing the anoxic conditions of porewaters in that section, thus increasing the discharge of metal-loaded porewaters via PEX (Figure 4.7b). The occasional recharge of the coastal aquifer and the subterranean estuary by the infiltration of freshwater from rainfall or ephemeral streams enhances the terrestrial hydraulic gradient and, consequently, the export of water and dissolved metals to the sea through SGD (Santos et al., 2012; Cerdà-Domènech et al., 2017). However, under a climate change scenario, the predicted reduction of rainfall in the study area and in the Mediterranean Basin more generally (IPCC (Intergovernmental Panel on Climate Change), 2007) could lead to a reduction in the volume of fresh groundwater. Under such circumstances, the consequent reduction of SGD and, therefore, the reduction of the flux of dissolved Fe and the abundance of Fe-hydroxides in seawater, may increase the offshore export of dissolved metals driven by PEX in Portmán Bay.

The persistence of the flux of dissolved metals more than 25 years after the cessation of tailings disposal suggests that the impact on the ecosystem may remain significant. Permanent pollution decades after the end of dumping of tailings in coastal environments has been shown in other places (e.g. Olsgard and Hasle (1993); Josefson et al. (2008)). However, there is a lack of studies showing the actual impacts of metal pollution by both, the particulate and the dissolved fractions, in coastal ecosystems (Nicolaidou et al., 1989; Olsgard and Hasle 1993; Burd, 2002; Lancellotti and Stotz 2004; Josefson et al., 2008).

The significance of SGD as a source of trace metals to the ocean has been highlighted in previous studies (Charette and Buesseler, 2004; Windom et al., 2006; Beck et al., 2007, 2009). In the Mediterranean Sea, it has been also shown by Trezzi et al. (2016b), who noticed the need of considering SGD in the calculation of metal budgets in the basin and the investigation of biogeochemical cycles in coastal areas. The present work represents one of the first assessments including and differentiating both SGD and PEX as sources of dissolved metals to the coastal sea. Our results demonstrate that both mechanisms are relevant pathways delivering dissolved metals to the coastal sea in polluted areas. For Portmán Bay, whilst the short- and small-scale recirculation of coastal waters through the mine tailings deposit (PEX) favors the remobilization of large amounts of dissolved metals, the discharge of anoxic low-salinity groundwaters (SGD) contributes to the supply of dissolved Fe. Altogether, PEX and SGD supply dissolved metals to the seawater of Portmán Bay, thus increasing their concentrations. Indeed, even the dissolved metal concentrations measured at 2000 m offshore (which appear to be low in comparison to the large concentrations measured in nearshore stations; Figure 4.3) were much higher than offshore concentrations measured in some open ocean stations from the same region (e.g. Alboran Sea; Yoon et al., 1999).

The significant SGD- and PEX-driven fluxes of dissolved metals to the coastal sea documented in this study might produce significant impacts on coastal biogeochemical studies, and it would deserve further investigation. A comprehensive understanding of the impacts of the Portmán mine tailing deposit on coastal biogeochemical cycles would also require evaluating the particulate fraction, including the potential remobilization of metals in storm-driven resuspension events and the metal export offshore.

Chapter 5 *The connection of Submarine Groundwater Discharge to seawater quality: The threat of treated wastewaters injected into coastal aquifers*

5.1. Introduction

Nutrients supplied by SGD to the coastal ocean can have important implications for coastal ecosystems, such as triggering hazardous algal blooms or leading to eutrophication of coastal waters (Johannes, 1980; Knee and Paytan, 2011; Lecher and Mackey, 2018; Santos et al., 2021; Valiela et al., 1992). SGD can thus have an important impact on leisure activities, such as those related to the quality of bathing waters. These leisure activities are fundamental for coastal tourism, an industry that represents a fundamental pillar for many coastal economies and societies. This is the case of Mediterranean islands, where tourism has provided high incomes and socioeconomic growth (Apostolopoulos et al., 2002). However, due to their insularity, small land surface and limited natural resources, the environmental impacts associated with tourism activities in these regions cause rapid deterioration of the environment (Davenport and Davenport, 2006; Garcia and Servera, 2003). To mitigate this deterioration and integrate the different European Directives addressed to control the quality of water bodies (91/271/EEC; 98/15/EEC; Water Framework Directive, 2000), numerous environmental infrastructures were built in the last decades to provide services or control waste disposal and pollution (e.g., water distribution pipes, pumping stations, wastewater treatment plants (WWTP), septic tanks or desalination plants). However, many of those infrastructures, such as WWTP, work at their maximum capacity during the high tourism season (i.e., summer). The high performance of WWTP in summer months can compromise their efficiency (i.e. capacity to reduce the nutrient load) or become under-dimensioned for the present tourist volume (EEA, 2019). Therefore, the overload of anthropogenic pressure and reduction of efficiency of WWTP may turn into a surplus of nutrients and pollutants into the environment (Orhon et al., 1999).

Most coastal WWTP discharge their effluents into the marine environment through submarine outfalls or into other superficial water bodies (e.g., rivers, ephemeral streams, or small lagoons). Alternatively, effluents of WWTP can be discharged into aquifers via injection wells, benefiting from the natural solute filtering that occurs in coastal aquifers when groundwaters are transported through small aquifer pores. However, coastal aquifers are often connected with the coastal sea and SGD can thus represent a potential pathway delivering nutrients and pollutants injected into coastal aquifers from WWTP effluents to the sea. The injection of WWTP into coastal aquifers could thus impact marine ecosystems.

The Illes Balears, with 1.1 million residents, ranks amongst the top touristic destinations in the Mediterranean Sea, where 16 million tourists are received every year. These islands are a hotspot of high-intensity tourism, an industry accounting for ~50% of the Balearic GDP (i.e. gross domestic product) (Manera et al., 2018). Among all WWTP in these islands, there are 32 along the coasts that either discharge into ephemeral streams, lagoons, or directly inject (injection wells) their treated wastewater into the aquifer. In aquifers formed by unconsolidated deposits or permeable rocks, the geological matrix act as a natural filter for pollutants, preventing their transfer to the coastal sea. However, we hypothesize that in heavily fractured systems such as karstic aquifers located along the coastline of the Illes Balears, the preferential conduits can rapidly transfer the solutes injected into the aquifer from WWTP to the coastal sea.

The aim of this study is to evaluate the potential transference of nutrients injected into a karstic aquifer from a WWTP to the coastal sea via SGD, and the impacts of this process on the quality of coastal waters. This study is conducted in Deià (Mallorca), a highly touristic small village where the effluents of the WWTP are injected into a coastal karst aquifer connected to a cove (Cala of Deià).

5.2. Methodology

5.2.1. Study site

The Cala of Deià is a small cove of 80 m shore length composed of big blocks and gravels (Pujol et al., 2017), and patched with *Posidonia oceanica* meadows. The cove is located at the shores of the village of Deià, on the northeast coast of the Island of Mallorca (western Mediterranean) (Figure 5.1). The village is located in the Tramuntana mountain chain, which is composed of highly karstified limestone from Mesozoic era (Gelabert and Sàbat, 2002; Onac et al., 2005). The coastal karstified calcareous aquifer of Valldemossa discharges into the Cala of Deià through small fractures and preferential conduits (PUMO, 1990). The cove is located at the end of a torrent that has a 300 m gradient.

Although Deià is a village of only 700 inhabitants, it constitutes one of the most important touristic poles of Mallorca due to its important cultural and natural heritage. The main economic activities developed in the area are based on tourism (GOIB - Observatori del treball). The climate in Deià is governed by mild winters (~9.3ºC) and hot summers (24.6ºC). It has a precipitation regime well differentiated between the wet season (autumn and spring) and dry season (summer) ranging between 600 and 800 mm y^{-1} (AEMET). The population living in the town varies drastically due to the tourist pressure, high in summer and very low during winter. Indeed, during summer the population increase by up to 2.5 times, relative to winter, due to the tourism offer (475 vacancies from hotels and ~700 from tourism residencies; IBESTAT, 2022; INE, 2022), resulting in high water consumption (Deyà Tortella and Tirado, 2011; Garcia et al., 2022). In Deià (as well as in most of the Illes Balears), groundwaters constitute the main source of freshwater (~95%; GOIB, 2022) for the population for most of the year (Giménez et al., 2014). Both, the demand for freshwater and the volume of wastewater increase significantly in summer because of tourism, resulting in an increase in the volume of treated wastewater in the local WWTP by a factor of ~ 4.

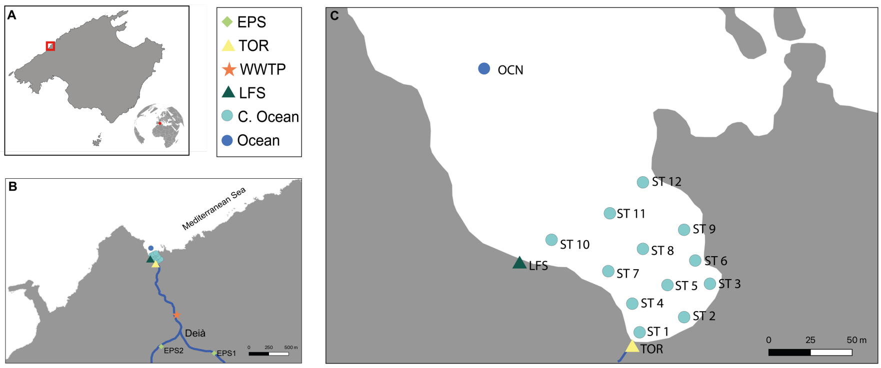

Figure 5.1. The study site is located at the western Mediterranean basin, at the N-E side of the island of Mallorca (Illes Balears). A) Location of the sampling site on the island of Mallorca. B) The locations of an ephemeral streams draining to the cove (blue line), freshwater springs that nourish the stream (green diamond) and the injection well of the WWTP (orange star) are represented. Samples were collected from the WWTP, the two freshwater springs, SGD endmembers, including the end of the Torrent Major (yellow triangle) and a freshwater spring at the eastern side of the cove (green triangle). Coastal seawater stations and the offshore station are represented with light and dark blue circles, respectively. C) Detailed location of the sweater stations, Torrent Major and karst spring.

5.2.2. Sampling methods

Two campaigns were conducted in April and August 2019 to assess the influence of WWTP effluents on the magnitude of groundwater discharge and associated nutrient fluxes to the coastal ocean. Twelve stations were distributed throughout the cove plus an extra sample outside of the cove (OCN) for superficial seawater samples (Figure 5.1). In August, additional deep samples (ranging between 2.5 and 4.5 m depth and sampled at ~50 cm above the seafloor) were collected at stations 5, 8 and 10. All surface (~50 cm below the water surface) and deep seawater samples were collected directly using a submersible pump. Groundwater was pumped using a submergible electric pump from 20 cm depth hole manually excavated at the end of the Torrent Major ephemeral stream (TOR). Two superficial water samples were collected from the ephemeral stream (EPS-1 and EPS-2) and one at the WWTP effluent (Figure 5.1). The ephemeral stream stations (EPS-1 and EPS-2) could not be sampled in August as both were completely dry. A submarine brackish groundwater spring, located inside the limestone fractures, that directly discharged into the cove seawaters was also sampled in August (LFS, Figure 5.1). This spring was not identified in April and could not be sampled.

All seawater, groundwater, ephemeral streams and WWTP samples were measured for temperature, salinity, pH and ORP with a multiparametric probe (YSI 670). Vertical profiles of temperature and salinity were also recorded using the multiparametric probe. In each seawater station, 60 L, 240 mL and 20 mL samples were collected to quantify Ra isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra, which are commonly used tracers of SGD; Garcia-Orellana et al., 2021), Chl-*a* and dissolved nutrients (NO_x (NO_3^- + NO_2^-), NH_4^+, SiO_2, PO_4^{3-}, TN, TP), respectively. All surface (~50 cm below the water surface) and deep seawater samples (~1 m above bottom sediments) were collected directly using a submersible pump. In August, the karstic spring (LFS) was sampled for Ra (60 L), nutrients and Chl-*a*. At the station TOR, located at the end of the ephemeral stream, which was completely dry during both seasons, 25 L of groundwater were pumped for Ra and dissolved nutrients analyses. Superficial waters from the two different ephemeral streams (EPS-1 and EPS-2) and the WWTP effluent were only sampled for physicochemical parameters and nutrients. In addition, water samples to determine nitrogen signatures ($\partial^{15}N$), which are used as tracers to determine the N source origin, were taken from all seawater, groundwater, ephemeral streams and WWTP samples in August. Furthermore, three different replicates of leaf shoots were taken from the seagrass meadow of *P. oceanica* at stations 7, 10, 12 and OCN to determine $\partial^{15}N$.

Seawater and groundwater samples collected for Ra isotopes were filtered (<1 L min^{-1}) through 20 g of dry acrylic fibers impregnated with MnO_2 to adsorb Ra isotopes (Moore and Reid, 1973). Samples for Chl-*a* were filtered through GF/F filters (0.7 μm), then filters were refrigerated and frozen for further analysis. Nutrient and $\partial^{15}N$ samples were filtered through nylon syringe filters (ϕ 0.45 μm) and stored in 10 mL polyethylene vials, which were immediately refrigerated and then frozen until analysis. Leaf shoots were stored in zip lock plastic bags and refrigerated until arriving at the lab where they were dried at 60 ºC for 48h.

5.3. Results

5.3.1. Groundwater, ephemeral stream and WWTP

Groundwater from the final part of the ephemeral stream (TOR) presented similar salinities in April and August with values of 9.3 and 9.1, respectively. Waters from the upstream part of the ephemeral stream (EPS1 and EPS2) had salinities of < 1. and the WWTP effluent waters had salinities of 1.0 and 1.8 in April and August, respectively. Groundwater from the karstic spring (LFS), which was only discharging in August, had salinities of 29, mainly because this sample was collected below surface seawater and has already undergone mixing with seawater.

Groundwater activities of ^{224}Ra in the ephemeral stream (TOR) were three times higher in April (96±9 dpm 100L^{-1}) than in August (33±4 dpm 100L^{-1}). However, concentrations of long-lived Ra isotopes were similar in April (41±1 and 27±2 dpm 100L^{-1} for ^{226}Ra and ^{228}Ra, respectively) and August (30±3 and 24±3 dpm 100L^{-1} for ^{226}Ra and ^{228}Ra, respectively). Groundwaters from the karstic spring (LFS) had much higher concentrations for all Ra isotopes compared to TOR (160±4, 57±5 and 98±8 dpm 100L^{-1} for ^{224}Ra, ^{226}Ra and ^{228}Ra, respectively). It should also be noticed that groundwaters from TOR and LFS have a similar and low $^{224}Ra/^{228}Ra$ ratio (1.4±0.2 and 1.6±0.2 for TOR and LFS, respectively), indicating that groundwater transit time through the aquifer is long enough to reach equilibrium for these isotopes (Diego-Feliu et al., 2021; Garcia-Orellana et al., 2021).

Groundwater nutrient concentrations also presented important differences between April and August (see Appendix A.2). While groundwater DIN was mainly composed of NO_3^- (66%) in TOR in April, NH_4^+ (95%) was the main component of DIN in August. For PO_4^{3-} concentrations, the difference in TOR during April with respect to August was almost one order of magnitude higher (0.78 and 11 µmol L^{-1}, respectively). However, the nitrogen concentrations in TOR in August (0.5 µmol L^{-1}, 0.35 µmol L^{-1}, and 16 µmol L^{-1} for NO_3^-, NO_2^- and NH_4^+ respectively) were significantly lower than those measured in the karstic spring (LFS) (1.5 µmol L^{-1}, 0.52 µmol L^{-1}, and 240 µmol L^{-1} for NO_3^-, NO_2^- and NH_4^+, respectively). Concentrations for SiO_2 were comparable between TOR between April (9.1 µmol L^{-1} and 16.5

μmol L^{-1} for April and August, respectively) and LFS (17.4 μmol L^{-1}). In April, both surface waters from the upstream (EPS-1 and EPS-2) had their DIN concentrations mainly composed of NO_3^- (90% and 97%, respectively). The composition of DIN in the WWTP effluent followed a similar pattern to that of TOR and LFS; the main component of DIN was NO_3^- in April and NH_4^+ in August (77% and 75%, respectively). While PO_4^{3-} concentrations in both springs were negligible (< 0.05 μmol L^{-1}), the WWTP had similar concentrations during April and August (73 and 66 μmol L^{-1}, respectively). The SiO_2 concentrations in EPS-1, EPS-2 and WWTP (48, 31, 40 μmol L^{-1}, respectively) were much higher than in TOR and LFS.

5.3.2. Seawater

Salinities inside the cove ranged from 36.7 to 38.4 in April and, and were slightly fresher in August, ranging from 36.2 to 38.0, with offshore salinities of 38.4 and 38.1, respectively. During both seasons, seawater salinities were fresher on the western side of the cove. The fresher salinities were reported in samples collected in front of the end of the ephemeral stream (TOR) in April and in front of the groundwater spring (LFS) in August. However, during August there was a clear stratification, with a fresher layer of ~ 0.7 m at the surface on the western half of the cove.

Radium concentrations in coastal waters were higher than in open seawater (Figure 5.2), except for ^{226}Ra in April, most likely reflecting Ra inputs from groundwater at the stations nearer to TOR and LFS. In April ^{224}Ra ranged from 1 to 14 dpm 100 L^{-1} inside Cala Deià and showed a downward offshore gradient from ST1 to the exterior of the cove. However, ^{226}Ra (ranging from 11.8 to 19.6 dpm 100 L^{-1}) and ^{228}Ra (ranging from 0.8 to 6.2 dpm 100 L^{-1}) had a scattered distribution along the cove, although the highest activities were always measured at ST1 (19.6 ± 0.6 dpm 100 L^{-1} and 6.2 ± 0.9 dpm 100 L^{-1}, respectively). In August, seawater activities of ^{224}Ra and ^{228}Ra (ranging from 3.8 to 33 dpm 100 L^{-1} and from 1.8 to 21 dpm 100 L^{-1}, respectively) were higher compared to those measured in April and showed a clear gradient starting from the western side towards the exterior of the cove (Figure 5.2). Contrarily, ^{226}Ra had relatively low activities (ranging from 9.5 to 19 dpm 100 L^{-1}) presenting a scattered distribution, except for sample ST10 (19 dpm 100 L^{-1}), which is the nearest sample to the LFS.

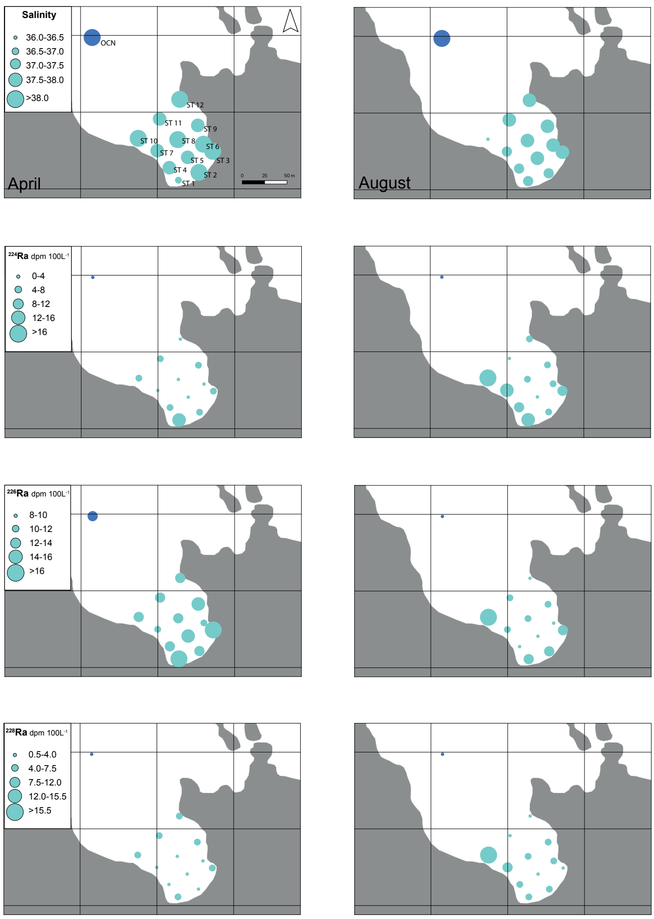

Figure 5.2. Distribution of salinity and Ra isotope activities during April and August sampling campaigns. The size of the circle scales with salinity and Ra activities.

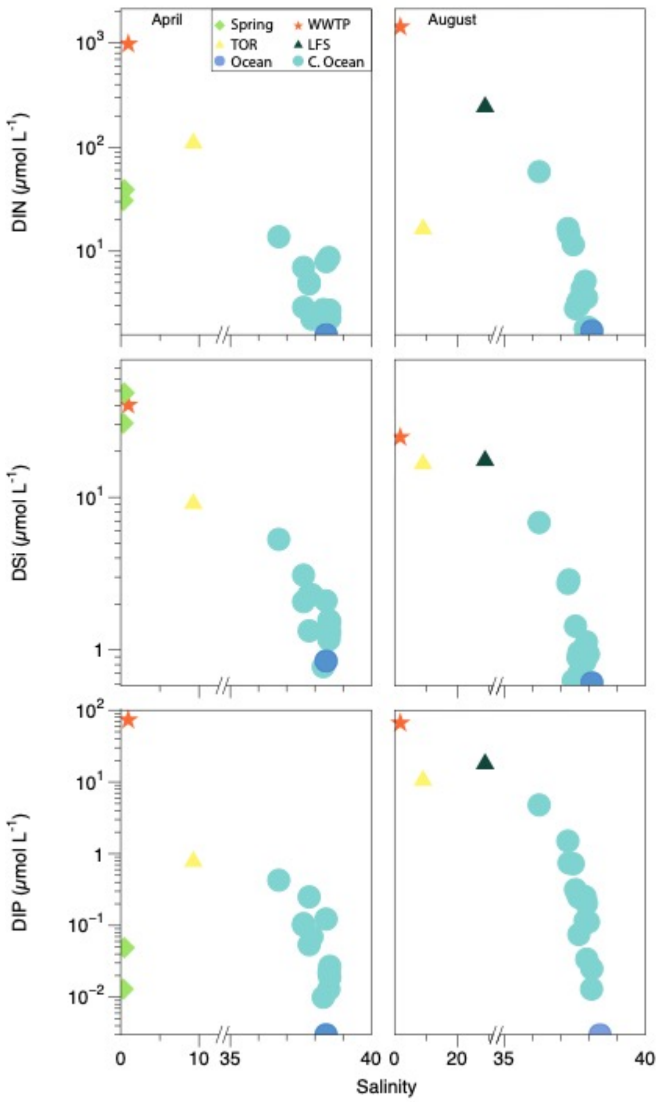

Figure 5.3. Nutrient concentrations along the salinity gradient in the study site. Samples correspond to freshwater upstream samples (EPS-1 and EPS-2) (April), WWTP, TOR and LFS at the end of the ephemeral stream (TOR) and the limestone fracture groundwater discharge located at the eastern side of the cove (LFS), coastal seawater stations and the offshore station.

Nutrient concentrations in coastal waters with fresher salinities were higher than in open seawater (Figure 5.3). Nutrient concentrations and the dominance of the inorganic nitrogen speciation varied significantly between seasons. In April there was a clear gradient of NO_3^- (0.4 - 7.6 µmol L^{-1}) on the western side of the cove towards the open ocean (0.4 µmol L^{-1}), with maximum values (7.6 µmol L^{-1}) at the nearest sample to the ephemeral stream (ST 1). Ammonia (NH_4^+ 0.2 – 7.4 µmol L^{-1}) did not show such a clear gradient and had similar concentrations to NO_3^- around the cove (see Figure 5.4). However, for NO_2^- (0.02 – 0.15 µmol L^{-1}) there was no significant gradient or enrichment relative to open ocean. Concentrations of SiO_2 (0.8 – 5.3 µmol L^{-1}) and PO_4^{3-} (0.003 – 0.430 µmol L^{-1}) in April also presented a moderate gradient offshore, although the concertation differences were not as large as for NO_3^-. Concentrations of NH_4^+ and PO_4^{3-} in seawater were one order of magnitude higher in August than in April (Figure 5.4). There was a marked gradient of NH_4^+ (1 – 56 µmol L^{-1}) in August along the cove, from high levels on the western and central areas of the cove, especially ST10, towards the open ocean (Figure 5.3). The other nitrogen species concentrations (NO_2^- (0.02 – 0.17 µmol L^{-1}) and NO_3^- (0.3 – 1.3 µmol L^{-1})) were relatively low and did not show any clear gradient or pattern. Although SiO_2 (0.6 – 6.8 µmol L^{-1}) and PO_4^{3-} (0.03 – 4.80 µmol L^{-1}) were also enriched in nearshore seawater (especially at ST10) relative to open ocean values, they did not show the same clear trends as observed for NH_4^+ (Figure 5.3).

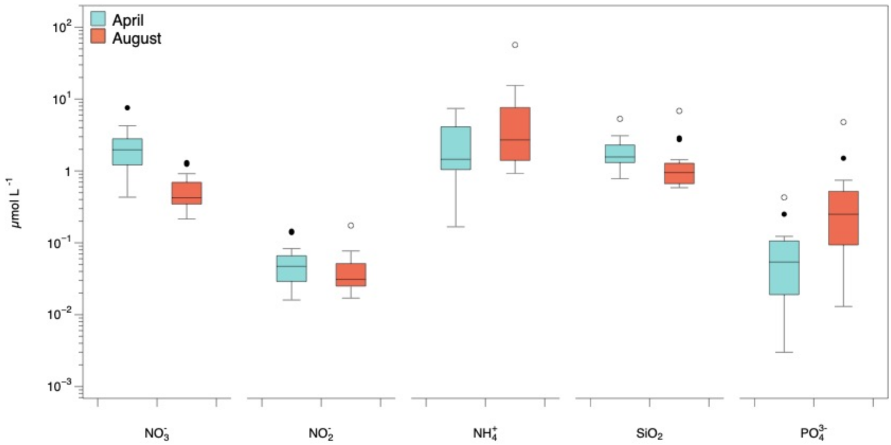

Figure 5.4. Dissolved inorganic nutrient concentrations in coastal waters during April and August.

Chlorophyll *a* (Chl-*a*) concentrations in April were low (0.03 – 0.11 mg Chl-*a* L^{-1}) with maximum concentrations at the nearshore seawater samples (ST1, 2 and 3). During August, the concentrations ranged between 0.05 and 4.46 mg Chl-*a* L^{-1} with maximum values of 4.5, 3.6, 1.5 and 1.7 mg L^{-1} at the shallowest stations ST 1, 2, 3 and 4, respectively.

Most water samples had low DIN concentrations that prevented the determination of $\partial^{15}N$. Isotopic signatures of $\partial^{15}N$ for the WWTP effluent, the karstic spring (LFS) and the station in front of the spring (ST10) were 15.2‰, 10.3‰ and 8.7‰, respectively. *Posidonia oceanica* leaves inside the cove presented a mean $\partial^{15}N$ value of 4.1±1.5‰ (n=4) and a maximum of 6.2‰, and samples collected in meadows farther from the coast (ST-OCN) presented the highest $\partial^{15}N$ value (7.2 ‰).

5.4. Discussion

5.4.1. Water flows driven by SGD

To evaluate the role of SGD in the cove of Deià as a conveyor of nutrients from a WWTP, which injects its effluents into the coastal karstic aquifer, it is necessary to identify all sources of SGD into the cove. The geological karst formation of the cove and the distribution of salinities, nutrients and Ra isotopes in the cove reveal that the main pathway of SGD nutrient supply into the cove is the karst point-sourced discharge. We have identified two predominant discharge point sources: subterranean flows from the stream (TOR) and inputs from the karstic spring (LFS), the latter only inflowing to the cove in summer.

The use of these isotopes to assess the role of SGD in Deià requires constraining all sources and sinks of these radionuclides in and out of the cove. A mass balance of the long-lived ^{228}Ra isotope has been used to assess SGD and associated nutrient fluxes in the Cala de Deià. Notice that we have preferably used ^{228}Ra because (i) coastal seawater is enriched in this radionuclide relative to the open ocean, and (ii) this radionuclide is indicative of relatively long pathways and groundwater transit times as those occurring at the study site (e.g., terrestrial groundwater discharge through karstic springs). Thus, we avoid using the short-live ^{224}Ra since it may include other short-scale processes (e.g., porewater exchange) which may play a minor role, relative to point-sourced discharge, transporting nutrients to the coastal ocean relative to terrestrial discharge.

To estimate the flow of SGD a ^{228}Ra box model was used assuming steady-state conditions (see Equations 5.2 and 5.3).

$$F_{^{228}Ra-SGD} + F_{sed} + F_{atm} + F_{stream} = \frac{(^{228}Ra_{cw-ex}) \cdot V}{\tau_r} + [\lambda \cdot {}^{228}Ra_{cw} \cdot V]$$

Eq.5.2

In Equation 5.2, the terms found on the left represent the inputs of Ra into the system and those on the right the outputs. On the left, $F_{^{228}Ra}$ is the ^{228}Ra flux from SGD (dpm ·d^{-1}), F_{sed} is the ^{228}Ra flux from the sediments (dpm ·d^{-1}), F_{atm} is the ^{228}Ra flux from the atmospheric deposition (dpm ·d^{-1}), and F_{stream} the ^{228}Ra flux from superficial waters (dpm ·d^{-1}). On the right we account for the Ra losses due to radioactive decay $[\lambda \cdot {}^{228}Ra_{cw} \cdot V]$, which depends on the decay constant of ^{228}Ra (λ; d^{-}), the activity of ^{228}Ra in the system ($^{228}Ra_{cw}$; dpm m^{-3}) and the volume of the box (V; m^{3}). The volume was obtained from the area of the cove (constrained by the 12 stations, 10,200 m^{2}) and a depth determined by the water stratification in summer (0.7 m), resulting in a more conservative result. Finally, the offshore outputs ($\frac{(^{228}Ra_{cw-ex}) \cdot V}{\tau_r}$), which depend on the Ra excess in the cove relative to offshore concentrations ($^{228}Ra_{cw-ex}$; dpm m^{-3}), the volume of the box (V; m^{3}) and the flushing time of the isotopes in coastal waters (τ_r; d^{-}). The SGD water flow (F_{SGD}; m^{3} ·d^{-1}) can be obtained by dividing the $F_{^{228}Ra}$ by the ^{228}Ra activity in the discharging groundwater endmember ($^{228}Ra_{SGD}$; dpm m^{-3}) (Equation 5.3).

$$F_{SGD} = \frac{F_{^{228}Ra-SGD}}{^{228}Ra_{SGD}} \qquad \text{Eq.5.3}$$

During both samplings, the ephemeral stream was completely dry, and precipitations have not occurred during the previous 15 days (Figure 5.5). No other water inputs are known or could be identified in the cove during the study. Thus, inputs of ^{228}Ra from streams can be neglected. The flux from the sediments can also be neglected since the deeper samples on the different samplings did not show a clear enrichment of Ra in comparison to the surface samples. In addition, the Ra sediment flux was also discarded due to the composition of the seabed, formed by stones and coarse-grain sands, which can be considered to have low U/Th content (Luek and Beck, 2014) and often represent a minor contribution of Ra (< 10%) compared to total Ra inputs, particularly for long-lived Ra isotopes such as ^{228}Ra (Beck et al., 2007; Garcia-Orellana et al., 2021, 2014). The atmospheric input was neglected as a Ra source because its contribution in small-scale study sites is often not higher than 1% (Garcia-Orellana et al., 2021). Inputs of Ra in the cove are thus only dependent on the supply via SGD, which is mainly inflowing to the cove through the karstic spring (LFS) only discharging in summer, and subterranean flows from the stream area (TOR). This assumption is indeed consistent with the highest activities of Ra isotopes observed in near-shore areas close to the ephemeral stream and the limestone fracture.

As a proxy of flushing times in the cove, we have used the activity ratios (AR) of $^{224}Ra/^{228}Ra$ to estimate the apparent water age (τ_r). Following (Moore, 2000a), we estimated the τ_r using Equation 5.4. We used ^{224}Ra since it is the isotope with the shortest half-live (3.6 d) and thus best suited for estimating short temporal scales as those expected in the cove, and ^{228}Ra to normalize for mixing.

$$\left[\frac{^{224}Ra}{^{228}_{ex}Ra}\right]_{end} = \left[\frac{^{224}Ra}{^{228}_{ex}Ra}\right]_{cw} \cdot e^{-\lambda_{224} \cdot \tau_r} \qquad \text{Eq.5.4}$$

Where, $[\frac{^{224}Ra}{^{228}_{ex}Ra}]_{end}$ and $[\frac{^{224}Ra}{^{228}_{ex}Ra}]_{cw}$ are the AR between the excess activities of ^{224}Ra and ^{228}Ra (which corresponds to the difference between the coastal water samples and the background concentration at the open ocean (OCN)) in the endmember (as detailed in the next paragraph) and coastal waters, respectively. The τ_r was calculated for April (3.0±0.7 d) but could not be estimated for August due to the relatively short τ_r. Subsequently, we estimated the maximum τ_r (1.5 d) that can be estimated using Ra isotopes when considering the relative average errors associated to the ^{224}Ra and ^{228}Ra ($d^{224}Ra$ and $d^{228}Ra$) in the coastal stations (see Equation 5.5) (Knee et al., 2010b), as follows:

$$\tau_r = \frac{ln\left(1-\sqrt{(d^{228}Ra)^2+(d^{224}Ra)^2}\right)}{-\lambda_{224}} \qquad \text{Eq.5.5}$$

This is the minimum time that can be estimated with Ra isotopes, thus we can only infer that the flushing times are < 1.5 d in August. Notice that using 1.5 d as an upper estimate of the Ra water age, results in conservative estimates of SGD (see Equation 5.1). Considering the temporal scales of transport processes for Ra, this short time also suggests that steady-state conditions is a valid assumption for the system (Rodellas et al., 2021).

As derived from the distribution of Ra isotopes and salinity, as well as from visual identification, the main source of groundwater to the cove in August appears to be the karstic spring inflowing at the western part of the cove. Therefore, the sample collected in this spring (LFS) is considered the best representation of the SGD endmember for ^{228}Ra ($^{228}Ra_{SGD}$). However, since the spring discharges below the water surface, the sample collected had a significant mixture with saline water (as derived from its salinity: 28). Thus, the ^{228}Ra concentration in this sample cannot be used to estimate the SGD flow because the signal of Ra was clearly diluted. In order to provide a conservative estimation of SGD, we extrapolated the ^{228}Ra concentration to an effective zero-salinity endmember using a linear regression (Beck et al., 2009; Tamborski et al., 2020). The estimated zero-salinity ^{228}Ra endmember concentration in August is 3.5±0.3 10^3 dpm $100L^{-1}$, resulting in a conservative SGD flow of 65±6 m^3 d^{-1}. Normalizing the SGD by the length of the cove mouth (80 m), the estimated SGD flow rate of 3.0±0.3 10^5 m^3 km^{-1} y^{-1} is similar in magnitude to SGD flows in other small coves in the Island of Mallorca (Rodellas et al., 2014; Tovar-Sánchez et al., 2014). SGD flows in April could not be computed due to the low water flow into the cove and therefore low ^{228}Ra concentrations.

5.4.2. Groundwater flows associated with the wastewater treatment plant

The higher ^{228}Ra concentrations and the lower salinities in the cove during August in comparison to April, suggest a higher inflow of SGD in summer. Since our study site is located on a karstic aquifer characterized by high transmissivities (Giménez et al., 2014), SGD is expected to rapidly respond to precipitation. However, this result disagrees with the precipitation regime in the area during the sampling periods, which were comparable during both samplings (Figure 5.5). Radium excess inventories inside the cove were ~21% higher in August than in April and thus they cannot be attributed to changes in the natural recharge of the coastal aquifer. This is also consistent with the visual observations of the karstic spring, which was only identified in August.

Since no other process can explain the increase of SGD in summer, we hypothesize that this difference in magnitude of SGD is likely to be linked with the increase of the wastewater volume injected into the aquifer during summer months. Indeed, the increase in SGD is strongly linked with the higher volume of injected water into the aquifer from the WWTP in Deià (from 4400 m^3 in April to 12800 m^3 in August), which results from the significant increase in tourism population in the village of Deià during summer (Figure 5.5).

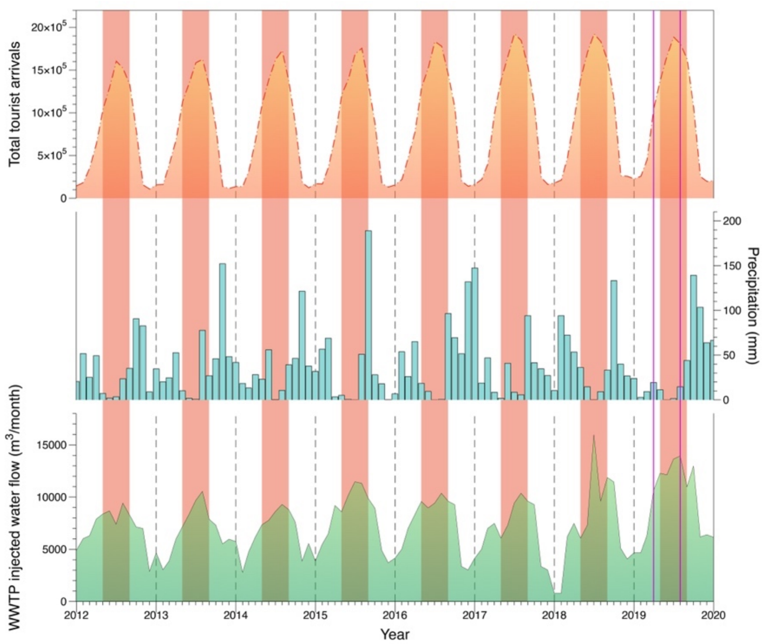

Figure 5.5. Time evolution (2012-2020) of precipitations and injected water flow in Deià. Orange area corresponds to the total number of tourist arrivals to Mallorca per month. Green area corresponds to the volume of water injected into the aquifer by the WWTP of Deià. Blue bars correspond to the accumulated precipitations per month. Red shadowed areas correspond to the high tourism season. Purple lines correspond to the two different samplings of April and August 2019.

These changes in the demographic pressure in the village and its water resources result in an increase in the volume of WWTP effluents injected into the aquifer during the high tourism season which might increase the aquifer water table elevation and, therefore, the flow of groundwater discharging through the spring (LFS).

5.4.3. Nutrient Fluxes

SGD inputs might be a relevant source of nutrients to the cove of Deià, particularly considering that groundwaters are likely influenced by effluents of the WWTP and that Deià is a small and semi-enclosed system, which favours nutrient accumulation. Thus, relatively small nutrient inputs from SGD can have a significant impact on coastal ecology. The SGD-driven nutrient flux can be directly estimated by multiplying the Ra flux supplied by SGD by the nutrient to ^{228}Ra ratio concentration from the SGD endmember (LFS) (Cook et al., 2018; Olid et al., 2022; Santos et al., 2008; Tovar-Sánchez et al., 2014). The estimated SGD-driven nutrient fluxes for DIN, DIP and DSi are $2.0 \pm 0.2\ 10^3$ mmol m^{-2} y^{-1}, $1.5 \pm 0.2\ 10^2$ mmol m^{-2} y^{-1}, $1.4 \pm 0.1\ 10^2$ mmol m^{-2} y^{-1}, respectively. The calculated SGD-driven DIN fluxes in Deià are comparable with mean global estimates in carbonate coastal systems (1.2 10^3 mmol m^{-2} y^{-1}; Santos et al., 2021), but they fit in the lower 25% fluxes estimated for local sites (<1 km^2) and rocky areas. The high DIP fluxes in Deià are up to three times the maximum values reported in karst aquifers and similar to the mean values in rocky areas. DIP fluxes supplied by SGD to the cove of Deià fit in the higher 75th percentile of total reported cases in Mediterranean sites (Rodellas et al., 2015a). Estimated DSi fluxes are in the lower ranges of the world karst or rocky areas (Santos et al., 2021). Moreover, the fluxes estimated in Deià are similar or higher to other sites influenced by WWTP or sewage in other locations of the globe. For instance, in the La Palme lagoon in July (high tourism season) the groundwater fluxes of DIN are similar but, DIP fluxes in Deià are one third of the reported there (Rodellas et al., 2018). Contrarily, in another study in Les Calanques (France), Deià estimates for DIN fluxes corresponded to one third, but DIP was up to 3 magnitude orders higher than in Calanques (Tamborski et al., 2020). In Hawai'i the maximum fluxes of DIN are one order of magnitude higher than in Deià, but the DIP maximum fluxes are similar (Bishop et al., 2017). In addition, it should be taken under consideration that such comparisons are qualitative since each study used different methods to estimate the SGD which will capture its different components characterized by having different spatial and temporal scales.

Besides SGD inputs, there are no other potential inputs of nutrients into the Deià cove, since no superficial waters were discharging into the cove and the sediment of the cove (mostly composed of stones and coarse-grain sands) is often considered negligible nutrient sources (Lü et al., 2005). Atmospheric deposition could also contribute as a net supplier of nutrients to the cove. However, considering the cove area and mean atmospheric nutrient fluxes in the region (Markaki et al., 2010), it produces atmospheric nutrient fluxes that would be 2 to 3 orders of magnitude lower than SGD-driven nutrient fluxes and thus can be neglected. Since nutrient fluxes supplied by SGD were only estimated for August, a quantitative comparison of nutrient fluxes between seasons cannot be conducted. A semi-quantitative evaluation can be conducted by considering nutrient inventories in the cove for April and August, together with the nutrient inventories that could be attributed to SGD in August (i.e., SGD nutrient inputs divided by the residence time) (see Figure 5.6). The measured DIN, DIP and DSi inventories in the cove are much larger in August than in April (3, 10 and 1.5 times higher, respectively), potentially responding to a higher input of nutrients in August compared to April. The nutrient inventories that could be attributed to SGD are comparable in magnitude to the inventories measured in the bay for DIN and

DIP, indicating that SGD is most likely the main source of these nutrients. Regarding DSi, SGD could only contribute to 50% of the DSi inventories observed in the cove, implying that another DSi source is needed to justify the observed inventories. This missing source could be associated with the constant erosion of the stones and sand of the shore (Tréguer and De La Rocha, 2013), a hypothesis that is consistent with the higher DSi concentrations measured on ST1, 2 and 3.

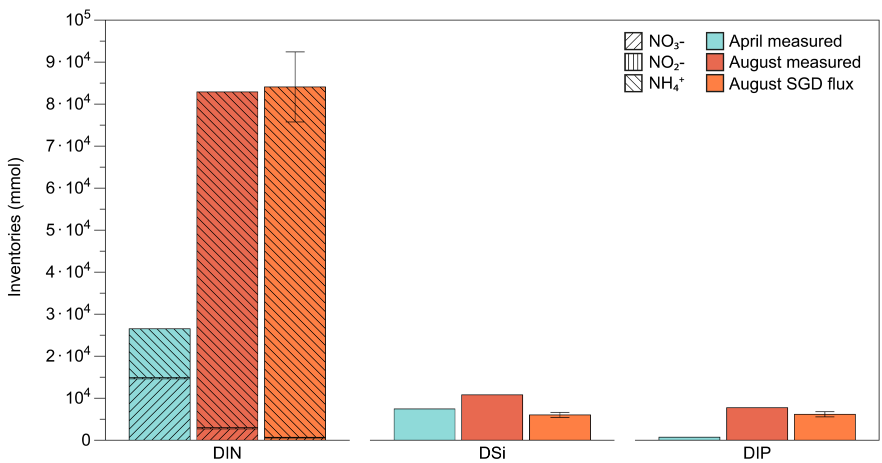

Figure 5.6. Dissolved inorganic nutrient inventories during April (blue), August (red) and inventories attributed to SGD (orange). Speciation for DIN is also represented.

Focusing on the nitrogen species (Figure 5.6), the DIN inventory in the cove is mostly composed of NO_3^- in April (55 %), whilst the main specie is NH_4^+ in August (96 %). The contribution of NO_2^- in the total DIN inventories is insignificant during both seasons (≤ 1 %). Such differences in nitrogen speciation in cove waters can be partially explained by the groundwater sources of these nutrients; in April, most of the N is most likely provided from the subterranean flows from the ephemeral streams, which are enriched in NO_3^-. On the contrary, the most important source of N is the karstic spring, which is mainly composed of NH_4^+ (99 %) most likely as a consequence of the water injected from the WWTP, which is also rich in NH_4^+.

Both the seasonal pattern of groundwater discharge (i.e., higher SGD in dry periods) and N concentrations in the karstic spring (i.e., DIN mainly composed of NH_4^+) suggest that the effluent of the WWTP is the main source of N to the cove of Deià via the wastewater injection into the aquifer and the subsequent discharge to the sea as SGD. To better establish the potential origin of the N concentrations in the cove of Deià, we used the isotopic signature of N ($\partial^{15}N$). According to the published literature, $\partial^{15}N$ values from WWTP and sewage waters are between +10 and +22‰, between +2 and +8‰ for groundwaters from natural systems and 1 and 3.8‰ for western Mediterranean seawaters (Cole et al., 2005; Kendall et al., 2007; Pantoja et al., 2002). The $\partial^{15}N$ signatures for the karstic spring (LFS; 10.3‰) fall within the range of waters impacted by wastewater effluents and sewage waters (Figure 5.7), suggesting that the high N loads could be released by the WWTP effluents. This is consistent with the distribution and temporal variability of salinity and Ra concentrations in the cove, as well as with the observed variability of nutrient inventories and N speciation. The relatively high values also observed in cove waters (8.3‰ in ST10) also reflect the contribution of anthropogenic sources (i.e., WWTP effluents) in the nutrient inventories observed in the cove of Deià.

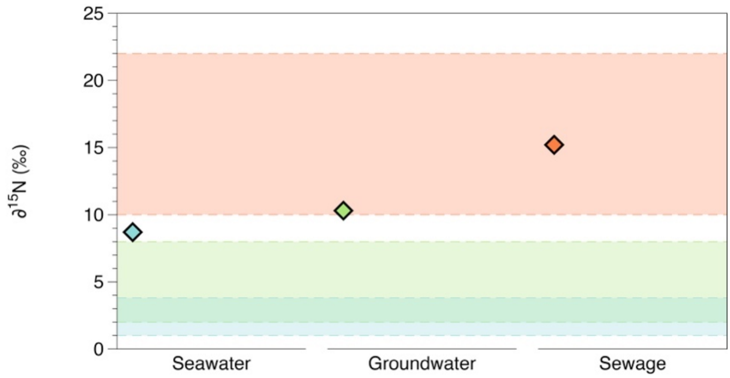

Figure 5.7. The $\partial^{15}N$ from Deià in comparison to average values reported in the literature (Cole et al., 2005; Kendall et al., 2007; Pantoja et al., 2002). Blue, green and orange areas correspond to seawater, groundwater and sewage values from the literature. Diamonds to samples measured in Deià.

Besides N, the contribution of natural sources alone cannot explain the large flux of DIP in summer in the cove of Deià (0.66 mmol m^{-2} d^{-1}), especially in comparison to other carbonate karstic systems (average SGD fluxes of 0.021 mmol m^{-2} d^{-1}; Santos et al., 2021) where phosphate is removed and easily gets attached to the carbonate surfaces by co-precipitating with dissolved Ca, Al or Fe (De Jonge and Villerius, 1989; Price et al., 2010; Weiskel and Howes, 1992; Zanini et al., 1998). Considering the large amount of water injected into the aquifer from the WWTP (412 m^3 d^{-1}) and the high DIP concentrations of these effluents (66.3 mmol m^{-3}), the high SGD-driven DIP fluxes are also consistent with the influence of the WWTP injection flux, where most DIP would come from human excreta, soaps and detergents. Notice that no important farms or industries using fertilizers exist in the area but there is a significant increase in the population living in the village during August.

5.4.4. Impact on the water quality and coastal ecosystem

The discharges of nutrient rich groundwaters into coastal areas have been globally reported as a key factor to trigger high productivity of phytoplankton blooms and, in some cases eutrophication (e.g., Amato et al., 2016; Andrisoa et al., 2019; Basterretxea et al., 2010; Garcés et al., 2011; Garcia-Solsona et al., 2010a; Machado and Imberger, 2014; Yoshioka et al., 2016). The Mediterranean Sea is characterized by its oligotrophic conditions, with an important deficit of phosphorus (Krom et al., 2010; Rodellas et al., 2015a). In this direction, the European Marine Strategy Framework Directive, or the European Water Framework Directive, contemplates limitations on the load of nutrients into the coastal systems to preserve the water quality and prevent the eutrophication of the environment.

- Phytoplankton blooms

In the Cala Deià, the mean coastal water ratio DIN:DIP in August (31:1) was above the Redfield ratio (16:1), indicating phosphorus as a limiting nutrient. Therefore, inputs of DIP can be particularly relevant to sustain productivity or trigger phytoplankton blooms in the cove of Deià (as well as on other coasts of the Illes Balears). The high SGD-driven nutrient fluxes and the relatively low DIN:DIP ratio of discharging groundwaters (5:1 in groundwaters from the karstic spring) can thus play a major role in regulating the important phytoplankton blooms recurrently occurring in the cove during summer months.

In this sense, the concentration of Chl-*a* can be used as an indicator of the risk of eutrophication and thus a degradation of the seawater quality (Colella et al., 2016). According to UN/MAP (2017) the threshold limits for moderate/good coastal water quality for the Mediterranean north western islands should be below 1.20 mg Chl-*a* L^{-1}. During August, Chl-*a* concentrations in the closest stations to the shore, which had eutrophic levels, were three times above those limits, with maximum concentrations of ~4 mg Chl-*a* L^{-1}, while the rest of the cove stat had concentrations above 0.1 mg Chl-*a* L^{-1}. These high Chl-*a* concentrations are indicative of an algal bloom occurring during the survey. Since the main source of nutrients into the cove is SGD enriched in nutrients due to the injection of WWTP effluents into the aquifer, this mechanism appears to play a significant role in the degradation of the seawater quality according to EU standards (UN/MAP, 2017). It should be noted that episodic blooms during summer are not exclusive to this site, but are common in Mediterranean enclosed areas influenced by SGD (Basterretxea et al., 2007), where usually are dominated by *Alexandrium minutum*, *Dinophysis sacculus*, *Karlodinium spp*. and *Gymnodium spp*. in the first meters from the shore (Basterretxea et al., 2018).

- Seagrass meadows

The long-term effect of the SGD-driven nutrient inputs to the cove can also be observed in the seagrass present in the cove, which integrate the isotopic signature of the nutrient sources used to support their growth. *Posidonia oceanica* usually inhabits in pristine transparent waters, under oligotrophic conditions and carbonate sediments that confer a P-limited environment (Short, 1987). By means of their roots and leaves, *Posidonia oceanica* can incorporate inorganic or organic nutrients present in seawater (Garcias-Bonet et al., 2016; Welsh, 2000). Depending on the main source of nitrogen the seagrass will vary its isotopic ratio ($\partial^{15}N$), presenting low isotopic signatures (<4‰; Illes Balears) if the main source is atmospheric (Bedard-Haughn et al., 2003) or higher if nitrogen is mainly sourced by anthropogenic activities (Apostolaki et al., 2012; Fernandes et al., 2009).

The mean value reported in leaves tissues of *Posidonia oceanica* in this study (4.7±1.9‰) is relatively high compared to the mean $\partial^{15}N$ signal of 3.7±1.1‰ in leaves from the plant in other sites of the Illes Balears (Fourqurean et al., 2007). These relatively high values, together with the maximum $\partial^{15}N$ signature of 7.2‰ measured in the site, most likely reflect the relevant contribution of N from anthropogenic sources (i.e., WWTP effluents via SGD). Indeed, the mean value in the cove of Deià is similar to the signatures of seagrass meadows in highly pressured areas with emissaries discharging near the seagrass meadows or irrigated coastal areas with WWTP treated waters (Fourqurean et al., 2007; Garcias-Bonet et al., 2016). The maximum in Deià ($\partial^{15}N$=7.2‰) is almost as high as the two maximum values reported (7.41‰ and 7.54‰ in Santa Eulària and Can Picafort, respectively) in the Illes Balears, which correspond to highly impacted areas. Thus, the isotopic signatures in seagrass meadows in Deià are consistent with the influence of anthropogenic nutrient loads delivered to the cove by SGD. In addition to acting as a nutrient source, these SGD-driven nutrient inputs can turn into algal blooms that can affect the clearance of the waters of the cove and/or enrich the sediment with organic matter, enhancing sulfide toxicity and hypoxia, and therefore directly affect the *Posidonia oceanica* ecosystem (Alcoverro et al., 2001; Calleja et al., 2007).

5.4.5. Water management potential impact on SGD Ecosystem Services

Submarine Groundwater Discharge plays an important role in the provision of Ecosystem Services to coastal societies (Chapter 6). For instance, fresh water and food related to SGD in different sites around the globe can be crucial for local communities (Chapter 6; Moosdorf and Oehler, 2017). The tourism industry benefits from these Ecosystem Services (Apostolopoulos et al., 2002), but the massive development of this industry endangers or even destroys the same Ecosystem Services that it nurtures from. These Ecosystem Services have also been reported to be endangered by high anthropogenic pressure on beaches of California (Yau et al., 2014) or Hawai'i (Knee et al., 2008), where the transference of pathogens through SGD could endanger the swimmers' health, and therefore their well-being. In addition, cultural Ecosystem Services could also be negatively affected, such as recreational activities or aesthetic values, due to the change of perception that beach users might have from those sites. In this direction, when algal blooms develop in a frequented coastal area due to the input of nutrients from SGD, changes of color can shape the perception of both tourists and local villagers who might decide not to go back, with an ultimate and direct impact on the local economy (Sanseverino et al., 2016). Nutrient rich SGD into coastal waters can also trigger deterioration of seagrass habitats and, thus, enhance deterioration of coastal quality (e.g., increase in water turbidity and beach erosion, decrease in marine biodiversity) and natural carbon sink capacity. The Cala of Deià seems to exemplify such potential changes in users' perception, especially when related to cultural Ecosystem Services. Tourists and villagers perceived the aesthetic value of the pristine Mediterranean cove fed by a fresh groundwater discharge could change to aversion for a cove with green waters with a groundwater discharge influenced by WWTP-treated waters. Moreover, the Ecosystem Service provided by the Cala of Deià related to develop recreational activities could also be negatively affected, moving from the enjoyment to swim in clean and pristine waters to the rejection to enter such waters due to their color. Consequently, the same industry that benefits from the Ecosystem Services threatens them through the increase of wastewater effluents injected into the aquifer that are subsequently channeled to the cove via SGD.

The same situation studied in Deià is likely to happen in many other sites of the Illes Balears. The four islands from the Illes Balears have 10 WWTP with injection wells into coastal aquifers, all of them located in sensitive touristic areas affected by its important seasonality. Additionally, there are up to 32 WWTP that discharge into ephemeral streams or lagoons, which can also leach into the aquifer or inflow to the coastal sea. Considering that the coastline of the archipelago is formed by karstified carbonate coastal aquifers, which are directly connected to the sea, aquifer fractures might represent rapid conduits that transfer WWTP effluents directly to the sea, having direct consequences for coastal ecosystems. SGD-driven nutrient inputs from WWTP with injection wells not only have an important impact on the coastal ecosystem with the proliferation of phytoplankton blooms that reduce the seawater quality but also to the societies that live there (Wada et al., 2021). Indeed the management of such services is crucial in Mediterranean regions due to the scarcity and high demand of freshwater resources (Erostate et al., 2020). Whilst this study focuses in a particular archipelago, the situation occurring in the cove of Deià is likely to occur in many other areas along the Mediterranean coast, which is characterized by karstic coastal aquifers (carbonate lithologies account for 46% of Mediterranean coastlines; (Hartmann and Moosdorf, 2012) and by ranking amongst the top touristic destinations.

Chapter 6 *The social implications of Submarine Groundwater Discharge from an Ecosystem Services perspective: A systematic review*

6.1. Introduction

Ecosystem Services provided by rivers or streams (Yeakley et al., 2016), lakes (Schallenberg et al., 2013), estuaries (Barbier et al., 2011) or mangroves (Queiroz et al., 2017) are well studied, but there is a lack of studies examining SGD from an ES perspective or evaluating the synergies and trade-offs derived from SGD-related ES. Only two studies have preliminary explored this topic; Erostate et al. (2020), who discussed the policies and management of ES linked to groundwater-dependent coastal ecosystems in Mediterranean regions; and Moosdorf and Oehler (2017), who reviewed social uses of SGD-derived freshwater (e.g., drinking, hygiene, agriculture, fishing, tourism or culture).

In this chapter, we conduct a systematic review of the scientific literature to gather the available and existing knowledge on the social implications of SGD worldwide. Specifically, we review the peer-reviewed scientific academic literature published in English to analyze coastal ES derived from SGD, understood as both positive and negative effects on human well-being and quality of life, and classify the information obtained using the Millennium Ecosystem Assessment (MEA, 2005) as a conceptual framework baseline. Furthermore, we review the direct social impacts of SGD, in terms of synergies and trade-offs towards well-being, and the research gaps and opportunities for further studies. The new insights derived from this review will allow the development of an ES-based analytical framework that will guide future research on the social implications of SGD. This review also highlights the importance of SGD from a social perspective, closing the gap between physical and social disciplines that have often worked independently.

6.2. Analytical framework

Submarine Groundwater Discharge is defined as "*the flow of water through continental and insular margins from the seabed to the coastal ocean, regardless of fluid composition or driving force*" (Burnett et al., 2003; Taniguchi et al., 2019). SGD includes thus both fresh groundwater discharge (fresh or terrestrial SGD) and seawater circulating through the coastal aquifer (saline or marine SGD). Fresh and marine SGD can be supplied via 5 different pathways (see Chapter 1). In this chapter, we will only refer to the fresh or saline fraction of SGD, regardless of the pathway driving the discharge of groundwater (Figure 6.1). Previous research has highlighted that coastal ecosystems provide diverse and valuable goods and services as a result of fresh SGD (Erostate et al., 2020; Moosdorf and Oehler, 2017). However, coastal ecosystems can also be supported by saline SGD, which constitutes a relevant source of dissolved solutes to the coastal ocean (Cho et al., 2018; Moore et al., 2008; Rodellas et al., 2015a). Following Erostate et al. (2020) and Richardson et al. (2011), we define coastal groundwater dependent ecosystem (coastal GDE) as the marine coastal ecosystems that require permanent or intermittent access to groundwater (including fresh and saline SGD) for maintaining their biological communities, their ecological processes, and the associated ecosystem services. Furthermore, we define the ecosystem services inherent to coastal GDE, that are directly provided by submarine groundwater discharge as SGD-ES.

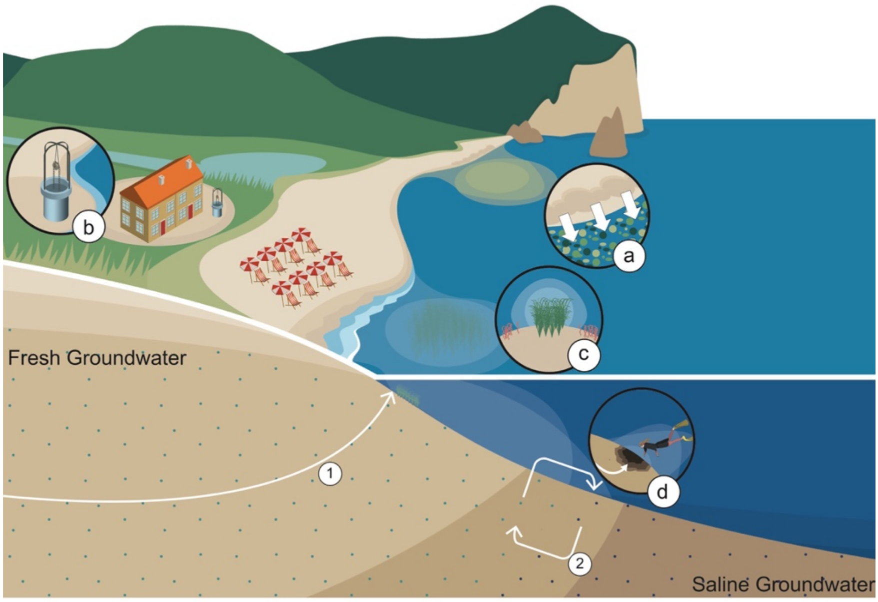

Figure 6.1. Conceptual diagram of a coastal society influenced by Submarine Groundwater Discharge and its four categories of Ecosystem Services: a) Supporting; b) Provisioning; c) Regulating; d) Cultural. The different components of SGD are also shown: 1) Fresh component of SGD; 2) Saline component of SGD. Figure based on Garcia-Orellana et al. (2021).

To develop a common and interdisciplinary framework to assess the social implications of SGD, we used the ES approach based on the Millennium Ecosystem Assessment (MEA, 2005). The MEA (2005) was used as baseline due to its sound relevance as the first robust framework to classify and quantify the social benefits and losses that humans obtain from the functioning of ecosystems.

We divided our conceptual framework into the four broad ES categories identified in the MEA (Figure 6.2): (i) Supporting; (ii) Provisioning; (iii) Regulating; and (iv) Cultural, which are in turn subdivided in Outcomes, reflecting the different services of each category. A wide range of outcomes derived from each ecosystem service category were already established by MEA (2005) framework, but only those relevant for SGD-influenced ecosystems have been selected in the framework.

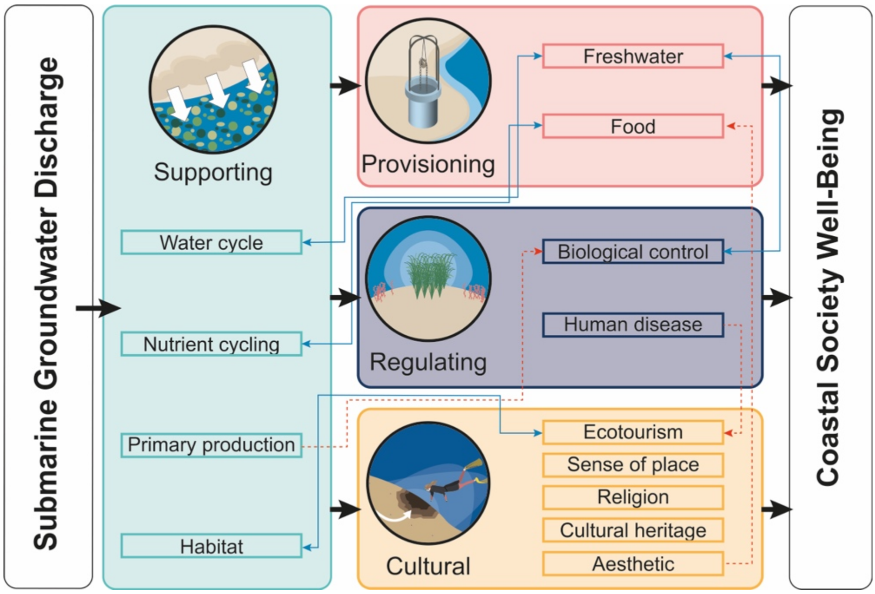

Figure 6.2. SGD-ES conceptual framework. SGD derives into the four ES categories and their outcomes (represented by squared boxes). Those outcomes depend on each other by creating synergies or trade-offs shown with blue and red arrows, respectively, as an example. Finally, those interactions influence the coastal society well-being, based on the MEA (2005).

Supporting ES are defined as services provided by SGD that sustain the existence of other ecosystem services. These services are indirect since they do not directly affect human well-being but are fundamental to the existence of the other categories identified in the MEA (2005). In this sense, we consider any SGD-driven input of water and solutes, including chemical dissolved compounds (e.g., nutrients, bacteria, trace metals, oxygen, or rare-earth elements) or water that modifies the physicochemical characteristics (e.g., salinity, temperature, or pH) of the coastal environment, and the biogeochemical implications of these inputs. For example, coastal human societies do not use nutrients as they are delivered to the environment, but they are essential to support the photic zone, where primary production will be produced, and therefore will be able to support the production of food (e.g., algae or fish) for human and animal consumption, or to maintain the habitat. As Outcomes derived from this category, we consider Water Cycle, Nutrient Cycling, Primary Production, and Habitat.

- Water Cycle as the role of SGD within the hydrological cycle.
- Nutrient cycling as the transfer of nutrients delivered by SGD from the coastal aquifer into the coastal GDE, from the inorganic compounds to the assimilation of super depredators at the top of the chain.
- Primary Production as the transformation of energy and inorganic compounds delivered by SGD into organic compounds by those organisms living in the coastal GDE.
- Habitat as the coastal GDE that promotes life due to the physicochemical and biological conditions which are sustained by SGD.

Provisioning ES are defined as products that SGD provides to society. As Outcomes we consider Freshwater and Food.

- Freshwater as the fresh component of SGD that is directly used as a water resource for human consumption, agriculture, or other industrial purposes.
- Food as organisms that have their habitat in coastal GDE or that their survival depends on SGD and are consumed by society.

Regulating ES are defined as services that control crucial processes for habitats and coastal ecosystems influenced by SGD. As Outcomes we consider Biological Control and Human Disease (as Disease Regulation in the MEA (2005)).

- Biological control as those changes or conditions induced by SGD that affect the prevalence of certain species, ecosystems, or limit the entrance of other species into coastal GDE.
- Human Disease refers to the transport or restriction of pathogens or pollutant compounds delivered by SGD that can compromise human health.

Cultural ES are defined as the non-material benefits provided by SGD that contribute to human values and influence behavior. The perception of those ES can vary across stakeholders or communities, due to the subjectivity of the observer. As Outcomes we consider Recreational Activities or Ecotourism, Sense of Place, Religion, Cultural Heritage and Aesthetic or Inspirational values.

- Recreational Activities or Ecotourism as any leisure activity (economically exploited or not) developed in an environment influenced by SGD.
- Sense of place as the feeling of belonging to a certain site or toponyms that have been given to certain places after the occurrence of SGD, as well as buildings' names.
- Religion as those stories, tales, myths, or religious ceremonies that are based on SGD.

- Cultural heritage as those ways of doing, traditions, knowledge, objects, or values related to SGD that the present society continues from older generations.
- Aesthetic or Inspirational values as the subjective sensory-emotional values provided by SGD, such as inspiration, intrigue to explore nature, or beauty.

Each of those Outcomes can be related to each other by means of synergies or can be prioritized by coastal societies by trade-offs to achieve their well-being. Following the MEA (2005) we define:

- *Well-being* as "the capacity of an ES to provide the conditions for physical, social, psychological, and spiritual fulfillment".
- *Synergies* as the relation between two or more outcomes that benefit mutually due to their existence.
- *Trade-off* as the choice taken by society that involves prioritizing one outcome in exchange of another one or more.

6.3. Data collection and analysis

The scientific literature review process has been carried out in five stages (Table 6.1). In order to provide an overview of the state of the art of the SGD-ES, according to well-established guidelines for systematic reviews by Petticrew and Roberts (2006), a systematic literature review was conducted by using the search engine Web of Science (hereinafter, WoS). As a preliminary review, we used "submarine groundwater discharge" and "soci*" as keywords in WoS. Results from this preliminary review search provided 30 studies of which only two (i.e., Duarte et al., 2010; Moosdorf and Oehler, 2017) explicitly reported direct social implications.

Table 6.1. Data selection criteria

Stage	Criteria	Screened studies	Selected studies
Preliminary	*Key words*	30	2
	"Submarine Groundwater Discharge"		
	"Soci*"		
First	*Key words*	1532	503
	"Submarine Groundwater Discharge"		
	"Submarine Spring"		
Second	*Title analyses*	503	92
	SGD impacts		
Third	*Abstract analysis*	92	32
	Social implications		
Fourth	*Detailed review*	32	32 (114 cases)
	Social implications		

Considering the limited number of studies obtained from the preliminary review, a broader search using the terms "Submarine Groundwater Discharge", or "Submarine Springs" was conducted as the first stage of the systematic review. A total of 1532 studies were registered with these search terms from 1900 to April 2020. Considering the MEA (2005) as a baseline, a research within this sample of articles was done by establishing a set of keywords for each ES category and outcome derived from SGD-ES (see Appendix A.3).

The content of the articles (reported in Supplementary material) indicated that most studies could be categorized as Supporting ES, suggesting that these articles did not explicitly examine the social implications of SGD. To readdress the review and focus on the social implications of SGD, the title of all the publications identified at the first stage (n= 1532) was reviewed to only include those studies which focused on SGD impacts as the second stage of the systematic review. With the remaining (n=503), a detailed publication review was made to double check for suitable publications that established direct relations between SGD processes, ES, and social implications. As third stage the abstracts of the manuscripts were screened to select only publications that referred to the social implications of SGD. The fourth and final stage consisted in the full text analysis of the selected manuscripts (n= 92), which was carefully reviewed to identify the social implications of SGD. As a result, 32 publications were finally included in the analysis of social implications, in which a total of 114 cases from different locations worldwide were identified and analyzed by using the MEA-based framework described in section 6.2 as a baseline (Figure 6.3).

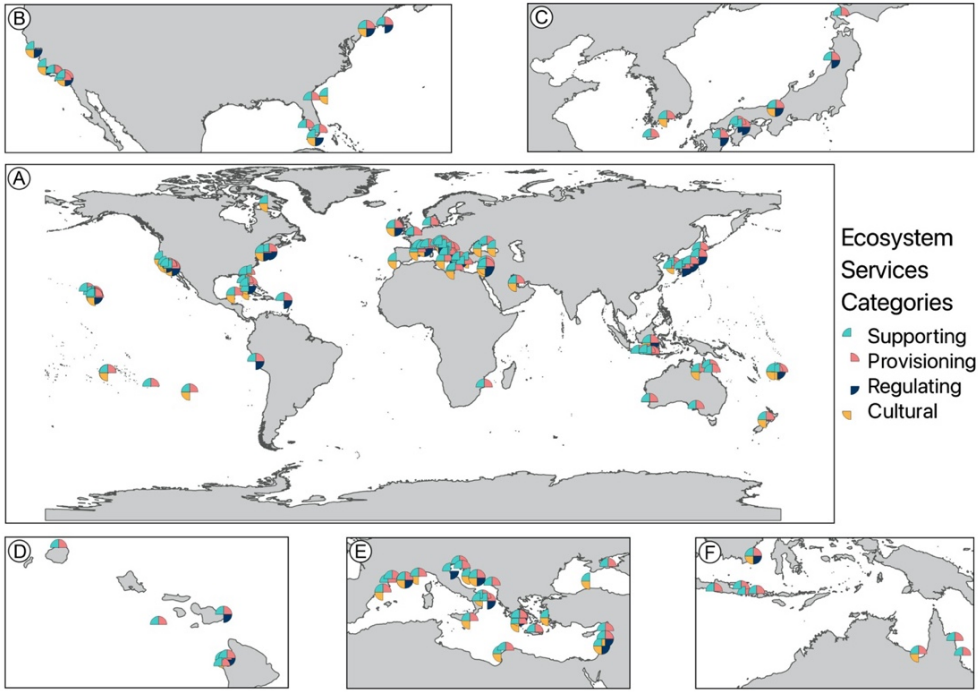

Figure 6.3. Worldwide distribution of locations where Ecosystem Services provided by SGD were identified and reported in scientific literature (A). Pink, turquoise, dark blue and yellow quadrant of the circle corresponds to sites where Provisioning, Supporting, Regulating and Cultural Ecosystem Services were identified, respectively. Zooms into the areas where most of the studies are located are also provided: B) North America; C) Japan and the Korean peninsula; D) Hawaiian archipelago; E) Mediterranean Sea; F) Indonesia and North Australia.

6.4. Results and Discussion

In the following sections we describe how SGD is directly related to those ES and how those interact with each other, what dependencies they have and what consequences affect the coastal societies. As it will be explained, Supporting, Provisioning, Regulating and Cultural ES can have multiple synergies between them (see section 6.4.1). In any case, those ES do not interact spontaneously but the different stakeholders from any coastal society interact with the SGD process. Either to take advantage or remove the threat to guarantee their well-being, there are trade-offs between ES that will take place in each society (see section 6.4.2). Therefore, those situations will make it difficult to achieve a win-win scenario, which can result in social conflicts.

6.4.1. Submarine Groundwater Dependent Ecosystem Services

Most of the SGD studies are focused on understanding the role of SGD in the water cycle and its biogeochemical impacts on coastal and marine ecosystems. Indeed, the results derived from the first stage of the systematical review reinforce this fact; 55% of the literature has been focused on evaluating Supporting ES of SGD. This evidences that direct ES such as Providing, Regulating, and Cultural, which only comprise 7%, 8%, and 3%, respectively, of the examined literature, have been significatively overlooked in research pertaining to SGD (Figure 6.4). Notice that according to the MEA (2005), Supporting ES are services that create synergies between categories, or their effects are so long term that they cannot be perceived by the coastal societies (Figure 6.2). Therefore, according to this definition, any provisioning, regulating, or cultural ES are related to the Supporting category and there is an overlap of some SGD-ES. In this direction, the same study can be accounted for the supporting category and any other. For instance, Duarte et al. (2010) showed that an aquiculture macroalgae farm that is provided by the nutrients of SGD is directly related to the provision of food by the algae farm (Provisioning ES) and, indirectly, but not less important, the support of habitat for those organisms (Supporting ES). In this direction, any other example described in the following sections is always related to Supporting ES.

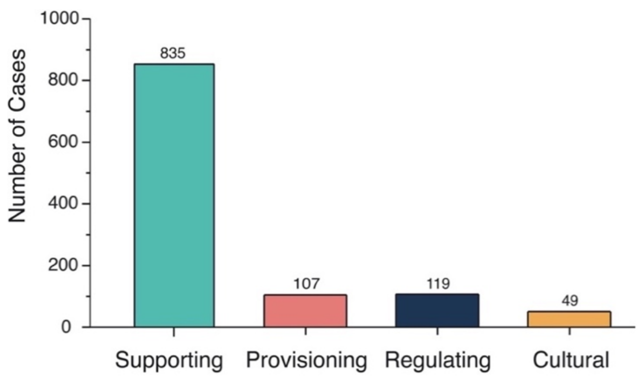

Figure 6.4. Number of reported cases in the first stage for each SGD-ES for the systematical search key words using WoS.

Focusing on the studies explicitly referring to SGD social implications (fourth stage), the identified 114 cases from the 32 publications in the systematic review showed the following results in terms of the reported ES: 100% Supporting, 80% Provisioning, 25% Regulating, and 41% Cultural ES (Figure 6.5). The higher incidence of Provisioning services seems to be the result of the major scientific effort done over the last 40 years to link SGD as a fresh water resource (Moore, 2010b; Taniguchi et al., 2019). Accordingly with results obtained in the first stage, the smaller relevance of Regulating and Cultural ES suggests that these topics have only recently received scientific attention.

The analyzed 114 cases where at least one SGD-ES can be identified with a direct social implication correspond to 96 different locations worldwide (Figure 6.3). Nevertheless, there were vast areas of the planet where few SGD studies were performed and little scientific information is available on ES provided by SGD. These areas include the coast of Africa, South America, the Arabian Peninsula, Antarctica, or the Indian subcontinent, which altogether represent less than 10% of the cases found in the review (Figure 6.3). This distribution of case studies is mainly explained by the inherent bias in this search since most of the research conducting SGD studies is concentrated in specific areas (e.g., USA, Australia, Europe) and the selection of scientific publications written only in English.

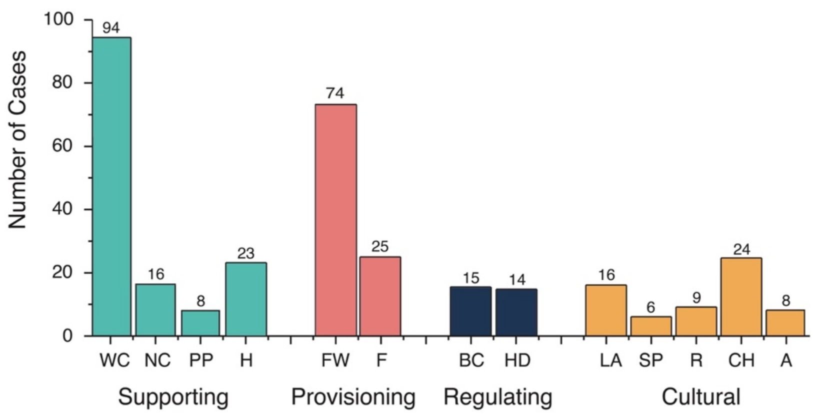

Figure 6.5. Number of reported cases for each SGD-ES categories and derived outcomes from the fourth stage. WC: water cycle; NC: nutrient cycling; PP: primary production; H: habitat; FW: freshwater; F: food; BC: biological control; HD: human disease; LA: leisure activities or ecotourism; SP: sense of place; R: religion or myth; CH: cultural heritage; A: aesthetical values.

6.4.2. Supporting Ecosystem Services

As one process involving the transference of water across the land-ocean interface, SGD has a role in the global Water Cycle (Church, 1996; Zhou et al., 2019), which is understood as a SGD-ES. During the 1960s, several studies were conducted to evaluate the fresh groundwater driven by SGD as part of the local water budget (Burdon and Papakis, 1961; Isbister, 1966; Muir, 1968; Newport and Haddor, 1963) and as part of the global budget that was estimated to represent 5% of surface runoff (Nace, 1967). Since then, other attempts were performed to estimate the fresh SGD contribution to the water cycle (Church, 1996; Taniguchi, 2002; Zektser and Loaiciga, 1993), including the recent investigations that have estimated that the fresh component of SGD represents ~1.3% of river discharge (Zhou et al., 2019) or ~0.6% of the total freshwater into the global ocean (Luijendijk et al., 2020). However, when the saline or brackish component of SGD is integrated, SGD has a broader influence on the world oceans representing between 80% and 160% of the amount of freshwater entering the Atlantic Ocean from rivers (Moore et al., 2008), or up to 4 times taking also into account the Indo-Pacific Oceans (Kwon et al., 2014).

In addition to its relevance for the hydrological cycle, SGD also supplies nutrients from natural or anthropogenic sources into the coastal ocean (Basterretxea et al., 2010; Johannes, 1980; Johannes and Hearn, 1985; Lecher and Mackey, 2018; McClelland et al., 1997; Santos et al., 2021; Slomp and Van Cappellen, 2004; Valiela et al., 1990). Nutrients supplied to the coastal sea by SGD, which form part of the nutrient cycling, continue their cycle interacting with the biota. Indeed, microbiota (bacterioplankton or phytoplankton) are the first organisms to transform those nutrients and make them available for other secondary producers (Lecher and Mackey, 2018). One of the most important processes in this nutrient cycling is to support primary production. Many publications have related the role of SGD-driven nutrients to support higher productivity of phytoplankton blooms in coastal areas (Garcés et al., 2011; Machado and Imberger, 2014; Troccoli-Ghinaglia et al., 2010), cyanobacteria blooms (Blanco et al., 2011, 2008; Umezawa et al., 2002), macroalgae blooms (Amato et al., 2016; Derse et al., 2007; Ouisse et al., 2011; Yoshioka et al., 2016) or enhance macrophytes spatial coverage, leaf growth and meadow productivity (Carruthers et al., 2005; Dadhich et al., 2017; Darnell and Dunton, 2017; Kamermans et al., 2002; Peterson et al., 2012). Primary producers, from both the benthos and the water column, are able to incorporate inorganic nutrients into the trophic chain upholding nutrient cycling and food for more complex organisms (Lecher and Mackey, 2018). Isotopic analysis of $\partial^{15}N$ and $\partial^{13}C$ and N:P ratio have allowed identifying the direct uptake of inorganic nutrients by phytoplankton (e.g., diatoms and dinoflagellates) and macrophytes (Amato et al., 2016; Andrisoa et al., 2019b; Hata et al., 2016; Lecher and Mackey, 2018; McClelland et al., 1997). The utilized nutrients can then be transferred to zooplankton and to higher trophic levels in the food web (Lecher and Mackey, 2018).

The discharge of groundwater to the coastal sea can also modify or stabilize temperature, pH, salinity, or water transparency conditions of the receiving water bodies, which might be essential to maintain or support many coastal habitats and ecosystems (e.g., coral reefs or seagrass meadows). However, the effects of SGD also may harm those habitats. For instance, SGD from karst springs may reduce the net calcification capacity of corals, and therefore the extension of habitat that they can provide to other species by provisioning high amounts of CO_2 stabilizing low pH (Álvarez-Góngora and Herrera-Silveira, 2006; Crook et al., 2012; Troccoli-Ghinaglia et al., 2010). Also the low salinities provided by fresh SGD were reported to reduce the diversity and richness in coral reefs (Lirman et al., 2003) and meiofaunal communities (Kotwicki et al., 2014; Migné et al., 2011). Contrarily, diatoms (Welti et al., 2015), cyanobacteria from benthic communities (Lee and Kim, 2007) and juvenile snails (*Lobatus gigas*) showed to find stable habitats due to freshwater conditions supported by SGD (Stieglitz and Dujon, 2017). Moreover, SGD inputs from karstic springs showed to represent the principal source of freshwater to some coastal lagoons, contributing to maintain them under non-hypersaline conditions for most of the year and thus playing a relevant role in coastal lagoon ecosystem functioning (Rodellas et al., 2018; Stieglitz et al., 2013).

Submarine Groundwater Discharge can also contribute to stabilize temperatures of coastal ecosystems, which might have a key role in the maintenance or weakening of coastal habitats. On the one hand, SGD-driven inputs of nutrients accompanied by stable temperatures promote primary production and support more complex organisms across the trophic chain and richer habitats. Such effects are known to create biological hotspots, where biomass, richness, diversity, net community production and ecosystem complexity are enhanced (Encarnação et al., 2015; Foley, 2018; Garcés et al., 2011; Utsunomiya et al., 2017). For example, in Salses - Leucate coastal lagoon (France) the higher temperature and nutrients availability related to SGD were correlated to the higher growth of Mediterranean mussels (*M. galloprovincialis*) (Andrisoa et al., 2019a). On the other hand, the same constant supply of nutrients and stable temperature can enhance the dominance of opportunistic species, which can displace others or affect them by cascading effect (Lecher and Mackey, 2018). The dominance of opportunistic species inevitably reduces richness and diversity in some coastal ecosystems. These consequences were studied in coral reefs of Japan (Blanco et al., 2008) and benthic communities in Delaware (USA) (Miller and Ullman, 2004), where zones directly influenced by SGD had communities with less ecological richness than others which were not influenced.

In addition, such processes can support Harmful Algal Blooms (HABs) such as red tides, brown tides, cyanobacteria blooms or macroalgal green tides (e.g., Gobler and Sañudo-Wilhelmy, 2001; Hu et al., 2006; Hwang et al., 2005; Kwon et al., 2017; Lapointe, 1997; Lapointe et al., 2005; Laroche et al., 1997; Lee et al., 2009; Su et al., 2012) enhancing primary production but at the same time destroying the habitat of other species and ecosystems. The presence of HABs supported by SGD-driven anthropogenic nutrients may have cascading effects on entire ecosystems, as the massive kills observed in the USA (Hu et al., 2006) and South Korea (Lee et al., 2010). The presence of dense phytoplankton blooms was reported to reduce light availability for benthic communities, in seagrass meadows (Short and Burdick, 1996) and coral reefs (Laroche et al., 1997a; Richardson et al., 2017). Similar effects were produced by macroalgal blooms in coral reefs and turf algae in Hawaii, where the massive presence of those organisms covering the benthos has prompted the habitat to change (Amato et al., 2016).

6.4.3. Provisioning Ecosystem Services

Freshwater resources in coastal areas, particularly in arid or semi-arid zones, are of vital importance to any type of human settlement. Several studies documented the use of the freshwater component of SGD since the Phoenician times along the Mediterranean coasts (Kohout, 1966) and the ancient Rapa Nui civilization in Easter Island (Brosnan et al., 2018). In this regard, SGD has been intensively studied in several countries (e.g., southern coasts of France, Lebanon, Libya and Greece) to be exploited as a freshwater resource (Bakalowicz, 2018; Fleury et al., 2007; Mijatović, 2006; UNESCO, 2004). Fresh SGD is also used for other purposes, such as agriculture or livestock (Moosdorf and Oehler, 2017; Pereira et al., 1996). Still today, fresh SGD is used for drinking, laundering, or hygiene in several islands of Indonesia (e.g., Java, Lombok, Bali) (Moosdorf and Oehler, 2017) or built-in tap water facilities in the Mediterranean (e.g., Trieste bay, Italy; Port-Miou, France; Chekka, Lebanon; or Benghazi, Libya) (Mijatović, 2006). This SGD-ES can be crucial in semi-arid regions, which are strongly dependent on groundwater resources, especially under climate change forecasts that consider these regions as hot spots due to their sensitivity to climatic disturbances (IPCC, 2014). Forecasting models predict changes in rainfall seasonality patterns, an increase of evapotranspiration and a decline of groundwater reserves (IPCC, 2007). Aside from its importance as a direct good, fresh SGD has numerous synergies with supporting, regulating and cultural ES provided by SGD that are explored in the following sections (see 6.4.3, 6.4.4 and 6.4.5).

The provisioning of food through fishing or aquaculture activities is another ES provided by SGD (UNEP-MAP, 2015). SGD can play a key role on the support of productivity and functioning of coastal ecosystems, resulting in favorable habitat conditions to provide food to human societies. This creates a synergy between the supporting ES and this provisioning ES. Due to the enhancement of high productivity derived from the SGD-driven nutrients, secondary producers can grow, habitats and ecosystems can develop, and ultimately, human consumed species are present in those areas. Sites where SGD contributes to provisioning of food include algae aquaculture in Hawaii (Duarte et al., 2010; Pongkijvorasin et al., 2010), crustacea in Portugal (Silva et al., 2012), fish in Japan (Burnett et al., 2018, 2015; Fujita et al., 2019; Utsunomiya et al., 2017), mussels in south France (Andrisoa et al., 2019a), or oysters in China and USA (Chen et al., 2018a;

Spalt et al., 2020). SGD can also endanger the provision of food through the supply of pollutants by deteriorating the ecosystems that support aquaculture and fisheries and endangering local communities' health (Erostate et al., 2020). SGD can also introduce large amounts of metals from mining activities (Chapter 4; Trezzi et al., 2016b), which can act as pollutants instead of micronutrients, affecting primary producers and subsequently higher trophic levels used for human consumption. In addition, SGD-driven HABs may not directly affect humans but their toxins can be accumulated in food that then will be consumed by humans (Lee et al., 2010).

6.4.4. Regulating Ecosystem Services

Biological control has been observed where fresh SGD influences the salinity levels of coastal areas. This process regulates the presence of species depending on their tolerance to low salinities as in Okinawa (Japan) (Blanco et al., 2008), Florida (USA) (Lirman et al., 2003) and Roscoff Aber Bay (France) (Migné et al., 2011). This process, often referred to as zonation (Kohout and Kolipinski, 1967), can also be produced by the reduction of the pH due to the influence of SGD and, therefore, the difficulties of some organisms with external carbonate or silicate structures to live (e.g., coral reefs or foraminifera) (Crook et al., 2013, 2012; Martinez et al., 2018; Prouty et al., 2017). For example, it was recognized that juvenile teleost fish had higher growth rates in coastal GDE (Lilkendey et al., 2019) or that the higher temperatures in winter supported by SGD provided shelter for other species (Miller and Ullman, 2004). SGD may thus concurrently provide habitat (Supporting ES) and biological control (Regulating ES). Excessive nutrient or contaminants loadings supplied by SGD can enable the presence of those species that are adapted to these live conditions (e.g., *Ulva spp.*) (Hwang et al., 2005; Kwon et al., 2017; Yoshioka et al., 2016) or opportunistic species of diatoms, dinoflagellates or cyanobacteria (Blanco et al., 2011). SGD investigations showed that eelgrass living in coastal GDE can have fewer herbivory organisms (Peterson et al., 2012). Turtle grass (*Thalassia testudinum*) can change its biological strategy, under high nutrient levels, by not growing flowers and developing bigger leaves (Darnell and Dunton, 2017), while the Australian dhufish (*Glaucosoma hebraicum)* can use low salinities to remove parasites (Pironet and Jones, 2000). Humans take direct advantage of such sites, where the abundance of certain species are a source of food to catch fish in Australia (Stieglitz, 2005), or create aquaculture in Japan (Hosono et al., 2012; Utsunomiya et al., 2017).

Human diseases can also be introduced into the coastal waters by bacteria or viruses supplied by SGD. Polluting microorganisms can be driven by groundwater (Abaya et al., 2018; De Sieyes et al., 2016; Paytan et al., 2004; Yau et al., 2014), delivering bacterial foreign communities (Knee et al., 2008) or viruses (Futch et al., 2010) into the coastal environments. Either from leaks or spills from septic tanks or injection wells from water treatment plants, sewage can infiltrate in coastal aquifers polluting groundwater with high concentrations of fecal bacteria and viruses, which can be transported by SGD to the coastal seawater. In different study sites in California (De Sieyes et al., 2016; Paytan et al., 2004; Yau et al., 2014), Florida (Futch et al., 2010) and Hawaii (Knee et al., 2008) it was demonstrated that zones influenced by SGD from coastal aquifers contaminated with wastewater, had elevated levels of Fecal Indicator Bacteria (FIB). According to Yau et al. (2014), the discharge of fecal bacteria into Avalon beach (California, USA) could be directly related to certain diseases among swimmers who entered in contact with the SGD influenced zones.

The provisioning of freshwater is also used to reduce human diseases and improve hygiene. Moosdorf and Oehler (2017) reported the use of groundwater to make laundry, bathing or to heal wounds in Indonesia, Fiji and Mozambique. The use of SGD in these societies contributes to the citizens health via two ways: directly, by using SGD for hygiene purposes, and indirectly, by allowing saving their cleaner freshwater resources only for drinking purposes. SGD can also represent a pathway delivering pollutants into the coastal ocean from anthropogenic activities and settlements (e.g., cities, harbors, or mines), which could represent a great threat towards people's health that have not yet been evaluated. These pollutants supplied by SGD include nutrients, which can trigger HABs that may liberate toxins and can pollute commercial species of shellfish (Anderson et al., 2000; Laroche et al., 1997b), and finally endanger the health of the consumers; metals, which can accumulate on commercial mussel species (e.g., *M. edulis* grown in SGD-influenced sites had twice the concertation of Hg on soft tissue compared to non-SGD influenced mussels (Laurier et al., 2007); as well as other contaminants such as radionuclides from nuclear power plant accidents (Fukushima, Japan) (Sanial et al., 2017) or from high naturally occurring radioactive areas (Garcia-Orellana et al., 2013), which can bioaccumulate in fish tissues (Garcia-Orellana et al., 2016). Other studies have reported that SGD can also supply pharmaceutical and caffeine residues (CEC's) (Knee et al., 2010a; Szymczycha et al., 2020), pesticides and persistent organic pollutants (POP's) (Dzierzbicka-Głowacka et al., 2019; Pavlidou et al., 2014) to the coastal ocean.

6.4.5. Cultural Ecosystem Services

Recreational activities or Ecotourism resulting from the existence of SGD are mainly linked to the presence of submarine springs (Burnett et al., 2015;

Lougheed, 2006; Moosdorf and Oehler, 2017). Sites influenced by submarine springs receive the attention of divers and swimmers due to the existence of a biodiversity hotspot supported and regulated by SGD. A clear example of the cultural relevance that these springs have is the case of La Source ("The Spring", in French) in Tahiti, where leisure companies have established guided routes to visit SGD-influenced sites as a result of their enhanced biodiversity (Moosdorf and Oehler, 2017). Other recreational activities linked to the occurrence of SGD can also be found in grey literature sources. On the coasts of the Balearic Islands (western Mediterranean Sea), several caves in karstified limestone massifs influenced by SGD are visited by divers, swimmers, and recreational underwater fishermen due to the specific low light biodiversity that lives in them (Rützler, 1996). During the cold winters of Canada, it was also reported that a polynya was maintained due to the discharge of groundwater with higher temperatures, allowing Arctic shipping (Sadler and Serson, 1980). SGD can also affect recreational activities, particularly when SGD-driven HABs are occurring or when swimming beaches are closed for sanitary reasons due to the presence of FIB derived from SGD inputs (Yau et al., 2014). Although less frequent, it was observed that navigation of recreational small boats was compromised along Croatian shorelines as a result of point-sourced large-flow groundwater discharge (Alfirevic, 1966; Keller, 1963).

Several toponyms along world shorelines were named after the occurrence of SGD, especially in areas where groundwater inputs represented a freshwater resource or led to biological hotspots, giving people a sense of place. Examples of such particularity are: "Olhos de Água" in Portugal ("eyes of water" in Portuguese) (Carvalho et al., 2013; Encarnação et al., 2015; Foley, 2018), "Punalu'u" in Hawaii (USA) ("diving spring" in Hawaiian language) (Moosdorf and Oehler, 2017), "Es Dolç" or "Sa Font de Sa Cala" in the Balearic Islands ("the fresh water" and "the spring of the cove" in Catalan) (Tovar-Sánchez et al., 2014). Symbolic constructions and places were also built in areas linked to SGD. Some human settlements located in coastal areas with a semi-arid climate were built near SGD springs because they depended on the freshwater resource provided by SGD. These sources of fresh water were often protected or venerated through the construction of defense, strategic or mystical buildings. Examples of such are the Cala Figuera in Maó (Menorca, Balearic Islands, western Mediterranean), where the Romans already exploited a spring with the construction of a nymphaeum and ships stopped to load fresh water (Murray-Mas, 2006). In Rapa Nui (Easter Island), it is believed that the original civilization that built the famous face statues (moai) around the island were able to survive thanks to the construction of wells and "punas" (dams) taking advantage of the fresh SGD, which created a sense of belonging to the place (Brosnan et al., 2018). The Yokokujo Castle of Hiji, Ohita Prefecture (Japan), was built at the shores of the beach to allow the catchment of the Marbled flounder (*Pseudopreulonectes yokohamae*), a highly-prized fish species that thrive in a SGD-dependent ecosystem (Shoji and Tominaga, 2018).

Submarine Groundwater Discharge is also related to religion or myths, both through iconic buildings and legends. A clear example is the Hindu temple Tanah Lot, Bali (Indonesia), which was built to protect a spring that was magically moved from inland to the sea (Lubis and Bakti, 2013; Moosdorf and Oehler, 2017). The ancient Greek civilization also created different myths and legends related to the occurrence of SGD. According to the ancient Greek geographer Pausanias (2.5.3), an old legendary tale explained how the Turkish River Meander went under the Aegean seabed to the surface 390 km away, in the northeast Peloponnese (Clendenon, 2009). This same legend, according to Strabo (6.2.271) was originated by the Greek lyric poet

Ibycus around the 6th century B.C. (Clendenon, 2009). Pausanias (8:VII) also described how the inhabitants of Argos made sacrifices to Poseidon in the location of a SGD spring, currently named Kiveri spring (Leake, 1830; Moosdorf and Oehler, 2017). One of the best-known and oldest myths related to SGD is the story of the spring nymph Arethusa and the river god Alpheus, which originated in the 8th century B.C. (Bilić, 2009; Clendenon, 2009). In this Greek myth, Arethusa transformed into water and traveled underground through the Ionian Sea to escape from Alpheus's amorous advances. Arethusa resurfaced as a freshwater spring in Syracuse (Sicily, Italy) together with Alpheus that had followed her and traveled the same submarine journey, remaining always fresh by never mixing with the sea (Clendenon, 2009).

These SGD-linked myths, stories, buildings and villages have become part of the current Cultural Heritage. Different cultures around the globe place high value to keep alive the old uses that SGD had for their ancestors. In Australia, the Aboriginal community of Kaurna finds an important part of their identity to the story of the ancient creator Tjilbruke, who wept for his nephew, and from his tears freshwater springs were created on the beach (Amery, 2016; Moosdorf and Oehler, 2017). In the Island of Kona, Hawaii (USA), many of the algae (e.g., limu manauea (*Gracilaria coronopifolia*)), which are harvested in sites influenced by SGD, are valued by the indigenous cultures for centuries (Duarte et al., 2010; Pongkijvorasin et al., 2010). Fishing spots related to SGD has been part of communities' traditional knowledge, which has passed across fishers' generations. Examples of SGD-linked fishing hotspots that can be considered cultural heritage include the "wonky holes" of the Great Coral Reef in Australia (Stieglitz, 2005), the "Mud Hole" in Florida (USA) (Kohout et al., 1979) and in the Yucatan Peninsula (Mexico) (Stieglitz and Dujon, 2017).

Additionally, Zektser et al. (1973) mention submarine springs as "the most spectacular manifestation of groundwater discharge to the seas", indicating the aesthetic value of SGD. Submarine springs or SGD continue to inspire and motivate new generations of authors and researchers. The inspiration has gone from one of the first documents that explained SGD, where Aristotle in his treatise "Meteorology" (ca. 350 BC), explains how karstic streams sink underground and travel short distances to discharge into sea (Clendenon, 2009), to today's latest publications on SGD. This aesthetical value of SGD has reached ancient poets such as Lucretius or geographers such as Pausanias and Strabo, to inspire songs in the Hawaiian folklore (Pukui, 1949). Nowadays, people continue to find the aesthetic value to SGD by visiting submarine springs on scuba diving experiences or by discovering new features in new SGD investigations.

6.4.6. SGD trade-offs

The ES provided by SGD and the synergies between them cannot be fully understood without detailed consideration of the interactions of the different stakeholders from any coastal society with SGD-influenced ES. Therefore, trade-offs (i.e., the prioritization of one service in exchange for another one) play a key role in understanding the social implications of SGD. For example, if a community perceives SGD as a freshwater resource and decides to collect and use this water for their own consumption, this action could reduce the flux of water and solutes to the coastal ecosystem. In that case, the community will trade-off the provision of freshwater resource in exchange to reduce the regulating and supporting services of SGD derived from the supply of water and nutrients to the ecosystem. This action might be to the detriment of nearby coastal communities that could see their provision of food reduced (Duarte et al., 2010; Pongkijvorasin et al., 2010), or also see affected their cultural heritage if those consumed SGD dependent species formed part of their culture (McDermid et al., 2019). This example is summarized in Figure 6.6, highlighting the synergies between the four categories of ES (blue double arrows) and the effects of a human decision that chooses to trade-off most of the outcomes by just the provision of the freshwater (red arrows). Further trade-offs related to SGD-ES can become especially complex when economic, cultural, or political interests are at stake. Thus, in order to achieve or maintain the well-being of a coastal community, policies and management strategies need to be developed considering the synergies and trade-offs between the different SGD-ES.

One of the main targets of the coastal policies and management strategies dealing with coastal ecosystem services is to guarantee the supply and shortage of materials or goods necessary for good life and economic sustainability (Costanza et al., 2017). In this regard, SGD has been used and managed for centuries as a freshwater resource. Nowadays, climate change-induced drought and high anthropogenic pressure (e.g., groundwater withdrawal, irrigation) make management of fresh SGD more necessary (Stigter et al., 2014; UNEP/MAP, 2012). This is critical for those societies that have scarce supplies of freshwater (e.g., North African and Middle East coasts). However, management strategies rarely take trade-offs into account.

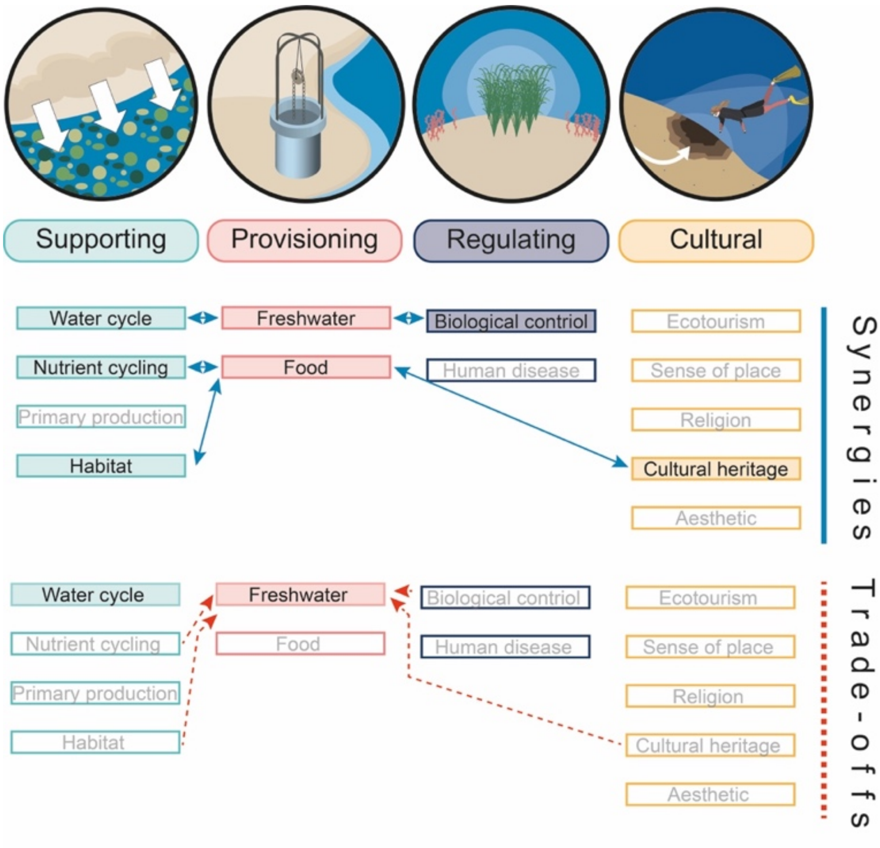

Figure 6.6. Diagram exemplifying how the SGD-ES framework is applied to a hypothetical case described in the text. Filled boxes correspond to outcomes identified and empty boxes to outcomes that have been removed or do not exist. Blue double arrows correspond to synergies between outcomes and red arrows correspond to trade-offs between outcomes that were preferred (filled box) in exchange of those renounced (empty box).

Research findings have assessed, conceptually and economically, the impacts of management interventions aimed to exploit such resources in these regions. For example, Ayoub et al. (2002) developed a cost-benefit survey in order to identify the viability of exploiting offshore SGD through a pumping freshwater project in Cheka Bay (Lebanon). They found that the exploitation of fresh SGD would drastically reduce the marine zonation around the submarine springs, and consequently the availability of commercial fish species, affecting the well-being of fishermen communities. In contrast, local citizens and industries would gain an additional volume of fresh water and therefore security for their future good living. Other concerning trade-offs that exist between freshwater and SGD-dependent commercial species have been described for algae in Hawaii (USA) (Duarte et al., 2010; Pongkijvorasin et al., 2010) and fish in Obama Bay (Japan) (Burnett et al., 2018, 2015). In these cases, there were direct linkages between the use of groundwater as a freshwater resource and the exploitation of nearshore biomass productivity fueled by SGD, where a gain of one goes to the detriment of the other. Guaranteeing a minimum provision of food stock might require significantly decreasing groundwater extraction (Duarte et al., 2010; Pongkijvorasin et al., 2010). On the contrary, according to another investigation in Japan (Burnett et al., 2018), the economic benefits that provisioning of groundwater might provide, in terms of freshwater stock, could be greater than the losses to the nearshore fisheries. The management strategy implemented should thus deal with the dichotomy between the benefits of provisioning freshwater and the benefits of provisioning food stock.

Anthropogenic actions devoted to improve the management of hydrological or biological coastal resources can also indirectly affect other ES (e.g., the construction of subterranean dams, grout curtains, conducts or pipes, and tapping water plants) (Mijatović, 2006; Tamborski et al., 2020; Tardieu and Poité, 2015). Similarly, in the exploitation of brackish submarine springs as a freshwater resource, desalinization of mined groundwater is required and the brine produced can have hazardous consequences for the social-ecological system when it is discharged into the sea (e.g., destruction of the surrounding habitats and potential commercial species, Bakken et al., 2012).

Coastal management strategies shaping the SGD-ES can lead to confrontation between the different stakeholders involved. When one individual or group perceives that their gains on the SGD-ES are threatened by another individual or group that is also exploiting the same resource, confrontation can converge into a social conflict. Access to fresh water is the ES provided by SGD that is more likely to lead to conflicts, due to its importance for human survival. Due to the political need and willingness to explore SGD as an option to face fresh water shortages, fresh groundwater is widely studied around the Mediterranean (Ayoub et al., 2002; Bakalowicz, 2018; Bakken et al., 2012; Fleury et al., 2007; Ghannam et al., 1998; Mijatović, 2006; Tardieu and Poité, 2015). In Hawaii (USA), serious political battles are already raging with respect to terrestrial anthropogenic impacts on nearshore environments related to the supply of terrestrial anthropogenic pollutants through SGD (Duarte et al., 2010; Pongkijvorasin et al., 2010). These impacts can in turn affect the algae aquaculture, feeding social conflicts because the cultural ES of the algae aquaculture are deeply rooted in the Hawaiian community (McDermid et al., 2019). On the one side, most political parties understand that groundwater extraction reduces SGD and can impact coastal marine ecosystems. On the opposite side, landowners and developers insist that the effects of reducing SGD in exchange for the freshwater supply are irrelevant. Such discrepancy between both sides is what leads to a conflict in the future management of this coastal society (Duarte et al., 2010). Recently, for the first time, the US Supreme Court has ruled in favor to protect the connection between the coastal aquifer and the coastal ocean (SGD) (Cornwall, 2020). The case was based on the demonstration that the injection of wastewater effluents into the coastal aquifer directly affected the coastal ecosystem (Glenn et al., 2013) and should be protected according to the Clean Water Act. That sets a new base on the social conflicts induced by SGD (Santos et al., 2021).

6.5. Further steps

This review has also identified that studies on direct ES (Provisioning, Regulating or Cultural ES) are vastly outnumbered by publications related to Supporting ES. This is a consequence of the large effort made during the last 40 years in the SGD research field to demonstrate the importance of this process on the hydrological and biogeochemical cycles. The consulted scientific literature has also evidenced a lack of attention towards potential impacts and benefits that Supporting ES have on coastal societies or other Provisioning, Regulating or Cultural ES. In this regard, future studies on ES provided by SGD should consider expanding their research to address how their findings could have potential social implications or be related to any of the other SGD-ES categories and outcomes. There is thus a need in the SGD research field to develop more interdisciplinary studies involving social scientists, hydrologists and oceanographers to work together.

6.5.1. Exploration of grey literature

This review reveals that the published scientific literature on Submarine Groundwater Discharge has neglected its social dimension, particularly regarding those cultural ecosystem services provided by SGD. Rather than being reported in conventional scientific research, many of the cultural ES related to SGD have only been published through grey literature publications. This grey literature can be defined as "all documents except journal articles that appear in widely known, easily accessible electronic databases will be considered grey literature" (Rothstein and Hopewell, 2009). These publications are generally written in local languages, and thus we acknowledge that by only focusing on English written scientific publications, this review has excluded both academic publications in other languages and grey literature. Gathering all the available information on social implications of SGD is challenging both because local and regional documents are not easily accessible and also because this research requires involving people proficient with those local languages. As an example to highlight this complexity, there are more than 85 languages spoken in the Mediterranean region. Focusing on the 44 submarine springs around the Mediterranean mentioned by Gilli (2020), the systematic review conducted in this study only allowed identifying direct ES (providing, regulating, or cultural) in two sites. If literature available online (both scientific and non-scientific) is screened using English, Italian, French, Catalan and Spanish (languages in which the authors are proficient) the number of sites with reported ES increases to 14. For example, in France, the spring of Estramar is related to leisure activities such as fishing and speleology. The springs of Port-Miou (France) are documented as an important freshwater resource for human consumption and used as a diving spot by different companies. In Italy, the spring of Galeso has become a Tourist attraction to go and see the "citri", terminology used to describe the bubbling pools inside the sea surface that SGD creates under vigorous flow. Widening the search possibilities (e.g., more languages, including paper-based documents) would have surely resulted in a significant increase in the reported ES. A comprehensive understanding of the ES provided by SGD should thus try to incorporate this locally-based knowledge, and this can only be attained by conducting local investigations that focus on social and cultural perceptions and local people's experience and knowledge. Further research should thus attempt to incorporate this grey literature, dealing with the challenge of tackling different languages in which most of the information is provided. In this regard, engaging citizens and communities (citizen science) to inform about these SGD-social links can decisively contribute to produce a comprehensive understanding of social implications of SGD.

Chapter 7 *Ecosystem services derived from SGD: a perspective from traditional and academic knowledge in Mediterranean societies*

7.1. Introduction

Grey literature offers a deep information resource where both academic and local ecological knowledge can be found (Macdonald et al., 2015; Mahood et al., 2014; Rothstein and Hopewell, 2009). Thus, grey literature can be defined as all documents except journal articles that appear in widely known, easily accessible databases in physical or electronic format (Rothstein and Hopewell, 2009). Whilst grey literature lacks peer revisions and permanent accessibility that can hamper its quality, it becomes a fundamental source of information for academic research thanks to its wider pool of participants, diversity of ideas, and different perspectives or easy access formats (Mahood et al., 2014; Seymour, 2010). The analysis of grey literature has been indeed applied to different scientific disciplines, including medicine (Pappas and Williams, 2011), hydrology (Uhlemann et al., 2013), oceanography (Sáenz-Arroyo et al., 2005) or social sciences (Schöpfel and Farace, 2010). Besides grey literature, there is a large body of information that is not always printed or published, commonly referred to as local knowledge. Local ecological knowledge is defined as a cumulative body of knowledge, practices and beliefs about local ecosystems and their management that is handed down through generations by cultural transmission and supported by customary institutions (Berkes et al., 2000; Molnár and Babai, 2021; Olsson and Folke, 2001; Ostrom, 1990). The information compilation of such know-how is difficult and many times may be biased but is essential to understand the role of some ecosystem services to the society out of the more quantitative scientific approach. Consequently, direct consultation with key local stakeholders is often needed to have access to this body of knowledge. Combining all the academic and local knowledge available regardless of language, format support, or accessibility can thus be essential to understand the social impacts of SGD in coastal communities, overcoming the limitations and biases of reviews based on scientific literature. The local approach has been demonstrated crucial to understand the importance of the potential ecosystem services and its degradation through time (Mallo et al., 2022).

The aim of this study is to obtain a comprehensive understanding of the social dimension of Submarine Groundwater Discharge by exploring both academic literature and local knowledge on the social implications and perception of SGD and its ecosystem services. To this aim, we selected to study areas in the Mediterranean region, the island of Mallorca and the peninsula of Salento. This allowed us to provide evidence from different contexts while characterizing the links between coastal societies and SGD, the similarities and differences of each Mediterranean society in relation to ES provided by SGD and identify the historical evolution of the perception of SGD and the services it provides.

7.2. Study areas

7.2.1. Mallorca

The island of Mallorca is in the northwestern Mediterranean Sea, in the Balearic archipelago (Figure 7.1). The island hydrology is governed by the two limestone mountain chains on the eastern and western sides of the island. Groundwaters are mainly governed by karst formations which confer highly permeable superficial aquifers that discharge into the sea (Giménez et al., 2014). Submarine Groundwater Discharge plays an important role in the island's nearshore waters, which is the major contributor of dissolved inorganic nutrients and trace metals (Tovar-Sánchez et al., 2014). Submarine Groundwater Discharge has been shown to play a major role in enhancing primary production (phytoplankton growth and stimulating seagrass growth; Basterretxea et al., 2010).

The island has been habited since 7000 B.P. by numerous cultures from the Mediterranean, such as Phoenicians, Greeks, Romans, or Arabs, from which today has an important cultural and historical heritage. Today's population is 912,000 inhabitants and is distributed unevenly around the Island (~50% lives in the capital of the Balearic Islands, Palma, and the rest is distributed in the other villages and cities around the island; INE, 2022). The main economic activity is tourism, which is concentrated all along the coast, although recently has started to diversify in the country sites of the island (Garcia et al., 2022). Due to the lack of natural superficial water resources, most water consumed on the island comes from groundwater resources (ABAQUA, 2022; Kent et al., 2002). The overexploitation of some aquifers (mainly due to tourism and agricultural industries) has led to seawater intrusion, which in turn threatens the freshwater resources end economy of the island (Custodio, 2017; Deyà Tortella and Tirado, 2011).

Figure 7.1. Study site locations. In red squares the island of Mallorca (1) and the Region of Salento (2).

7.2.2. Salento

The Salento peninsula (Province of Lecce, Brindisi and Taranto) is located at the southeastern end of the Italian Peninsula (Figure 7.1). The Salento peninsula aquifer is characterized by strongly fractured and karstified limestones, which confers it a high permeability (Balacco et al., 2022). The territory is flat with very small hydraulic gradients except in the basin of Taranto (De Filippis et al., 2016). Most of the hydraulic recharge is produced through the Murgia area, in the northwest, and then flows through the Salento aquifer until reaches the sea (Cotecchia et al., 2005). Submarine groundwater discharge is an important asset for fisheries (Mulazzani et al., 2016), especially for the historical mollusk fishery in the Mare Piccolo of Taranto (Cardellicchio et al., 2016; Parenzan, 1969).

The first testimonies of civilization in the region date from 4500 B.C. and have been followed by historical cultures such as Greeks and Romans, but Neanderthal people inhabited coastal caves until 25,000 years ago in the Uluzzo bay (D'Antoni and Onorato, 1995). The Salento region has 1,500,000 inhabitants and are distributed unevenly, with ~40% living in the municipalities which have a coastline (only five urban centers out of 40, stay on the seacoast) (ISTAT, 2022). The main economic activities in the area are agriculture and tourism, being important industrial settlements of Taranto and Brindisi located just at the extreme borders of the Salento.

The main freshwater supply for the region are groundwater sources (ISTAT, 2022). However, due to the important agricultural and tourist industries, there is overexploitation of the aquifers (Cotecchia et al., 2005; Mulazzani et al., 2016; Polemio, 2016). In this direction, the aquifer suffers important problems of contamination (Lugoli et al., 2011) and seawater intrusion (Cotecchia et al., 2005; Masciopinto and Liso, 2016; Polemio, 2016; Polemio and Limoni, 2006). In addition, climate change is expected to increase seawater intrusion due to sea-level rise and reduce the amount of groundwater resources (Masciopinto and Liso, 2016).

7.3. Analytical framework

Coastal groundwater dependent ecosystems have been defined as "the marine coastal ecosystems that require permanent or intermittent access to groundwater (including fresh and saline SGD) for maintaining their biological communities, their ecological processes, and the associated ecosystem services" (Chapter 6). Therefore, in this study, we consider Ecosystem Services provided by Submarine Groundwater Discharge (SGD-ES) as those services inherent to coastal groundwater dependent ecosystems (Chapter 6). This definition incorporates those ES categorized as supporting, which is defined in the MEA (2005) as necessary for the existence of the other three categories of ES (provisioning, regulating and cultural). In this direction supporting ES are related to long term ecosystem functionalities that are not perceived by society or have an indirect contribution to their well-being. Therefore, since we aim to analyze the social perception towards SGD, in this study the supporting category is not analyzed and is focused on the other three categories. Following Chapter 6 we define the ES categories and outcomes as follows:

Provisioning ES are defined as products that SGD provides to society. As outcomes, we consider Freshwater and Food:

- *Freshwater* as the fresh component of SGD that is directly used as a water resource for human consumption, agriculture, or other industrial purposes (e.g., coastal water springs).

- *Food* as organisms that have their habitat in coastal GDE or that their survival depends on SGD and are consumed by society (e.g., fishery).

Regulating ES are defined as services that control crucial processes for habitats and coastal ecosystems influenced by SGD. As outcomes we consider Biological Control and Human Disease (as Disease Regulation in the (MEA, 2005)).

- *Biological control* as those changes or conditions induced by SGD that affect the prevalence of certain species or ecosystems, or limit the entrance of other species into coastal GDE (e.g., fish nesting area).
- *Human Disease* refers to the transport or restriction of pathogens or pollutant compounds delivered by SGD that can compromise human health (e.g., Fecal bacteria driven by SGD).

Cultural ES are defined as the non-material benefits provided by SGD that contribute to human values and influence behavior. The perception of those ES can vary across stakeholders or communities, due to the subjectivity of the observer. As outcomes we consider Recreational Activities or Ecotourism, Sense of Place, Religion, Cultural Heritage and Aesthetic or Inspirational values.

- *Recreational Activities or Ecotourism* as any leisure activity (economically exploited or not) developed in an environment influenced by SGD (e.g., bathing area with lower temperatures).
- *Sense of Place* as the feeling of belonging to a certain site or toponyms that have been given to certain places after the occurrence of SGD, as well as buildings names (e.g., "Aigua dolç" translates to fresh water).

- *Religion* as those stories, tales, myths, or religious ceremonies that are based on SGD (e.g., Goddess Arethusa).
- *Cultural heritage* as those ways of doing, traditions, knowledge, objects, or values related to SGD that the present society continues from older generations (e.g., Fishing spot where SGD is produced).
- *Aesthetic or Inspirational values* as the subjective sensory-emotional values provided by SGD, such as inspiration, intrigue to explore nature, or beauty (e.g., poetry inspired by a coastal spring).

7.3.1. Data collection and analysis

The data collection for this study has been carried out through three different approaches that allowed us to gather the information available in i) academic literature, ii) grey literature and iii) local ecological knowledge.

First, we conducted a review of the academic literature by using the keywords "Salento", "Mallorca" and "submarine groundwater discharge", "SGD" or "submarine spring" in Web of Science (WoS). This search produced 12 articles, but only 7 of them (5 in Mallorca and 2 in Salento) reported SGD-ES. Due to the reduced number of results and the academic articles published in local languages in scientific journals from non-English countries, we translated the search to the local official languages of the regions (Catalan and Spanish for Mallorca, and Italian for Salento). In addition, we added to our search the term "submarine caves" in the corresponding local languages (both areas are characterized by karstic systems). This search produced 6 in Mallorca and 13 in Salento.

Second, we used the same terms for searching in the grey literature by using Google browser. By grey literature we consider “all documents except scientific journal articles that appear in widely known, easily accessible electronic databases” (Rothstein and Hopewell, 2009). Therefore, we searched for electronic and paper-based documents, cartographies, encyclopedias, catalogs, and books, from which we obtained 87 different information sources. These sources are included in the supporting information.

Third, we designed a semi-structured interview guide (see supporting information) that included questions from three main topics: i) Knowledge and location of SGD; ii) Characterization of each SGD point; iii) New information sources or further contacts to be interviewed. Interviews were conducted were done with people who lived in coastal villages or professional workers potentially related to the SGD such as fishermen or divers who were identified by using a snow-ball sampling procedure (Newing, 2011). Interviews were conducted in the corresponding local languages and responses were recorded in notes and properly anonymized. We obtained oral informed consent prior to the interview, following the university code of conduct. In total we interviewed 13 people in Mallorca and 11 in Salento, reporting a total of 17 and 18 sites, respectively.

All the data collected from the three different information sources were used to create a dataset on the different sites where SGD-related ecosystem services were identified into seven pre-established categories. The dataset includes information on: i) GPS location; ii) name of the site; iii) Information source (interview, Internet webpage, Governmental, book, news media or scientific publication; iv) Ecosystem Service (following the analytical framework); v) Temporality of the service (if the ES was from the past or the present); vi) references; vii) description of the site and ES. All grey literature references and interview model are presented in Appendix A.4 and A.5, respectively.

7.4. Results

7.4.1. Submarine Groundwater Discharge ES in Mallorca and Salento

The review conducted in this study allowed identifying 206 SGD sites in Mallorca and Salento where knowledge of Ecosystem Services provided by Submarine Groundwater Discharge is available (Figure 7.2). In both study areas, the sites are distributed all along their coastlines, pointing out the ubiquity of SGD. In Mallorca 140 of those SGD sites were found. The wetland area of "s'Albufera" in Mallorca was accounted as a unique site instead of accounting for the numerous springs it has. The remaining 66 sites were located in the region of Salento. All the sites identified have reported at least one Ecosystem Service (Provisioning, Regulating or Cultural ES). Notice that no supporting ES are presented in this study or discussed since they are implicitly present when any other category is identified (see Chapter 6).

Considering all the data review of WoS, grey literature and interviews with local stakeholders, the three ES categories were reported in almost the same proportion in both regions (see Figure 7.2). Despite the sample size being significantly different (n=140 and n=66, for Mallorca and Salento, respectively), provisioning and cultural ES are perceived in ~70% of cases, and regulating is only perceived in ~30% of the cases.

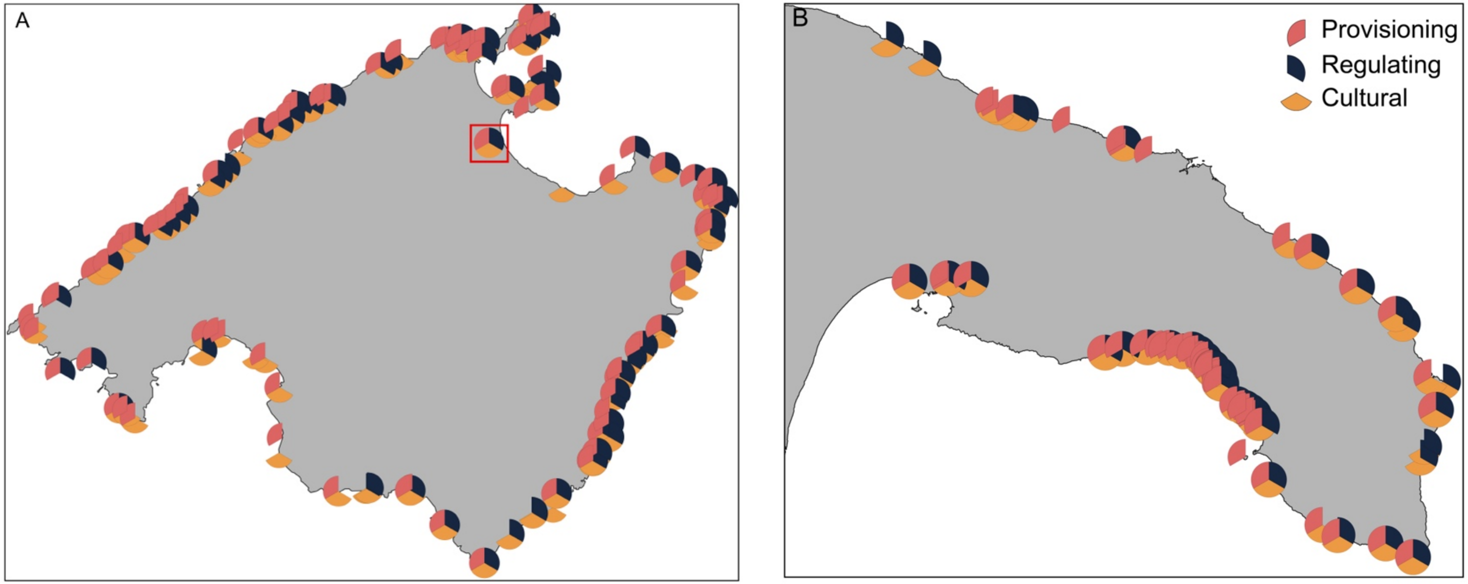

Figure 7.2. Ecosystem services distribution along the island of Mallorca (A) and the region of Salento (B). Every third of a cycle corresponds to a different ES category. Pink corresponds to provisioning, dark blue to regulating, and orange to cultural. Red rectangle corresponds to the coastal lagoon of s'Albufera.

7.4.2. The provisioning ES-SGD

- Freshwater

The freshwater outcome was the most reported service considering all categories in Mallorca and the second in Salento, with a total of 83 (59%) and 37 (56%) cases respectively (Figure 7.3). There is evidence that suggests that SGD was used for freshwater provisioning since ancient times. On the Island of Mallorca, ceramics were found in nearshore caves suggesting their use to recollect the groundwater filtering through the stalagmites before reaching the sea (Encinas, 2014). Romans used to reach the shores of Salento by boat to collect fresh water from the SGD springs to continue their journeys (Parise et al., 2017). In the XIII century in Italy, defense towers were built to protect against invaders. In the XVI century, a complete fortification was constructed along the coast to guard against the Ottoman army and pirate invasions (Corchia, 1961; Torri Costiere del Salento, 2023). Many defense towers were strategically placed in front of SGD springs to safeguard freshwater sources, as invaders looked for those water sources. The location of these sites has endured over time and are used nowadays by old fishermen in Mallorca and Salento to obtain fresh water (Gual and Albertí, 2000; Inguscio et al., 2007; Inventari de fonts a Mallorca, 2023). Besides human use, the villagers of Gallipoli in Salento used to have cattle at the Isola di Sant'Andrea so they could drink from the SGD spring of the island (itLecce, 2023). Also in Mallorca, many springs along the coast are frequented by goats and sheep to drink from the groundwaters discharging into the sea (Inventari de fonts a Mallorca, 2023). As an example of modern freshwater usage, in Mallorca the SGD spring of "Sa Costera" was canalized in 2009 and can deliver up to 4.5 $hm^3\ y^{-1}$ to the main city of the island, Palma, representing one of the most important water supplies for the island. In addition, when the demand for water is lower than the water flow provided by the spring, four different injection wells canalize the remanent water back into the aquifer (ABAQUA, 2022). Other uses for these fresh groundwaters in Mallorca are for watering the orchards, laundry, or other domestic porpoises (Aguiló, 1996; Berenguer, 1738; Salvator, 1884). In areas with high water flow, according to interviewees SGD has also been used in the past to refrigerate the different components of an old electric station.

- Food

The provisioning of food was more reported in Salento than in Mallorca, with a total of 23 (13%) and 18 (35%) cases respectively. Fishing and harvesting goods from the sea is an essential but often challenging activity for coastal societies. It has been demonstrated that certain species live, reproduce or hide in sites influenced by SGD, since it represents a source of nutrients for coastal ecosystems that can increase the biodiversity and abundance of marine organisms (Lecher and Mackey, 2018). Interviewed fishermen reported having used these hotspots for generations to obtain the catches they needed. These SGD-influenced sites are sometimes named after the fishing activities or species captured in the area, such as “Cova de sa pesquera” (cave of the fishery), “Cova de ses llises” (cave of the mullets (*Mujil cephalus*) (Encinas, 2014)) in the island of Mallorca or the “Grotta delle Corvine” (Submarine cave of the Croaker (*Argyrosomus regius*) (Costa del Sud, 2023; Eloisa Malagoli, 1977)). Besides using SGD sites as fishing spots, interviewees explained that these areas have been transformed and modified in order to perform aquiculture of different species. Some sites were used in the past as artisanal aquacultures, such as “sa cova des torrentó” (the torrent cave) in Mallorca to feed and grow small prawns (*Palaemon elegans*) that were used as bate for the fishermen (Encinas, 2014), or the numerous “bacini” along the western coast of the Salento peninsula, which were intensely used as aquacultures during the ’70s and ’80s. Indeed, because of the numerous brackish SGD spots along the coast of Salento, the industrial aquiculture located at SGD discharging points was an important economic activity since the year 1000 A.D. This industry became the most important activity in the region during the last half of the XX century, thanks to the culture of the "cozze nere" (mussel (*Mytilus galloprovincialis*)) production at the Mare Piccolo of Taranto (Cardellicchio et al., 2016; Parenzan, 1969). Mare Piccolo and Mare Grande, which are clearly influenced by SGD springs, are indeed unique sites to harvest mussels in the world and the biggest mussel farm in Italy. There are 34 main SGD springs (locally named "Citri") between the two basins, being the Galeso the most important with an average flow of 600 L s^{-1}. Especially in the Mare Piccolo, the amount of freshwater discharged into the basin confers stable salinity, temperature, and nutrient conditions year-round, which allow the Mussel farms to produce up to 30,000 tons y^{-1} (Cardellicchio et al., 2016).

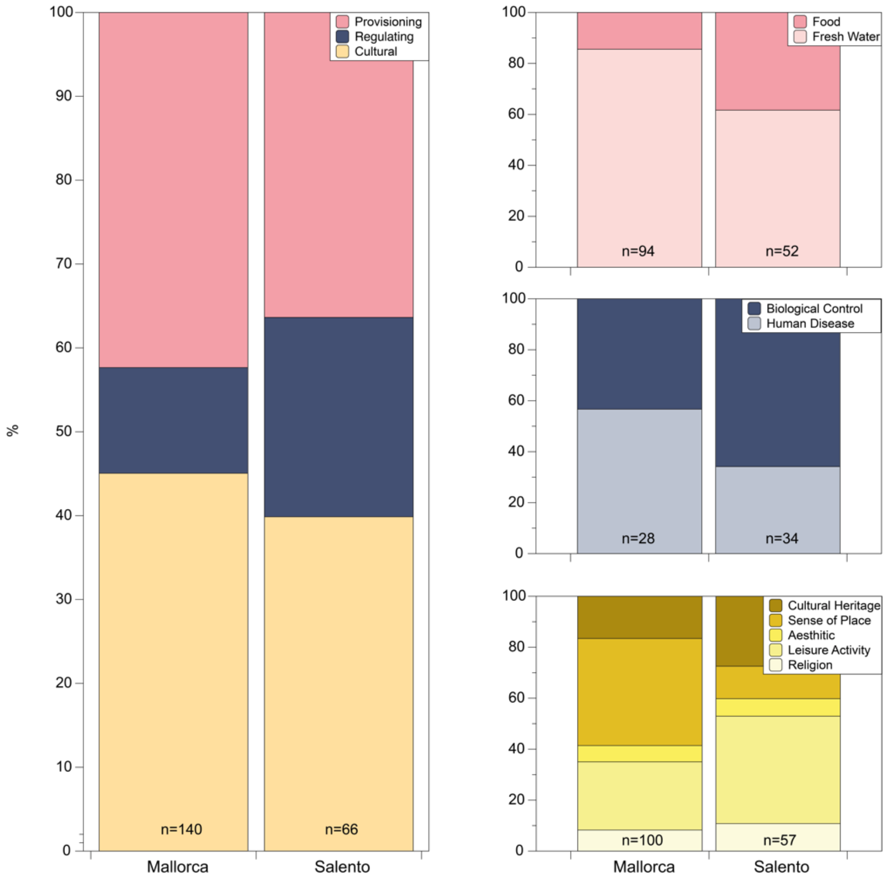

Figure 7.3. Categories and outcome of SGD-ES in Mallorca and Salento. A represents the percentage of cases of the three different categories of the SGD-ES. B, C and D represent the percentage of cases for the different outcomes of the provisioning, regulating and cultural categories, respectively.

7.4.3. The Regulating ES-SGD

- Biological control

The regulating ES is the least studied ES provided by SGD and coastal societies seem to be less perceived by local users than the provisioning and cultural ES (as shown in the next section). Considering the biological control, only 17 (12%) and 27 (41%) cases have been reported in Mallorca and Salento, respectively. Examples of biological control provided by SGD include the anchialine environments, which are clearly linked to SGD and are characterized by constant physicochemical conditions that allow certain species to survive in those environments. In addition, fresh and brackish SGD inputs often produce a marked stratification that acts as a biological barrier, protecting and isolating the species that live in this environment. Since the two study sites have karstified geologies, many caves and fissures in Mallorca and Salento have been described to host endemic species. For instance, the "Cova de sa Gleda" in Mallorca, known as the longest submarine cave in Europe, hosts the endemic amphipod species *Bogidiella balearica*, known to live only in the eastern karstic area of the island (Fornós et al., 1989). Similarly, the Grotta Zinzulusa and Grotta Lu Bissu in Salento host the endemic isopod of the Puglia region *Trichoniscus ruffoi* or the endemic acarus *Lohmannella stammeri*, among others (Inguscio et al., 2009). It should be noticed that the biological control outcome can usually be perceived in synergy with the provision of food. As explained before, numerous species used for food provisioning such as mullets (*Mujil cephalus*), eels (*Anguilla anguilla*), croakers (*Argyrosomus regius*) or mussels (*Mytilus galloprovincialis*) are sustained by the regulating biological control provided by SGD (Eloisa Malagoli, 1977; Encinas, 2014; QuiValleditria, 2023; Soler, 2004).

- Human Disease

The regulating ES is the least studied ES provided by SGD and coastal societies seem to be less perceived by local users than the provisioning and cultural ES (as shown in the next section). Considering the biological control, only 17 (12%) and 27 (41%) cases have been reported in Mallorca and Salento, respectively. Examples of biological control provided by SGD include the anchialine environments, which are clearly linked to SGD and

are characterized by constant physicochemical conditions that allow certain species to survive in those environments. In addition, fresh and brackish SGD inputs often produce a marked stratification that acts as a biological barrier, protecting and isolating the species that live in this environment. Since the two study sites have karstified geologies, many caves and fissures in Mallorca and Salento have been described to host endemic species. For instance, the "Cova de sa Gleda" in Mallorca, known as the longest submarine cave in Europe, hosts the endemic amphipod species *Bogidiella balearica*, known to live only in the eastern karstic area of the island (Fornós et al., 1989). Similarly, the Grotta Zinzulusa and Grotta Lu Bissu in Salento host the endemic isopod of the Puglia region *Trichoniscus ruffoi* or the endemic acarus *Lohmannella stammeri*, among others (Inguscio et al., 2009). It should be noticed that the biological control outcome can usually be perceived in synergy with the provision of food. As explained before, numerous species used for food provisioning such as mullets (*Mujil cephalus*), eels (*Anguilla anguilla*), croakers (*Argyrosomus regius*) or mussels (*Mytilus galloprovincialis*) are sustained by the regulating biological control provided by SGD (Eloisa Malagoli, 1977; Encinas, 2014; QuiValleditria, 2023; Soler, 2004).

7.4.4. The cultural ES-SGD

- Recreational activities

Outcomes related to cultural ES have been largely reported, especially those linked to recreational activities, which account for 42 (30% of total) and 43 (65%) cases in Mallorca and Salento, respectively. Groundwater discharging into the sea, as reported by interviewees produces specific characteristics that can attract locals and visitors. For instance, local swimmers in Mallorca recognize different sites such as "Es dolç" or "Cova es Coloms in Cala Varques" as special spots to go swimming in the sea in summer months, due to the relatively cold waters of these sites produced by groundwater inputs (Encinas, 2014). Also, in Salento, there are numerous sulfuric coastal springs that provide this same outcome but with warm waters. These features also attract tourists, since differences in temperature produced by SGD are advertised on commercial and official web pages (Playas Baleares, 2023). SGD also attracts the interest of excursionists that visit these springs (Encinas, 2014), or tourists that get covered in the mud that the SGD produces humidifying the clays at the shore in the “Cova des Xalar” (Mallorca) (Maestre-Janer, 1980). Other leisure activities such as scuba diving or cave diving are also attracted by sites where SGD occurs due to the intricate morphology often linked to karstic SGD springs and the high biodiversity and richness that these sites host. For instance, diving companies from Mallorca (Tramuntana Diving, 2023) or Salento (Scuba Diving Otranto Salento, 2023) offer guided trips into the caves (e.g., "Coves de ses fontanelles" or "Grotta Lu Lampiune", respectively). The species richness in SGD-influenced sites additionally constitute an attraction for locals enjoying recreational fishing both in Mallorca and Salento (Itineraridipesca, 2023).

- Sense of place or toponymies

The outcome related to the sense of place was also very common in Mallorca and Salento, where up to 66 (47%) and 13 (20%) sites, respectively. The sites where the ES provided by SGD are perceived can represent a reference point for the coastal societies who live there. The most reported examples by interviewees were those related to the provision of fresh water for coastal societies, since has always been a scarce resource in the Mediterranean basis. Numerous beaches, caves, or localities are named after the fresh discharge of groundwater, since water resources constitute a valuable resource (e.g., “Es Dolç” or “Acquaviva di Marittima” in Mallorca (Gran Enciclopèdia de Mallorca, 1989) and Salento (FAI, 2023), respectively). Other SGD-related names originate from antique cultures, like the cave of na

Juliana (Mallorca) which derives from the term springs in Arabic (Encinas, 2014). Several SGD-influenced sites have also been named after the biological species that live therein (e.g. Cova de ses llises in Mallorca (Encinas, 2014) (the cave of the mullets) or Spiaggia di Lido Conchiglie (beach of the shells) in Salento (SpiaggeSalento, 2023)). Other sites are named after the activities conducted owing to SGD (e.g. "Rentador de sa senyora" (the woman's laundry site) or "Sa font de sa Pesquera" (Spring of the fishery) in Mallorca (Aguiló, 1996; Encinas, 2014)).

- Myths and tales

The myths and tales outcome accounted for a total of 13 (9%) and 11 (17%) sites in Mallorca and Salento, respectively. Submarine groundwater discharge has inspired many cultures to attribute mythical and magical properties to those waters due to their unknown origin and differentiated properties in comparison to seawater. Common beliefs exist on the healing powers of SGD sites in both Mallorca and Salento regions (Inventari de fonts a Mallorca, 2023; Malagoli, 1977; Rizzelo, 2018). In Salento, some SGD points are related to the Greek gods due to due to the strong historical influence of the Greek culture; e.g., "Fiume Tara" takes the name after Poseidon's son, Taras, whose legend tells that Taras went into the river to join his father after building the city of Taranto. In Mallorca folklore, different tales about coastal sites are related to SGD. For instance, the "Cova Xica des Drac" and the "Cova del Dull" (Encinas, 2014) have tales related to the morphology of these systems (reminding a water dragon and the long hair of a goddess, respectively), which are produced by SGD. In addition, due to the importance of the Catholic religion, several SGD sites in both Mallorca and Salento are related to miracles or actions performed by figures of the catholic religion (e.g. "Sa Cova Plana" (Mallorca) (Encinas, 2014) and "Fiume Chidro "(Salento) (Malagoli, 1977) both have stories with Saint Peter related to SGD).

- Cultural heritage

The cultural heritage outcome has been reported in 26 (19%) and 28 (42%) cases for Mallorca and Salento, respectively, often in synergy with food provisioning. Coastal societies of Mallorca and Salento have interacted with SGD for millennia, and today there is still knowledge, heritage buildings and objects, culture and perspectives linked to these past interactions. A great example of such inheritance is the different fishing spots that today's ancestors used as fisheries for commerce, and which today are used for recreational fishing (see Recreational activities). In Mallorca, different mine springs to obtain fresh water, the old paper industry (Salvator, 1884) or the archeologic ceramic remains (Coello, 1850; Encinas, 2014; Salva, 1997) which were used to recover groundwater from caves; and, in Salento according to interviewees, the bacini to drain the wetlands, the surveillance towers that guarded the springs (Torri Costiere del Salento, 2023) or the remains of the aquaculture industry (Malagoli, 1977). However, most of the cultural heritage remains on the intangible inheritance, such as the places named after the SGD, where references to the old practices people used to have can be found (see Sense of place). This inheritance does not only refer to the old usage, but also the folklore, myths, and tales that remain from the past cultures, where those waters could be sinuous water dragons coming out of the caves or radiant long hair from a goddess falling into the sea (Encinas, 2014) (see Myths and tales).

- Aesthetical values

The aesthetical outcome, which is the most subjective outcome, was reported in 10 (7%) and 7 (11%) cases in Mallorca and Salento, respectively. The aesthetics linked to SGD have become an inspiration to different individuals to write, sing or paint about it. The different artistic authors that have seen their inspiration motivated by the SGD, describe it as beautiful, intriguing, or magnificent (Mateos and González Casasnovas, 2009; Serra, 1991). However, the aesthetic value of SGD in most sites is not exclusively expressed by artists, but rather by the people interacting with these sites (Villaggi Estivi, 2023). Some representative examples are “Sa porta del Cel” (Heavens Door), a cave in Mallorca whose name refers to the aesthetics of the geological features created by SGD (Gràcia et al., 1997); or the "Fiume Galeso" (Salento), a SGD spring from which the city of Taranto was greatly dependent hydrologically and economically for centuries and represents a great value for the habitants of the city.

7.5. Discussion

7.5.1. Differences in societies' perceptions of ES provided by SGD between case studies

The peninsula of Salento and the island of Mallorca are great examples of ES's diversity and richness related to SGD. Both regions are located at the shores of the Mediterranean Sea, influenced by similar cultures and host karstic systems which favor a large number of located SGD spots along the shore (Balacco et al., 2022; Giménez et al., 2014). The proportion of the different ES categories for both sites (Figure 7.3) is relatively alike and they have many similarities that have been presented in the previous sections. However, the comparison of the outcomes for both sites reveals that there are important differences that respond to geographical, historical, and cultural differences between these two study sites (Figure 7.3).

The provisioning ES in both sites is dominated by the freshwater outcome since both sites lack rivers and obtain most of their water resources from groundwater. However, there is a relevant difference between the proportion of food services in Salento in comparison to the island of Mallorca. Such difference is likely related to the different historical practices in both regions. In Salento, its society has historically been profiting from the SGD sources as hotspots for fisheries and aquaculture, thus the second most iconic sector after tourism is fisheries in Salento (Mulazzani et al., 2016). However, in Mallorca although many areas profited from SGD as fishing spots, those have never represented an important industry for the island and thus seem to have been less explored than in Salento.

In the Regulating ES category, there are also differences in the relative importance of the outcomes depending on the study site. These differences are most likely linked to two different patterns: The higher incidence of biological control in Salento is likely related to the major number of sites used for food provisioning, and thus to the higher perception of coastal societies on habitat-related issues. The higher presence of sites with human disease control in Mallorca is likely influenced by the higher contribution of freshwater provisioning ES, and thus by a higher perception of issues related to water quality. In addition, a more developed tourist industry along the coast is likely to increase the probability of cases where SGD spots can be polluted and therefore reported (Gössling et al., 2012). Thus, the bigger proportion of cases in Mallorca could also be influenced by the higher tourist pressure.

In the category of cultural ES, leisure activities represent the most prevalent outcome in Salento and the second one in Mallorca. The tourism industry in both sites has profited from goods and services provided by SGD (e.g., diving companies or tourism agencies that promote sites or beaches influenced by SGD). The higher proportion of this outcome in Salento than in Mallorca responds to the rise of recreational fishing spots in Salento (Mulazzani et al., 2016). Instead, in Mallorca the most recurrent outcome was the sense of place which is less prevalent in Salento. The difference may respond to the numerous freshwater points along the coast of Mallorca, which have been documented through the grey literature to be an important water resource for its inhabitants. Indeed, ~50 % of the total "sense of place" outcome inventoried in Mallorca contains a reference to the word "dolç" (fresh water in Catalan). On the cultural heritage and religious ES, both sites have experienced the influence of different cultures characteristic of the NW Mediterranean region, from the Greek and Roman empires, the Arabic caliphates, or the catholic kingdoms. However, in each site, the different cultures that passed through these areas left different references related to the SGD (e.g., more references to Greek gods in Salento; more references to Arabic eras in Mallorca).

7.5.2. Historical and present Ecosystem Services provided by SGD

Different coastal societies perceive the ES provided by SGD in a diverse manner. Besides this spatial variability, also show a large variability in time, which is an indicator of the dynamism of the ES of SGD that are not only associated with physical or natural factors but also with socio-economic and cultural elements. Thus, ES that were perceived in the past may become ecosystem functionalities since the perception of the coastal society changes as it evolves culturally and technologically (Costanza et al., 2017). As a consequence of this evolution, new ecosystem services can be perceived by coastal societies or the ES provided by SGD can even disappear (Queiroz et al., 2017).

As part of this review, we have compared the historical evolution of the outcomes provided by SGD on the island of Mallorca and the region of Salento. As shown in Figure 7.4, most ES outcomes experience a relative increase from past to present. This is mainly an artifact produced by the significant reduction in the relative importance of outcomes such as provision of freshwater and religious and myths in both regions. The reduction of freshwater provisioning may be related to three important changes that both sites have experienced during their societal evolution. First, fresh water in both areas has historically been a precious good due to the lack of surface sources and SGD represented a major fresh water resource for coastal communities. Although there existed other methods as cisterns during all historical periods (Mays et al., 2013), this dependence changed in the second half of the XX century when most southern European countries started to have canalized tap water for domestic consumption (García-Ruiz et al., 2011). Second, groundwaters have been historically a soil destabilizer for buildings and infrastructures and an important focus of human diseases (such as malaria; Boualam et al., 2021; Sánchez-Carrillo and Angeler, 2010). Coastal societies have drained, blocked, or deviated groundwaters from coastal lagoons or coves since the Roman era to prevent these issues. The massive transformation of Mediterranean coastlines during the last decades to develop the tourism industry (Segreto et al., 2009) has produced the drainage of large groundwater bodies, reducing thus the availability of this freshwater resource (García-Ruiz et al., 2011). Third, the increased human pressure in coastal areas and overexploitation of coastal aquifers over the last century has produced seawater intrusion and pollution of coastal aquifers (Michael et al., 2017). A reduction in the quality of fresh groundwater has resulted in a reduction in the use of groundwater resources for freshwater provisioning (García-Ruiz et al., 2011).

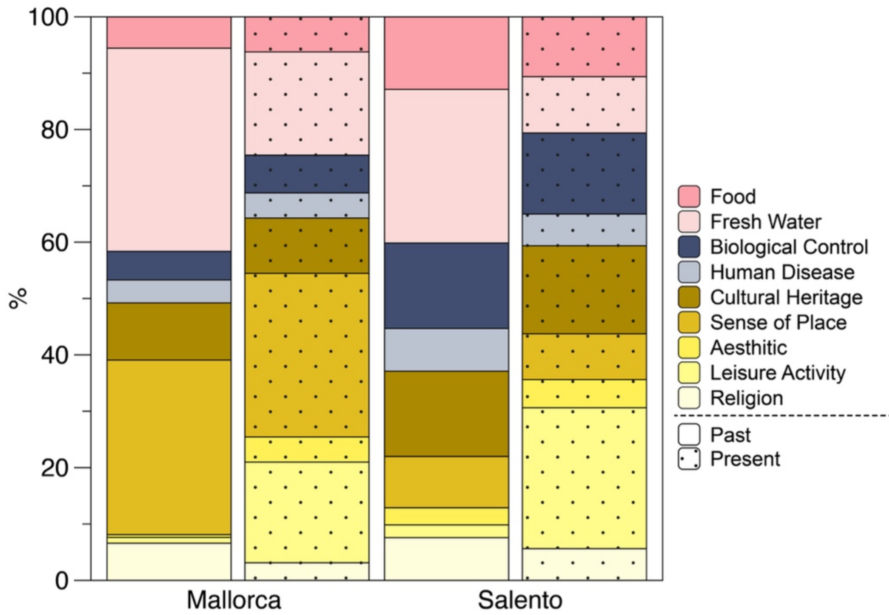

Figure 7.4. Historical change on SGD-ES outcomes in Mallorca and Salento.

On the Regulating ES we observed an important increase in biological control. Such change mostly responds to the change of professional fishermen towards leisure fishermen. Such change, reported in both study sites (Morales-Nin et al., 2005; Mulazzani et al., 2016), responds to a change in coastal societies' main economic drivers which have changed towards the tourism industry (Garcia and Servera, 2003; Mulazzani et al., 2016). Therefore, most fisheries are now frequented by fishermen who practice this activity as a sport. In addition, the technological techniques that allow people to dive into the oceans have allowed exploring inaccessible SGD areas, which in turn have become hotspots for diving companies. In this direction, the cultural SGD-ES have experienced a general increase in people's perception. On the one hand, such change relies on the coastal tourism industry, which profits from the leisure activities that SGD offers and which has given bigger visibility to this process to be perceived. A clear example can be found in Mallorca with the beach s'Estany d'en Mas, which is related to the water accumulated by

SGD, and now has changed to Cala Romantica, a name given to increase the attractiveness of the beach towards the visitors[26]. On the other hand, the strong resilience of the cultural heritage and toponymy in these areas (Ordinas Garau and Binimelis Sebastián, 2021) has resulted in the preservation of this ES (see examples in section 4.4.2). The Mediterranean regions (such as Spain and Italy) have undergone significant transformations during the last fifty years, including changes in the domain of myths and religion. Consequently, there has been a noticeable decline in religiosity in these areas, resulting in consequential shifts in political and social structures, such as the rise of non-confessional countries and a preference for cohabitation over traditional marriage (Berger, 1985; García Pereiro et al., 2014). However, those countries have also become a religious tourism system, that does not only rely on the devotion of their visitants anymore but due on the historical and artistic values (Nolan and Nolan, 1992). Thus, those transformations may have also been accompanied by a loss of the societies toward acknowledging and identifying the ES related to myths and religion in turn to the leisure activity that tourism implies. Indeed, many of the remaining ES provided by SGD related to myths and religion are nowadays promoted by the tourism industry, which are presented in travel guides or tourism websites.

7.5.3. Study limitations

The approach that we have followed to assess the ecosystem services provided by SGD have several limitations and biased. The main limitations that we have identified are:

1) The availability of information from the present (e.g., last 50 years) is much higher than the information available from the past. This prevents conducting an accurate historical evolution of ES provided by SGD, particularly when referring to absolute values.

2) Scientific literature mostly focuses on provisioning ES categories, whilst traditional knowledge is likely to incorporate the cultural dimension. The proportion of each category can thus be biased depending on the relative contribution of the different information sources used in the study (i.e., higher scientific literature and thus the proportion. Similarly, the regulating does not need a specific interaction with humans, they can be more independent since they control environmental factors which are secondary to human contact. Such difference in comparison to the cultural and provisioning that does need such interaction creates a significant difference in the perception societies will have towards this ES category (Bürgi et al., 2015).

3) There exists a notable disparity in the number of cases examined across different regions, which can be attributed to the unequal amount of time allocated to Mallorca compared to Salento, owing to logistical and temporal constraints during the course of the study. As a result, while the findings presented offer valuable insights into the perception of ES provided by SGD in these two Mediterranean societies, it is crucial to acknowledge that there may be additional sites that were not included in this investigation, which could potentially expand the information presented in this study.

Chapter 8 *Conclusions and future perspectives*

8.1. Conclusions

The aim of this thesis was to advance understanding of the social dimension of Submarine Groundwater Discharge (SGD), contributing to address the existing disconnection between the natural and social sciences in this field. This involved examining the impacts of human activities on the fluxes of solutes supplied by SGD to the coastal ocean as well as evaluating the existing evidence on ecosystem services associated with SGD. From one side, metal and nutrient fluxes driven by SGD have been quantified in two areas heavily impacted by mining activities and tourism, respectively. On the other side, academic literature and local knowledge concerning the perceived social implications of SGD have been analyzed from an ecosystem services perspective. Collectively, this thesis has allowed obtaining a comprehensive understanding of the social dimension of SGD, including both the human impacts on SGD and the influence of SGD on coastal communities. This thesis also has identified opportunities for future research and management practices that address the disconnection between the natural and social sciences in the SGD field. Detailed conclusions for the different chapters of this thesis are summarized below.

First, findings from this thesis confirm that anthropogenic activities can have a determinant impact on SGD-driven fluxes. As it was shown in Chapters 4 and 5, polluting anthropogenic activities can induce important dissolved metals and nutrients into the coastal ocean, having a significant impact on their ecosystems. Moreover, a relevant contribution of this thesis is that the diversity of pathways of SGD plays an important role in diversifying the different solutes driven into the coastal ocean. In Portmán Bay, whilst the short- and small-scale recirculation of coastal waters through the mine tailings deposit (PEX) favors the remobilization of large amounts of dissolved metals, the discharge of anoxic low-salinity groundwaters (SGD) contributes to the supply of dissolved Fe. However, concentrations of dissolved metals in coastal waters are significantly reduced due to (i) the removal of dissolved metals before discharging to the sea by an "iron curtain" that acts as a geochemical barrier, and (ii) the co-precipitation of dissolved metals with iron hydroxides supplied by SGD. Differentiating the respective pathways of PEX and SGD becomes necessary to properly assess dissolved metal fluxes to the coastal sea, as PEX mainly remobilizes dissolved metals stored in the uppermost part of the deposit, whereas SGD affects larger spatial scales. The differentiation and characterization of both pathways are thus critical to understanding the transfer of metals in anthropogenic polluted coastal zones, allowing an appropriate assessment of their impacts on coastal biogeochemical cycles.

Second, coastal areas where leisure activities take place can be negatively affected by SGD in specific seasons. The seasonal fluctuations in tourism can result in changes in the volume of wastewater treated at local wastewater treatment plants (WWTP) and the volume of effluents injected into a highly permeable aquifer, which will cause alterations in aquifer hydrology. This, in turn, leads to an increase in groundwater discharge to nearby coves and the supply of nutrient fluxes. As a result of these inputs of SGD-driven nutrients, inventories of DIN and DIP in the coastal waters of Deià increase significantly during the high tourist season, i.e., summer months. These high nutrient fluxes can contribute to algal blooms in the cove, leading to the degradation of seawater quality for local swimmers and tourists. The anthropogenic origin of SGD-driven nutrients can also be traced in seawater and seagrass meadows, as evidenced by high $\partial^{15}N$ signatures indicative of polluted areas. Chapter 5 demonstrates that the high pressure exerted on coastal areas by tourism activities can lead to alterations in SGD fluxes, thereby endangering coastal ecosystems and the services they provide. This finding is particularly relevant for highly touristic regions such as the Mediterranean coast and specific areas such as the Illes Balears. Therefore, these results provide an opportunity for researchers, managers, and policymakers to better understand and manage coastal areas under high anthropogenic pressure by considering the potential role of SGD.

Third, this thesis develops and applies for the first time a conceptual and analytical framework based on the Millennium Ecosystem Assessment (MEA, 2005) for identifying and classifying the ecosystem services (ES) provided by SGD and their effects on the well-being of local societies (Chapter 6). This framework provides new evidence on the social implications of SGD. Results show that SGD, from its use as a water resource to its cultural influence, is deeply rooted in many coastal societies, and its zones of influence have a significant impact on the local communities. Thus, findings presented in Chapter 6 suggest that coastal ecosystem services linked to SGD are crucial for many coastal societies, especially in the context of climate change. However, the different ES provided by SGD are rarely in a win-win scenario and trade-offs among different ES categories are common. Such trade-offs may lead to social confrontation or conflicts, necessitating further interventions in terms of policies and management strategies. Even though the evaluation of monetary and non-monetary services is not addressed in this thesis, it is worth noting that the Ecosystem Services framework places significant emphasis on valuing these services. As such, the framework proposed in this thesis has the potential to expand and incorporate this aspect of the Ecosystem Services framework in the future. Thus, Chapter 6 offers new evidence and understanding of SGD from a social-ecological systems perspective, which brings an opportunity to explore the different roles of SGD in societal well-being and better understand the relations between SGD and society through an interdisciplinary approach.

Fourth, Chapter 7 provides a comprehensive understanding of the perception of Mediterranean societies towards SGD, including its uses and its role in coastal communities. This is obtained by integrating the information available in the scientific literature, grey literature and traditional knowledge. Findings show that the limited historical documentation on SGD causes bias in reporting present ecosystem services (ES) compared to the past in the two studied areas (Mallorca and Salento). SGD-related ES are sensitive to localities due to strong dependence and variability at spatial scale despite their distribution along both study sites' shores. It also offers a historical evolution of the ES provided by SGD, which can often change as a consequence of temporal cultural and technological variability. Finally, results from Chapter 6 show that peoples' perceptions towards SGD can also change due to the different economic pressures, which introduces an interesting dimension to guide future research on this topic.

In sum, this thesis is an interdisciplinary walkthrough of the strong bounds between SGD and coastal societies, a topic that has received very little attention to date. By examining the impact of highly polluting anthropogenic activities on this process and constructing a framework for identifying and analyzing the social-ecological system underlying SGD, this study provides both solid scientific evidence and robust methodological guidance on the influence of SGD on coastal societies from a social-ecological approach.

8.2. Future perspectives in management and research

Submarine Groundwater Discharge has been largely investigated during the last three decades and numerous recent reviews have highlighted the findings from a natural sciences perspective (Adyasari et al., 2023; Garcia-Orellana et al., 2021; Lecher and Mackey, 2018; Santos et al., 2021; Taniguchi et al., 2019). However, as it has been presented in this thesis, little information was available on the linkages between natural and social sciences in the SGD field. The interdisciplinary approach followed in this thesis represents a novelty and brings new knowledge and evidence to guide policy and management strategies regarding SGD. The following topics have been identified as key areas for future research on the social dimension of SGD:

- *Policies and management.* Management strategies and policies to manage coastal resources and ecosystems have been implemented since the 70's. However, although the Integrated Water Resource Management (IWRM) (Petit and Rivière-Honegger, 2006) and Integrated Coastal Zone Management (ICZM) (Deboudt et al., 2005) are being applied in different parts of the world, especially Europe, there are still important gaps in these strategies (Erostate et al., 2020). Both management protocols consider an integral vision of the coastal waters, and SGD should be regarded as one important component of the connectivity between land and oceans. Cases such as those described in Chapters 4 and 5 exemplify the linkages between human activities, groundwater and the coastal ocean. In both study cases, the infiltration of dissolved solutes resulting from human activities into coastal oceans remains unmonitored. Furthermore, the absence of monitoring is accompanied by the local manager's disregard for SGD as a significant process within coastal waters. Consequently, the potential of SGD is undervalued, and no comprehensive policies or management strategies exist that adequately address SGD's role in the prosperity of coastal societies. To date, only a single instance exists in the United States where a judge has ruled in favor of preserving the hydrological land-ocean continuum, with SGD serving as the subject of preservation and monitoring. In this sense, there is a lack of communication between legislators, lawyers, and scientists in order to develop integrative management and political actions that integrate SGD.

- *Valuation of SGD.* Monetary and no monetary valuation of SGD are needed in order to promote future management and political interventions. To date, only four studies (Burnett et al., 2018, 2015; Duarte et al., 2010; Pongkijvorasin et al., 2010) have attempted to monetarily evaluate localized SGD (case studies in Japan and Hawaii). There are no studies where non-monetary evaluations have been made in contrast to other land-ocean pathways such as rivers (Boithias et al., 2016; Brouwer et al., 2016), glaciers (Cook et al., 2021) or streams (Marsh et al., 2011; Yaacovi et al., 2021). Important efforts can be made in the coming future in order to properly address the value of SGD for coastal societies. The present thesis constitutes an initial contribution towards this objective. The ecosystem services framework provides a wide and common ground where social-ecological systems can work together to conceptualize the different interactions where ecosystems intervene for the better well-being of societies (Costanza et al., 2017).

- *From Ecosystem Services to Nature Contribution to People.* One of the key points from the ES framework that has been recurrently criticized (which has not been addressed in this thesis), refers to the above mentioned valuation of the ES (monetary and non-monetary). This criticism arises from the perspective that while the MEA (2005) facilitates accounting for tangible services such as food or water supplies, it is unclear and ambiguous on non-tangible services such as those related to cultural services (Díaz et al., 2018). Thus, the Intergovernmental Platform on Biodiversity and Ecosystem Services (IPBES) has suggested the approach of Nature Contribution to People framework (NCP) in order to increase the inclusivity of scientific research, particularly by giving greater consideration to the humanities and social sciences, as well as incorporating knowledge systems used by indigenous peoples and local communities (Ellis et al., 2019). Thus, this framework does not exclude the ES but integrates them as part of the new conceptual model. Social-ecological academics continue to advance their research and future SGD investigations should try to integrate these advancements in social sciences in order to continue progressing towards a more comprehensive understanding of SGD.

- *Spatial, temporal and social biases.* Over the past decade, the prevalence of SGD has been discussed and documented, with much of the research taking place in areas where groundwater flow is anticipated and under base-flow conditions. This limits the ability to extrapolate findings from local samplings on a temporal and spatial scale (Adyasari et al., 2021; Diego-Feliu et al., 2022; Luijendijk et al., 2020; Santos et al., 2021). Likewise, during the elaboration of this thesis, the SGD-ES and derived social implications are locally dependent on time, space and social context. The same SGD-ES can be perceived as a different category in different historical moments, sites, or by different individuals or groups (see Chapter 7). Therefore, the inclusion of a social perspective in SGD introduces an additional level of complexity that must be carefully untangled to effectively scale up the numerous local studies conducted to date. To do so, alongside the development of regional and global approaches to quantify SGD, a broad and continuous global network should be developed to gain insights into the perception, utilization, and conservation of the ecosystem services provided by SGD.

- *A global change perspective*. This thesis provides, for the first time, an overview and classification of the Ecosystem Services linked to SGD (SGD-ES), as well as the synergies and trade-offs between different SGD-ES. However, the scarcity of literature relating SGD to ES and the fact that the results obtained provide a point-in-time view, means that we only understand a small fraction of the current interactions between coastal dwellers and SGD-ES. Importantly, the links between SGD and ES are of a dynamic nature, implying that their synergies and trade-offs are likely to continuously evolve together with societies and the coastal environment, both at a local, regional and global scale. This is particularly relevant in the actual context of global change. In this regard, the overpopulation of coastal areas is likely to continue increasing, rising the demand of fresh water and therefore the provisioning SGD-ES. In addition, fresh resources would be prejudiced by the likely decrease of mean precipitations, due to climate change, and increase of evapotranspiration in many mid-latitude and subtropical regions (IPCC, 2023). Such change could involve a major reduction on the fresh SGD input into the oceans (Kundzewicz and Döll, 2009; Stigter et al., 2014). Sea level rise is also expected to reach up to ~0.8 m by 2100 (IPCC, 2014), affecting large coastal areas and reducing the hydrologic gradient and consequently the quantity of fresh SGD (Robinson et al., 2018). Moreover, important disruptions are expected in the biogeochemical cycles due to contamination by multiple anthropogenic factors (e.g., nutrient pollution of aquifers due to agriculture, mining and industrial wastes and waste waters from growing cities) (Lafortezza and Chen, 2016). Such changes in coastal aquifers will directly affect the quality of SGD inflowing into the coastal ocean (e.g., fluxes of nutrients, trace metals, contaminants) and thus the role of SGD on the nutrient cycle, productivity, or habitat support. Sea level rise will also likely affect nutrient cycling and productivity in coastal areas, mobilize terrestrial anthropogenic pollutants to the sea and critically impact those habitats with low-salinity conditions that are supported by SGD (Danielopol et al., 2003; Michael et al., 2013; Pope et al., 2011). Global change will thus definitely impact the Supporting Ecosystem Services supported by SGD, including water cycle, nutrient cycle, primary production, or habitats. Once the Supporting ES are affected, all the other dependent ES could be affected by cascading effects. For instance, the reduction of the habitats, due to the lack of freshwater, could make disappear the biological control, reduce the amount of food due to a reduction of productivity or displacement of species. In addition, some of the cultural ES could disappear or be endangered (e.g., leisure activities related to the fresh SGD). Therefore, to develop new management programs to preserve SGD-ES for the next generations, it is necessary to study the evolution of SGD-ES under the current global change scenario, with special emphasis on new synergies and trade-offs.

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Appendix

A.1. Dissolved metal concentrations in seawater.

Sample	Ag	Cd	Co	Fe	Pb	Zn
				nM		
W1	206	3.6	0.3	7.7	5.6	488
W2	33	0.5	0.2	4.6	3.8	53
W3	15	0.4	0.2	4.9	3.0	24
W4	13	0.3	0.2	4.4	2.4	18
W5	11	0.3	0.2	4.0	1.6	12
W6	12	0.3	0.2	5.2	1.6	16
W7	7	0.2	0.2	3.7	1.2	6
W8	8	0.2	0.2	3.7	0.9	4
C1	n.m	n.m	n.m	n.m	n.m	n.m
C2	30	0.5	0.2	4.1	2.8	51
C3	15	0.3	0.2	3.9	1.9	20
C4-sup	8	0.2	0.1	5.3	1.4	8
C4-7	8	0.2	0.1	5.3	1.0	10
C4-bot	9	0.3	0.2	4.6	1.0	n.m
C5	9	0.2	0.2	n.m	1.2	8
C6-sup	8	0.2	0.2	n.m	1.3	8
C6-7	6	0.2	0.2	4.2	0.6	5
C6-bot	5	0.2	0.2	4.1	0.6	4
C7	9	0.2	0.2	n.m	1.3	9
C8-sup	6	0.2	0.2	n.m	1.1	6
C8-7	5	0.2	0.2	3.7	0.4	2
C8-bot	7	0.2	0.1	4.5	0.5	3
E1	124	2.6	0.2	5.0	5.3	403
E2	45	0.8	0.2	4.7	3.2	124
E3	19	0.3	0.2	4.3	2.3	24
E4	14	0.3	0.2	5.5	1.8	13
E5	10	0.3	0.2	7.4	1.9	10
E6	8	0.2	0.2	5.9	1.4	10
E7	9	0.2	0.2	4.2	1.5	9
E8	5	0.2	0.2	6.3	1.2	9

n.m: Not measured

A.2. Nutrient concentrations in waters during April and August samplings.

Sample	Season	NO_3^-	NO_2^-	NH_4^+	SiO_2	PO_4^{3-}	TN	TP
		μmol L^{-1}						
WWTP	April	753	33.8	194	40	73.2	1581	116
EPS1	April	35	0.02	3.8	48	0.05	39	0.7
EPS2	April	30	0.07	0.9	31	0.01	36	0.5
TOR	April	72	1.04	36	9.1	0.78	16	0.5
1	April	7.6	0.15	6.1	5.3	0.43	12	0.3
2	April	0.8	0.04	1.4	1.5	0.02	18	0.5
3	April	1.5	0.03	1.2	1.3	0.03	10	0.4
4	April	2.7	0.06	0.2	3.1	0.10	20	0.4
5	April	2.0	0.05	0.2	2.3	0.07	10	0.4
6	April	1.2	0.07	7.4	1.2	0.01	20	0.4
7	April	2.8	0.08	4.1	2.1	0.11	16	0.4
8	April	1.2	0.03	1.2	1.6	0.02	7.9	0.5
9	April	2.3	0.03	2.7	1.3	0.05	28	0.2
10	April	3.7	0.14	4.1	2.1	0.12	16	0.4
11	April	4.3	0.02	0.6	2.3	0.25	10	0.4
12	April	0.4	0.05	2.3	0.8	0.01	7.9	0.2

OCN	April	0.5	0.02	1.0	0.8	0.00	16	0.5
WWTP	August	278	88.0	1064	25	66.3	1646	151
TOR	August	0.5	0.35	16	17	10.5	70	15
LFS	August	1.5	0.52	242	17	17.9	351	29
1	August	0.4	0.07	14	2.9	0.74	31	1.0
2	August	0.3	0.03	2.5	1.4	0.32	27	0.5
3	August	0.4	0.03	3.1	1.1	0.20	20	0.5
4	August	0.9	0.06	11	0.6	0.72	28	0.8
5	August	0.4	0.03	1.4	0.9	0.11	12	0.5
6	August	0.5	0.03	3.9	1.0	0.26	13	0.5
7	August	0.9	0.08	16	2.7	1.50	35	1.9
8	August	0.5	0.02	4.6	1.0	0.25	12	0.4
9	August	0.4	0.04	2.6	1.0	0.25	13	0.6
10	August	1.3	0.17	57	6.8	4.78	80	6.8
11	August	0.4	0.04	2.8	0.9	0.27	21	0.4
12	August	0.4	0.03	1.4	0.8	0.12	12	0.4
OCN	August	0.2	0.02	2.3	0.6	0.03	19	0.5

A.3. SGD-ES Systematic search at WoS by ES category. All searches correspond to the "Submarine Groundwater Discharge" OR "Submarine Springs" and all the corresponding keywords for each ES category outcome. The * corresponds to any termination for that word.

Ecosystem service category	Ecosystem service outcome	Number of results	Searching criteria ("Keywords")
SUPPORTING	Water cycle	21	Water cycle Hydrological cycle
	Nutrient cycling	781	Nutrient Nitrate Nitrite Phosphate Ammonia Silica Carbon Methane Micronutrients Macronutrients
	Primary production	198	Primary produc* Chlorophyll Phytoplankton
	Habitat	76	Habitat Zonation
PROVISIONING	Freshwater	21	Water provision Drinking water Water mining
	Food	89	Food Fishermen Fishing Fishery Sea food Farm Aquaculture Seaweed culture Fish culture
REGULATING	Biological control	9	Biological control Zonation

	Human diseases	110	Disease Bacteria Human health Viruses Fecal E. coli Escherichia HAB Human diseases Harmful algal
CULTURAL	Recreational	32	Recreational Tourism Ecotourism Recreation Vacation Leisure Bathing Swimming Diving Navigation
	Sense of place	0	Sense of place Toponym Named after
	Cultural Heritage	19	Cultural Heritage Local knowledge Indigenous knowledge Traditional knowledge Traditions Culture
	Religion	0	Religi* Myths Tales Beliefs Tradition
	Aesthetic	20	Aesthetic Inspiration* Culture Education Arts Poetry Poem

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A.5. Semi-structured interview model.

1. Knowledge and localization of the SGD spring
    1.1. Did you know about the discharge of groundwaters into the sea? (If needed show video and photos of SGD examples)
    1.2. Do you know an area of Mallorca/Salento that has this type of discharge?
    1.3. Can you locate the site on a map?
    1.4. Do you know any coastal springs?
    1.5. Is there any that is submarine?
2. Characterization of each spring
    2.1. Source of information
        2.1.1. How did you learn about the spring?
    2.2. Name
        2.2.1. Does it have a name?
        2.2.2. Has this name changed over time?
    2.3. Discharge
        2.3.1. Is the discharge produced all year long?
        2.3.2. Do you know if the discharging waters are fresh or salty?
    2.4. Ecological impacts
        2.4.1. Do you know if there is more life? More fish, mollusks, birds, etc?
        2.4.2. Are there certain species that live in these influenced areas?
        2.4.3. Are the discharging waters smelly?
        2.4.4. Have you ever seen a change of color of the surrounding waters?
        2.4.5. Every when does it happen?
    2.5. Anthropic interactions
        2.5.1. Is there any sign or post that marks the discharging point?

2.5.2. Is there any construction that channelizes the discharge?

2.5.3. Do you know if there is any tale, myth or religious meaning related to the spring?

2.5.4. Does anyone use the spring for any reason?

2.5.5. And in the past? (For hygiene, drinking, cattle)

2.5.6. Is there any future action that you know on the discharging point?

2.5.7. Has ever created any kind of problem or conflict between different groups or citizens?

2.5.8. Do you consider that it has enough value to be known about or be taught to future generations?

2.5.9. Do you know if any song, painting or other inspirational or aesthetical value is related to it?

3. New grey literature sources

3.1. Do you know where I could find any documentation related to the spring?

3.2. Do you know any document physical or electronic where I could find more information about this process?

3.3. Do you know anyone who might have more information?