

**Tracing submarine groundwater discharge pathways
and their ecological impacts using radium isotopes**

Júlia Rodríguez Puig

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**Tracing submarine groundwater discharge pathways and
their ecological impacts using radium isotopes**

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Abstract

Submarine groundwater discharge (SGD), the subterranean counterpart of rivers, has long been acknowledged by ancient societies as a valuable source of freshwater. However, its scientific understanding has only advanced in recent decades, largely due to its hidden and diffuse nature, the limitations of available methodologies, and the complexity of the process, which includes both terrestrial groundwater discharge and seawater recirculation through the sediments. These two broad components encompass multiple pathways that vary across space and time, making SGD highly heterogeneous. The importance of SGD is now recognized from local to global scales, with hydrological, biogeochemical, and social implications. The transition from a single-pathway to a multi-scale perspective of SGD has opened new research frontiers, particularly regarding the identification and quantification of individual pathways in complex systems. Bulk estimates of SGD-driven solute fluxes remain unreliable without proper pathway discrimination, as pathways differ in magnitude, seasonality, and biogeochemical signature. Accurately resolving these differences is essential to incorporate SGD into biogeochemical budgets and link it to ecosystem functioning.

In this context, radium isotopes are powerful SGD tracers due to their range of half-lives, which capture processes from cm-scale porewater exchange to km-scale oceanic circulation. This thesis advances the understanding of SGD by **i) refining the quantification of pathway-specific water flows using radium isotopes, ii) improving estimates of chemical inputs to coastal systems by resolving pathway-specific fluxes, and iii) linking them to ecological outcomes such as eutrophication and hypoxia.** By combining an advective transport model of Ra in the aquifer with a transient radium mass balance model in the Mar Menor coastal lagoon, this work demonstrates how Ra isotopes can be applied to quantify the contribution and seasonality of different SGD pathways and identify their main driving mechanisms. The results reveal that short-scale porewater exchange (PEX) exhibits strong seasonality, with increased discharge in summer likely driven by enhanced sediment bioturbation. This thesis also integrates the specific biogeochemical processing within each pathway to resolve pathway-specific nutrient fluxes, demonstrating that origin (continental vs. marine) and temporal scale (long-scale vs. short scale) control nutrient composition and flux magnitude. These findings highlight the need to reconsider solute flux calculations, given the large discrepancies between bulk and pathway-resolved estimates. Furthermore, the information generated challenges the prevailing assumption that eutrophication and overall ecological degradation in the Mar Menor is solely

driven by continental nitrogen inputs, instead pointing to a significant role of recirculated flows. Finally, the distinction between SGD pathways is used to assess their impact on chemical oxygen demand through the delivery of reduced compounds, representing the first assessment of this kind. Results indicate a stronger impact during summer, driven by large PEX supply, which can be particularly relevant under stratified conditions. The findings presented represent an important step to understand the role of SGD on chemical oxygen demand by providing qualitative guidelines based on the magnitude of groundwater flow rate and composition. Overall, this thesis demonstrates how radium isotopes can be used to resolve pathway-specific SGD fluxes and provides new insights into their role in coastal biogeochemistry and ecosystem functioning.

List of articles

The content presented in this thesis is based on three research articles, developed in Chapters 4, 5, and 6:

- **Chapter 4:** Seasonality of submarine groundwater discharge pathways in a coastal lagoon revealed by radium isotopes: The importance of porewater exchange in summer (2025). **Rodríguez-Puig, J.**, Rodellas, V., Diego-Feliu, M., Alcolea, A., Jiménez-Martínez, J., Alorda-Montiel, I., Alorda-Kleinglass, A., Pereira, F., Manzano, M., Gilabert, J., & Garcia-Orellana, J.; *Journal of Hydrology*, 661, 133616. <https://doi.org/10.1016/j.jhydrol.2025.133616>.
- **Chapter 5:** Recirculated submarine groundwater discharge dominates nutrient inputs and enhances eutrophication risk in a coastal lagoon (2026). **Rodríguez-Puig, J.**, Ruiz-González, C., Diego-Feliu, M., Alorda-Montiel, I., Alorda-Kleinglass, A., Romano-Gude, D., G. Bravo, A., Dordal-Soriano, J., Gilabert, J., Bergeler, S., Lavergne, C., Casas, G., Manzano, M., Garcia-Orellana, J., and Rodellas, V.; *Limnology and Oceanography*. <https://doi.org/10.1002/lno.70371>.
- **Chapter 6:** Impact of submarine groundwater discharge pathways on chemical oxygen demand. **Rodríguez-Puig, J.** et al. *To be submitted to Environmental Science & Technology*.

Additionally, the candidate has contributed to the following manuscripts:

- Unveiling Hidden Mercury and Methylmercury Sources: The Role of Submarine Groundwater Discharge in Coastal Lagoons (2025). Lavergne, C., **Rodríguez-Puig, J.**, Ruiz-González, C., Montero-Curiel, M., Casas, G., Romano-Gude, D., Alorda-Montiel, I., Dordal-Soriano, J., Alorda-Kleinglass, A., Diego-Feliu, M., Gilabert, J., Campillo-de La Maza, A., Romera-Castillo, C., Torres-Rodríguez, N., Heimbürger-Boavida, L.-E., García-Orellana, J., Rodellas, V., & G. Bravo, A. *Environmental Science & Technology*. <https://doi.org/10.1021/acs.est.5c07191>
- A century of sediment metal contamination of Mar Menor, Europe's largest saltwater lagoon (2025). Alorda-Montiel, I., Rodellas, V., Arias-Ortiz, A., Palanques, A., Bravo, A. G., **Rodríguez-Puig, J.**, Alorda-Kleinglass, A., Green-Ruiz, C., Diego-Feliu, M., Masqué, P., Gilabert, J., & Garcia-

Orellana, J. *Marine Pollution Bulletin*, 220, 118347.
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- Large scale hydrogeochemical and isotopic observations in the Baltic Sea system (2025). McKenzie, T., Majtényi-Hill, C., Henriksson, L., Ljungberg, W., Reithmaier, G. M. S., Cotovicz, L. C., Lencina-Avila, J. M., Mitschke, N., Böttcher, M. E., Szymczycha, B., Ulfssbo, A., Tomer, A. S., Cardis, T., Hall, P. O. J., Holloway, C., **Rodriguez-Puig, J.**, Börjesson, S., Yau, Y. Y. Y., Zhao, S., ... Santos, I. R. *Scientific Data*, 12(1), 1757.
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- Impact of Submarine Groundwater Discharge on Microbial Communities in a Highly Anthropized Coastal Lagoon (Mar Menor, SE Spain) (2025). Romano-Gude, D., Dordal-Soriano, J., **Rodriguez-Puig, J.**, Bravo, A. G., Alorda-Montiel, I., Alorda-Kleinglass, A., Diego-Feliu, M., Romera-Castillo, C., Mallenco-Fornies, R., Gilabert, J., Garcia-Orellana, J., Rodellas, V., & Ruiz-González, C. *Molecular Ecology*, 34: e70201.
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Thesis structure

This dissertation is organized into seven chapters:

Chapter 1 provides a general introduction to the topic of submarine groundwater discharge (SGD), divided into five main sections:

- i) A general description of SGD, including its definition, main pathways, and relevance.
- ii) An overview of the methods for the identification and quantification of SGD, highlighting their target processes, limitations, and strengths.
- iii) A description of biogeochemical processes occurring in subterranean estuaries and the controls on solute fluxes to coastal waters.
- iv) An integrated perspective on SGD, synthesizing the different knowledge spheres related to its study.
- v) A general overview of coastal lagoons, with a particular focus on Mar Menor, where the core studies of this thesis have been developed.

In **Chapter 2**, the objectives of the thesis are presented.

Chapter 3 describes the collection and analysis of radium isotopes, including the Radium Delayed Coincidence Counter and gamma spectrometry, as well as other chemical species in water samples. The chapter also includes a description of the mass-balance approach for quantifying SGD and an overview of the main sources of uncertainty.

Chapters 4 to 6 correspond to three independent studies linked to specific research papers:

Chapter 4 simultaneously quantifies the contribution of different SGD pathways (fresh SGD, long-scale recirculated SGD, and porewater exchange) to the Mar Menor by combining a transient radium mass balance in the lagoon with an advective transport model of radium in the aquifer. This model is applied over different periods, enabling the temporal assessment of the dynamics and drivers of SGD pathways over an annual cycle.

Chapter 5 assesses the pathway-resolved nutrient fluxes in Mar Menor and links them to eutrophication processes. The study characterizes the biogeochemical signature of each pathway and its ecological effects, underscoring the importance of including all contamination pathways in lagoon management plans.

Chapter 6 investigates the impact of SGD pathways on chemical oxygen demand via the supply of reduced substances, a process that remains poorly understood. The chapter identifies the main factors governing a coastal system's susceptibility to SGD-induced oxygen depletion. It also provides qualitative guidelines for assessing it based on water flow and groundwater composition.

Chapter 7 presents the main conclusions of the dissertation and identifies key knowledge gaps and research opportunities.

1. Introduction

1.1. Submarine groundwater discharge

1.1.1. Definition, pathways, and relevance of submarine groundwater discharge

About 30% of freshwater on Earth is in the form of groundwater, representing up to 99% of all liquid freshwater, while surface water, such as rivers and lakes, accounts for less than 1% (Gleick, 1993; UN Water, 2022). As a resource, groundwater represents the main drinking water supply for over 50% of the global population, particularly in rural areas, and is essential for food and energy security (UN Water, 2022). Zooming into the coastal area, the current near-coastal population (<50 km) exceeds the world population that existed less than a century ago, representing 29% of the global population (Cosby et al., 2024). Moreover, coastal populations are growing faster than inland populations, particularly in South America and Asia (Cosby et al., 2024). Groundwater systems are not isolated but are hydrologically connected to surface waters, including rivers, streams, lakes, and the coastal ocean. As a result, there is a continuous exchange of water through recharge and discharge from or to surface water bodies. In coastal environments, groundwater can indeed reach the ocean through submarine groundwater discharge (SGD), which is recognized as a major process of the global hydrological cycle (Fig. 1.1) and plays a critical role in biogeochemical cycles, linking terrestrial and marine environments (Douglas & Murgulet, 2025).

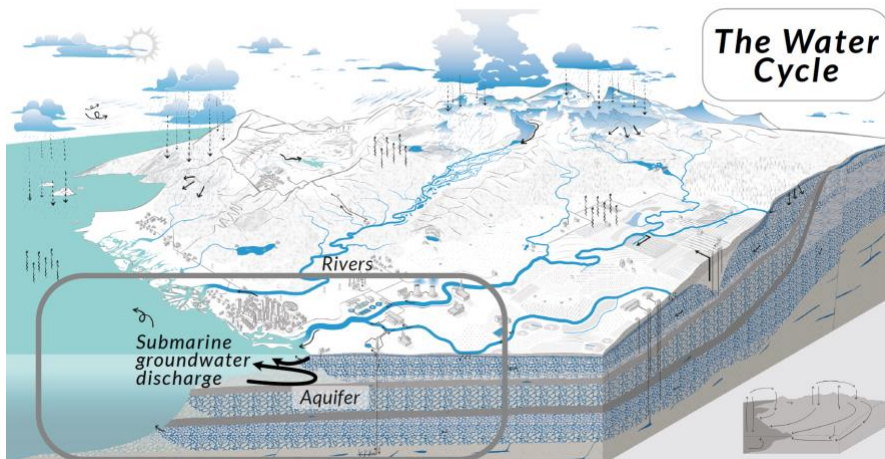


Figure 1.1. Submarine groundwater discharge within the water cycle. The coastal area is highlighted. Adapted from Corson-Dosch et al. (2023).

The discharge of groundwater in the coastal area has long been recognized in the traditional knowledge of many ancient societies. Indeed, the earliest recorded observations of SGD date back to the 1st century, when Strabo, an ancient Greek geographer, described submarine springs off the Syrian coast (Moosdorf & Oehler, 2017). However, the scientific study of SGD only began ~50 years ago, and it was not until 1970 that the term “submarine groundwater discharge” was coined. In 1999, following growing scientific interest in the topic, Moore described the term “subterranean estuary” to denote the biogeochemical mixing zone of fresh groundwater and seawater beneath the coast. By the early 2000s, SGD was recognized as an important process contributing to the hydrological cycle (Moosdorf & Oehler, 2017), and in 2003, Burnett et al. formally defined SGD as “any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition.” By this definition, any process representing water advection between sediments and overlying water along continental margins qualifies as SGD and thus it includes not only fresh but also saline groundwaters. Note that groundwater refers to *any water in the ground*, and therefore water in the pores of submerged sediments (i.e., porewater) is considered synonymous with groundwater (Burnett et al., 2006).

Groundwater discharge to the coastal ocean is controlled by different driving forces and composed of numerous flow pathways, which vary across locations, space, and time, making SGD a highly heterogeneous process (Garcia-Orellana et al., 2021a; Taniguchi et al., 2019). The characteristics of the different pathways, including transit times, groundwater-aquifer interactions, and hydrogeological properties, determine the extent and nature of chemical reactions occurring within the subsurface (Robinson et al., 2018; Santos et al., 2012b). Consequently, recent research has moved beyond the traditional distinction between fresh and saline groundwater and increasingly focuses on identifying and characterizing the different pathways through which SGD occurs (Cabral et al., 2023; Rodellas et al., 2017; Sadat-Noori et al., 2016a). Pathways can be classified according to their origin, driving forces, and spatial scales (Garcia-Orellana et al., 2021a) (Fig. 1.2):

(1) Terrestrial groundwater discharge

Driven by terrestrial hydraulic gradients, which generate the pressure required for fresh groundwater to flow seaward. The magnitude of this pathway depends on groundwater recharge patterns, mainly controlled by climate factors (chiefly precipitation), land-use (e.g., agriculture or urban soils), soil structure and texture, topography, aquifer permeability, and beach morphology (Condon & Maxwell, 2015; Jafari et al., 2019; Rukundo & Doğan, 2019; Y. Zhang et al., 2017). For

instance, fresh discharge can increase under conditions of enhanced recharge, such as precipitation events (Diego-Feliu et al., 2022b; McKenzie et al., 2020), but it can decrease due to human activities such as groundwater pumping for extraction (Nazari et al., 2025). The most evident expressions of this process (although not the most common worldwide) occur in areas of heterogeneous geology that create preferential focused discharge pathways, such as submarine springs in karst systems (Hoffmann et al., 2025; Savatier et al., 2023; Tamborski et al., 2020b) and in volcanic formations (Cardenas et al., 2020; Oehler et al., 2019a). Aside from these heavily fractured systems, terrestrial discharge can also occur in unconsolidated surficial deposits created by alluvial, lacustrine, glacial, deltaic, or eolian processes or in permeable rocks like sandstones or limestones, particularly when high permeabilities and strong hydraulic gradients occur (Erkul et al., 2025; Tur-Piedra et al., 2024). Although this discharge typically occurs at the coastline, fresh groundwater can also be found km away from the coast, sometimes known as offshore freshened groundwater (Micallef et al., 2020).

(2) Density-driven seawater circulation

Driven by temperature- and salinity-induced density gradients. Denser seawater infiltrates the coastal aquifer, mixing with fresh groundwater (Robinson et al., 2006). This creates the so-called saltwater wedge at the freshwater-saline mixing zone (Santos et al., 2012a). Along the mixing zone, the salt concentration and the fluid density vary due to mechanical dispersion and molecular diffusion, resulting in a convection cell (Werner et al., 2013). Besides mechanical dispersion and molecular diffusion, the amount of fresh discharge and the density gradient determine the thickness of the mixing zone (Werner et al., 2013).

(3) Seasonal exchange of seawater

Driven by the movement of the freshwater-saltwater interface, which responds to changes in the hydraulic pressure inland or sea-level changes. Reduced groundwater recharge allows seawater to penetrate further into the coastal aquifer (Palacios et al., 2020), while decreased sea levels can increase saline SGD rates (Gonneea et al., 2013; Ten Hietbrink et al., 2025). Such dynamics can result in a displacement of the mixing zone, which can become particularly pronounced during storm surges, sometimes persisting for years (Mondal et al., 2024).

(4) Shoreface circulation of seawater

Driven by tidal pumping or wave action. Tidal pumping, which occurs within the range of hours to days (Craddock et al., 2024; Greskowiak & Holtappels, 2026),

promotes increased recirculation of seawater during high tide, particularly in locations with higher tidal ranges and wave setup (McKenzie et al., 2021). Wave-driven shoreface recirculation creates convection cells that flush the upper sediments within seconds to minutes (Diego-Feliu et al., 2025; Santos et al., 2012b). Due to the high frequency of this process, mixing with the fresh groundwater is less pronounced compared with tidal effects (Xin et al., 2010).

(5) Porewater exchange (PEX)

Driven by a variety of mechanisms, this is arguably the most heterogeneous SGD pathway. Some drivers originate at the surface and propagate downward into the bottom sediments, such as wave-driven oscillatory flows. Others are linked to processes occurring at the sediment-water interface, such as pressure gradients induced by flow or topography, ripple migration, fluid shear from currents, and density-driven convection. Additional mechanisms occur within the sediments themselves, such as bioirrigation by burrowing organisms or plant roots, gas bubble upwelling, and sediment compaction (Santos et al., 2012b). Note that PEX occurs at small spatial scales, ranging from mm to cm, and is thus characterized by rapid transit times (Cook et al., 2018a).

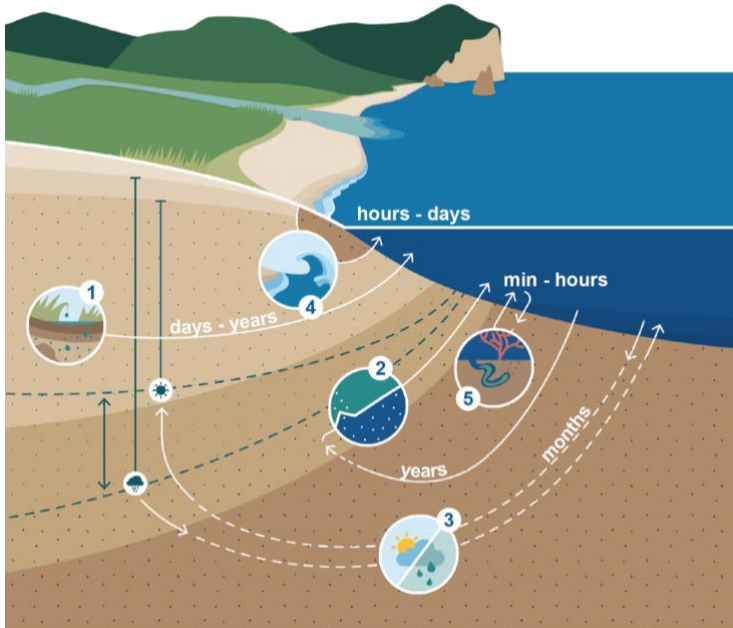


Figure 1.2. Pathways of submarine groundwater discharge: (1) terrestrial groundwater discharge, (2) density-driven seawater circulation, (3) seasonal exchange of seawater, (4) shoreface circulation of seawater, and (5) porewater exchange. The timescale of each pathway is indicated along its flow path or at the discharge point, based on Kiro (2025). Adapted from Garcia-Orellana et al. (2021).

Although this classification is useful for understanding advective groundwater processes occurring in the coastal zone, it should be noted that separating the different processes remains a major challenge. They often overlap in time and space, and the observed flows are frequently the interaction of multiple forces that combine in nonlinear ways (Taniguchi et al., 2019). Because of the diversity of pathways, SGD occurs in virtually all coastal systems worldwide: in karstic aquifers (Y. Chen et al., 2025), sandy beaches (Greskowiak & Holtappels, 2026), mangroves (B. Zhang et al., 2025), glacial landscapes (Bullock et al., 2024a), and coral reefs (Tait et al., 2023). Despite its ubiquity, SGD studies are mainly concentrated in regions with high gross domestic product, revealing important geographic and socioeconomic gaps in our understanding of SGD (Fig. 1.3).

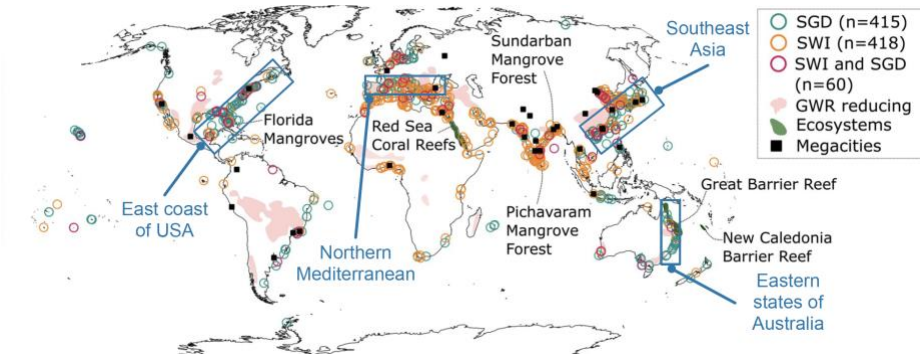


Figure 1.3. Locations of SGD studies as of 2024 (green circles), mainly conducted in basins with gross domestic product above the global median. In particular, studies concentrate in the East coast of USA, Northern Mediterranean, Southeast Asia, and the Eastern states of Australia. Adapted from Kretschmer et al. (2025).

Another key characteristic of SGD is its high variability both in space and time. This variability is primarily controlled by the interaction of the strength of driving forces, with stronger forcings resulting in larger magnitudes, and the aquifer geology, including subsurface heterogeneity and groundwater flow architecture (e.g., diffuse or focused) (Geng et al., 2026).

Understanding the ubiquitous and dynamic flowpaths of SGD and its magnitude is essential, as it plays a key role in coastal hydrology, biogeochemical cycles, and human society. From a hydrological perspective, recent water budgets and numerical models estimate that fresh SGD delivers between 0.6% and 1.3% of the total freshwater inputs to the ocean (Luijendijk et al., 2020; Zhou et al., 2019), although earlier estimates suggested relatively higher contributions, up to ~10% (Taniguchi et al., 2002). However, this picture changes substantially when all SGD pathways are considered. In fact, Ra-based total SGD estimates suggest that it can

reach flows up to four times larger than global river discharge (E. Y. Kwon et al., 2014). This difference arises because saline SGD typically dominates the total discharge, often accounting for more than 90% of total SGD fluxes (e.g., Zhu et al., 2025). However, high relative contributions of fresh SGD have been reported linked to seasonal exchange (Michael et al., 2005) or after strong recharge events, such as monsoons (Lino et al., 2023). The global median of lineal velocities of total SGD is $\sim 20 \text{ cm d}^{-1}$, but it can range from a few cm per day to a few hundreds of cm d^{-1} (Santos et al., 2021).

From a biogeochemical perspective, SGD is often highly enriched in dissolved solutes and can therefore contribute disproportionately to nutrient fluxes to the coastal ocean (e.g., Yu et al., 2024). Total SGD nutrient fluxes exceed river inputs in more than 60% of locations with available data (Santos et al., 2021) and frequently exhibit elevated N:P ratios relative to the Redfield ratio, which can alleviate nitrogen limitation and significantly alter coastal biogeochemical dynamics (Santos et al., 2021). Because SGD encompasses both fresh and saline pathways that behave differently in terms of origin, water–rock interaction, residence time, and redox conditions (Garcia-Orellana et al., 2021a), its biogeochemical influence is far more complex than that of rivers alone (see section 1.3). Each pathway can deliver distinct suites of nutrients, trace elements, and organic matter, and is subject to different driving forces, meaning that their contributions to solute fluxes should be assessed individually and may exhibit different temporal behavior. For instance, fresh SGD reflects terrestrial sources, often dominated by nitrate and dissolved organic carbon, and can be enhanced after precipitation events. In contrast, recirculated seawater is frequently enriched in ammonium and phosphate generated through organic matter remineralization and can penetrate deeper into the aquifer with sea level rise, releasing reduced compounds such as ferrous iron (Fe^{2+}) (Alorda-Kleinglass et al., 2019; Diego-Feliu et al., 2022b; Santos et al., 2021; Slomp & Van Cappellen, 2004). Despite these differences, the majority of SGD studies do not distinguish between the fresh and saline components (Kretschmer et al., 2025).

1.1.2. Identification, quantification, and reporting of submarine groundwater discharge

The magnitude of SGD to coastal waters is poorly constrained compared to the well-characterized global magnitude of river discharge (Douglas & Murgulet, 2025). This arises from three main challenges: i) the identification of SGD, which requires determining where, how, and when it occurs, is hindered by its inherent

spatiotemporal variability; ii) the quantification of SGD, since it is an invisible process occurring at low flow rates but over large areas and composed of multiple pathways; and iii) the reporting of SGD rates, which requires consistent measurement approaches and standardization to enable comparisons across studies.

The first step in assessing SGD is selecting the most appropriate method, considering available resources, existing knowledge, and the limitations of each approach. With ongoing technological advances, new techniques are developed while existing methods are refined. A brief overview of the main approaches is provided below.

▪ Geochemical tracers

Radium (Ra) and radon (Rn) isotopes are the most widely used tools for SGD identification and quantification (Diego-Feliu, 2022a). In SGD studies, the most commonly used isotopes include the four naturally occurring Ra isotopes and one Rn isotope: ^{226}Ra ($T_{1/2} = 1600$ years) and ^{222}Rn ($T_{1/2} = 3.83$ days) belonging to the ^{238}U decay series, ^{224}Ra ($T_{1/2} = 3.66$ days) and ^{228}Ra ($T_{1/2} = 5.75$ years) from the ^{232}Th series, and ^{223}Ra ($T_{1/2} = 11.4$ days) from the ^{235}U series (Fig. 1.4).

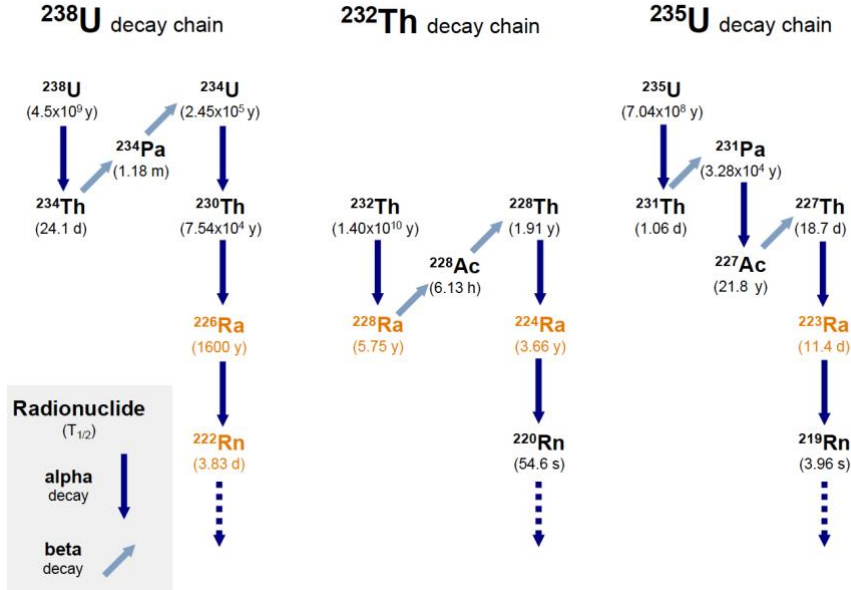


Figure 1.4. Schematic diagram of the ^{238}U , ^{232}Th , and ^{235}U decay series. Adapted from Rodellas (2014).

These radioisotopes have five key tracer properties that make them particularly effective compared to other geochemical tracers (Fig. 1.5): i) groundwater

becomes enriched in these isotopes as it flows through the coastal aquifer, where they are produced by the radioactive decay of sediment- or rock-bound parent isotopes, resulting in a strong signal in seawater when groundwater discharge occurs relative to background ocean concentrations; ii) they behave conservatively once released to seawater; iii) their half-lives range from days (^{224}Ra) to thousands of years (^{226}Ra), which determine their ingrowth rate in the aquifer and decay rate in the ocean, allowing for tracing processes over different temporal scales and estimating water ages; iv) they belong to different decay chains of the Uranium and Thorium series, allowing differentiation of sources or origins; and v) the coastal water column integrates their signal, which smooths local-scale variations (Burnett et al., 2001).



Figure 1.5. Key tracer properties of radium and radon.

Ra- or Rn-based SGD flows are usually calculated with a mass balance approach, in which the main sinks (radioactive decay, mixing with offshore waters, internal cycling, and atmospheric evasion in the case of radon) and sources (surface runoff, sediments, precipitation, radioactive production, and atmospheric deposition) are estimated, and the excess tracer flux is attributed to SGD, which usually represents the main source of Ra and Rn (Adyasari et al., 2023; Garcia-Orellana et al., 2021a). In addition, the water volume affected by SGD and the residence time of coastal waters must be well constrained, along with a representative tracer concentration in discharging groundwater (Burnett et al., 2006), which is arguably the largest source of uncertainty in Ra- or Rn-based SGD estimates (Cook et al., 2018a; Rodellas et al., 2021). Radon can also be measured continuously, enabling the localization and estimation of SGD (Burnett, 2003b; S. Zhao et al., 2022).

Radium and radon-based applications provide SGD estimates that can integrate from beach scales to entire ocean basins. These radionuclides can also be applied as point measurements, using depth profiling coupled with one-dimensional exchange models to trace processes at much smaller scales, such as PEX (e.g., Cable & Martin, 2008). Vertical profiles of radon in porewater are based on radon porewater deficit in the upper sediment layers relative to in situ sediment production, indicating exchange with the overlying water (Cook et al., 2018b). This method requires information on sediment porosity and radon production rates in

the sediment (Cook et al., 2018b). Radioactive disequilibrium in sediments, such as the $^{224}\text{Ra}/^{228}\text{Th}$ ratio, can also be used to estimate benthic fluxes (Q. Wang et al., 2023; Wei et al., 2026). This technique relies on the different geochemical behavior of the parent-daughter isotopes: ^{228}Th is bound to the sediment particles, while ^{224}Ra is desorbed upon contact with seawater through cationic exchange (P. Cai et al., 2012). Again, a deficit of ^{224}Ra relative to ^{228}Th in the upper centimeters of the sediments indicates advective exchange across the water-sediment interface (P. Cai et al., 2014).

Aside from radioactive isotopes, stable isotopes have also been applied in SGD studies, although much less frequently. In particular, $\delta^2\text{H}$ - $\delta^{18}\text{O}$ signatures are commonly used in hydrological studies to fingerprint water origin and mixing (Duque et al., 2019a; Rocha et al., 2016). However, they usually need to be combined with radioactive tracers to provide quantitative estimates of SGD flows (Rocha et al., 2016). Dissolved silica mass balances can also be used to estimate SGD flows, but unlike Ra or Rn, silica does not behave conservatively, as it can be incorporated by phytoplankton species to form their frustules and is therefore better used as a complementary tracer (Oehler et al., 2019b). Similarly, salinity can be employed in multi-tracer approaches, either as a discrete measurement to detect fresh SGD or within a mass balance to estimate fresh groundwater flows (McCormack et al., 2014; Schubert et al., 2023a).

▪ Water balances and modeling of groundwater flow

Water mass balances, Darcy's law estimates, and hydrogeological models primarily quantify terrestrially derived SGD (i.e., net flow of fresh groundwater to the coastal ocean). Water balances are performed at a hydrological basin scale and account for all inputs (recharge) and outputs (groundwater extraction, evapotranspiration, and surface runoff), with the remaining water volume attributed to groundwater discharge (Cave & Henry, 2011). Because extensive knowledge on the hydrological basin is often lacking, the main source of uncertainty lies in accurately constraining all the water inputs and outputs. Consequently, the estimated fresh groundwater discharge may be comparable in magnitude to the uncertainties in the other terms (Burnett et al., 2006). In addition, water budgets tend to underestimate fresh SGD compared to in situ measurements (Y. Zhou et al., 2018).

Estimates based on Darcy's law rely on hydraulic conductivity, the area of the discharge zone, and the hydraulic gradient (A. M. Wilson et al., 2015). Accurate calculations, therefore, require detailed information on the groundwater table, sea

level, and aquifer conductivity. As with many hydrological methods, a key limitation is the assumption of a homogeneous aquifer, which is rarely true in natural systems, as hydraulic conductivity can vary over several orders of magnitude over short distances (Burnett et al., 2006).

Hydrogeological models provide another approach to estimate fresh SGD (Alcolea et al., 2019) and can also be used to investigate terrestrial and oceanic forcings on the freshwater-saltwater interface (J. Zhang et al., 2025) as well as the related biogeochemical reactions through reactive transport models (Robinson et al., 2018).

▪ **Direct measurements with seepage meters**

Seepage meters are benthic chambers deployed on the sediment bed to directly measure groundwater seeping from the bottom sediments. They were originally designed for freshwater systems but were adapted to marine environments by Lee (1977) and have since been modified to withstand rougher coastal conditions (Duque et al., 2020b). A typical seepage meter consists of a bottomless cylinder with an outlet connected to a plastic collection bag (Lee, 1977). Each device samples approximately 0.25m² of sediment (Rosenberry, 2005), although smaller designs have also been used (Diego-Feliu et al., 2025). Seepage meters are usually deployed for a fixed period, usually on the order of hours, allowing the estimation of a seepage volume per unit area and time. They are widely used (~100 studies worldwide as of 2020) because their simple design is low-cost and relatively easy to construct (Duque et al., 2020b).

Despite their evident strengths, several factors must be considered when designing and deploying seepage meters. The radius of the chamber and the tubing of the collection system can influence measured rates due to head losses within the device (Murdoch & Kelly, 2003), while some designs can induce artificial advection due to the Bernoulli effect (Shinn et al., 2002). In addition, exposure of the collection bag to currents, leakage around the base of the chamber, or attenuation of pressure signals at the sediment bed can produce anomalous measurements (Burnett et al., 2001; Russoniello & Michael, 2015). Beyond the physical characteristics of the device, deployment conditions can also affect the measured seepage rates. To ensure stable geochemical conditions, seepage meters should be installed two days before sampling (Murdoch & Kelly, 2003). Deployment during rough sea conditions may result in measurement errors because of wave setup or currents. Consequently, most of the studies conducted have been in sheltered environments (Duque et al., 2020b). Deployment in coarse sediments can also be nearly impossible, as the chambers cannot be adequately

seated in the sediment. When metallic devices are used, chemical alteration of discharged water should be considered if used for estimating solute fluxes (Duque et al., 2020b). Another limitation is the short deployment duration, which is constrained by the capacity of the collection bag and the discharge rate. Automated seepage meters allow much finer temporal resolution but with increased costs (Taniguchi et al., 2003).

Regarding the quantification of seepage rates, the main limitation lies in upscaling point measurements, as variability at the meter scale can be substantial and may hinder accurate estimation of beach-wide SGD rates. Some studies address this issue by deploying multiple seepage meters to capture spatial heterogeneity (Rosenberry, 2005). In addition, seepage is highly dynamic, with rates varying over time (Taniguchi et al., 2003), which makes repeated or time-series measurements recommended to obtain representative estimates.

▪ **Geoelectrical methods**

Electrical properties of the subsurface allow mapping the subsurface distribution of groundwater salinity in coastal areas, allowing the identification of the freshwater-saltwater interface and other key processes in the aquifer (Ayari et al., 2023). The electrical resistivity of the subsurface, which is the inverse of conductivity, depends both on the physicochemical characteristics of porewater, including salinity and temperature, and the properties of the aquifer solids, including porosity, tortuosity, and clay content (Palacios et al., 2020). In general, higher resistivity values correspond to freshwater-saturated sediments, while lower resistivity values indicate seawater intrusion (Paepen et al., 2020). Consequently, both a detailed understanding of aquifer characteristics and the inversion strategy used to interpret geophysical data are critical, as they strongly influence the accuracy of the resulting resistivity distribution (Costall et al., 2018).

Terrestrial electrical resistivity tomography, marine continuous resistivity profiling, and amphibious electrical resistivity tomography, which covers both land and sea, can be used to map subsurface electrical resistivity along the land-ocean continuum (Diego-Feliu et al., 2025; Paepen et al., 2020; Tur-Piedra et al., 2024). These methods have been successfully applied to understand climatologically induced freshwater dynamics (Tur-Piedra et al., 2024) and tidal-induced recirculated seawater dynamics (Águila et al., 2022). One of the key setup parameters is the distance between electrodes, as increasing the electrode spacing allows greater depth of investigation but reduces the resolution of subsurface features, with full-depth resolution limited to the central zone of the

transect due to inversion strategy limitations. Additionally, the accuracy of the resistivity profile can be affected by line straightness, surface or subsurface infrastructure, and terrain irregularities, which can distort apparent resistivity and create false anomalies (Żogała et al., 2025). Electromagnetic methods, which require less time and resources than traditional resistivity surveys, are particularly useful in areas with strong salinity contrasts (Kirkegaard et al., 2011) and can also be performed via airborne measurements (Werner et al., 2013).

▪ Thermal methods

Thermal methods include all temperature-based approaches, such as remote sensing thermal infrared (TIR), and in-situ temperature profiling. Thermal infrared is based on thermal contrast between discharging groundwater and the sea surface, as groundwater bodies typically have a stable thermal signal over time, while surface water temperatures fluctuate daily and/or seasonally. This contrast allows the identification of SGD locations through thermal anomaly mapping (Hare et al., 2015; K. Ye et al., 2025). Remote sensing TIR is an effective exploratory tool for identifying SGD hotspots, as the data is publicly accessible and allows coverage of large areas with minimal human resources (K. Ye et al., 2025). Its main limitations are temporal and spatial resolution: temporal coverage can be restricted by environmental factors like cloud cover (Weng & Fu, 2014), while the highest spatial resolution achievable is 30 m with Landsat 8, preventing detection of small or low-discharge SGD (Jou-Claus et al., 2021). Airborne TIR, usually unmanned aerial systems, can improve spatial resolution to the centimeter scale (Lee et al., 2016) and identify locations where diffuse fresh groundwater mixes with recirculated seawater (Tamborski et al., 2015). It also allows the acquisition of time-series plume imagery with precise control over spatial resolution and flexible field operations (Lee et al., 2016). Handheld TIR technologies are also commonly used and have resolutions of ~50 cm (Williams et al., 2024).

In situ temperature measurements can be performed as vertical thermal profiling to identify SGD zones, such as fiber-optic distributed temperature sensing and temperature profiling probes (Hare et al., 2015; LeRoux et al., 2021; Williams et al., 2024). Vertical groundwater fluxes are estimated using 1D heat transport models based on Darcy's law (Anderson, 2005). The vertical resolution is determined by the spacing between sensors along the profile. Common discrete profiling probes such as the TROD, feature 10 cm intervals to resolve fine-scale thermal gradients in sediments.

Although each method described above provides valuable insights into specific aspects of SGD, multi-method approaches are essential to overcome the limitations of individual methods, particularly regarding the conceptualization of groundwater dynamics, the multiple temporal scales at which SGD pathways operate simultaneously, and operational constraints. In particular, the spatiotemporal resolution of the selected method(s) should match the spatiotemporal scale of the processes being studied (Fig. 1.6), which can range from short-term pulse inputs to long-term fluxes, while also accounting for their temporal variability (Rodellas et al., 2023). For instance, Ra isotopes and Rn can be combined to distinguish between long-scale and short-scale pathways (W. Liu et al., 2026), aerial surveys and electrical resistivity tomography techniques can be used for ground truthing prior to in situ porewater sampling (Erkul et al., 2025), radionuclides and stable isotopes can be combined to estimate SGD rates and identify water origins (Rocha et al., 2016), salinity and temperature measurements can be combined to produce fluid, salt and heat transport models to estimate the dynamics of groundwater fluxes from different drivers (Rodellas et al., 2020), thermal methods can study SGD at different spatial scales (Williams et al., 2024), and TIR methods can be used in combination with in situ methods for determining the relation between SGD flux and plume area (Young & Pradhanang, 2021).

Because different methods target distinct processes and operate at different spatial and temporal scales, estimates from different techniques are not directly comparable. In addition, there is a lack of standardization in reported units in SGD. Typical reporting formats include: i) volume per time unit (e.g., L d^{-1}), ii) linear velocity of flow across the seabed (e.g., cm d^{-1}) or its equivalent volumetric flux per area per time (e.g., $\text{cm}^3 \text{cm}^{-2} \text{d}^{-1}$), and iii) volume per length of shoreline per time (e.g., $\text{L m}^{-1} \text{d}^{-1}$) (Burnett et al., 2003a). Converting between these units often requires site-specific information, such as the width of the discharge area or the total area sampled, which is not always reported in published datasets (Santos et al., 2021). Furthermore, some parameters are chosen in an arbitrary way, including the selection of the normalization area or the estimation of coastline length, which is scale-dependent.

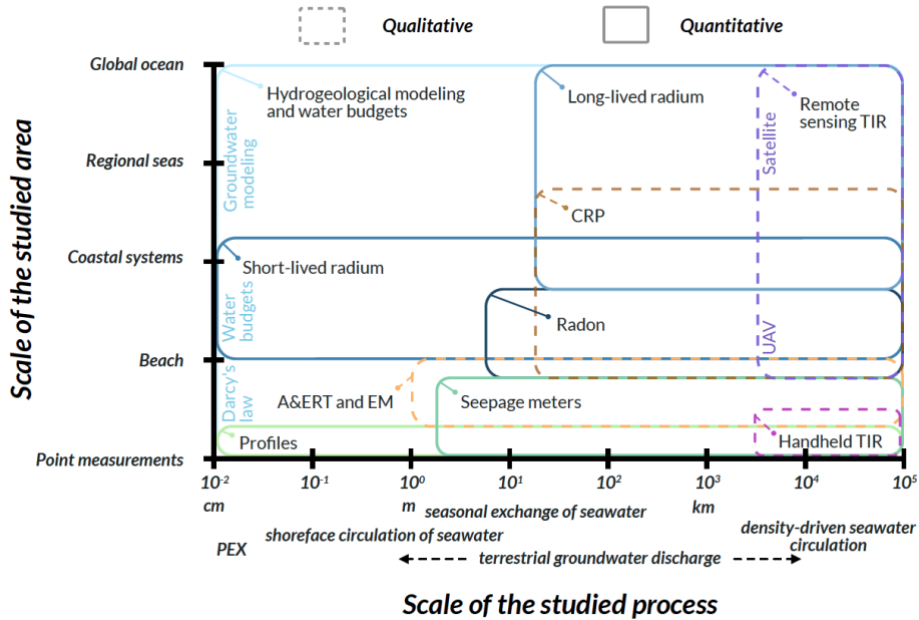


Figure 1.6. Spatial resolution according to scale of the studied area and scale of the studied process for each SGD identification/quantification method. Dashed lines indicate qualitative methods while solid lines indicate quantitative methods. Profiles include $^{224}\text{Ra}/^{228}\text{Th}$, ^{222}Rn deficit, and thermal profiles. TIR: Thermal infrared, UAV: Unmanned aerial vehicles, A&ERT: Amphibious and terrestrial electrical resistivity tomography, EM: electromagnetic methods.

1.1.3. Biogeochemical processes in the subterranean estuary and solute transport via submarine groundwater discharge

At the boundary between continents and oceans, subsurface waters create a transitional zone, with strong geochemical gradients at the meter scale (Waska et al., 2008). Recognizing the importance of this boundary, Moore (1999) described this reaction zone as *subterranean estuary* (STE). This concept embedded the geochemical dimension of coastal aquifers, similar to surface estuaries (Duque et al., 2020a). Current definitions of STE further emphasize a net freshwater flow on at least decadal timescales, advective water movement, and salinity gradients that promote reactive mixing between fresh and saline waters (Rocha et al., 2021).

The steep gradients in STEs, together with long groundwater residence times (hours to hundreds of years), drive microbially mediated chemical transformations that modify groundwater solute concentrations, thereby controlling temporal and spatial variability of biogeochemical conditions and influencing the enrichment or attenuation processes of key elements prior to groundwater discharge (Heiss et al., 2017; Robinson et al., 2018). Groundwater within the STE is usually anoxic,

exhibiting a shift from oxidants to reductants along the land-sea gradient. While most of the transformations occurring within the STE are microbially mediated, little is known about the abundance and composition of microbial communities (Ruiz-González et al., 2021). Although it is well established that groundwater composition changes as it flows through the STE, many SGD flux studies still rely on concentrations from upstream groundwater, neglecting the cycling of solutes occurring within the STE (Moore, 2010; S. J. Wilson et al., 2024a).

Many SGD studies quantify nutrient fluxes reaching the coastal zone. Nutrients delivered by SGD originate from the degradation of organic matter in sediments, direct percolation from the surface to the aquifer, and interaction with the geological matrix (Santos et al., 2021). Redox conditions, salinity, and groundwater residence time control the dominant nutrient species in SGD (Pain et al., 2021). Fresh SGD often transports new nutrients (e.g., nitrates) derived from anthropogenic sources, such as agricultural runoff, while recirculated SGD remobilizes recycled nutrients from the sediments (Santos et al., 2021). Saline SGD is typically enriched in ammonium relative to dissolved organic nitrogen due to the reducing conditions, although the dynamics of dissolved organic nitrogen remain less studied (Robinson et al., 2018; Santos et al., 2021). In addition, saline SGD can attenuate nitrate contamination by driving denitrification (Wei et al., 2026). Phosphorus in fresh water is mainly bound to Fe or Mn oxides or precipitated with calcium carbonate, but in saline groundwater it can be released through reductive dissolution of iron or sulfate minerals (Cable et al., 2002; Slomp & Van Cappellen, 2004). Dissolved silica generally increases with groundwater transit times via mineral dissolution (Rahman et al., 2019), although biogenic Si can be an important source in locations with abundant siliceous phytoplankton (Oehler et al., 2019b).

Nutrient fluxes from SGD exceed river contributions in many regions, including the Mediterranean Sea (Rodellas et al., 2015), the coast of China (Zhu et al., 2025), and the Great Barrier Reef (Tait et al., 2023). In most systems, SGD delivers nutrients at N:P ratios higher than the Redfield ratio, particularly in coastal aquifers impacted by anthropogenic activities (Santos et al., 2021). The supply of SGD-derived nutrients can influence primary production, trigger harmful algal blooms, drive hypoxic conditions, and contribute to N₂O emissions (H. K. Kwon et al., 2017; Montiel et al., 2019; Reading et al., 2021; Rocha et al., 2022).

Submarine groundwater discharge is also a key component of coastal dissolved carbon cycles (J. Liu et al., 2025), with important implications for greenhouse gas emissions, blue carbon, and coastal acidification models. Groundwater circulating

through organic-rich systems, such as peatlands and marshes, becomes enriched in DOC and dissolved inorganic carbon (DIC), including CH_4 and CO_2 , as a result of microbial respiration and mineral alteration processes (Tamborski et al., 2025). Carbon delivery via SGD is dominated by DIC, with fluxes an order of magnitude higher than those of dissolved organic carbon (DOC) (M. Zhao et al., 2026) and surpassing riverine input in bays (Wang et al., 2025). This process is the primary pathway for the lateral transport of DOC in mangroves (B. Zhang et al., 2025), karstic environments (Y. Chen et al., 2025), saltmarshes (Wang et al., 2025), and volcanic islands (Fang et al., 2025). Estimated DIC supply rates exceed net carbon burial and are comparable to the carbon sequestration capacity of saltmarsh systems, highlighting their importance in blue carbon estimations not only in saltmarshes but also in mangroves (X. Chen et al., 2018; M. Zhao et al., 2026).

Among DIC components, SGD represents an important pathway for CH_4 emissions in saltmarshes, contributing up to ~50% of total CH_4 exports in these systems (Schutte et al., 2020). Such emissions of greenhouse gases from SGD are particularly relevant when assessing the global cooling potential derived from soil carbon sequestration, yet they are often neglected. Tidal pumping appears to be a dominant control on SGD-driven CH_4 fluxes in Arctic settings (Lecher et al., 2016) and also influences CO_2 fluxes in mangroves and saltmarshes by accelerating organic matter respiration (Tomer et al., 2025). Although SGD can also carry some alkaline elements, most SGD studies report high DIC/Talk (total alkalinity) ratios, reflecting its potential to reduce coastal alkalinity and contribute to local acidification (Cardenas et al., 2020b; Z. Zhang et al., 2024). From a biological perspective, total SGD-derived carbon fluxes have been shown to enhance nearshore primary productivity in the Japan Sea (Cabral et al., 2023).

Numerous studies demonstrate that SGD can be a major source of trace metals across diverse coastal settings, including mine tailing deposits (Ag, Cd, Co, Pb, Zn, and Fe; Alorda-Kleinglass et al., 2019), coastal wetlands (Cu, Pb, Zn, Cd, Cr, and Hg; Qu et al., 2020), and coastal bays, where it contributes 20-50% of trace metal fluxes (Pb, Zn, Cd, Cr, and As; Xue et al., 2023). At a regional scale, SGD has been shown to be source of trace metals comparable to riverine discharge and atmospheric deposition, particularly in coastal areas of relatively dry areas like the Mediterranean Sea (Trezzi et al., 2016). The STE acts as a reactive zone where changing environmental conditions, particularly redox potential, control the release or uptake of metals and their transformation to other bioavailable species (McKenzie et al., 2024). For example, when reduced groundwater meets oxygenated seawater or porewater, Fe^{2+} is oxidized to Fe^{3+} , leading to its precipitation as iron-rich minerals. This process forms a geochemical barrier

known as the iron curtain (Charette & Sholkovitz, 2002), which results in an attenuation of dissolved Fe commonly observed in STEs (e.g., Tamborski et al., 2025). Conversely, reductive conditions can mobilize certain metal species, such as Hg, its bioavailable form, MeHg, or Mn from the sediments (Ahrens et al., 2020; Emili et al., 2011). Indeed, oxygen-poor recirculated SGD has been shown to deliver Hg and MeHg to a coastal lagoon at magnitudes comparable to atmospheric deposition (Lavergne et al., 2025), while in a salt marsh setting, SGD has been identified as the main source of Mn (Tamborski et al., 2025). Trace metals can also play an important role regulating ecosystem functioning: for instance, Fe supply has been linked to enhanced nitrogen fixation and higher Chl-a concentrations (Tamborski et al., 2020b; Tovar-Sánchez et al., 2014). Lastly, the metal contamination risk associated with SGD is influenced by high population density, high SGD fluxes, and the presence of acid sulfate soils (McKenzie et al., 2024).

Contaminants of emerging concern are increasingly recognized as widespread pollutants in groundwater systems worldwide. These contaminants can reach the ocean via SGD, with large concerns and uncertainties regarding their impact on aquatic life, particularly due to endocrine disruption and toxicity (Kasonga et al., 2021), and SGD has been identified as an important source of these contaminants (Szymczycha et al., 2020). In a coastal aquifer in Spain, up to 92 chemicals have been detected, with ~50% also detected in adjacent coastal waters. Moreover, perfluoroalkyl and polyfluoroalkyl substances were identified for the first time in this aquifer and were particularly widespread in highly contaminated sites, along with pharmaceuticals (Gutiérrez-Martín et al., 2023). Similarly, in Australia, caffeine, carbamazepine, and dioxins have been detected in groundwater, with ibuprofen and dioxins at concentrations posing a threat to the ecosystem (McKenzie et al., 2020). In the Baltic Sea, caffeine and diclofenac have been identified as the most widespread contaminants (Szymczycha et al., 2020).

Microplastics are another emerging concern in groundwater, although studies remain limited (Khant & Kim, 2022). Higher concentrations of microplastics have been observed in SGD-influenced locations along the Indian coastline (Purushothaman et al., 2023; Valsan et al., 2023). On Dawanshan Island, China, microplastic abundance in groundwater appears to decrease with depth, linked to inland plastic usage, while marine-derived microplastics were found in recirculated SGD in Laizhou Bay, China, where they may enhance dissimilatory nitrate reduction to ammonium in the intrusion zone (Xiong et al., 2025).

1.1.4. An integrated perspective on submarine groundwater discharge

Submarine groundwater discharge is an inherently interdisciplinary process linking the hydrosphere, lithosphere, geochemical sphere, biosphere, atmosphere, and anthroposphere in a context of global change (Fig. 1.7). Its role in coastal systems extends beyond a purely hydrological process and should be considered from an integrated, cross-disciplinary perspective. Within this conceptual framework, the main dimensions (or spheres) of SGD can be summarized. Notice that most processes described occur at the interfaces of multiple spheres, highlighting their interconnectivity:

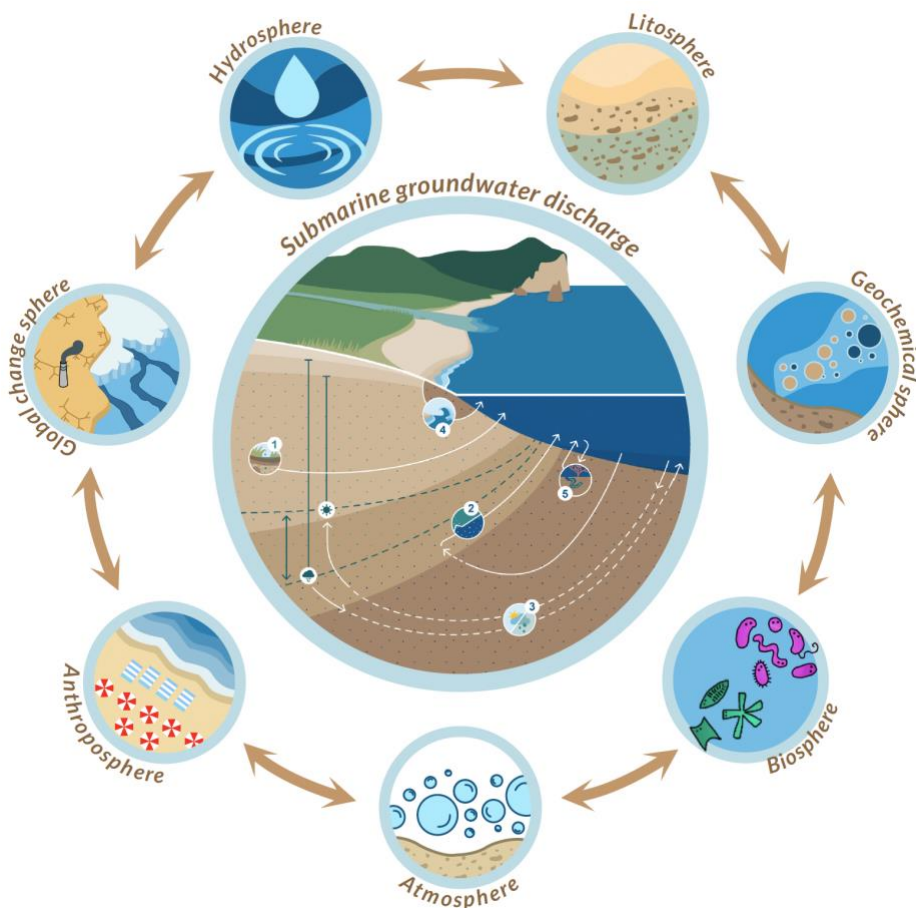


Figure 1.7. The main spheres of submarine groundwater discharge. Submarine groundwater discharge iconography from Garcia-Orellana et al. (2021).

▪ **Hydrosphere**

Submarine groundwater discharge is a key component of the coastal water cycle, involving the transport of both fresh groundwater derived from terrestrial recharge and recirculated seawater (Moore, 2010). Its magnitude, flow paths, and temporal variability are controlled by hydraulic gradients, tides, waves, and density differences, making SGD a highly dynamic heterogeneous pathway connecting land and ocean (e.g., Rocha et al., 2022; see section 1.1). Precipitation influences groundwater level, shaping the timing and magnitude of fresh SGD (McKenzie et al., 2021), with higher fresh SGD observed in areas with higher precipitation (Jung & Yoon, 2025), while evaporation can cause denser porewaters to infiltrate in the aquifer (Geng & Boufadel, 2017). Oceans act as drivers of SGD through currents, tides, sea level, and density gradients, among others (Taniguchi et al., 2019), influence the geochemical gradients in the STE (Moore, 1999), and are the receivers of SGD-derived geochemical inputs, altering coastal ecology (Lecher & Mackey, 2018; Santos et al., 2021).

▪ **Lithosphere**

Lithology, permeability, and aquifer structure determine transit times, weathering reactions, and spatial extent of the discharge (Tovar-Sánchez et al., 2014). For example, SGD from karstic submarine springs in Spain exhibits transit times on the order of days, as water travels rapidly through conduits and fracture networks (Garcia-Solsona et al., 2010). In limestone environments, confined aquifers can transport groundwater until it discharges hundreds of meters offshore, influencing coral reef systems (Hagedorn et al., 2020). In sandy beaches, which represent around 30% of global ice-free coasts (Luijendijk et al., 2018), SGD generally occurs as diffuse seepage through permeable sediments rather than focused springs (Diego-Feliu et al., 2025; Santos et al., 2012b). Multi-layered coastal aquifers with distinct lithologies can create complex discharge patterns at different depths (Martínez-Pérez et al., 2022).

▪ **Geochemical sphere**

Physical forcing and biogeochemical processes result in salinity and redox zonation in the STE that strongly shape solute fluxes to the ocean (Slomp & Van Cappellen, 2004; Snyder et al., 2004). The discharge of groundwater to the sea is a significant source of nutrients, carbon, metals, rare earth elements, gases, and other contaminants across the land-sea interface (extensively described in section 1.3; Kim & Kim, 2014). Its magnitude is relevant for biogeochemical cycles at coastal scales, such as carbon budgets in saltmarshes (M. Zhao et al., 2026), basin

scales, such as nutrient inputs to the Mediterranean Sea (Rodellas et al., 2015), and global scales, such as calcium and alkalinity fluxes (Kiro, 2025), and its role in global cycles of silica or strontium, among others. Despite the evident need to incorporate SGD fluxes in global biogeochemical cycles, many recent regional or global budgets still poorly constrain or neglect the input from SGD, including the Mediterranean Mercury Assessment (Cossa et al., 2022) and nutrient budgets in the Great Barrier Reef, Australia (Furnas et al., 2011; Tait et al., 2023).

▪ **Biosphere**

The biosphere is perhaps one of the most complex and diverse spheres because SGD affects organisms ranging from microbes to larger fauna. At the microscopic scale, microbial communities drive many biogeochemical processes within the STE, modifying groundwater composition, although connectivity pathways within aquifers remain poorly understood (Ruiz-González et al., 2021). Submarine groundwater discharge also seems to influence microbial composition, abundance, and heterotrophic activity of receiving water bodies (Garcés et al., 2011; Romano-Gude et al., 2025). A link between SGD and high chlorophyll *a* concentrations, indicative of primary production in phytoplankton, has been reported in highly anthropized areas, sometimes leading to green tides (Alorda-Kleinglass et al., 2024; N. Su et al., 2014). Beyond plankton, SGD provides macrophytes with nutrients, as observed in a variety of global settings, such as coastal lagoons and coral reefs (Amato et al., 2016; Andrisoa et al., 2019b).

Submarine groundwater discharge can also impact higher up the food web, but the ecological effects of SGD are highly system-dependent and have been barely demonstrated beyond indirect evidence. In some cases, SGD can be beneficial to mid-distance coral reefs (Yeo et al., 2026), enhance growth rates of mussels in a coastal lagoon (Andrisoa et al., 2019a), increase species richness and abundance of fish and benthic invertebrates in a bay (Utsunomiya et al., 2017), and enhance productivity and fish abundance near a submarine spring in a coastal lagoon (Starke et al., 2020). On the other hand, SGD can cause declines in meiofaunal communities in a coastal embayment (Kotwicki et al., 2014), lead to the bioaccumulation of metals in fish tissues (Garcia-Orellana et al., 2016), or hinder the growth of some macrophytes and phytoplankton species due to competitive interactions (Lecher & Mackey, 2018).

▪ **Atmosphere**

Submarine groundwater discharge plays an important role in the exchange of gases between coastal waters and the atmosphere. Greenhouse gases are

produced or consumed within the SGD flow path, including CO₂, CH₄, N₂O (Maher et al., 2019). In addition, SGD can carry toxic gases such as H₂S that can negatively impact the ecosystems (Moore et al., 2024) and can incorporate dissolved black carbon from the combustion of biomass and fossil fuels (W. Zhao et al., 2025). Hydroclimatic variability, such as increased precipitation, can drive influx of fresh SGD and increased supply of inorganic nutrients to the ocean (Douglas et al., 2021a).

▪ **Anthroposphere**

From a social perspective, SGD provides a wide range of ecosystem services (Alorda-Kleinglass et al., 2021; Moosdorf & Oehler, 2017). Ecosystem services provided by SGD include i) supporting services that are embedded in the water cycle and include nutrient cycling, primary production, and habitat maintenance; ii) provisioning services that relate to freshwater supply and food resources; iii) regulating services that influence key ecological processes, such as biological control and the mitigation of human diseases; and iv) cultural services that encompass non-material benefits, including ecotourism, sense of place, and cultural heritage (Alorda-Kleinglass et al., 2021).

Anthropogenic pressures on SGD include overexploitation of groundwater resources, impacts of land use (e.g., agriculture and mining activities), legacy contamination, and sewage system leakage. For example, sewer network overflows have been reported in shallow aquifers in coastal urban areas (X. Su et al., 2020), fecal indicator bacteria have been identified in SGD, affecting 40% of western Hawai'i reefs (Hondula et al., 2025), and human-specific enteric viruses have been detected in Florida (Futch et al., 2010). Legacy pollution can persist long after the cessation of industrial or agricultural activities, as observed in Hawai'i due to past sugarcane and pineapple production (Bishop et al., 2017).

Conflicts over coastal groundwater use are also common. At a local scale, disputes have arisen in Hawai'i over the effects of anthropogenic activities on SGD-sustained traditional algae aquaculture (McDermid et al., 2019). In Brazil, competition between private sector extraction and community needs has led to unsustainable overexploitation, highlighting social and class inequalities (Petelet-Giraud et al., 2018). At the regional scale, groundwater has even been a strategic resource in conflicts, as seen in Israel's control over groundwater resources in Palestine, perpetuating water insecurity and driving seawater infiltration into the Gaza coastal aquifer (Abualtayef et al., 2017; Muratoglu & Wassar, 2024).

Legal regulations for groundwater vary across jurisdictions but commonly focus on controlling pollution, sustainable use, and protecting connected ecosystems. Since 2000, the European Union regulates groundwater through the Water Framework Directive, which requires member states to prevent deterioration of groundwater quality and quantity, control pollution inputs, and maintain or achieve good chemical and quantitative status. In the USA, groundwater was formally included under the Clean Water Act two decades later, being recognized as a “functional equivalent” of a point source pollutant. Indirect economic valuations of groundwater resources have been performed, mainly through agriculture and fishery yields, but remain scarce to date (Alorda-Kleinglass et al., 2021). Management and monitoring efforts, along with research initiatives, are also components of the anthroposphere, reflecting our role in understanding, quantifying, and achieving sustainable management of SGD in coastal systems.

▪ Global change sphere

Global change refers to the widespread, human-driven alterations to Earth, impacting planetary processes and the conditions necessary for human well-being (Steffen et al., 2005). Hence, global change encompasses a broad range of processes, including climate change and human activities, which have profoundly shaped SGD and are expected to continue doing so. The latest report (AR6) from the Intergovernmental Panel on Climate Change (IPCC, 2023) states with *high* or *very high confidence* that climate change, derived mainly from greenhouse gas emissions, is increasing global mean sea level, inducing changes in extreme events, such as heavy precipitation, droughts, and tropical cyclones, and pushing some ecosystems to irreversibility, such as Arctic permafrost thaw. The IPCC concludes that “*every increment of global warming will intensify multiple and concurrent hazards.*” The consequences of these intensifying events are already evident in increased coastal risks. Hurricanes and cyclones have caused damage to water supply and salinization in the USA and the Philippines (Cardenas et al., 2015; Carlson et al., 2008), while flooding has led to contamination of coastal aquifers, deterioration of nearshore waters, and increased coastal erosion (Richardson et al., 2024).

On the human side, growing coastal populations place additional pressure on groundwater resources, with seawater intrusion observed several kilometers inland in aquifers with groundwater pumping and extraction activities (Jeen et al., 2021; Peters et al., 2022), and water sanitation systems exceeding capacity due to increased tourism (Alorda-Kleinglass et al., 2024). Land use changes further influence SGD: the disturbance of native forests reduces infiltration rates by 50%

globally (Meli et al., 2024), and land use development has been shown to increase coastal vulnerability to offshore contamination, as observed in South Korea (Jung & Yoon, 2025).

1.2. Coastal lagoons and Mar Menor

Coastal lagoons occupy 13% of the world's coastline (Alongi, 1997), ranging from small sized to vast lagoons such as Lagoa dos Patos in Brazil (10100 km²). They are water bodies typically located parallel to the coastline, separated from the ocean by natural barriers such as sandbars, and connected to the sea by at least one inlet (Kjerfve, 1994). The term derives from the Latin word *lacus* (i.e., lake) and originally referred to the waters surrounding the city of Venice (Cataudella et al., 2015). Coastal lagoons are often characterized by shallow depths, with most lagoons being around 1-2 m deep, which facilitates the resuspension of bottom sediments (Davis & FitzGerald, 2019; Pérez-Ruzafa et al., 2020b). These systems are usually located in low-lying coasts and frequently receive substantial inputs from large watershed basins (Davis & FitzGerald, 2019). The salinity regime of coastal lagoons depends on the balance between freshwater inputs and losses (e.g., evaporation or mixing with seawater). Salinity can vary widely, but most commonly observed salinities are schizohaline conditions (large salinity variations), such as Lake Reeve in Australia, or hypersaline (>40) conditions, such as Laguna Madre in the USA.

Based on their geomorphology, coastal lagoons can be classified into three main categories: i) choked lagoons, characterized by one or more long and narrow inlets and located in high-energy coasts ii) restricted lagoons, featuring two or more inlets and generally dominated by wind forcing, often exhibiting vertical stratification, and iii) leaky lagoons, which contain several inlets along the coastline, can extend for several kilometers, and are commonly located along current-dominated coasts (Kjerfve & Magill, 1989). These different geomorphologies and dominant forcing determine the dominant physical processes in coastal lagoons and lead to different hydrodynamic regimes, with choked lagoons exhibiting longer residence times (Kjerfve & Magill, 1989). In general, residence time in coastal lagoons can vary on the order of days to months and can show strong seasonal and spatial variability (Honfo et al., 2024; Soria et al., 2021).

Because they are situated at the land-ocean-atmosphere interface, coastal lagoons are characterized by strong physicochemical gradients that facilitate intense matter exchange (Kjerfve, 1994). Their vulnerability to external inputs

largely depends on the residence time, as higher times lead to the accumulation of pollutants and can amplify their ecological effects (Anthony et al., 2009; Kennish & Paerl, 2010). Their geographical, morphological, and hydrodynamic context makes coastal lagoons highly productive ecosystems, with annual primary production between 50 and 500 g m⁻² y⁻¹, comparable to that of upwelling regions (Pérez-Ruzafa et al., 2024). As a result, coastal lagoons provide numerous contributions to human well-being, including supporting services (primary and secondary production), regulating services (climate regulation and water purification), provisioning services (food and raw material), and cultural services (aesthetics and educational) (Rodrigues-Filho et al., 2023). These ecosystems also support livelihoods mainly through activities such as fishing, salt extraction, tourism, and recreation (Newton et al., 2014; Velasco et al., 2018). This diversity of economic uses has resulted in significant pressures exerted on lagoon resources and their surrounding areas, leading to profound modifications through urban development, aquaculture, agricultural practices, the construction of coastal defenses and port structures, and land reclamation (Newton et al., 2014). Indeed, human modification of lagoonal landscapes can be traced back to the Roman Empire, with land reclamation practices already documented in 5000 BC (Cataudella et al., 2015).

Currently, coastal zones, and coastal lagoons in particular, are considered hotspots of global change due to increasing human pressures and their high vulnerability to perturbations, a phenomenon referred to as the “coastal syndrome” (Newton et al., 2012). Moreover, most of these ecosystems are groundwater-dependent, especially in regions with water scarcity. However, overpopulation and overexploitation of groundwater resources have led to a degradation of groundwater quality and, consequently, overall ecosystem health (Eröstate et al., 2020).

More than 400 lagoons have been identified in the Mediterranean region (Cataudella et al., 2015), with 37 of them having an area greater than 10 km² (Soria et al., 2022) and almost half of them situated in Italy. Mar Menor (SE Spain) is one of the biggest Mediterranean lagoons, spanning 135 km² with a maximum depth of 7 m and a mean depth of 4.5 m. It is separated from the Mediterranean Sea by La Manga, a 22-km-long sandbar, with only three inlets: Las Encañizadas, Marchamalo, and El Estacio (Gilabert et al., 2023) (Fig. 1.9). El Estacio is the only channel wide and deep enough to allow boat navigation. Hydrodynamic conditions vary across the lagoon: the northern sector has water renewal times on the order of months, influenced by the general circulation of the lagoon and the proximity to El Estacio, while the southern sector has slower renewal times

(up to 400 days) and higher salinities. Overall, water renewal is poor, with current velocities around 0.03 m s^{-1} , and a generally well-mixed water column (García-Oliva et al., 2018; Morote-Sánchez et al., 2025a).

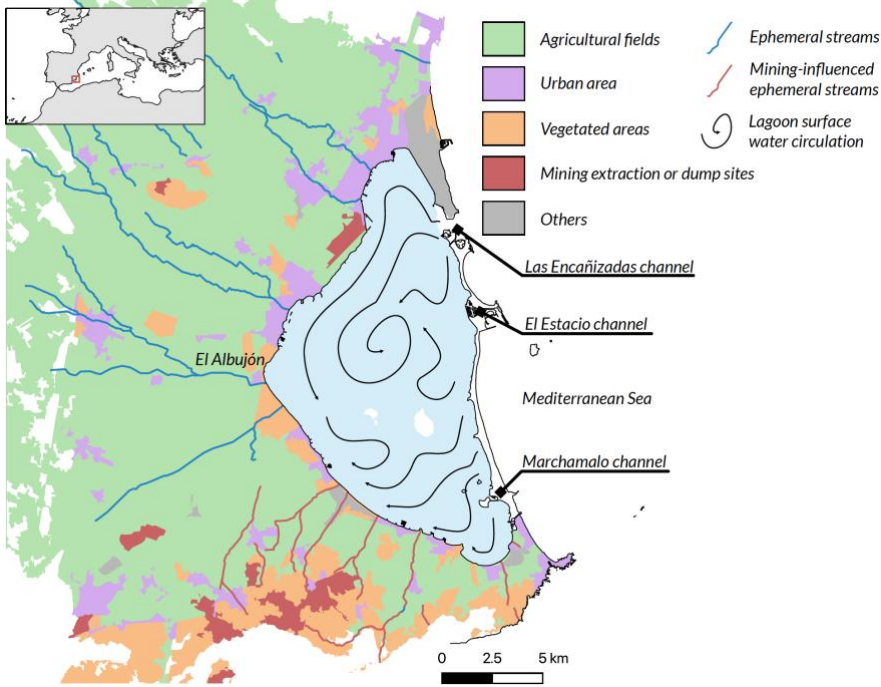


Figure 1.8. The Mar Menor coastal lagoon, showing the main land uses, channels, ephemeral streams, the permanent stream (El Albuñón), and the main surface circulation patterns under easterly winds based on López-Castejón et al. (2026).

The region experiences a semi-arid climate characterized by low annual precipitation ($\sim 300 \text{ mm}$; M. N. G. Alcaraz et al. (2024), occurring mainly during episodic events in spring and autumn. The lagoon features seasonal temperature variations, ranging from 10 to 31°C (mean $\sim 18^\circ \text{C}$), reflecting the typical Mediterranean climate pattern. Because evaporation exceeds rainfall and water renewal is limited, the lagoon has a hypersaline regime (40 to 46), above the mean Western Mediterranean salinity of 38 (Aydogdu et al., 2023). Dissolved oxygen concentrations in the lagoon range between 2.9 and 9.9 mg L^{-1} , with the lowest values during summer (López-Andreu et al., 2023).

Winds mainly modulate circulation in the lagoon, with minimal influence from astronomical tides (López-Castejón et al., 2026). The lagoon is characterized by weak winds ($\sim 6 \text{ m s}^{-1}$), with eastern thermal winds predominating in summer and western winds in autumn and winter (Morote-Sánchez et al., 2025b). Sea level is

primarily influenced by atmospheric pressure variations through the inverse barometer effect, but wind also plays a key role, causing water-level accumulations of up to 6 cm under peak wind conditions and triggering seiche oscillations within the lagoon (López-Castejón et al., 2026).

The lagoon's bottom sediments are dominated by a ~1 m layer of fine-grained muds, covering ~87% of the area (with 65% silt content), while sandy sediments dominate shallower coastal zones (~10%) (Alorda-Montiel et al., 2025; Gómez-Ballesteros et al., 2017). These muddy sediments are colonized by *Cymodocea nodosa*–*Caulerpa prolifera* meadows, which occupy ~90% of the lagoon floor (Pérez-Ruzafa et al., 2020a). Although fine sediments typically exhibit low intrinsic permeability, the high abundance of benthic fauna and extensive seagrass meadows enhance permeability through burrows and root structures, promoting advective flow (Sandonnini et al., 2024; Santos et al., 2012b).

Mar Menor has a high ecological importance, supporting a wide range of species and habitats (León & Bellido, 2016), and provides valuable ecosystem services (Velasco et al., 2018). Its ecological value is recognized through multiple national and international conservation designations, including the Ramsar Convention on Wetlands of International Importance, the Specially Protected Areas of Mediterranean Importance, the European Union Bird Directive from the Natura 2000 Network, and Sites of Community Importance.

The lagoon receives contamination from both diffuse and point sources generated by human activities in its adjacent watershed, the Campo de Cartagena (1316 km²), (León & Bellido, 2016) (Fig. 1.9). These activities include: i) historical mining in the La Unión mountain range to the south (M. N. G. Alcaraz et al., 2024), ii) urbanization and tourism development along the coast, including discharges from wastewater treatment plants (Álvarez-Rogel et al., 2006), iii) extensive agricultural practices, particularly along the western border of the lagoon, which constitute the main sources of nutrient pollution (Arauzo et al., 2024). These activities generate contamination from metals, including Ag, Pb, Zn, Cu, Fe, and Mn (Alorda-Montiel et al., 2025), nitrogen and phosphorus (Pérez-Martín, 2023), and polycyclic aromatic hydrocarbons and current-use pesticides, among others (Carratalá et al., 2017). These pressures reflect the region's intensive human use: agriculture underwent a profound transformation in the late 1970s, shifting from dry crops to irrigated fields following a main river transfer (Tajo-Segura water transfer), and agricultural land use currently covers about 50% of the catchment, making the area one of the most productive in Europe (Pacheco et al., 2025; García-Ayllón, 2018). Overall, the cumulative effects of human pressures have

driven ongoing ecological degradation in the lagoon over the past decades (León & Bellido, 2016).

The lagoon experienced an environmental collapse in 2016 after evolving from an oligotrophic state before the 1970s, similar to the nearby Mediterranean Sea, to its current eutrophic state as a result of these human-induced pressures, suffering an environmental collapse in 2016 (Álvarez-Rogel et al., 2020). The largest degradation event occurred later in 2019, when a cut-off low (locally known as *DANA*) dragged large amounts of pollutants to the lagoon, causing oxygen concentrations to drop to hypoxic and anoxic levels and triggering a euxinic episode (sulfur waters), resulting in a dystrophic crisis (Álvarez-Rogel et al., 2020). Another localized anoxia event affected the southern part of the lagoon in 2021. These episodes led to the loss of seagrass meadows and massive fish die-offs (Pérez-Ruzafa et al., 2019). The widespread perception of the environmental impacts and risks, particularly those related to water pollution, urban development, and ecosystem and species loss (Velasco et al., 2018), has contributed to Mar Menor becoming the first ecosystem in Europe to gain legal personality recognition (Law 19/2022), granting it legal status and the ability to defend its ecosystem.

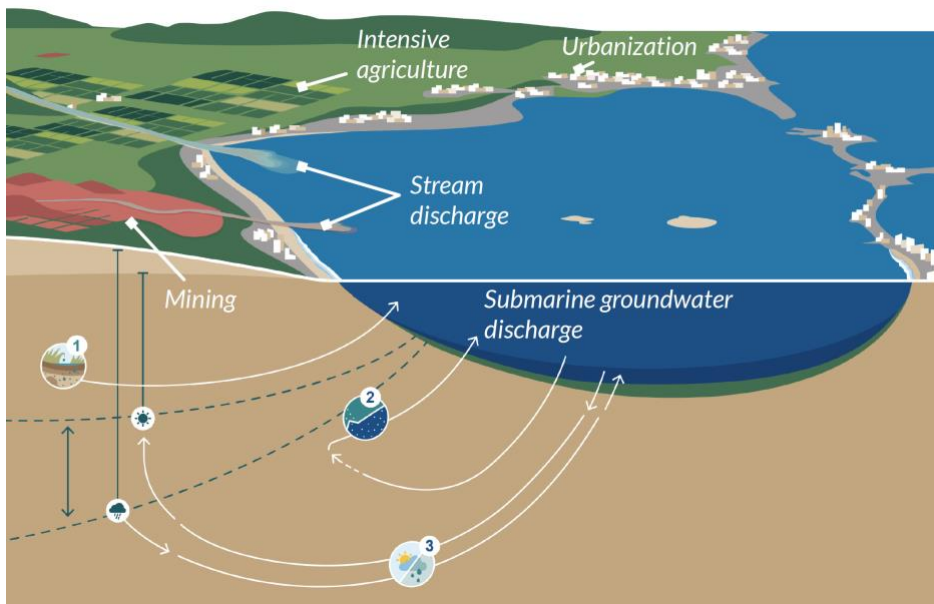


Figure 1.9. Schematic representation of the Mar Menor coastal lagoon, highlighting its main anthropogenic pressures and solute input pathways.

Although Mar Menor is one of the most researched lagoons in the Mediterranean (Soria et al., 2022), there is still disagreement over the primary routes by which pollutants enter the lagoon and the relative contributions of groundwater and surface runoff (Cabello & Brugnach, 2023). In addition to the permanently flowing *Rambla del Albujón*, which delivers an estimated mean runoff of $20 \text{ hm}^3 \text{ y}^{-1}$ to the lagoon (Senent-Aparicio et al., 2021), multiple intermittent watercourses, locally known as *ramblas*, discharge only during intense rain events. At a subsurface level, the lagoon is connected to the upper Quaternary layer of the Campo de Cartagena aquifer, an unconfined aquifer composed of gravels, sands, and clays (Alcolea et al., 2019). This aquifer borders the lagoon along a 30 km-long and 5 m-deep contact front (Martínez-Alvarez et al., 2011), with an average thickness of 50 m that increases from west to east, reaching up to 150 m near the coast (Jiménez-Martínez et al., 2012). The aquifer extends beneath the lagoon, allowing for water and solute exchange between the lagoon water and the sediments. Intensification of irrigation following the shift to intensive agriculture raised the water table, leading to increased terrestrial groundwater discharge to the lagoon (Velasco et al., 2006). Current hydrogeological models estimate fresh groundwater discharge to the lagoon between 11 and $68 \text{ hm}^3 \text{ y}^{-1}$ (Alcolea et al., 2019; Domingo-Pinillos et al., 2018; Jiménez-Martínez et al., 2016; Senent-Aparicio et al., 2021). However, the magnitude of other SGD pathways, including recirculated seawater, remains largely unknown, and their contribution to contaminant transport and the ongoing ecological degradation of Mar Menor has yet to be fully assessed.

2. Objectives

This thesis explores knowledge gaps in the understanding of submarine groundwater discharge (SGD) and its implications for coastal biogeochemistry and ecosystem functioning. While the importance of SGD in hydrological and biogeochemical cycles is well-established, the research frontier has now shifted towards a multi-pathway conceptualization of SGD, and bulk estimates of solute fluxes remain unreliable without proper pathway discrimination. In particular, current challenges include: i) the characterization and quantification of overlapping pathways, constrained by methodological limitations; ii) understanding how biogeochemical transformations within the subterranean estuary modulate solute fluxes; iii) quantifying pathway-specific solute fluxes, given that different pathways often exhibit distinct geochemical signatures; and iv) linking these fluxes to seasonal ecological responses, which remains limited due to a lack of studies targeting annual-scale variability in SGD pathways.

To bridge these gaps, the general objective of this thesis is to **resolve overlapping submarine groundwater discharge pathways** by using radium isotopes and to **quantify pathway-resolved solute fluxes** to determine their role in ecosystem degradation. To achieve this, the research presented here follows a sequential approach that first frames SGD from a hydrological perspective by quantifying water flows, then incorporates the biogeochemical dimension to understand biogeochemical transformations within the subterranean estuary, and finally integrates ecosystem-scale impacts, such as eutrophication and coastal hypoxia. This framework is particularly relevant for vulnerable coastal lagoons like Mar Menor, where the core research of this thesis has been conducted. In this lagoon, limited water exchange with the ocean and high sensitivity to external chemical loading amplify the ecological consequences of SGD.

The main goal is divided into three specific aims, which are addressed in Chapters 4 to 6 of this thesis:

1. To quantify the **magnitude and temporal variability of different SGD pathways** (fresh SGD, long-scale recirculated SGD, and porewater exchange) in Mar Menor using radium isotopes. (*Chapter 4*)
2. To determine **nutrient fluxes associated with different SGD pathways** while accounting for reactive transport within the subterranean estuary and to evaluate their **ecological implications** for the Mar Menor ecosystem. (*Chapter 5*)
3. To assess the **contribution of SGD to coastal hypoxia** by quantifying the supply of **reduced compounds** and their direct dissolved oxygen demand. (*Chapter 6*)

3. Methods

3.1. Sample collection

Here we provide a general description of the methods used to collect water and sediment samples. Specific details on these methods are included within each chapter. Water samples were collected with different methods according to the sampled compartment. Water samples from the Mar Menor lagoon and in the neighboring Mediterranean Sea were collected using a submersible pump at a fixed depth, allowing the collection of samples directly from the boat. Similarly, water from streams was collected directly with a syringe or a submersible pump near the mouth. A submersible pump was used to extract groundwater from wells, which were first purged to guarantee that the water was fully renewed. Beach groundwater samples were collected using stainless steel shielded-screen well-point piezometers deployed at different depths (from 0.1 to 1 m) (Fig. 3.1). The piezometer was connected to a manual or peristaltic pump through acid-washed silicon tubing. Prior to sampling, the system was purged (~300 mL) to remove stagnant water within the tubing and to rinse the system. Radium (Ra) samples were collected from a Büchner flask coupled to the vacuum pump system, while samples for other solutes (nutrients and reduced species) were retrieved directly from the silicon tube through a three-way stopcock with a pre-rinsed syringe, minimizing oxygen exposure (Fig. 3.1).

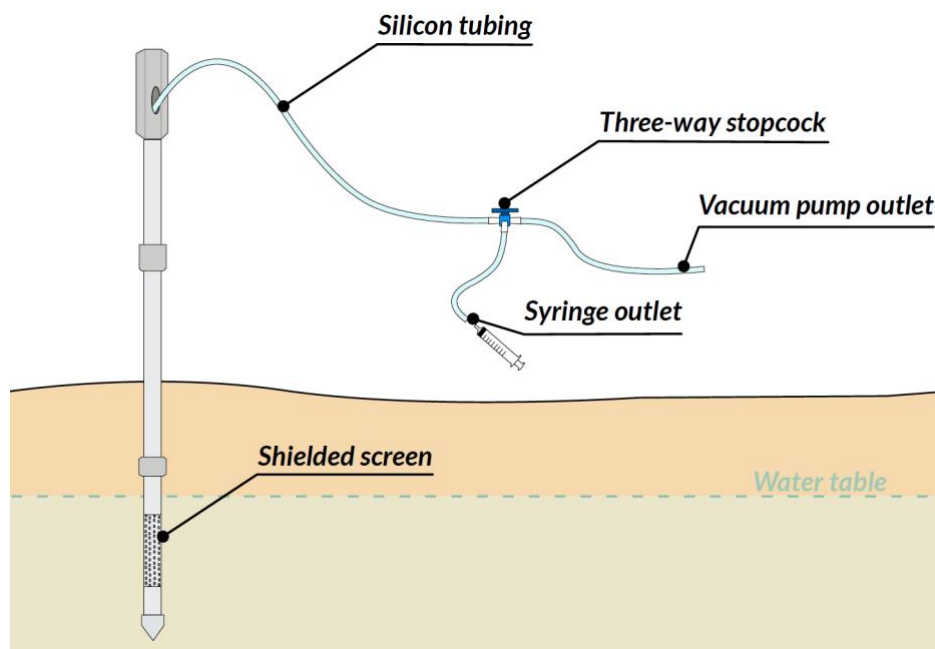


Figure 3.1. Schematic diagram of a manual push-point shielded-screen piezometer.

For groundwater collection within the lagoon at considerable depths below sea level (hereafter referred to as lagoon porewater), two different methods were employed depending on the required sample volume and target depth. The first approach consisted of manual piezometers connected to long tubing and deployed by scuba divers, allowing sampling from the boat. Alternatively, lagoon porewater samples were obtained from shallow sediment cores collected by scuba divers. The sediment cores were sliced at 2 cm intervals in an anoxic glove bag using an acid-cleaned PVC core cutter. Sections from the upper 4 cm were transferred to 50 mL centrifuge tubes and centrifuged at 4500 rpm for 30 minutes, after which the supernatant waters were collected with clean syringes without disturbing the sediment.

Additional sediment cores in the lagoon were collected by scuba divers, which were left undisturbed for further analysis. Emerged and submerged sediments in shallow areas were also directly collected with a shovel and stored in plastic bags.

3.2. Radium isotopes

3.2.1. Collection of samples for dissolved radium

Radium isotopes are the main tracers used in this thesis to quantify the magnitude of submarine groundwater discharge (SGD) fluxes. Ra isotopes must be pre-concentrated from large sample volumes, usually between 5 and 200 L, because they are naturally found in water at very low concentrations (Garcia-Orellana et al., 2021). Radium can be concentrated using MnO₂-impregnated acrylic fibers, which quantitatively extract Ra isotopes from water through cation exchange (Fig. 3.2) (Moore & Reid, 1973). Water samples are filtered through a column containing 20 g of Mn-fiber at a flow rate below 1 L min⁻¹. For samples containing reduced species, such as low-oxygen groundwater, the water should be oxygenated prior to filtration, as reducing agents can dissolve the MnO₂ coating on the fiber and interfere with complete Ra adsorption (Dulaiova & Burnett, 2004). After filtration, Mn-fibers are rinsed with Milli-Q ultrapure water (Ra-free water) to remove particles and sea salts and then dried down to 50% moisture content to ensure optimal Rn emanation efficiency during the analysis of short-lived Ra isotopes (Sun & Torgersen, 1998).

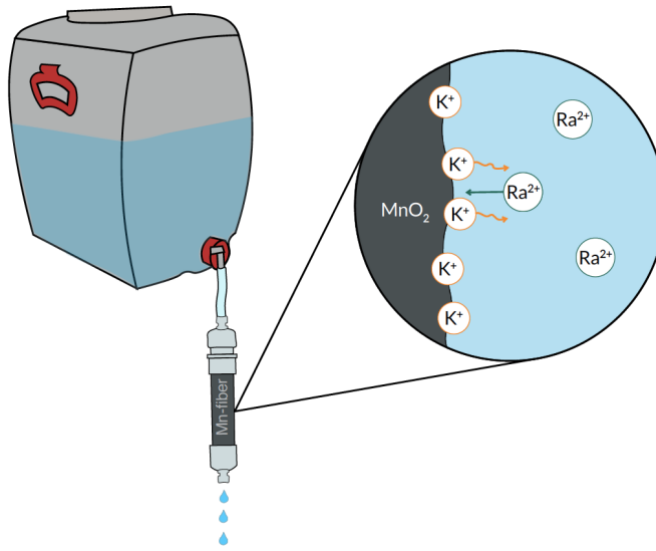


Figure 3.2. Schematic diagram of water sample filtration through columns filled with Mn-fibers for Ra analysis. Adapted from Diego-Feliu (2022a).

3.2.2. Measurement of radium isotopes with RaDeCC and gamma spectrometry

Short-lived Ra isotopes (^{223}Ra and ^{224}Ra) were measured using a solid scintillation detector, the Radium Delayed Coincidence Counter (RaDeCC) (Fig. 3.3), which is the most extensively used instrument for this purpose (Moore & Arnold, 1996). Columns loaded with pre-conditioned Mn-fiber (see "1" in Fig. 3.3) are connected to a closed helium circulation loop ("2"). An air pump ("3") circulates helium through the sample, transporting the decay products of ^{223}Ra and ^{224}Ra (^{219}Rn and ^{220}Rn , respectively) into a 1.1 L ZnS phosphor scintillation cell (Lucas cell) ("4"). When an alpha particle from the decay of Rn or its daughters strikes the cell walls, the resulting light signal is converted to an electronic pulse by the photomultiplier tube ("5"). An electronic gateway system ("6") records the pulses (or counts) and sorts them into three channels ("Total," "219," and "220") based on the time interval between two consecutive decay events. After an initial alpha decay is detected, the 219 channel is opened for 5.6 ms ($\sim 3 \cdot T_{1/2}$ of ^{215}Po , daughter of ^{219}Rn), followed by the 220 channel, which opens for 600 ms ($\sim 4 \cdot T_{1/2}$ of ^{216}Po , daughter of ^{219}Rn). The total channel continuously records every decay event during the measurement period (Diego-Feliu et al., 2020). Count rates from the 219 and 220 channels are then used to estimate ^{223}Ra and ^{224}Ra activities, accounting for detector efficiency and 219-220 cross-talk interferences (Moore

& Arnold, 1996), following the quantification guidelines provided in Diego-Feliu et al. (2020).

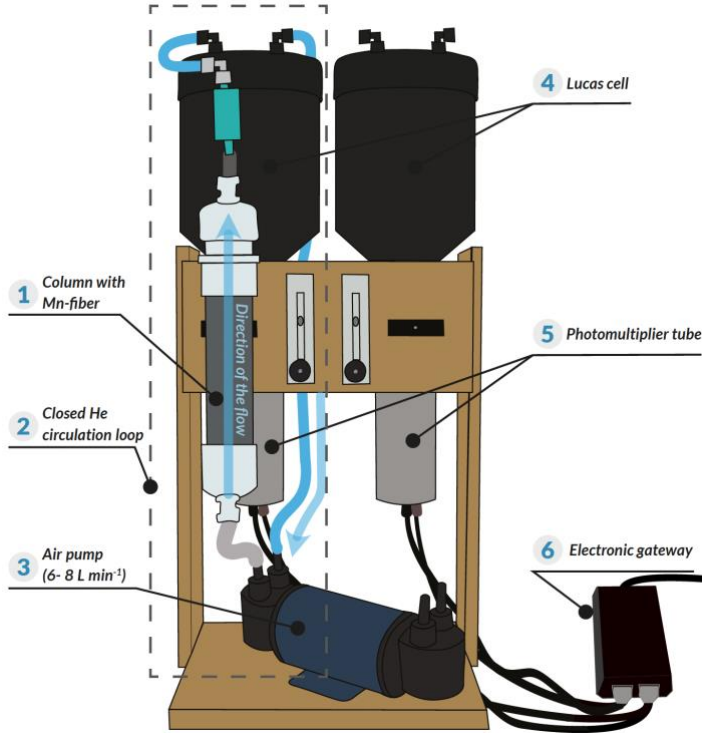


Figure 3.3. Schematic diagram of the Radium Delayed Coincidence Counter system. Adapted from Diego-Feliu (2022a).

Samples for ^{223}Ra and ^{224}Ra analysis require several measurements. The first measurement was conducted within a week of sampling to determine ^{223}Ra and ^{224}Ra activities. A second measurement was performed 7-21 days after sample collection to prevent ^{223}Ra overestimation. This isotope was directly estimated from the first measurement unless the total channel count rate exceeded 200 cpm, or the 220/219 ratio was above 10, or the 220/219 ratio exceeded 4 with the 220 count rate above 5 cpm (Diego-Feliu et al., 2020). To determine the excess activities of ^{224}Ra , an additional measurement was performed ~21 days after sample collection to quantify the ^{224}Ra activity supported by its parent (^{228}Th), thus determining ^{228}Th activities. Before each measurement, the RaDeCC system was purged for at least 15 minutes, along with background measurements (Moore, 2008). The efficiency of the 219 and 220 channels was calibrated using three different Mn-fiber tracer standards with known activities of ^{223}Ra and ^{224}Ra , respectively, which are in equilibrium with their parent isotopes, ^{227}Ac and ^{232}Th

(Scholten et al., 2010). The efficiencies ranged from 34 to 38% (± 3.0 to $\pm 3.2\%$) for the 219 channel and from 50 to 53% (± 1.7 to $\pm 2.9\%$) for the 220 channel.

Long-lived Ra isotopes (^{226}Ra and ^{228}Ra) are typically measured using a well-type high-purity germanium semiconductor detector via gamma spectrometry from Canberra. First, Mn-fibers are placed in a porcelain crucible and incinerated at 820°C for 16 hours. Then, the resulting ashes are ground and placed into sealed vials to prevent ^{222}Rn outgassing (Charette et al., 2001). The vials are aged for a minimum of three weeks to achieve secular equilibrium between ^{226}Ra (and ^{228}Ra) and their daughter radionuclides (^{214}Pb). Within the detector, gamma radiation interacts with the germanium crystal (see “1” in Fig. 3.4), producing electrical pulses that are recorded by a multichannel analyzer that generates an energy spectrum (“2”). The detector is surrounded by thick lead shielding to minimize background radiation (“3”) and cooled with liquid nitrogen to reduce interference by current generated by thermal energy (“4”). Samples were measured in well-type configurations (“5”) to maximize detection efficiency (Rodellas et al., 2023) (Fig. 3.4).

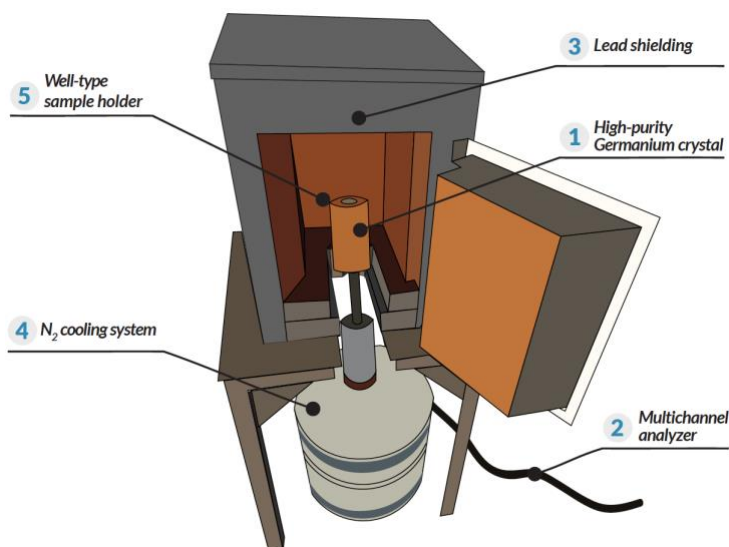


Figure 3.4. Schematic diagram of the HPGe gamma spectrometer system. Adapted from Diego-Feliu (2022a).

Measurement times varied from 1 to 4 days, depending on sample activity. The activities of ^{226}Ra and ^{228}Ra were determined based on the intensity of the photopeaks of their daughters, ^{214}Pb (351.9 keV) and ^{228}Ac (911.6 keV), respectively. Gamma spectrometry software (Genie 2000 Gamma Analysis Software) was used to locate the target peaks, calculate their area, and correct for

background and detector efficiency. The detection efficiencies for ^{226}Ra and ^{228}Ra were calibrated for different ash volumes in each detector, ranging from 18 to 29% for ^{226}Ra and 5.3 to 9.0% for ^{228}Ra .

3.2.3. Radium mass balance approach for quantifying submarine groundwater discharge and associated solute fluxes

Building a mass balance for the study area that takes into account all potential inputs and outputs of Ra is the most common method used to estimate SGD. The main sources of Ra to coastal waters include: i) atmospheric deposition, which is generally a minor input (<1% of the Ra budget) but can become relevant in large basins or areas with large atmospheric inputs; ii) surface water inputs from rivers, streams, storm runoff, and anthropogenic discharges, whose relative importance depends on their magnitude, contributing to both dissolved Ra and Ra released through desorption during freshwater-seawater mixing; iii) bottom sediments that release Ra isotopes via diffusion, erosion, bioturbation, and sediment resuspension, whose contribution depends on sediment grain size, mineral composition, and porosity and is typically more important for short-lived isotopes; iv) radioactive production, usually accounted for by reporting Ra activities as “excess” and representing a minor source; and v) inputs from SGD, which often represent a major source of Ra (Garcia-Orellana et al., 2021a).

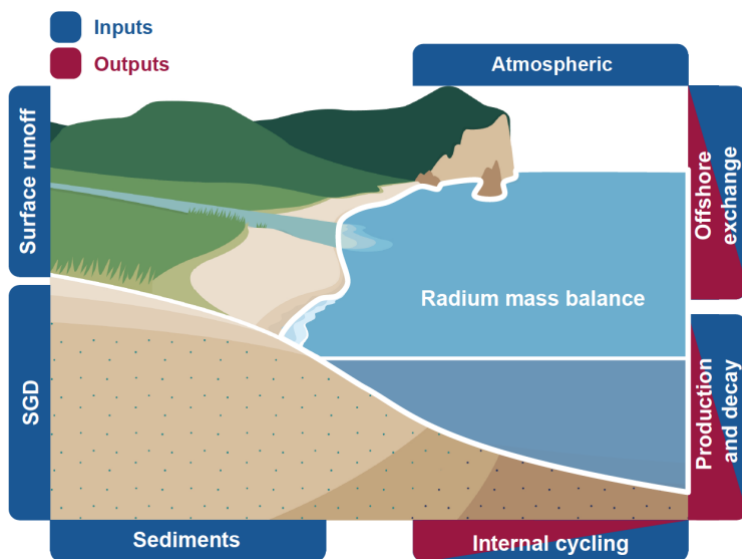


Figure 3.5. Main inputs and outputs of a Ra mass balance in the coastal ocean. Adapted from Garcia-Orellana et al. (2021).

The main sinks of Ra from coastal waters include: i) radioactive decay in the water column, which depends on the Ra inventory and the decay constant of the isotope considered and is more important for short-lived isotopes and in systems with long residence times; ii) net export to offshore waters, which is more relevant for long-lived isotopes and in systems with short residence; and iii) internal cycling, which represents a minor source and includes co-precipitation with salts, scavenging, or uptake by biota (Garcia-Orellana et al., 2021a).

The Ra flux supplied by SGD (F_{SGD}) can be estimated by a flux difference approach, provided all other major sources and sinks are constrained:

$$\frac{\partial I}{\partial t} = F_{atm} + F_{river} + F_{sed} + F_{prod} + F_{SGD} - F_{\lambda} - F_{ocean}, \quad \text{Equation 3.1}$$

where $\frac{\partial I}{\partial t}$ represents the change of the Ra inventory (Ra activity multiplied by the volume of the study area) over time. The most common approach to solving Eq. 3.1 is to assume steady-state conditions ($\frac{\partial I}{\partial t} = 0$), where the imbalance between inputs and outputs can be attributed to the Ra flux supplied by SGD (Fig. 3.5). The Ra flux (activity per unit of time, e.g. Bq d⁻¹) can be converted into a volumetric water flow (volume per unit of time, e.g. m³ d⁻¹) by dividing it by the characteristic Ra activity in the discharging waters (the groundwater endmember; activity per unit of volume, e.g. Bq m⁻³).

One of the main strengths of Ra isotopes is that they can be combined to differentiate processes occurring over different timescales by resolving concurrent mass balances (Rodellas et al., 2017). The enrichment rate of each isotope is controlled by the production rate, which is different for each isotope, and the retardation factor, defined as the reduction in solute velocity relative to groundwater due to interactions with the solid matrix, such as adsorption-desorption processes or weathering, until equilibrium with the parent isotope is reached (Diego-Feliu et al., 2021; McKinley & Russell Alexander, 1993). Consequently, short-lived isotopes can become enriched over short transit times (hours to days), while long-lived isotopes require longer transit times to become substantially enriched (Kiro et al., 2012; Y. Liu et al., 2018, 2025).

Although the Ra mass balance approach provides a robust framework for estimating SGD, inadequate characterization or conceptual assumptions regarding Ra activities can introduce considerable uncertainties (Rodellas et al., 2021). The spatial and temporal variability of Ra in groundwater, especially in complex systems, is one of the primary sources of error (A. L. H. Hughes et al., 2015). Indeed, groundwater Ra activities can vary up to nine orders of magnitude across

different settings (Girault et al., 2018). Despite this large variability, endmember characterization is often based on a limited number of samples and may neglect mixing between different water fractions (Cook et al. 2018a; Duque et al., 2019b). Strategies to overcome these limitations include field-based approaches, such as measuring Ra in a large number of samples or directly from discharging waters via springs or benthic chambers (Rodellas et al., 2023), and statistical analysis, such as Monte Carlo simulations, which involve stochastic sampling for different input parameters from probability distributions to constrain the potential range of SGD (S. J. Wilson et al., 2024c; Zhu et al., 2025). Additionally, reporting precautions, such as providing lower and upper limit estimates or the statistical distribution of groundwater activities, can further improve the uncertainty treatment of the results (J. Liu et al., 2021).

Another common source of uncertainty in Ra mass balance models is related to the temporal scale of the Ra isotope used. Most studies assume steady-state Ra conditions in the water column and for the model parameters, implying that tracer inputs equal tracer outputs over the timescale of the tracer. To validate this assumption, the tracer residence time (t_{tracer}) can be calculated following Rodellas et al. (2021):

$$t_{tracer} = \frac{1}{\lambda + \frac{1}{\tau}}, \quad \text{Equation 3.2}$$

where λ is the radioactive decay constant and τ is the surface water residence time.

The steady-state assumption, however, might not hold in extremely dynamic environments where transient processes take place over timescales shorter or comparable to the tracer residence time. Transient models that explicitly account for changes in the Ra inventory (e.g., by calculating finite differences between sequential samplings) are useful when the steady-state assumption is not valid. Weighting factors based on the temporal proximity of the disturbance in relation to the sample collection time can be applied to the model parameters to account for fluctuations that occur more quickly than t_{tracer} (Rodellas et al., 2021; Schubert et al., 2019).

After estimating the total or pathway-specific SGD flows, the solute fluxes (mass per unit of time, e.g., mol d⁻¹) associated can be calculated by multiplying the water flow (volume per unit of time, e.g., m³ d⁻¹) by the solute concentration characteristic of the discharging waters (endmember, e.g., mol m⁻³). However,

determining representative concentrations of SGD is often challenging because nutrients may undergo multiple biogeochemical transformations within the subterranean estuary (STE), thus displaying a non-conservative behavior (see section 1.3). Many studies address these challenges by directly sampling the discharge waters, similarly to Ra characterization, but others assume negligible transformations within the STE, which can introduce a source of bias (Santos et al., 2021; S. J. Wilson et al., 2024a).

3.3. Collection and analysis of dissolved chemical species in water samples

Nutrient samples were filtered in situ through 0.45 μm pore-size nylon syringe filters or, after centrifugation, through 0.45 μm Sterivex® units in the glove bag, and stored in 15 mL high-density polyethylene (HDPE) vials. In the field, samples were kept cold and frozen at -20°C upon return to the laboratory (<12 h after sampling). Nutrient analysis was performed using a colorimetric method with an Autoanalyzer AA3 HR for inorganic nutrients, with Fluorometer Jasco for ammonium determination, and an Autoanalyzer AA3 with Julabo Digestor for TDN at the Chemistry Service of the *Institut de Ciències del Mar* (Barcelona). The detection limits of the method were 0.006, 0.003, 0.003, 0.010, 0.016, and 0.071 μM for NO_3^- , NO_2^- , NH_4^+ , PO_4^{3+} , $\text{Si}(\text{OH})_4$, and TDN, respectively. For clarity, nitrate (NO_3^-) and nitrite (NO_2^-) are referred to as nitrogen oxyanions (NO_x), dissolved inorganic phosphorus (analyzed as orthophosphate; PO_4^{3+}) is referred to as DIP, while dissolved silicate (analyzed as silicic acid; $\text{Si}(\text{OH})_4$) is referred to as DSi. Dissolved inorganic nitrogen (DIN) is defined as the sum of NO_x and NH_4^+ , while total dissolved nitrogen (TDN) includes both inorganic and organic (dissolved organic nitrogen; DON) nitrogen fractions.

Samples for dissolved organic carbon (DOC) were filtered through pre-combusted (450°C for 4 h) glass fiber filters 0.7 μm (Whatman GF/F) and collected in pre-combusted acid-washed 20 mL glass vials. Samples were acidified using orthophosphoric acid to $\text{pH} < 2$ and stored at 4°C until analysis. DOC was measured with a TOC-L CSH Shimadzu organic carbon analyzer after removal of CO_2 by vigorous sparging with high-purity N_2 . The accuracy was tested daily with the DOC reference materials provided by D.A. Hansell (University of Miami).

For the determination of dissolved sulfide (H_2S , i.e., sum of H_2S , HS^- , and S_2^{2-}) concentrations, filtered porewater samples (1.5 mL) were fixed in situ with zinc acetate (5% final concentration, v/v) and stored at 20°C until analysis. Samples were thawed in the dark on ice, and H_2S was assessed using the colorimetric

methylene blue method (Cline, 1969; Cojean et al., 2020). Briefly, after dilution, 80 μL of stabilized Cline reagent was added to 1 mL of the sample. The mixture was shaken thoroughly, incubated in the dark for 15 min, and the absorbance was measured at 670 nm.

The collection and measurement of samples for methane (CH_4) followed two distinct methods, depending on the sampled compartment. For surface water and a subset of coastal groundwater samples, 4 mL of CH_4 samples were injected into 22 mL of gas-tight vials with a needle. Samples were stored cold and analyzed at Umea University via gas chromatography (Clarus 500, PerkinElmer Inc., USA) with prior addition of 20 μL of 4% HCl. A gas mixture with known concentrations of CH_4 (10 and 500 ppm) was prepared, stored, and analyzed as standards together with each batch of samples. For the remaining coastal groundwater samples and lagoon porewater samples, CH_4 collection and analysis were performed following the headspace equilibration technique (Striegl et al., 2012). Water samples were collected using a syringe equipped with a stopcock, drawing 30 mL of water and 30 mL of air to create the headspace. To facilitate equilibrium between water and air phases, the syringes were vigorously shaken for 1 minute and then kept at a constant temperature for 10 minutes. Subsequently, 30 mL of the gas phase was injected into a pre-evacuated 12 mL Exetainer® vial, creating overpressure to prevent contamination from external air. Ambient air samples were used as a reference for the headspace concentration. Samples were stored at $<4^\circ\text{C}$ until analysis. Methane concentrations in the gas phase were measured with an Agilent 7820A gas chromatograph equipped with a flame ionization detector (FID) and calculated based on the equilibration temperature, pressure, and Henry's law constant.

For dissolved iron (Fe^{2+}) determination, 3 mL of the filtered sample was fixed with 1 mL of HCl (2N) and stored at 4°C until analysis. Then, the dissolved Fe^{2+} concentrations were then determined using the Ferrozine method (Cojean et al., 2020; Stookey, 1970; Viollier et al., 2000). A total of 100 μL of fixed sample was transferred to a quartz microcuvette, to which 900 μL of ferrozine was added. The mixture was incubated for 2 min in the dark and absorbance was measured at 562 nm to determine the Fe^{2+} concentration.

4. Seasonality of submarine groundwater discharge pathways in a coastal lagoon revealed by radium isotopes

This chapter is based on:

Rodriguez-Puig, J., Rodellas, V., Diego-Feliu, M., Alcolea, A., Jiménez-Martínez, J., Alorda-Montiel, I., Alorda-Kleinglass, A., Pereira, F., Manzano, M., Gilabert, J., & Garcia-Orellana, J. Seasonality of submarine groundwater discharge pathways in a coastal lagoon revealed by radium isotopes: The importance of porewater exchange in summer (2025). *Journal of Hydrology*, 661, 133616.

4.1. Introduction

Submarine groundwater discharge (SGD) represents a complex process influenced by multiple driving mechanisms operating simultaneously across broad spatiotemporal scales, ranging from millimeters to kilometers and from seconds to years (Taniguchi et al., 2019). Quantifying different SGD pathways concurrently has historically been limited because most quantification methods target only specific SGD components or subsets of them. The accurate estimation of SGD using radium (Ra) isotopes presents several challenges, including quantifying the relative importance of each pathway, understanding the spatiotemporal scale of each process and selecting the appropriate Ra isotope(s) (Tamborski et al., 2020a), assessing the temporally variable nature of individual pathways, selecting representative endmembers while considering mixing between water fractions (Cook et al., 2018a), and including and reporting both conceptual and analytical uncertainties in estimated flows (Rodellas et al., 2021). As a result, the majority of Ra assessments report SGD as a total water flow (Ma & Zhang, 2020), while studies simultaneously differentiating between pathways are scarce (e.g., Sadat-Noori et al., 2016; Santos et al., 2008; H. Xu et al., 2024). Although total SGD estimations may be appropriate in systems dominated by a single pathway, they are a source of bias in systems where multiple pathways are present (Garcia-Orellana et al., 2021b). Additionally, most SGD studies are conducted under steady-state conditions, and only a few seek to understand temporal variations in SGD processes and their drivers (e.g., Bullock et al., 2024; Douglas et al., 2021; Liefer et al., 2014; Rocha et al., 2016).

This study is conducted in the Mar Menor coastal lagoon, where SGD is recognized as a potentially relevant source of nutrients to this ecosystem (Ruiz, et al., 2020; Tragsatec, 2020). In fact, some studies have independently quantified the magnitude of different SGD pathways in the lagoon, including fresh and recirculated SGD (M. Alcaraz et al., 2024; Alcolea et al., 2019; Baudron et al., 2015; Domingo-Pinillos et al., 2018; Jiménez-Martínez et al., 2016; Senent-Aparicio et al., 2021). However, none have simultaneously accounted for all SGD components within the lagoon and assessed their seasonal variability, resulting in an incomplete, system-wide understanding of the processes at play. To fill this knowledge gap, a transient Ra mass balance, a groundwater advective transport model for Ra, and a regional hydrogeological model are combined to i) identify the **main SGD pathways** in Mar Menor, ii) estimate the **magnitude and variability** of the discharge rate associated with each SGD pathway throughout the year, and iii) explore the main **mechanisms driving SGD** seasonality and the potential

implications for biogeochemical cycles of this and other coastal lagoons. The Ra-based methodology presented is expected to serve as a basis for the future evaluation of SGD pathways in other coastal lagoons.

4.2. Methods

4.2.1. Sampling

Three intensive seasonal surveys were conducted in March, July, and November 2021. During each survey, samples were collected to characterize the concentration of Ra isotopes (in addition to physicochemical parameters) from lagoon waters, streams, and coastal groundwater from wells and piezometers (Fig. 4.1). To ensure clarity, the term “porewater” is used for samples collected along the coastline using manual piezometers and “groundwater” for samples collected from wells, although both are essentially forms of groundwater. Twenty-one stations were evenly distributed across the lagoon to obtain representative samples (L1 to L21 in Fig. 4.1). During each intensive survey, surface water samples from the lagoon were collected using submersible pumps at 0.5 m deep in all stations. Deepwater samples were taken approximately 1 m above the seafloor at stations L2, L11, L13, and L17, hereafter referred to as monitoring stations. Surface lagoon samples were collected regularly at monitoring stations from March 2021 until May 2022 to assess temporal variability. Porewater samples were collected at 10 different sites along the coast using a direct-push, shielded-screen well-point piezometer to characterize the Ra activity in porewater potentially discharging to the lagoon (Pz1 to Pz10; Fig. 4.1). At each site, samples were collected at different depths (0.1 to 1.0 m) and along shore-perpendicular transects, including porewater samples on land (up to 80 m landwards) and in the lagoon (up to 50 m offshore). Additional porewater samples were also collected in the middle of the lagoon, at stations L2 and L17, with manual piezometers deployed by scuba divers.

Groundwater samples were collected from various wells located in different areas and featuring different depths (7 to 18 m). Surface stream samples were collected in the Rambla del Albujón stream and Carmolí wetland (Fig. 4.1) in all campaigns and in the Rambla del Beal in November 2021, when this ephemeral stream carried water. Overall, 274 water samples were collected throughout the sampling period, including 161 samples from the lagoon, 72 from piezometers, 32 from wells, and 9 from streams.

In April 2023, shallow sediment cores (~30 cm) were collected along the shoreline at sites Pz1, Pz5, and Pz7, as well as in the lagoon monitoring stations, to assess Ra diffusion to the water column from underlying sediments and to conduct Ra equilibration experiments (Tamborski et al., 2019). See A2.2 in the Appendices for more detail. Surface sediment was also collected at different sites (Pz1, Pz5, Pz7, and L11) for Ra desorption experiments. Additionally, sediment cores were collected later in May 2024 at the lagoon monitoring stations to obtain an independent estimate of the Ra activity in interstitial water samples, used only for comparison with Ra equilibration experiments.

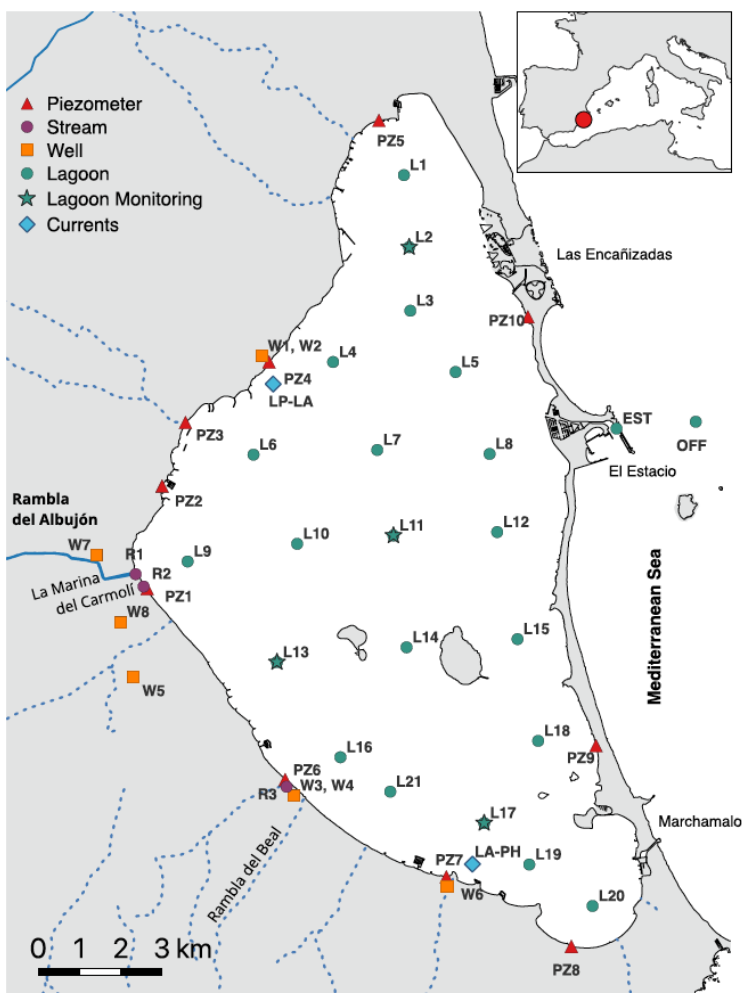


Figure 4.1. Sampling locations for wells (■), porewater collected from piezometers (▲), lagoon stations (●), and main streams (●). Lagoon monitoring stations are represented with ★. Data points for currents (◆) are also shown (see Discussion). Main ephemeral streams (Ramblas) are depicted by dashed blue lines, while the only permanent stream, the Rambla del Albuñón is depicted by a solid blue line.

Physicochemical parameters such as salinity, conductivity, specific conductivity, temperature, oxidation-reduction potential (ORP), pH, and dissolved oxygen (DO) were measured in situ with a multiparameter probe (YSI Professional Plus). Depth profiles of conductivity and temperature were conducted at each station using the SonTek CastAway CTD sensor. Large-volume samples were collected to determine Ra isotope activities (lagoon = 60 L, piezometer = 4–10 L, well = 15–60 L, stream = 5–60 L).

4.2.2. Radium mass balance

The magnitude of SGD into the Mar Menor coastal lagoon was estimated with a Ra mass balance approach. Considering all the relevant Ra fluxes in and out of the lagoon, an independent mass balance was used for each Ra isotope (except for ^{223}Ra due to larger relative uncertainties and lowest activities compared to the other isotopes) and sampling from March 2021 to May 2022 ($n = 17$). The Ra flux attributed to SGD was subsequently coupled to a one-dimensional advective transport model of radionuclides in groundwater to quantify the magnitude of water flows from different SGD pathways. The Ra mass balance can be expressed as follows:

$$\frac{dA_i V}{dt} = F_{\text{SGD},i} + F_{\text{Str},i} + F_{\text{Diff},i} + F_{\text{Des},i} - F_{\lambda,i} - F_{\text{Ex},i}, \quad \text{Equation 4.1}$$

where “i” refers to a specific Ra isotope, A_i is the Ra activity in the lagoon (dpm m^{-3}), V is the lagoon’s volume (m^3), and $\frac{dA_i V}{dt}$ is the change of Ra activity and volume over time (t ; d). The Ra inputs (dpm d^{-1}) are SGD ($F_{\text{SGD},i}$), permanent stream discharge ($F_{\text{Str},i}$), diffusion from bottom sediments due to concentration gradients ($F_{\text{Diff},i}$), and desorption from suspended sediments due to cationic exchange caused by bottom sediment resuspension ($F_{\text{Des},i}$). The Ra outputs (dpm d^{-1}) are radioactive decay ($F_{\lambda,i}$) and water exchange with the Mediterranean Sea through El Estacio and Marchamalo channels ($F_{\text{Ex},i}$). Input and output terms from Eq. 4.1 can be further developed as follows:

$$\frac{dA_i V}{dt} = F_{\text{SGD},i} + Q_{\text{Str}} A_{\text{Str},i} + J_{\text{Diff},i} S + V \tau A_{\text{Des},i} - \lambda_i V A_i - (Q_{\text{Out}} A_i - Q_{\text{In}} A_{\text{Est},i}), \quad \text{Equation 4.2}$$

where S is the surface area (m^2) of the lagoon and Q_x and A_x refer to water flows and Ra activities, respectively, and “x” refers to a specific output or input process. $Q_{\text{Str}} A_{\text{Str},i}$ is the Ra input via the Albuñón permanent stream, where Q_{Str} ($\text{m}^3 \text{d}^{-1}$) is

the water flow, retrieved from Canal Mar Menor streamflow monitoring database (<https://canalmarmenor.carm.es/>), and $A_{Str,i}$ (dpm m⁻³) is the Ra activity in Albuji3n, including dissolved and potentially desorbed Ra. Diffusive fluxes can be expressed as the product between the area-normalized Ra diffusive flux ($J_{Diff,i}$; dpm m⁻² d⁻¹) and the lagoon's surface area. The desorption flux is calculated considering the maximum desorbable activity ($A_{Des,i}$; dpm m⁻³) and the frequency of resuspension events (f ; d⁻¹). Regarding Ra outputs of the system, the first term is the Ra loss by radioactive decay, where λ_i is the decay constant of the given isotope (d⁻¹). The second output term is the water exchange with the Mediterranean Sea through the inlets, where Q_{In} and Q_{Out} (m³ d⁻¹) are the inflow and outflow rates, and $A_{Est,i}$ is the Ra activity at the mouth channel in the Mediterranean Sea. A detailed explanation of the estimation of each process can be found in Appendix A.1, while the definitions and values of the terms used in Eq. 4.2 and the calculated Ra fluxes for each process and isotope can be found, respectively, in Tables A.3 and A.4.

4.3. Results

4.3.1. Characterization of porewater, groundwater, and stream water

Porewater samples collected from piezometers close to the shoreline presented highly variable, site-dependent pH values, DO concentrations, ORP values, and salinities. Salinity ranged from 0.8 to 49, although most of the samples were brackish (median = 16.4). Fresh porewater, here defined as those samples with salinity values below 10, was found at all sampling sites, including piezometers placed in the submerged part of the beach, except for Pz9 and Pz10. These two sites are located in the La Manga sandbar, not connected to the aquifer, and therefore excluded from further analysis. The ubiquitous presence of fresh porewater at all the remaining sites is consistent with the high piezometric level in the Quaternary aquifer. Porewater salinity showed no correlation with depth, nor significant seasonal variations observed (one-way ANOVA p-value=0.30). Groundwater samples from wells generally had freshwater salinities, ranging from 3.9 to 7.3, except for W3, which was hypersaline (~65). Stream water salinity ranged from 4.1 to 12, with the Rambla del Beal stream (R3) exhibiting the highest salinity (12).

Radium activities showed strong variability between samples, as shown in Fig. 4.2. Samples were classified according to salinity and location: streams, well samples, porewater collected along the coastline, divided into fresh (<10), brackish (10–30),

and saline (>30), and lagoon waters. This classification is arbitrary and is used here solely to better distinguish between different types of water.

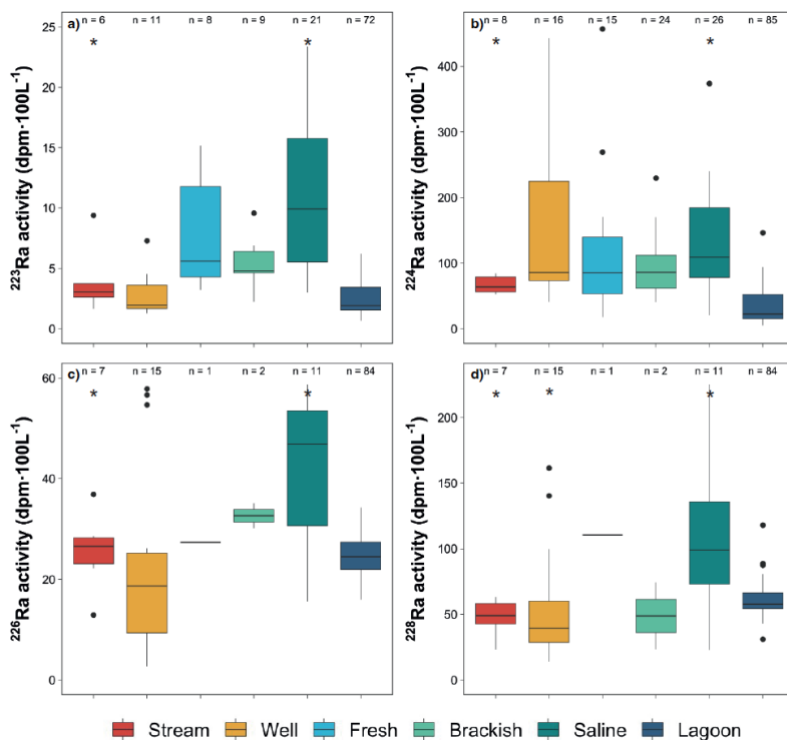


Figure 4.2. Activities of Ra isotopes in streams, wells, fresh (<10), brackish (10–30), and saline (>30) porewaters, and lagoon waters for a) ^{223}Ra , b) ^{224}Ra , c) ^{226}Ra , and d) ^{228}Ra in $\text{dpm } 100\text{L}^{-1}$. Asterisks (*) indicate that one or more samples exceeded the activity range of the plot and are therefore not displayed. Dots (·) represent statistical outliers.

Radium activities varied according to sample type and isotope (Table A.1 and Fig. A.1 in the Appendices). The highest Ra activities were found in saline porewater samples for all isotopes (Fig. 4.2). Porewater samples were enriched relative to lagoon activities, while stream waters showed comparable activity ranges to porewater activities for all isotopes. Most samples featured long-lived isotope activities below the detection limit due to low sample volumes. No significant seasonal variation in Ra activities was observed (one-way ANOVA p -values > 0.05 for all isotopes).

4.3.2. Characterization of lagoon water and its seasonal variability

Salinity in lagoon samples displayed a marked seasonality, with salinity increasing throughout the year (see Fig. A.3), peaking in October. A seasonal pattern was also observed for surface temperature in the lagoon, reflecting the climatic conditions of the area, with average temperatures ranging from 16 °C in January to 32 °C in August. DO also followed a seasonal pattern, with July samples featuring considerably lower concentrations (~60%) compared to November samples (~90%). The seasonal variability of salinity, temperature, and DO in lagoon waters is consistent with records from the Scientific Data Server of Mar Menor (SDC; <https://marmenor.upct.es>) and previous studies (Pérez-Ruzafa et al., 2019).

The salinity distribution in the lagoon was also heterogeneous in space, with increasing salinities from north to south in March and July (Fig. A.3). November did not follow the same spatial pattern, with the lowest salinities in the western part, possibly influenced by higher freshwater inputs from streams and runoff linked to precipitation during the previous days. In all three surveys, the Albuñón stream's freshwater discharge plume had an impact on L13, where surface waters had lower salinity levels than deep samples.

Radium activities in the lagoon showed a marked seasonal behavior for short-lived Ra isotopes (^{223}Ra and ^{224}Ra), as shown in Fig. 4.3. This seasonal pattern was also observed in the monthly samplings conducted from March 2021 until May 2022 (Fig. 4.4). Maximum ^{224}Ra activities were observed in June–July 2021, being 5.4 times higher than minimum activities (measured in October 2021–January 2022). This seasonal trend was less pronounced for ^{223}Ra , ^{226}Ra , and ^{228}Ra , with ratios of maximum to minimum average activities of 3.5, 1.5, and 1.8, respectively.

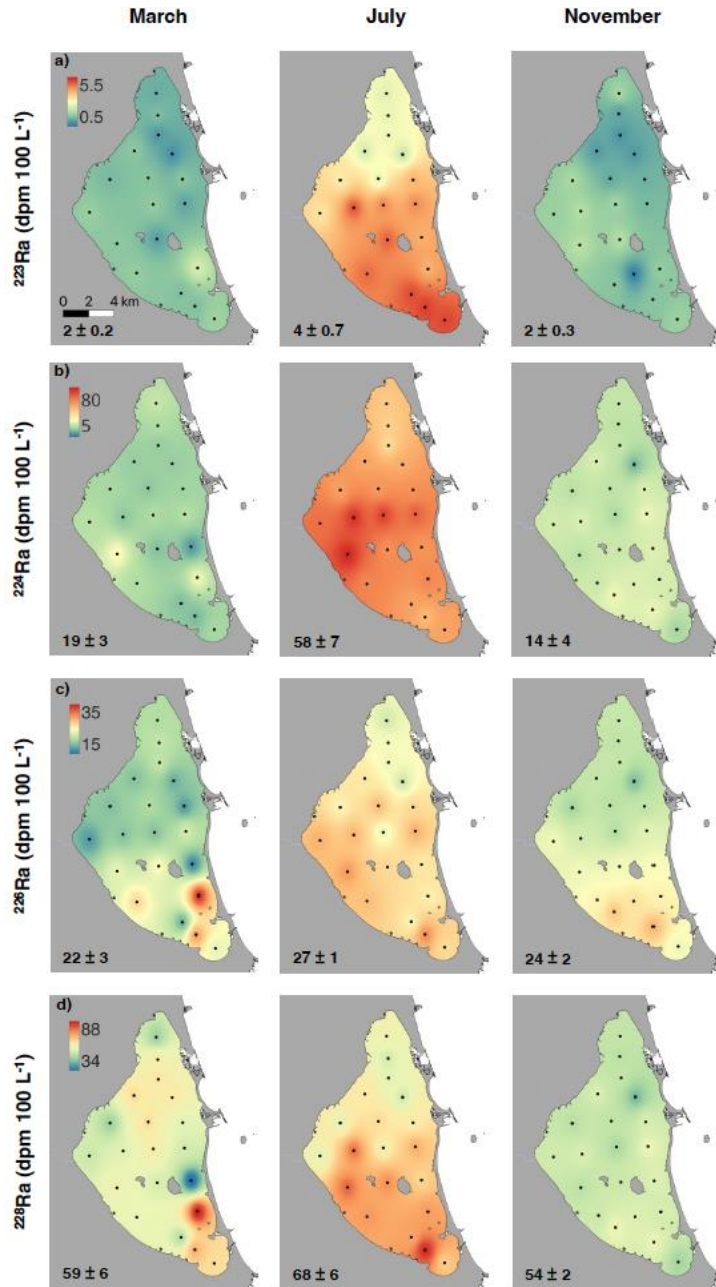


Figure 4.3. Seasonal surface distribution of Ra activity in the Mar Menor lagoon in March, July, and November 2021 for a) ^{223}Ra , b) ^{224}Ra , c) ^{226}Ra , and d) ^{228}Ra . Dots represent sampling stations used to derive the Inverse Distance Weight (IDW) interpolation. The average Ra activity and standard deviation for each sampling are also included in the insets.

The spatial data on Ra activities from all three campaigns also showed differences across seasons and sampling stations. In summer, an increasing north-to-south activity gradient was observed, especially for the long-lived isotopes and ^{223}Ra , possibly influenced by low-Ra Mediterranean Sea water entering the lagoon through the northern channels of Las Encañizadas and El Estacio. The main counterclockwise circulation pattern (Pérez-Ruzafa et al., 2023) likely contributes to this north-south imbalance. The activities of ^{224}Ra were homogeneously distributed over the lagoon surface. The vertical distribution of all Ra isotopes was homogeneous in all stations except for station L11, where ^{224}Ra values were twice as high in deep samples (~5 m) compared to surface ones in March and July 2021 (Table A.2).

In the offshore station in the Mediterranean Sea, Ra activities were 2–4 times lower (depending on the isotope) than in lagoon waters (0.23 ± 0.10 , 2.3 ± 0.3 , 7.6 ± 1.6 , and 2.0 ± 0.8 dpm 100L^{-1} for ^{223}Ra , ^{224}Ra , ^{226}Ra , and ^{228}Ra , respectively) as a consequence of the lack of significant sources of Ra in the open sea (Moore, 2010). Samples collected at the mouth of El Estacio channel showed a diluted signal from lagoon activities, with average activities of 1.2, 17, 13, and 18 dpm 100L^{-1} for ^{223}Ra , ^{224}Ra , ^{226}Ra , and ^{228}Ra , respectively.

4.3.3. Submarine groundwater discharge estimation

A common assumption in Ra mass balances is that the system is in steady state (i.e., Ra activities in the lagoon waters remain constant over time). However, the temporal evolution of Ra activities throughout the sampling period (Fig. 4.4) reveals that this assumption is not valid for ^{224}Ra and ^{228}Ra (i.e., $\frac{dA_i}{dt} \neq 0$). Considering the short half-life of ^{224}Ra , the changes in the ^{224}Ra inventory have been approximated using finite differences between two sequential samplings such as:

$$\frac{dI_i}{dt} \approx \frac{I_{(t+\Delta t),i} - I_{(t),i}}{\Delta t}, \quad \text{Equation 4.3}$$

where $I_{(t),i}$ and $I_{(t+\Delta t),i}$ are the measured Ra inventories at two sequential samplings, with Δt representing the elapsed time between these samplings. Because ^{228}Ra integrates longer times, rather than using differences between samplings (which introduces large uncertainties on the estimates), changes of inventories derived from the slope of linear long-term trends were used. Three trends were identified over the sampling period, which were significantly different (ANOVA test; p-value < 0.0005, F-statistic more than four times the F critical value). Conversely, ^{226}Ra activity variations (<25%) were comparable to analytical

uncertainties, therefore, inventories were assumed to remain constant over time. Ra inventories in the lagoon for each period were derived from the averaged Ra activities from stations L2, L11, and L17, sampled on a monthly basis. The inventories calculated using this three-station approach did not differ significantly from those obtained using data from the 20 stations sampled during the extensive campaigns ($p\text{-value} > 0.05$). Therefore, these three stations provide a reliable representation of the entire lagoon, consistent with the approach employed in Rapaglia et al.'s (2012) study on optimal sampling design. Lagoon volume variations were also included in the inventory calculations, using monthly average volumes derived from daily volume data (A1.4 in the Appendices).

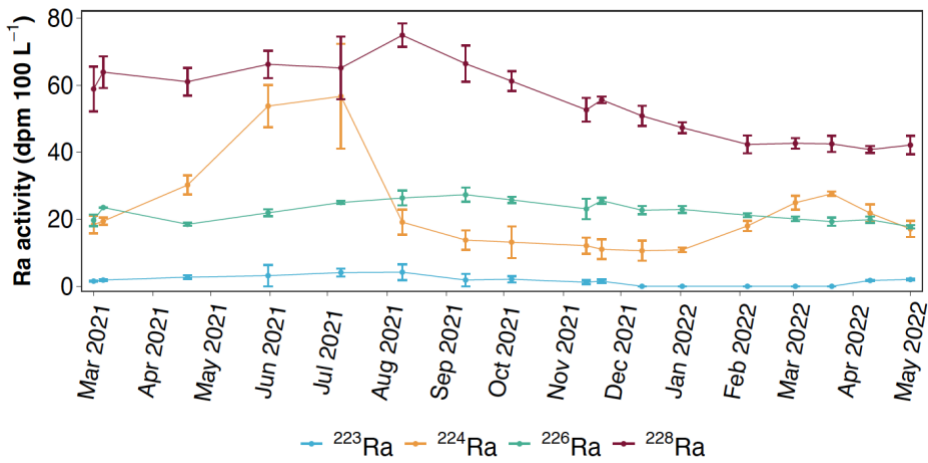


Figure 4.4. Evolution of Ra activities in the lagoon in dpm 100 L⁻¹ for ^{223}Ra , ^{224}Ra , ^{226}Ra , ^{228}Ra from March 2021 to May 2022 estimated from the monthly samplings ($n = 17$).

Another frequent assumption in Ra models is that all Ra fluxes are constant on a time scale comparable to the tracer residence time in the system (Rodellas et al., 2021). This assumption may not hold in a highly variable system where meteorological and oceanographic conditions fluctuate at a faster rate than the tracer timescale (i.e., particularly for long-lived isotopes). Tracer residence times for the Mar Menor coastal lagoon are calculated considering the average flushing time (refer to A1.5 in the Appendices) and the decay rate of each radionuclide following Rodellas et al. (2021). These residence times are relatively long (~ 5 d for ^{224}Ra , ~ 130 d for ^{226}Ra , and ~ 120 d for ^{228}Ra) compared to the scales of temporally variable flows, such as stream discharge and water exchange with the Mediterranean Sea. To account for faster variabilities, a weighting factor to stream discharge (Q_{str}) and water exchange (Q_{ex}) was applied depending on the temporal

proximity of the event relative to each sampling campaign, as shown in Eq. 4.4 and 4.5, following Schubert et al. (2019) and Rodellas et al. (2021):

$$W_{t,i} = e^{-\left(t \cdot \left(\lambda_i + \frac{1}{t_f}\right)\right)}, \quad \text{Equation 4.4}$$

and

$$Q_{x,i} = \frac{\sum_{t=0}^{t_{\max}} [W_{t,i} \cdot Q_t]}{\sum_{t=0}^{t_{\max}} W_{t,i}}, \quad \text{Equation 4.5}$$

where t are the different time steps before each sampling campaign, $W_{t,i}$ is the estimated weighting factor for each isotope, t_f is the average flushing time, and $Q_{x,i}$ ($\text{m}^3 \text{d}^{-1}$) is the weighted average water flow for Q_{Str} or Q_{ex} .

4.3.3.1. Quantification of Ra sources and sinks and the total SGD-driven Ra flux

The relative contribution of different sources and sinks of ^{224}Ra , ^{226}Ra , and ^{228}Ra for March, July, and November 2021 sampling campaigns is shown in Fig. 4.5. The magnitude of the input and output fluxes of ^{224}Ra , ^{226}Ra , and ^{228}Ra in each season is reported in Table A.4, and uncertainty treatment is detailed in A.1 in the Appendices. Due to its short half-life, radioactive decay was the main sink for ^{224}Ra , while water exchange between the lagoon and the Mediterranean Sea was the dominant sink for ^{226}Ra and ^{228}Ra . Submarine groundwater discharge was the main source of Ra isotopes to Mar Menor regardless of season, with a relative contribution of >85% of total inputs. Diffusion was the second most important contributor for ^{224}Ra , ranging from 2 to 10%, whereas the contributions of desorption and stream discharge were minimal (<2%) for all the isotopes. To minimize errors in the net Ra flux from SGD, the main contributors to the Ra budget were carefully evaluated. These included the Mediterranean Sea–Mar Menor water exchange, using a hydrodynamic model of the lagoon (Regional Ocean Model System; ROMS) (Moore et al., 2011; Shchepetkin & McWilliams, 2005), and ^{224}Ra diffusive processes from bottom sediments, assessed through sediment core incubations. An extensive explanation on the quantification of each sink and source can be found in section A.1. in the Appendices.

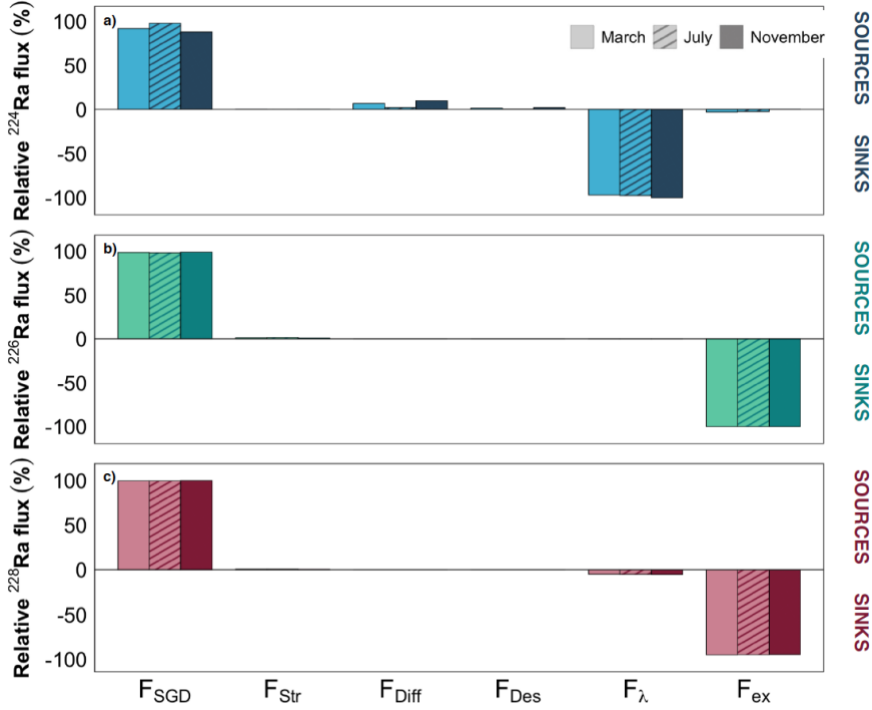


Figure 4.5. Relative contribution (in %) of each Ra sink and source to the total Ra inputs and outputs to Mar Menor by season for a) ^{224}Ra , b) ^{226}Ra , and c) ^{228}Ra . $F_{SGD,i}$ refers to total SGD, $F_{Str,i}$ is the permanent stream discharge, $F_{Diff,i}$ is the diffusion from bottom sediments, $F_{Des,i}$ refers to the desorption from suspended sediments, $F_{\lambda,i}$ is radioactive decay, and $F_{ex,i}$ is the water exchange with the Mediterranean Sea through the El Estacio and Marchamalo channels. The relative contributions of sources and sinks were calculated as percentages of the total inputs and outputs, respectively.

The ranges of SGD-derived Ra fluxes for all seasons ranged from 1.0×10^{10} to 6.4×10^{10} dpm d^{-1} for ^{224}Ra , from 6.5×10^8 to 7.2×10^8 dpm d^{-1} for ^{226}Ra , and from 0.5×10^9 to 3.5×10^9 dpm d^{-1} for ^{228}Ra . The ^{224}Ra fluxes are comparable to those previously estimated by Baudron et al. (2015). The SGD contribution to the ^{224}Ra and ^{228}Ra budgets varied across seasons, indicating higher SGD rates in summer. This was not observed for ^{226}Ra fluxes.

4.3.3.2. Groundwater dynamics in the Mar Menor lagoon explained by a three-SGD pathway system

The presence of fresh groundwater discharge to the lagoon is evidenced by findings from several studies (Alcolea et al., 2019; Domingo-Pinillos et al., 2018; Jiménez-Martínez et al., 2016; Senent-Aparicio et al., 2021). A first approximation of the ^{226}Ra flux associated with fresh SGD can be estimated using the fresh SGD flow derived from hydrogeological modeling (Alcolea et al., 2019) and the ^{226}Ra

activity in fresh shore samples (mean = 38 ± 11 dpm 100L^{-1}). This yields fluxes ranging from 4.6×10^7 to 4.8×10^7 dpm d^{-1} , implying that fresh SGD contributes only 6.4–7.1% of the total ^{226}Ra inputs from SGD. These results suggest that ^{226}Ra activities in the lagoon are not sustained solely by fresh SGD, but rather by a recirculation process with long transit times. Transit times determine groundwater enrichment in different Ra isotopes (Diego-Feliu et al., 2021; Michael et al., 2011). For instance, ^{226}Ra enrichment will only occur in processes with long temporal scales ($> \text{year}$) due to its long half-life, while all SGD pathways are typically enriched in ^{224}Ra due to its short regeneration time. The different seasonal oscillations of Ra isotopes observed in lagoon waters (i.e., more pronounced fluctuations of short-lived isotopes throughout the year compared to long-lived isotopes) can only be explained by the presence of a recirculation process with short transit times (i.e., enriched mainly in ^{224}Ra).

Taking this into account, three main SGD pathways are defined to explain groundwater dynamics in Mar Menor: i) **fresh groundwater discharge**, driven by hydraulic gradients in the Quaternary aquifer, ii) **long-scale recirculation through the sediments**, which responds to slow processes occurring in the freshwater–saltwater interface such as density gradients or seasonal oscillations, and iii) **cm-scale porewater exchange (PEX)**, driven by rapid processes such as wave pumping, ripple migration, or bioirrigation.

4.3.3.3. *Combining Ra isotopes and hydrological modelling to quantify SGD pathways*

In this section, the relative contribution of each pathway to the total SGD flow is assessed by integrating the outcomes of the non-stationary Ra mass balance in lagoon water (Eqs. 4.1 and 4.2) with a one-dimensional advective transport model of radionuclides in groundwater to evaluate the enrichment rate in Ra isotopes through various SGD pathways. The transport model (Eq. 4.6) has been detailed elsewhere (Garcia-Orellana et al., 2021b; Michael et al., 2011) and implies certain assumptions (e.g., homogeneous aquifer and groundwater composition, absence of weathering and Ra precipitation; see Diego-Feliu et al. (2021)). The application of this transport model allows for a first-order estimation of the Ra activities in different SGD pathways:

$$A_{\text{SGD},i} = A_i e^{-\lambda_i R \tau} + A_{\text{eq},i} (1 - e^{-\lambda_i R \tau}), \quad \text{Equation 4.6}$$

where the activity of the discharging groundwater for each pathway ($A_{\text{SGD},i}$) and radionuclide (i) depends on the Ra activity in infiltrated lagoon water (A_i ; only applied to recirculation processes), the Ra equilibrium activity in the aquifer or

permeable sediments ($A_{eq,i}$), i.e., the maximum Ra activity given the characteristics of the system (activities of parent radionuclides in sediment grains, porosity, and grain size), the decay constant (λ_i), the Ra retardation factor (R ; a measure of the Ra velocity relative to flow velocity), and the transit time of groundwater through the system (τ). Note that $A_{SGD,i}$ is equal to $A_{eq,i}$ for pathways and isotopes in radioactive equilibrium. The SGD-driven Ra flux to lagoon waters, estimated from the non-stationary Ra mass balances, includes the contribution of fresh SGD, long-scale recirculation, and PEX and can be represented as follows:

$$F_{SGD,i} = Q_F A_{F,i} + Q_L (A_{L,i} - A_i) + Q_S (A_{S,i} - A_i), \quad \text{Equation 4.7}$$

where $F_{SGD,i}$ is the Ra flux (dpm d^{-1}) delivered to the lagoon by SGD, derived from Eq. 4.1; Q_F , Q_L and Q_S are the water flows ($\text{m}^3 \text{d}^{-1}$) associated with fresh, long-scale recirculation, and PEX, respectively; $A_{F,i}$, $A_{L,i}$ and $A_{S,i}$ are the i isotope activities (dpm m^{-3}) in groundwater associated with fresh, long-scale recirculation, and PEX, respectively. Note that recirculation processes also imply the removal of Ra from overlying waters into sediments, and this loss term is accounted for by using net Ra fluxes (i.e., the difference of activities between the groundwater endmember ($A_{x,i}$) and overlying waters (A_i); Cook et al., 2018a). Assuming that Ra activities in fresh SGD are in equilibrium due to its long temporal scale, the combination of Eq. 4.6 and Eq. 4.7 can be expressed as:

$$F_{SGD,i} = Q_F A_{F,i} + Q_L (A_i e^{-\lambda_i R \tau} + A_{eq,L,i} (1 - e^{-\lambda_i R \tau_L}) - A_i) + Q_S (A_i e^{-\lambda_i R \tau} + A_{eq,S,i} (1 - e^{-\lambda_i R \tau_S}) - A_i). \quad \text{Equation 4.8}$$

For detailed information on the estimation of each term involved in Eq. 4.8 refer to A.2 in the Appendices. In the Mar Menor lagoon, the estimated Ra retardation factor for saline waters in lagoon sediments ranges from 4 to 80 (see A.2.3). Note that since both SGD recirculation pathways involve the circulation of saline groundwater through permeable sediments, the same retardation factor has been applied to both processes. Based on the estimated R , ^{224}Ra activities in PEX are expected to reach equilibrium (i.e., $A_{SGD,224}/A_{eq,224} \geq 0.95$, based on Eq. 4.6) for transit times of at least ~ 1 d. Conversely, only partial enrichments relative to equilibrium activities will occur for ^{228}Ra if PEX has a temporal scale longer than 1 d but shorter than ~ 100 d. ^{226}Ra , due to its long regeneration time, will not be significantly enriched in PEX processes with temporal scales < 100 d (i.e., $A_{SGD,226}/A_{eq,226} \leq 0.01$). Therefore, ^{226}Ra activities in PEX can be considered negligible, and short-scale recirculation can be excluded as a ^{226}Ra source. Refer to Text A.2.4 for more details on Ra enrichment and transit times in the aquifer.

For long-scale recirculation, high-salinity samples collected at the shoreline are assumed to represent the discharging groundwaters from this recirculation pathway. Thus, there is no need to account for Ra ingrowth along this pathway. Considering this, a simplified three-equation system for the different Ra isotopes can be derived from Eq. 4.8:

$$\begin{aligned}
 F_{\text{SGD},226} &= Q_F A_{F,226} + Q_L (A_{L,226} - A_{226}) \\
 F_{\text{SGD},224} &= Q_F A_{F,224} + Q_L (A_{L,224} - A_{224}) + Q_S (A_{S,224} - A_{224}) \\
 F_{\text{SGD},228} &= Q_F A_{F,228} + Q_L (A_{L,228} - A_{228}) + Q_S (A_{228} e^{-\lambda_{228} R \tau_S} + \\
 &\quad A_{\text{eq},S,228} (1 - e^{-\lambda_{228} R \tau_S}) - A_{228}),
 \end{aligned}
 \tag{Equation 4.9}$$

where Q_L , Q_S , and τ_S are the unknown terms. In this multi-pathway model, the freshwater flow has been independently assessed with a 3D surface-groundwater hydrogeological model of the Campo de Cartagena Quaternary aquifer. This regional-scale model, developed by Alcolea et al. (2019), accounts for all water inputs and outputs of the basin, except pumping and losses to underlying aquifers across leaky boreholes, which are accounted for by applying a correction to the groundwater mass balance. Fresh groundwater discharge is the main unknown term of the model (refer to A.2.1). The fresh SGD flow has also been weighted to account for fluctuations faster than the tracer timescale (see Eq. 4.5 in Results). Long-scale recirculation flows, PEX flows, and short-scale transit times have been subsequently quantified by solving the ^{226}Ra , ^{224}Ra , and ^{228}Ra mass balances, respectively (Eq. 4.9).

Selecting a representative isotope endmember activity ($A_{F,i}$, $A_{L,i}$, and $A_{S,i}$) of each SGD pathway is arguably one of the most challenging steps when estimating SGD flows, especially in complex systems with multiple sources (Cook et al., 2018a). In this study, the endmember activities for fresh SGD ($A_{F,i}$) and long-scale recirculation ($A_{L,i}$) are derived from a large pool of porewater samples collected near the shoreline during the March, July, and November surveys ($n=57$). All the samples are pooled together, as minimal seasonal variability has been observed, which allows for a better characterization of the SGD endmember (Charette, 2007). Well samples, located far from the shore, are excluded from the endmember pool due to the biogeochemical transformations that modify water composition (Ruiz-González et al., 2021; S. J. Wilson et al., 2024a). Although they are often used as endmembers in SGD studies, they are unlikely to be representative of the actual discharging water. Porewater samples with salinity values < 10 ($n=13$) are selected as representative of terrestrial freshwater

discharge ($A_{F,i}$), while porewater samples with salinity values > 30 ($n=12$) are selected as long-scale recirculation endmembers ($A_{L,i}$). Note that, while these thresholds are arbitrary, variations of ± 5 units (if $n \geq 5$) in the salinity threshold produce minor variations in the pool average, which remains within the range of uncertainties. The PEX endmember ($A_{S,i}$) pool is derived from Ra activity in interstitial water samples via ^{224}Ra equilibration experiments ($n=7$). The experiments were conducted in sediment cores collected at the inner part of the lagoon (A.2.2 in the Appendices). In this study, short-scale recirculation is assumed to occur all over the lagoon, as it is a ubiquitous process (Huettel et al., 2014; Santos et al., 2012a). This assumption is consistent with the observed homogeneous distribution of ^{224}Ra , which implies the widespread input of this isotope throughout the lagoon. Radium endmember activities in fresh SGD ($A_{F,i}$) are averaged from porewater samples collected near the shoreline (salinity < 10). Radium endmember activities in recirculation pathways ($A_{L,i}$ and $A_{S,i}$) are randomly selected from the sample pool using deterministic combinational analysis. The values for each Ra endmember activities ($A_{F,i}$, $A_{L,i}$, and $A_{S,i}$) can be found in Table A.5.

The quantification of long-scale recirculation (Q_L), PEX (Q_S), and PEX transit times (τ_S) is based on a Monte Carlo analysis (detailed in A.2.5.) of the model described in Eq. 4.9. In the analysis, 100,000 stochastic simulations were run for each mass balance and campaign with different key model parameter combinations. Water flows for PEX and long-scale recirculation are reported as the median and Interquartile Range (IQR) derived from the simulations.

4.3.3.4. *Magnitude and seasonal variability of SGD pathways: Recirculation processes dominate water flows into the lagoon*

The contributions of the main groundwater discharge processes to the Mar Menor lagoon throughout the year (fresh groundwater discharge, long-scale recirculation, and PEX) and stream discharge are presented in Fig. 4.6. The discharge rates associated with each SGD pathway estimated in this study reveal that Mar Menor is a recirculation-dominated environment, representing 96.1–99.9% of the overall water inputs.

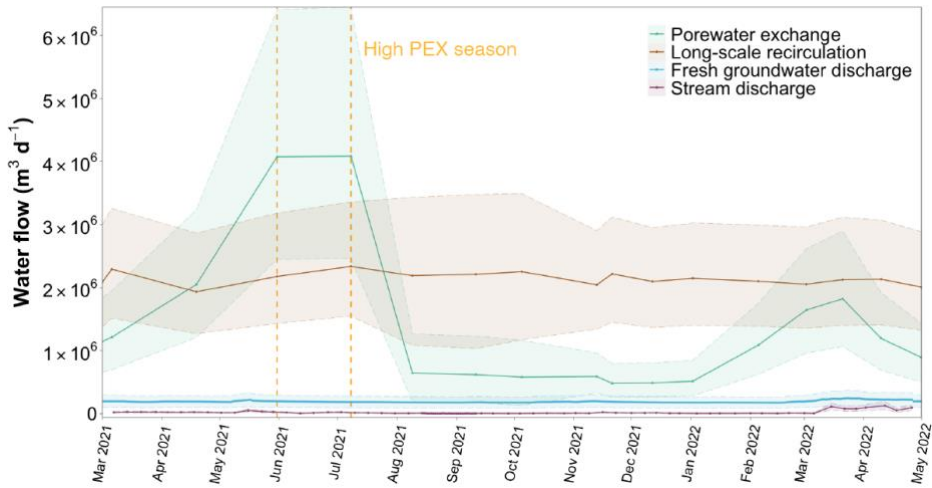


Figure 4.6. Estimated water flows ($\text{m}^3 \text{d}^{-1}$) for fresh groundwater discharge, long-scale recirculation, porewater exchange, and stream discharge, from March 2021 to May 2022. The shaded area represents uncertainty, estimated from IQR for porewater exchange and long-scale recirculation, or as a 50% error from the mean value for fresh groundwater discharge and stream discharge. Fresh groundwater discharge and stream discharge are represented here as a 10-day moving average, estimated from daily data and data of varying frequency, respectively. The area between the dashed lines indicates the period with the highest PEX flow.

Throughout the entire period (March 2021–May 2022), fresh groundwater discharge ranged from 5.4×10^3 to $130 \times 10^3 \text{ m}^3 \text{d}^{-1}$, long-scale recirculation rates ranged from 19×10^5 to $25 \times 10^5 \text{ m}^3 \text{d}^{-1}$, PEX ranged from 4.8×10^5 to $41 \times 10^5 \text{ m}^3 \text{d}^{-1}$, and stream discharge ranged from 5.1×10^3 to $240 \times 10^3 \text{ m}^3 \text{d}^{-1}$. The discharges associated with both recirculation processes are at least one order of magnitude higher than the freshwater inputs. If the discharge occurs along the coastline connected to the Quaternary Aquifer (i.e., excluding La Manga), water flows can be normalized to discharge per meter of coastline. This normalization yields discharge rates of $0.2\text{--}4.3 \text{ m}^3 \text{d}^{-1} \text{m}^{-1}$ for fresh SGD and $64\text{--}82 \text{ m}^3 \text{d}^{-1} \text{m}^{-1}$ for long-scale recirculation. If PEX is assumed to occur homogeneously over the lagoon's bottom sediment surface, the discharge rates can be down-scaled to area-normalized flows, resulting in PEX rates between 0.4 and 3.0 cm d^{-1} .

From a temporal perspective, both fresh SGD and long-scale recirculation remain relatively constant throughout the year. Conversely, PEX exhibits a marked seasonality (Fig. 4.6), with a progressive increase through spring, a peak in summer, and a decrease to its lowest discharge values in winter. In summer months, PEX rates are one order of magnitude higher than winter rates and account for up to 64% of the total SGD. The increase in PEX rates in summer leads to significantly higher total SGD rates during this season.

The estimated PEX transit times are between 2 and 14 days, based on the median from the Monte Carlo analysis. The shortest times are observed in June and July, and the longest in March 2021. However, the magnitude of the short-scale transit times (τ_S) should be restricted to a qualitative assessment, as this model is highly dependent on the ^{226}Ra flux of long-recirculated seawater and the subsequently derived Q_L , the Ra retardation factor (R), and the estimated inventory changes over time for ^{228}Ra . Therefore, small changes in these parameters can lead to different transit times. Further determination of transit times would thus be needed for more accurate results.

4.4. Discussion

4.4.1. A high water table elevation sustains relatively constant fresh SGD and long-scale recirculation

Water flows associated with fresh groundwater discharge and long-scale recirculation remain relatively constant throughout the year (Fig. 4.7a). Fresh SGD is typically driven by terrestrial hydraulic gradients. In the Mar Menor lagoon, the high elevation of the water table is sustained by infiltration from intensively irrigated agricultural fields in the watershed year-round (i.e., a constant hydraulic gradient)(García-Pintado et al., 2007; Martínez-Alvarez et al., 2011). As a result, the salt wedge toe remains virtually stable throughout the year (Alcolea et al., 2019).

Occasional events of intense precipitation can also cause variations in fresh SGD, as evidenced by its response to high precipitation levels in 2022, particularly during spring (Fig. 4.7), one of the wettest seasons in the entire data series available. Precipitation during the summer months in 2021 was as low as 5–6 mm, ~2% relative to total precipitation in spring 2022, according to monitoring data from regional water management agencies (*Confederación Hidrográfica del Segura and Sistema de Información Agroclimática para el Regadío*). Stream discharge is also mainly fed by agricultural drainages, although it can also be governed by peaks in precipitation and is positively related to monthly precipitation patterns ($r = 0.71$, $p \leq 0.05$), consistent with Velasco et al.'s (2006) findings.

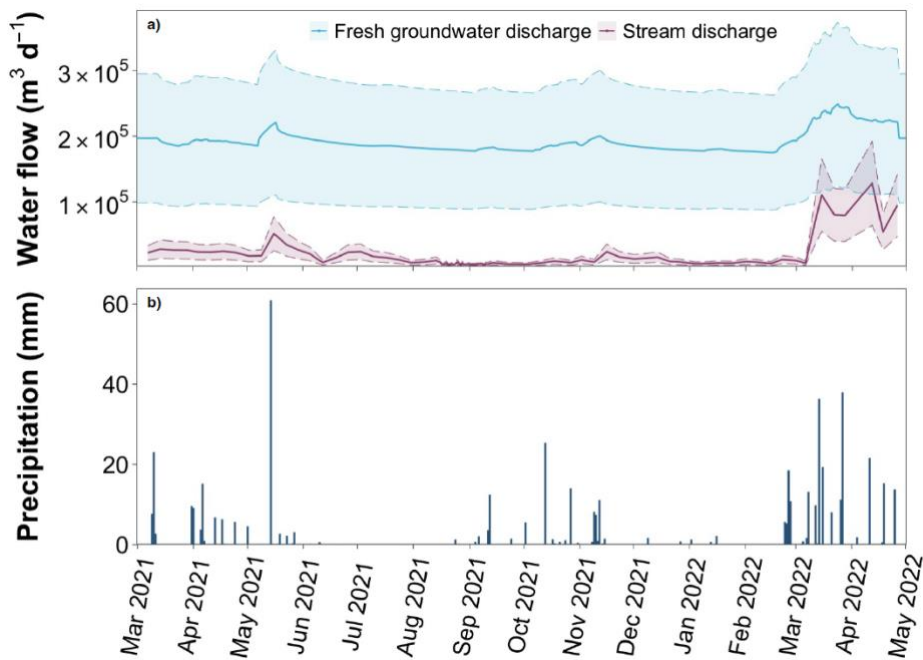


Figure 4.7. a) Estimated water flows ($\text{m}^3 \text{d}^{-1}$) for fresh groundwater discharge and stream discharge, represented as a 10-day moving average, estimated from daily data and data of varying frequency, respectively, from March 2021 to May 2022; b) Precipitation in Mar Menor lagoon for the same period. Data retrieved from San Javier meteorological station (*Sistema de Información Agroclimática para el Regadío* monitoring data; <https://servicio.mapa.gob.es/websiar/>).

4.4.2. What drives large porewater exchange flows in summer?

Although some studies have attempted to understand individual pathways and the drivers of their temporal patterns (e.g., Bullock et al., 2024; Ferrarin et al., 2008; Rodellas et al., 2017), information on the seasonal variability of SGD in multi-pathway systems is scarce. PEX, which occurs at a small scale (cm–m scale), can be driven by a wide range of processes, including shear flows, wave pumping, and bioirrigation, among others (Garcia-Orellana et al., 2021; Santos et al., 2012a). In this section, the primary known drivers of PEX that match the observed annual pattern in Mar Menor are discussed, and the presence of a seasonally variable driver is hypothesized. Drivers that are not primarily influenced by seasonal processes (e.g., flow and topography-induced pressure gradients), occur over longer timescales (e.g., sediment compaction), or are relevant only in sandy sediments (e.g., shear-induced flow) (Santos et al., 2012a) are thus excluded.

4.4.2.1. *Density-driven convection*

One of the driving mechanisms of porewater exchange is density-driven convection (Santos et al., 2012b), which can occur over different spatial scales. This process results from the higher density of the overlying water compared to porewater. In Mar Menor, the salinity of lagoon waters increases in summer as a result of evaporative processes, potentially inducing PEX flows through density gradients. According to Martínez-Alvarez et al. (2011), daily monthly evaporation rates are at their minimum in February (1.4 mm d^{-1}) and maximum in August (6.3 mm d^{-1}). However, measured porewater salinities in the lagoon bottom were slightly higher than those in the water column (40.2–47.8 in porewaters vs. 40.1–40.8 in the lagoon in June 2021, and 43.3–44.6 vs. 42.6–43.8 in May 2024). The denser porewater would thus prevent this type of convection.

4.4.2.2. *Wind conditions*

Wind patterns have been identified as major drivers of SGD in certain coastal settings (Bullock et al., 2024b; Guimond et al., 2023; Stieglitz et al., 2013). Wind conditions and fetch can enhance mechanisms like ripple migration and wave pumping by influencing sea level, wave heights, wave directions, and current speeds (King et al., 2009; Y. Li et al., 2017; Rodellas et al., 2020). This surface water hydrodynamics can thus drive PEX variations over the timescale of changes in winds patterns (e.g., weather conditions, fetch, and bathymetry). For instance, strong wind events have been shown to force PEX flows of up to 50 cm d^{-1} through wave pumping in another shallow Mediterranean coastal lagoon (Rodellas et al., 2020). In Mar Menor, the combination of wind effects and the lagoon's shallow depth (average of 4.5 m) could favor wave pumping, forcing the recirculation of water through sediments (Precht & Huettel, 2003). The region is characterized by thermal winds, driven by temperature differences between land and sea. During spring and summer, inland heat intensifies, generating longer and more sustained NE winds, which have the largest fetch. Despite more frequent NE wind events in summer, there is not a consistent increase in winds from winter to summer that could justify the progressive increase in PEX (Fig. 4.8b). Wind-induced wave height is generally low in the lagoon, with maximum heights occurring in winter during strong storm events, reaching up to 1 m. Wave pumping has been shown to drive PEX up to 1.5 cm d^{-1} with wind speeds of 5 m s^{-1} in a shallow estuary (Sawyer et al., 2013). During summer, there were only 22 daily events of wind $> 5 \text{ m s}^{-1}$ and NE direction, unlikely to drive sustained PEX flows in the summer of $2\text{--}3 \text{ cm d}^{-1}$. Surface currents in the lagoon are also wind-

dominated and generally weak ($<0.1 \text{ m s}^{-1}$) (Baudron et al., 2015), with three main currents flowing parallel to the coastline (Comité de asesoramiento científico del Mar Menor, 2017; Fraile-Nuez et al., 2016). From March 2021 to May 2022, the average surface current speed was 0.03 m s^{-1} . Currents were stronger in winter and spring (up to 0.27 m s^{-1}), showing opposite seasonality to PEX (Fig. 4.8c). Based on this, there is no clear evidence of wind-induced seasonality of PEX flows in Mar Menor to explain the highest discharge rates in summer. However, it is worth noticing the increase in PEX in Spring 2022, coinciding with a period of stronger currents and winds.

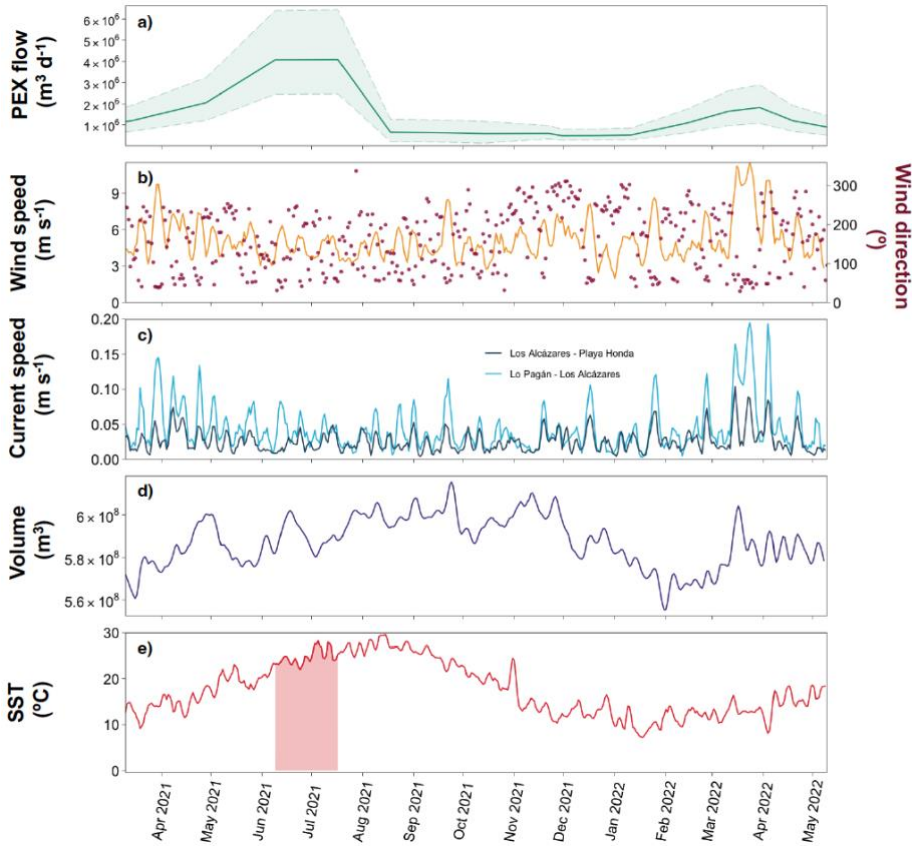


Figure 4.8. a) Porewater exchange rate ($\text{m}^3 \text{d}^{-1}$), b) wind speed (m s^{-1}), c) surface current speed (m s^{-1}), d) lagoon volume (m^3), and e) Sea Surface Temperature (SST; $^\circ\text{C}$) from March 2021 to May 2022. Data for wind speed and direction were retrieved from ERA5 reanalysis (Hersbach et al., 2020) and were averaged over Mar Menor surface. Data for lagoon's volume and current speed was retrieved from a ROMS hydrodynamic model of Mar Menor (Text A.1.4). Data for current speed was obtained from two points located on the main surface current flow paths (see Fig.4.1), Lo Pagán–Los Alcázares (LP–LA) and Los Alcázares–Playa Honda (LA–PH). Data for SST was retrieved from SDC Mar Menor. Wind speed, current speed, volume, and SST data are presented here as 5-day, 3-day, 5-day, and 3-day moving averages, respectively, calculated from daily measurements.

4.4.2.3. *Water-level variations*

Water-level variations can also promote lagoon water recirculation through sediments (Rodellas et al., 2020). Water level variations in coastal lagoons can be produced by fluctuations in winds or atmospheric pressure, as well as by the dynamic balance between evaporation and precipitation. In Mar Menor, the water volume of the lagoon primarily responds to seasonal pressure fluctuations that regulate the mean levels of the Mediterranean Sea and, therefore, the one of the lagoon (Gilabert et al., 2020). In summer, although atmospheric pressure is higher, warmer temperatures increase water evaporation. This causes a large amount of water from the Mediterranean Sea to enter the lagoon, raising the water level. The correlation between the two can be observed in Fig. 4.8. Although volume variations also seem to match the temporal PEX pattern in Fig. 4.8, literature suggests that these two processes tend to have opposing behaviors because higher water depths minimize the interaction between surface hydrodynamics and the seabed (Precht & Huettel, 2003).

4.4.2.4. *Bioirrigation*

Faunal activity in the sediment can also be a major contributor to water-pumping processes (Huettel et al., 2014). Infaunal organisms create burrows in the sediments, increasing sediment porosity and hydraulic conductivity, thus enhancing horizontal and vertical water fluxes (Garcia-Orellana et al., 2014; Santos et al., 2012a; Smith et al., 2008). This allows water to infiltrate and exfiltrate due to physical drivers like wave pumping. As a result, when high biomass density is present, bioirrigation can become a dominant driver of PEX (Volkenborn et al., 2007). Seasonality in bioirrigation has been previously observed (Dwyer et al., 2024), as faunal activity in sediments typically peaks during late spring or summer, driven by warmer temperatures and increased nutrient availability (Forster et al., 2003; Roskosch et al., 2012). The observed increase in PEX matches the temperature increase in Mar Menor lagoon waters. Previous studies show that the bioirrigation effect can drive exchange rates of 5 cm d⁻¹ (Martin et al., 2006), which are comparable to the PEX rates in Mar Menor in summer (3.0 cm d⁻¹). The invertebrate community in the lagoon's sediments includes 25 different taxa, representing Annelida, Mollusca, Nematoda, Arthropoda, and Phoronida, as of April 2018, with an infauna density of 2,200±1,000 ind. m⁻² (Sandonnini et al., 2024). In a similar shallow Mediterranean bay (Alfacs Bay), infauna densities of ~10,000 ind. m⁻² were linked to PEX rates of ~2 cm d⁻¹ (Rodellas et al., 2017). In the same bay, researchers reported up to a

fivefold increase in PEX during summer, suggesting the pumping activities of benthic fauna as the main driving mechanism of PEX. Other studies have reported similar seasonality in recirculation flows, often traced through short-lived isotopes (Garcia-Orellana et al., 2014; Luek & Beck, 2014). Despite the complexity of driving forces in the Mar Menor coastal lagoon and the likelihood that SGD magnitudes result from their combined effects, the seasonality of PEX is hypothesized to be primarily driven by elevated temperatures, which enhance infaunal activity within sediments during summer.

4.4.3. Recirculation pathways are likely to impact biogeochemical cycles in the lagoon

Groundwater is a crucial component of the hydrological cycle in coastal lagoons and plays a key role in nutrient dynamics (e.g., Ji et al., 2013; Rapaglia et al., 2012; Rodellas et al., 2018). In the Mar Menor lagoon, eutrophication events driven by increasing nutrient inputs mainly from agriculture have been occurring since 2016 (Ruiz Fernández et al., 2019). The presence of nutrients, metals, and other contaminants stored in the lagoon's sediments is well-documented (Alorda-Montiel et al., 2025; Moreno-González & León, 2017; Santos-Echeandía et al., 2023; J. Velasco et al., 2006), which are susceptible to remobilization processes driven by recirculated SGD. Estimates from our study show that recirculation represents between 96 and 99% of total SGD, suggesting that the high discharge rates may significantly influence the lagoon's biogeochemical cycles. Differentiating between fresh SGD, long-scale, and short-scale (PEX) recirculation is key to understanding nutrient speciation and assessing the biogeochemical impact of SGD on coastal ecosystems (Santos et al., 2021). Recirculated SGD delivers reduced substances, increasing oxygen demand and shifting the environment to hypoxic conditions (Moody et al., 2024). This, in addition to benthic coupling in summer months, can drive higher ammonium and phosphorus release rates (Jensen et al., 1995; Liefer et al., 2014). Previous studies have linked increased SGD rates and fish mortality in other environments (Moore et al., 2024; Sanial et al., 2021). Despite this, research in Mar Menor has predominantly focused on surface runoff and fresh SGD, leaving the potential contribution of recirculated SGD pathways to the nutrient budget overlooked.

Current knowledge of nutrient sources to the lagoon primarily focuses on surface runoff, reporting nutrient fluxes of 0.2×10^4 – 6.5×10^4 mol d⁻¹ for NO₃⁻, 1.4×10^4 mol d⁻¹ for NH₄⁺, 0.4×10^4 mol d⁻¹ for PO₄³⁻ (Álvarez-Rogel et al., 2020; J. Velasco et al., 2006). In contrast, groundwater-derived nutrient fluxes remain poorly

constrained. Only two studies have quantified NO_3^- fluxes associated with fresh groundwater discharge, reporting values between 1.8×10^2 and $6.0 \times 10^2 \text{ mol d}^{-1}$ (Alcolea et al., 2019; Tragsatec, 2020). A preliminary calculation of PEX-derived nutrient fluxes can be estimated from sediment core porewater concentrations, with total dissolved nitrogen (TDN) ranging from 0.15–3.9 mM (Amaral et al., 2023). This corresponds to a PEX-derived TDN input between 7.2×10^4 and $1.6 \times 10^7 \text{ mol d}^{-1}$. Global observations suggest that dissolved inorganic nitrogen (DIN) represents 57% of TDN in SGD (Santos et al., 2021), yielding a PEX-derived DIN flux between 4.1×10^4 and $9.1 \times 10^6 \text{ mol d}^{-1}$. These values are comparable to and may exceed by up to two orders of magnitude, DIN inputs from surface runoff ($\text{NO}_3^- + \text{NH}_4^+$; 1.5×10^4 – $7.8 \times 10^4 \text{ mol d}^{-1}$).

Higher PO_4^{3-} concentrations have been observed in Mar Menor during summer (maximum= $3.7 \text{ } \mu\text{g L}^{-1}$; mean= $1.7 \text{ } \mu\text{g L}^{-1}$), positively correlated with warmer temperatures but also increased population due to tourism (Gilabert, 2001). However, the sources driving these increases remain poorly understood. This seasonal pattern is consistent with the observed variability of PEX, suggesting a potential link between its discharge and nutrient enrichment. In addition to nutrients, PEX could also be a major source of metals and DOC, given the high concentration found in the lagoon's sediments (Alorda-Montiel et al., 2025; Amaral et al., 2023). This highlights that recirculation pathways likely play a critical role in biogeochemical cycles of the lagoon, impacting water quality. Particularly in summer months, the large PEX fluxes can potentially increase oxygen stress and exacerbate eutrophication processes. Further research is needed to better understand groundwater–sediment interactions, identify distinct endmembers representative of each driving mechanism, and quantify key pathways for nutrients, metals, carbon, and other solutes in the aquifer–lagoon continuum.

5. Recirculated submarine groundwater discharge dominates nutrient inputs and enhances eutrophication risk in a coastal lagoon

This chapter is based on:

Rodriguez-Puig, J., Ruiz-González, C., Diego-Feliu, M., Alorda-Montiel, I., Alorda-Kleinglass, A., Romano-Gude, D., Bravo, A. G., Dordal-Soriano, J., Gilabert, J., Bergeler, S., Lavergne, C., Casas, G., Manzano, M., Garcia-Orellana, J. & Rodellas, V. Recirculated submarine groundwater discharge dominates nutrient inputs and enhances eutrophication risk in a coastal lagoon (2026). *Limnology & Oceanography*

5.1. Introduction

Coastal lagoons often receive solute-rich groundwater through submarine groundwater discharge (SGD), with inputs of nutrients, trace metals, organic matter, and pollutants that can rival riverine contributions (Andrisoa et al., 2019b; Rodellas et al., 2018). While only fresh SGD represents a net water input, all pathways contribute to solute fluxes to the ocean and can have a significant ecological impact on coastal systems (Santos et al., 2021). The impact of SGD inputs on the coastal environment depends on the magnitude and chemical composition of each SGD pathway. However, independently quantifying the magnitude of pathway-specific fluxes remains challenging due to the inherent complexity of groundwater processes, which occur belowground, involve multiple subprocesses, and span diverse spatial and temporal scales. This knowledge gap hinders our ability to link SGD nutrient inputs to ecological dynamics. In Mar Menor, stream discharge and fresh SGD are recognized as major nutrient sources to the lagoon (Cabello & Brugnach, 2023; Martínez-Fernández & Esteve-Selma, 2020), but the role of lagoon water recirculation as a nutrient pathway and ecosystem degradation driver has not been previously assessed.

In this study, **stream discharge, fresh SGD, long-scale recirculated SGD, and short-scale porewater exchange nutrient fluxes** are simultaneously assessed, their **seasonal variability** is explicitly resolved, and their influence on nutrient **distribution and bioavailability within the lagoon** is examined, thereby evaluating their ecological consequences. By quantifying each pathway, **preferential nutrient inputs** and their volumetric contributions in a coastal lagoon system are identified for the first time, and a conceptual framework is provided linking SGD dynamics to changes in water quality.

5.2. Methods

5.2.1. Sampling strategy and determination of nutrient fluxes

Two-week field samplings were conducted in March, July, and November 2021 in the Mar Menor coastal lagoon to capture the main hydro-biogeochemical contrasts over an annual cycle. In two follow-up surveys in July 2024 and March 2025, lagoon porewaters were also collected (Fig. 5.1). In situ measurements of physicochemical parameters, nutrient concentrations, and radium isotopes in water samples were conducted (Chapter 3). Sample collection for surface waters and coastal groundwaters is described in section 4.2.1. Lagoon porewater samples

were retrieved from shallow sediment cores collected by scuba divers at L2, L11, L13, and L17 (Fig. 5.1).

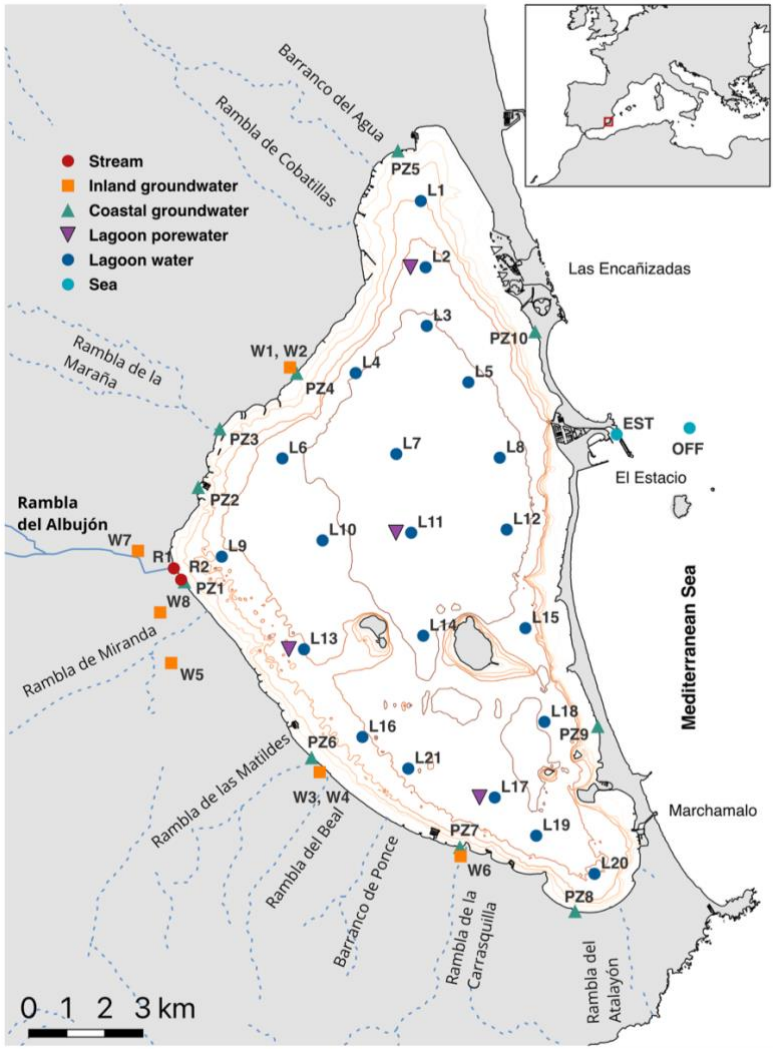


Figure 5.1. Geographical location of Mar Menor and location of sampling stations. Symbols indicate the different systems sampled: stream (i.e., “ramblas”; R), inland groundwater (i.e., wells; W), coastal groundwater (i.e., from manual piezometers; PZ), lagoon porewater (i.e., interstitial waters from the lagoon’s sediments; L), lagoon water (L), and sea water samples (EST and OFF, from Estacio site and offshore, respectively). Main ephemeral streams (*Ramblas*) are depicted by dashed blue lines, while the permanent stream, Rambla del Albuja, is depicted by a solid blue line and highlighted in bold. Bathymetry is shown with 1 m resolution (from 1 to 5 m), with darker orange lines for higher depths. The upper right map highlights the lagoon’s location within the Mediterranean region (red square).

The statistical analysis and interpolation methods, as well as the estimation of nutrient fluxes, are described in sections B.1 and B.2 in the Appendices. In short,

a Monte Carlo analysis was used to estimate the most likely nutrient fluxes from previously measured water flows and selected endmember concentrations that were considered to be representative of each pathway. For each nutrient species, water pathway, and season, 100,000 stochastic simulations were performed with different random combinations of model parameters.

5.3. Results

5.3.1. Nutrient distribution along the land–lagoon continuum

Physicochemical parameters varied markedly across streams, continental groundwater, fresh (< 10), brackish (10 – 30), and saline (> 30) coastal groundwater, lagoon porewater, and lagoon waters (B.4 in the Appendices). Concentration ranges for each sample type and nutrient species are given in Table B.2. Median dissolved nutrient concentrations were higher in all potential sources (i.e., streams, groundwater and porewaters) compared to lagoon waters (Fig. 5.2).

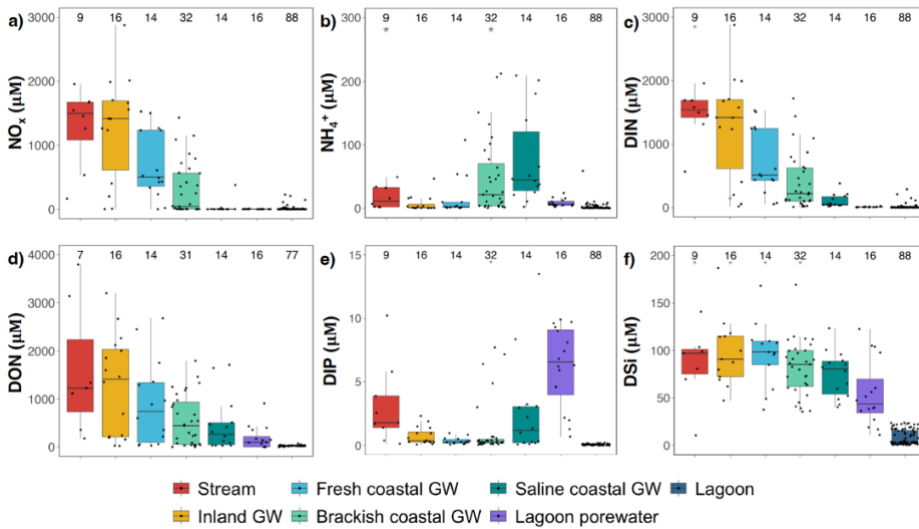


Figure 5.2. Nutrient concentrations in stream, inland groundwater (i.e., wells), fresh (<10), brackish (10–30), and saline (>30) coastal groundwater, lagoon porewater (saline), and lagoon water for a) NO_x , b) NH_4^+ , c) DIN, d) DON, e) DIP, and f) DSI, in μM . Grey asterisks (*) indicate that one or more samples exceeded the concentration range of the plot and are therefore not displayed. Numbers on top indicate the number of samples in each category. Samples from all the field surveys are pooled together. GW denotes groundwater.

Concentrations of nitrogen oxides ($\text{NO}_3^- + \text{NO}_2^-$; NO_x), dissolved inorganic nitrogen (DIN), and dissolved organic nitrogen (DON) decreased with salinity in coastal groundwaters, while ammonium (NH_4^+) followed the opposite trend, with the highest concentrations observed in coastal groundwater saline samples (Fig. 5.2). Stream samples were predominantly NO_x -dominated, whereas inland and fresh coastal groundwater showed mixed dominance of NO_x and DON. Brackish and saline groundwaters were generally enriched in DON or NH_4^+ . The highest dissolved inorganic phosphorus (DIP) concentrations were observed in lagoon porewaters. Median N/P ratios were >1000 in inland groundwater, stream, and fresh coastal groundwater and <50 in lagoon-influenced samples (Fig. B.2.b). Overall, differences in dissolved inorganic silica (DSi) concentrations across sample types were not observed, except for lagoon samples, which showed significantly lower concentrations.

5.3.2. Seasonal and spatial nutrient concentration patterns in lagoon waters

The dominant form of nitrogen in lagoon surface waters was DON, with higher concentrations in March compared to July and November (Fig. 5.3). Elevated NO_x concentrations were observed along the western shoreline both in March and November, near the Albuji3n mouth. Conversely, the lowest NO_x concentrations were found on the eastern side of the lagoon, along La Manga sandbar. Ammonium concentrations were elevated along the coastline in March, both north and south of the stream mouth, possibly linked to nearshore saline SGD or wastewater for neighboring urban areas (García-Pintado et al., 2007). DSi exhibited pronounced seasonality, with July concentrations up to 20 times higher than those recorded in March or November. Phosphate concentrations were consistently low ($<0.2 \mu\text{M}$) but tended to be higher in July and November relative to March.

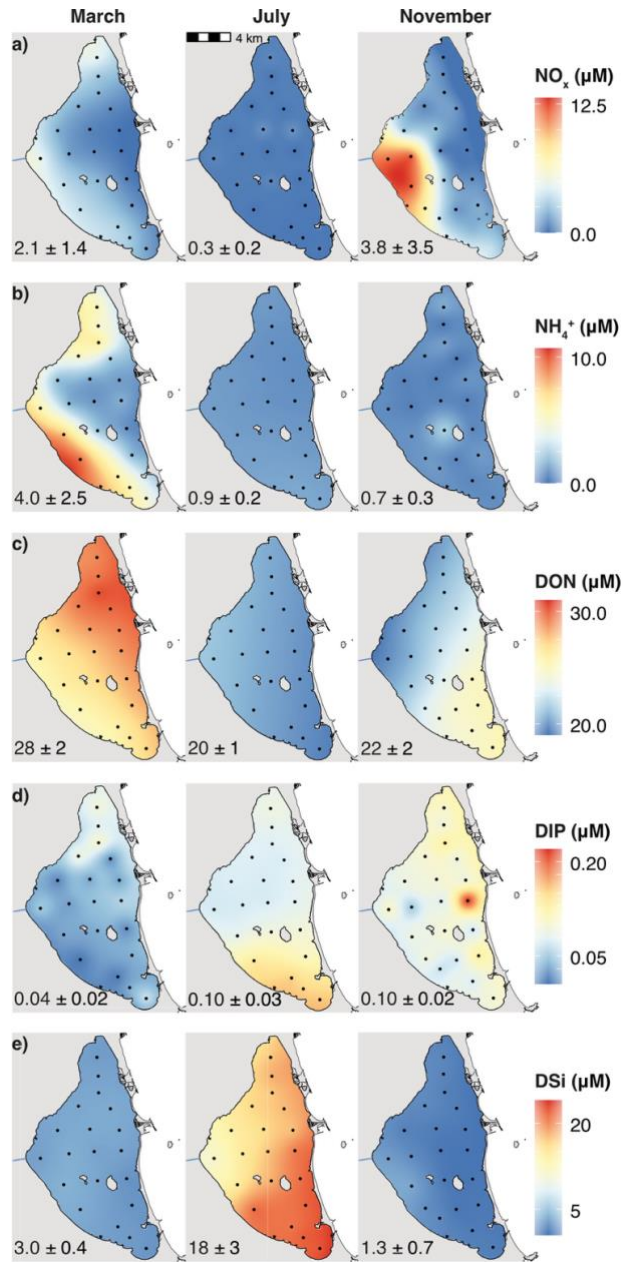


Figure 5.3. Seasonal surface distribution of nutrient concentration in the Mar Menor lagoon in March, July, and November 2021, from left to right, for a) NO_x , b) NH_4^+ , c) DON, d) DSi, and e) DIP in μM . Dots represent sampling stations used to derive the kriging spatial interpolation (see B.1). The mean (sd) concentrations for each sampling are also included in the insets. DIN spatial distribution is depicted in Fig. B.3.

The seasonal fluctuations observed in nutrient concentrations also influenced nutrient limitation patterns throughout the year. Based on the Redfield ratio, surface waters were generally N-rich (Fig. 5.4), indicating potential P or Si limitation during most of the year. In summer, however, a significant proportion of surface water samples (~90%) fell into the P-rich or Si-rich quadrants, emphasizing strong seasonality in nutrient availability in the lagoon. Regarding nitrogen speciation, ~90% of lagoon samples were dominated by DON (Fig. B.2a).

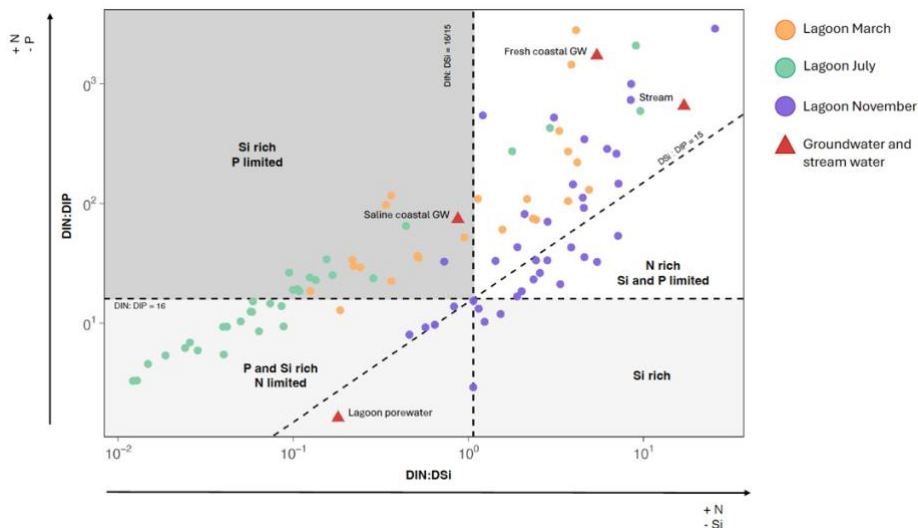


Figure 5.4. Nutrient limitation in lagoon surface waters. DIN:DIP ratios vs. DIN: DSi ratios in lagoon surface waters in March, July, and November, and in endmembers, including stream water, fresh coastal GW, saline coastal GW, and lagoon porewater, represented as the median values of each water type.

5.3.3. Nutrient fluxes associated with different hydrologic pathways

Nutrient contributions of stream discharge, fresh SGD, long-scale recirculation, and PEX were estimated for each sampling campaign (Fig. 5.5; Table B.3). Hereinafter, a distinction is made between continental sources (i.e., stream discharge and fresh SGD), which primarily originate from meteoric waters, and recirculation pathways (i.e., long-scale recirculation and PEX), which result from lagoon water recirculating through the sediments. Continental discharge primarily governed NO_x inputs, while NH_4^+ , DON, DIP, and DSi inputs were mainly supplied by recirculated SGD. Among SGD pathways, fresh SGD contributions were only relevant for NO_x and DON (accounting for 63–100%, and 1–17% of total SGD inputs, respectively), while it represented less than 5% of the total SGD flux for NH_4^+ , DIP and DSi (Fig. 5.5). Seasonal trends showed maximum NO_x fluxes in

March, while DON, DIP, and DSi fluxes peaked in July, driven by enhanced PEX, revealing that nutrient delivery mechanisms are dynamic and compound-specific (Fig. 5.5).

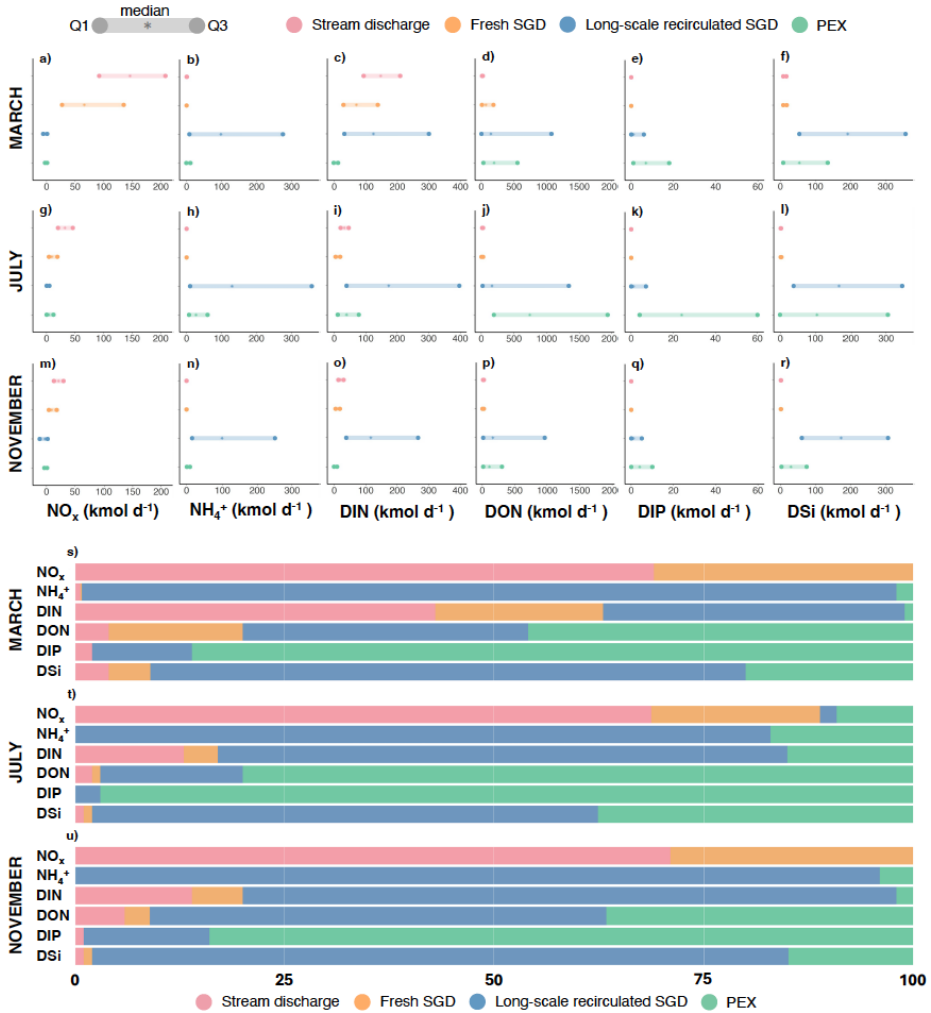


Figure 5.5. Nutrient fluxes (kmol d⁻¹; panels a–r) and relative contribution to overall fluxes (%; panels s–u) from stream discharge, fresh groundwater discharge, long-scale recirculated SGD, and PEX for each nutrient species (NO_x, NH₄⁺, DIN, DON, DIP, and DSi). In panels a) to r), the horizontal bars represent the interquartile range and the asterisk (*) represents the median values from the Monte Carlo-derived fluxes.

Total DIN inputs were delivered mostly by both stream (20–150 kmol d⁻¹; 10–40% of total DIN inputs) and SGD (130–220 kmol d⁻¹; 60–90%). NO_x fluxes were mainly delivered by stream discharge (20–150 kmol d⁻¹; ~70% of the total NO_x flux), followed by fresh SGD (9–70 kmol d⁻¹; 20–30% of the total NO_x flux) (Fig. 5.5). Because nutrient concentrations in the lagoon exceeded those in lagoon porewaters, recirculated SGD acted as a NO_x sink in March and November, driving an estimated net removal of 1.5–3.5 kmol d⁻¹, respectively, from the water column. The highest NH₄⁺ fluxes were associated with long-scale recirculation (98–130 kmol d⁻¹; >80% of total NH₄⁺ inputs), followed by PEX, which was only relevant in summer (~27 kmol d⁻¹; ~20%). Contribution from continental sources to NH₄⁺ fluxes remained low throughout the year (<1 kmol d⁻¹). DON fluxes were dominated by PEX (110–740 kmol d⁻¹; 40–80% of total DON inputs) and long-scale recirculation (150–160 kmol d⁻¹; 20–60%), although the contribution from fresh groundwater discharge was also important (10–70 kmol d⁻¹). DIP was primarily delivered by recirculation SGD processes (>98%), in particular by PEX (4–24 kmol d⁻¹), but also by long-scale recirculation (0.6–0.9 kmol d⁻¹). Continental inputs remained below 0.2 kmol d⁻¹ throughout the year. DSi was also predominantly sourced by recirculation (>90%), with fluxes ranging from 170 to 190 kmol d⁻¹ for long-scale recirculation, from 30 to 100 kmol d⁻¹ for PEX, and negligible for continental sources (Fig. 5.5). Nutrient fluxes from total SGD increased from winter to summer for most species, with percent changes ranging up to 400% for DIP (Table 5.1).

Table 5.1. Nutrient fluxes from total SGD (kmol d⁻¹) for each nutrient species in winter and summer and percent change (%) from winter to summer.

	Winter*	Summer	Change (%)
DIN	250	250	0
DON	360	930	+160
DIP	6	30	+400
DSi	240	280	+17

*Winter fluxes were calculated as the average of the median fluxes for March and November.

To provide context on the importance of SGD relative to other potential nutrient sources to the lagoon, SGD was compared with other inputs, including diffusion from the sediments, atmospheric deposition, inflow from the Mediterranean Sea, and stream discharge. This comparison revealed that SGD was the main nutrient source (70–90% of total inputs; Fig. 5.6), except for NO_x (Text B.4 and Table B.5).

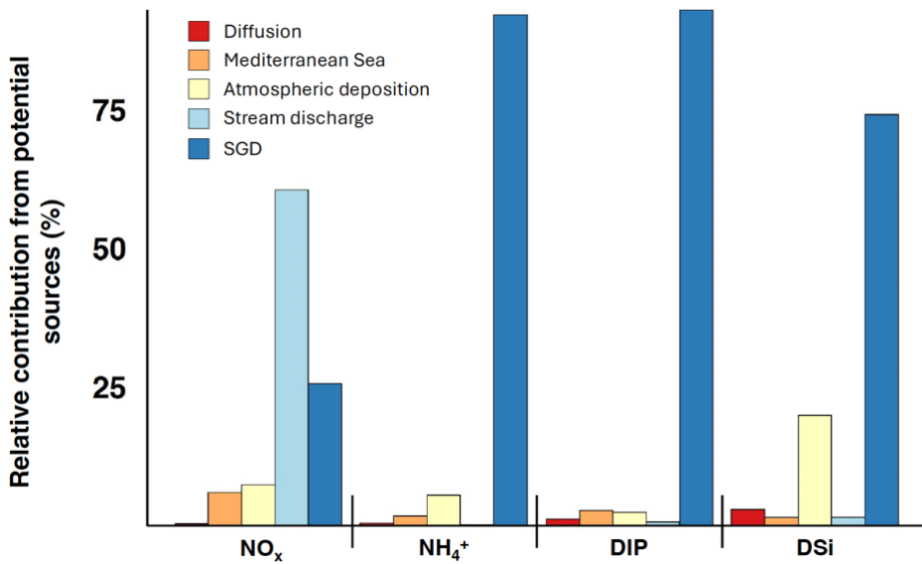


Figure 5.6. Relative contribution from diffusion, inflow from the Mediterranean Sea, atmospheric deposition, stream discharge, and SGD, for NO_x, NH₄⁺, DIP, and DSi.

5.4. Discussion

5.4.1. Continental discharge governs NO_x inputs, while recirculated SGD dominates NH₄⁺, DON, DIP and DSi inputs to the lagoon

Nutrient fluxes from stream discharge, fresh SGD, long-scale recirculated SGD, and PEX to the lagoon are controlled by large-scale watershed land use and local-scale biogeochemical processes, particularly redox conditions (section B.5).

Stream discharge is mainly fed by agricultural runoff, with previous studies estimating a delivery between 2 and 70 kmol d⁻¹ of NO_x, comparable to our estimates (Álvarez-Rogel et al., 2020; J. Velasco et al., 2006). Elevated NO_x concentrations in lagoon surface waters were detected near the influence of the stream discharge plume compared to inner lagoon waters during November, possibly linked to precipitation-driven runoff, and, to a lesser extent, in March. These spatial and seasonal concentration patterns are consistent with previous observations in the lagoon (Pérez-Ruzafa et al., 2005a, 2019), and the concentration ranges observed are also consistent with those reported in 2017, 2019, and 2020 by Ouaisa et al. (2023).

Fresh groundwater discharge delivers NO_x -rich water to the Mar Menor lagoon, sustained by decades of agricultural fertilizer application in the Campo de Cartagena catchment (Arauzo et al., 2024). NO_x concentrations decrease markedly along the land–lagoon continuum, from median values of $1600 \mu\text{M}$ in inland wells to $450 \mu\text{M}$ in fresh coastal groundwaters, indicating substantial attenuation within the subterranean estuary. This pattern aligns with the presence of microbial communities capable of denitrification (e.g., *Proteobacteria*, *Bacteroidetes*, *Thermodesulfobacterota*, *Verrucomicrobiota*) or dissimilatory nitrate reduction to ammonium (e.g., *Firmicutes*, *Nitrospirota*, *Proteobacteria*) in the same coastal groundwaters (Romano-Gude et al., 2025), which can reduce NO_3^- either to nitrogen gas or to NH_4^+ , depending on environmental conditions (D. Li et al., 2025) (Fig. 5.7). Consequently, fresh SGD flux estimates are approximately one order of magnitude lower than those of previous studies that relied on inland groundwater concentrations as endmembers, which did not capture nitrogen attenuation closer to the discharge zone (Alcolea et al., 2019; Comité de asesoramiento científico del Mar Menor, 2017).

Recirculation of lagoon water through sediments, including both long-scale recirculation and PEX, represents a major mechanism transferring nutrients to the lagoon, where N and P have been accumulating in the sediments for decades (Ruiz et al., 2020). These generally muddy and organic-rich sediments (Pérez-Ruzafa et al., 2005b) promote microbial processing that favors NO_x removal and NH_4^+ production via dissimilatory nitrate reduction to ammonium and ammonification (Porubsky et al., 2014). Consistent with these conditions, NO_3^- concentrations in long-scale recirculated groundwater are lower than surface lagoon waters, whereas NH_4^+ concentrations are significantly higher. This indicates that, overall, long-scale lagoon seawater recirculation is a net sink of NO_x and a source of NH_4^+ to the lagoon.

In contrast, NH_4^+ enrichment is limited in inner lagoon porewaters, resulting in negligible PEX contributions. The limited NH_4^+ -enrichment in PEX may reflect i) adsorption onto clay and organic-rich sediments (Boatman & Murray, 1982); ii) short transit times that limit biogeochemical transformations (Kroeger & Charette, 2008); iii) limited quantity and lability of organic matter (Porubsky et al., 2014); and/or iv) active microbial metabolisms such as coupled nitrification-denitrification or anammox (Gao et al., 2022), consistent with the low NO_2^- concentrations measured in lagoon porewaters.

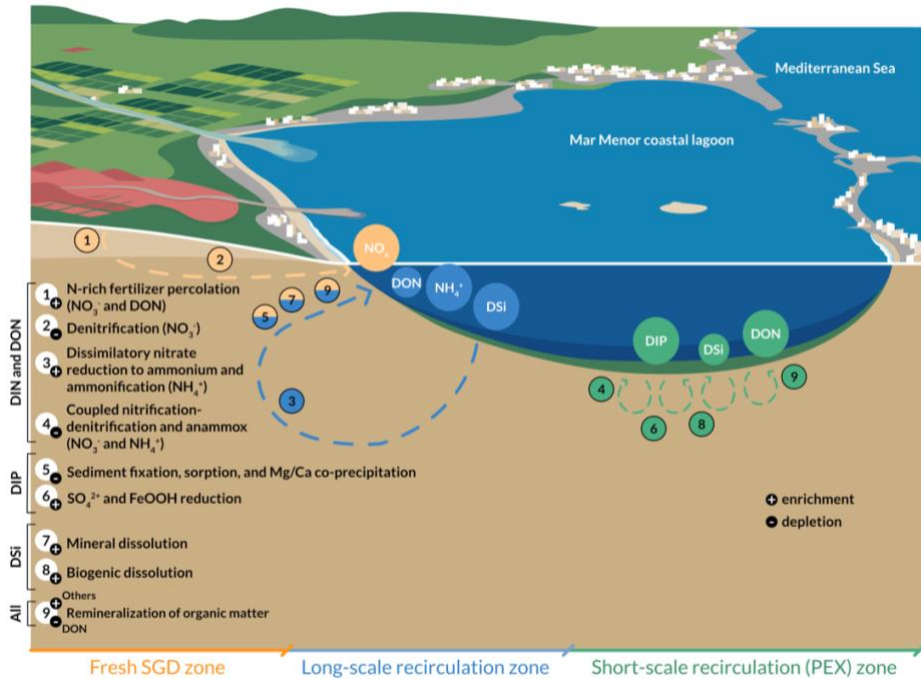


Figure 5.7. Conceptual diagram of nutrient inputs and associated biogeochemical processes along each SGD pathway. Bubble size represents the relative magnitude of nutrient fluxes. Numbers indicate the main nitrogen (1–4), phosphorus (5–6), silica (7–8), and shared (9) sources (+) and sinks (-) along the flow path of each pathway.

The elevated DIP concentrations in lagoon porewaters result in fluxes mainly controlled by short-scale lagoon recirculation. A substantial fraction of DIP entering the lagoon is likely retained within the sediments as insoluble forms (J. Velasco et al., 2006). Organic phosphorus remineralization and microbial sulfate and iron reduction release DIP to porewaters (Joshi et al., 2015; McAllister et al., 2015). Conversely, lower DIP in coastal groundwaters likely reflects a combination of soil P fixation (Schipanski & Bennett, 2021), sorption in mixing zones (the iron curtain; McAllister et al., 2015), or co-precipitation with Ca or Mg minerals (Corman, 2025).

Elevated DSi concentrations in coastal groundwater in Mar Menor originate primarily from silicate mineral dissolution, which increases with groundwater residence time (Rahman et al., 2019). However, high DSi concentrations are also observed in rapid-flushing lagoon porewaters, suggesting additional sources such as the dissolution of biogenic Si from diatom frustules and sponge spicules (Koné et al., 2019), a plausible scenario in diatom-dominated systems such as Mar Menor (Fernández-Alías et al., 2022). The measured porewater DSi aligns with reported

marine sediment dissolution rates ($15\text{--}57\text{ nmol g}^{-1}\text{ h}^{-1}$; Wu & Liu, 2020), assuming transit times longer than a few hours, consistent with typical porewater exchange timescales.

5.4.2. Nutrients from SGD impact the lagoon ecosystem by shifting nutrient limitation

Nutrient loading from SGD can negatively impact receiving ecosystems by triggering eutrophication processes (e.g., Alorda-Kleinglass et al., 2024; Luo et al., 2023). Alterations at the base of the food web can cascade upward, affecting the abundance and community composition of consumers and predators (Murphy et al., 2020). In Mar Menor, nutrient inputs from SGD have been linked to increases in abundance and activity and shifts in the taxonomic structure of bacterioplankton (Romano-Gude et al. 2025), and eutrophication has been shown to alter the abundance, biomass, and functional guild dominance of fish assemblages (Zamora-López et al., 2025). Similarly, SGD-derived nutrient inputs can alter lagoonal food webs by favoring filter-feeders and herbivores (Andrisoa et al., 2019a; Piló et al., 2018).

Moreover, seasonal variability across SGD pathways influences nutrient limitation dynamics and primary production, as shown in a eutrophic bay (C. Xu et al., 2024). In Mar Menor, seasonal shifts in nutrient limitation are recurrent and directly shape the phytoplankton community (Fernández-Alías et al., 2022). Increases in recirculated SGD flows during the summer cause the P and Si limitation in lagoon waters to decrease (Table 5.1), which raises the risk of hypoxia and eutrophication. P is the limiting nutrient in Mar Menor for the majority of the year, in contrast to the majority of coastal oceans, which are N-limited (Velasco et al., 2006; Fig. 5.4).

In this lagoon, recent phytoplankton blooms are mainly attributed to diatoms, with high abundances that result in a subsequent DSi depletion (Fernández-Alías et al., 2022; Ouaisa et al., 2023). Nutrients supplied by recirculated SGD directly benefit diatom populations (Lecher & Mackey, 2018). While previous studies in the lagoon attribute algal blooms to continental nutrient inputs (García-Pintado et al., 2007; Jiménez-Martínez et al., 2016), our results highlight that recirculated SGD plays a central role in nutrient cycles, certainly affecting algal blooms and lagoonal ecological responses. Notably, the ecological footprint of SGD seems to extend beyond the lagoon, as its nutrient-rich waters reach up to 1.8 km offshore, also affecting *Possidonia oceanica* meadows in the Mediterranean Sea (Jiménez-Casero et al., 2025).

The quality and quantity of discharging groundwaters highly influence Mar Menor ecosystem, positioning the lagoon as a groundwater-dependent ecosystem. Although current management measures largely target NO_3^- inputs, including wetland restoration or bioremediation techniques to enhance denitrification, little attention has been given to NH_4^+ and P, which accumulate in lagoon sediments as legacy pollution and can be transferred to the lagoon over decades, fueling eutrophication even after external loads are reduced or ceased (Schipanski & Bennett, 2021).

5.4.3. Implications of distinguishing SGD pathways for nutrient flux estimates

Recent studies in coastal environments report large nutrient fluxes attributed to SGD (e.g., X. Wang et al., 2018; Tait et al., 2023; Guldin et al., 2026), often emphasizing their ecological significance yet lacking an explicit differentiation between fresh SGD and saline recirculated SGD. This bulk approach remains far more common than pathway-resolved estimates of SGD (I. R. Santos et al., 2021), and it provides a first-order approximation on the relative importance of SGD compared to other sources. However, this approach can bias flux estimates and mask the biogeochemical role of different flow components, particularly the distinction between internally recycled and external inputs (J. Liu et al., 2021). For instance, J. Liu et al. (2021) found significantly higher SGD-driven nutrient fluxes in the Yellow Sea when using total SGD-based estimates than pathway-resolved quantifications. Similarly, this study shows that using a single radium isotope to estimate total SGD, which is the most common approach (Garcia-Orellana et al., 2021a), yields DIN fluxes 5–20 times higher than the pathway-specific approach, while NH_4^+ , DSi , and DIP fluxes are 2–17 times lower. These differences primarily arise because the bulk SGD approach is biased towards the most sampled pathways, which is commonly fresh SGD, even though this pathway only contributes minimally to nutrient budgets. As a result, recycled nutrients are often underestimated, highlighting that source attribution and pathway differentiation decisions can influence nutrient fluxes. Failure to distinguish internally recycled nutrients from externally derived inputs may misdirect management efforts toward land-based controls when internal recycling processes dominate solute fluxes via recirculated SGD.

6. Impact of submarine groundwater discharge pathways on direct oxygen demand

This chapter is based on:

Rodriguez-Puig, J., Lavergne, C., Bergeler, S., Alorda-Montiel, I., Bravo, A. G., Romera-Castillo, C., Gilabert, J., Garcia-Orellana, J. & Rodellas, V. Impact of SGD pathways on direct oxygen demand. To be submitted to Environmental Science & Technology

6.1. Introduction

Hypoxia is a major concern for water quality worldwide, with a trend of declining oxygen concentrations over the past few decades (Breitburg et al., 2018). Coastal areas are particularly exposed to hypoxia, with faster oxygen decline rates and more frequent hypoxic events than the open ocean (Gilbert et al., 2010). Hypoxic conditions are generally defined as dissolved oxygen (DO) concentrations below 2 mg L^{-1} . However, the tolerance to hypoxia differs across organisms, as hypoxic stress depends on the DO supply relative to metabolic demand, with sub-lethal conditions at higher DO concentrations ($3\text{--}5 \text{ mg L}^{-1}$) (Ekau et al., 2010; Roman et al., 2019). Hypoxic conditions can severely impact the ecosystem by increasing fish mortality, reducing biodiversity and ecosystem services, and altering element cycling (B. B. Hughes et al., 2015; Middelburg & Levin, 2009; Vaquer-Sunyer & Duarte, 2008).

Geographical and morphological characteristics, including low water renewal, water column stratification, and rising temperatures, often promote coastal hypoxia (Breitburg et al., 2018; Meire et al., 2013; Virtanen et al., 2019). Coastal hypoxia risk is further exacerbated by increasing anthropogenic stressors, particularly nutrient inputs (Simonetti et al., 2024). Allochthonous nutrients can stimulate microbial respiration fueled by photosynthetic-derived organic matter (Diaz & Rosenberg, 2008; Howarth, 2008). Beyond the well-established influence of different submarine groundwater discharge (SGD) pathways on primary production and indirect DO consumption via nutrient delivery, recent studies suggest that SGD can also increase oxygen demand through direct DO reduction (Moore et al., 2024). This occurs through the supply of reduced compounds such as dissolved NH_4^+ , H_2S , DOC, DON, CH_4 , and Fe^{2+} to the water column. Despite the potential biogeochemical implications of this process, only a limited number of studies have explored the role of SGD in delivering these reduced solutes (Guo et al., 2020; Sanial et al., 2021). In five Atlantic coastal settings, SGD-derived fluxes of NH_4^+ , H_2S , DOC, DON, CH_4 , and Fe^{2+} have been shown to significantly decrease DO concentrations (Moore et al., 2024). However, the impact of SGD to DO depletion remains largely unexplored. In this regard, it is particularly relevant to distinguish the individual contribution of different pathways to DO depletion. Each pathway is characterized by specific compositions and redox conditions, thus chiefly controlling the supply of reduced compounds and the potential impacts on oxygen demand.

This study aims to quantify the **contribution of different SGD pathways to direct DO consumption**. To this end, fluxes of NH_4^+ , H_2S , DOC, DON, CH_4 , and Fe^{2+} from fresh groundwater discharge, saline recirculation, and porewater exchange (PEX) are estimated in the Mar Menor coastal lagoon (SE Spain). The analysis is conducted for three different periods (March, July, and November) to evaluate their **seasonal variability**. Within the framework of this study, **hydrological, chemical, and temporal guidelines** are provided to assess the potential influence of SGD-derived chemical DO consumption across coastal systems worldwide, positioning SGD within the context of oxygen-depletion dynamics.

6.2. Methods

6.2.1. Sample collection and analysis

Groundwater and lagoon samples were collected over different field surveys (Fig. 6.1). A first set of surveys, conducted in March, July, and November 2021, allowed the collection of coastal groundwater samples for NH_4^+ , DOC, DON, and CH_4 analyses ($n=11-15$) (described in section 4.2.1). Another set of surveys was conducted in May, July, November 2024, and March 2025, under similar meteorological conditions to those in 2021. During these surveys, porewater from lagoon sediments was collected at four representative stations (M1 to M4; $n=4$ per season) to analyze NH_4^+ , H_2S , DON, and Fe^{2+} . Lagoon porewaters were retrieved using manual piezometers installed at 30 cm by scuba divers. Additionally, lagoon water samples were collected at the same locations for NH_4^+ and DON analyses at surface and near-bottom depths. The last field sampling was conducted in July 2025 to collect coastal groundwater at two different sites (Pz1 and Pz7) for H_2S and Fe^{2+} analysis ($n=3$), as well as lagoon porewaters for NH_4^+ , H_2S , DOC, DON, CH_4 , and Fe^{2+} ($n=4$).

Physicochemical parameters, including salinity, temperature, DO, and oxidation-reduction potential (ORP), were determined in situ with a YSI Pro Plus multiparametric probe. The analytical methods used to measure ancillary parameters are detailed in Chapter 3.

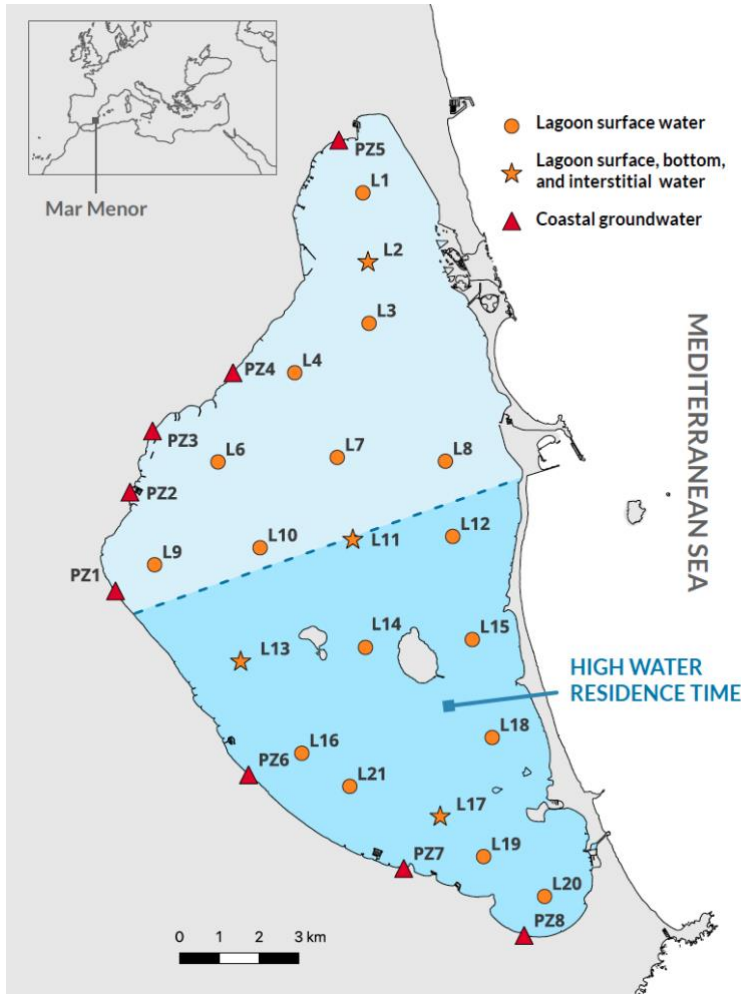


Figure 6.1. Geographical location of Mar Menor and location of sampling stations. Symbols indicate the different systems sampled. Residence time areas are based on a hydrodynamic model of the lagoon (Pereira et al., 2025). The upper left map highlights the lagoon's location within the Mediterranean region.

6.2.2. Determination of potential DO reduction from SGD-derived fluxes

The fluxes of reduced compounds (NH_4^+ , H_2S , DOC, DON, CH_4 , and Fe^{2+}) delivered to the lagoon via the three main SGD pathways in Mar Menor (fresh SGD, saline recirculation, and PEX) were assessed to estimate the rate of DO consumption ($\text{mg L}^{-1} \text{d}^{-1}$ or $\mu\text{M d}^{-1}$) via chemical oxygen reduction. The flux of reduced compounds (kmol d^{-1} or $\mu\text{mol d}^{-1}$) was estimated as described in section 3.1.4. The groundwater endmember concentrations were estimated as the median

of the samples representative of each pathway (see section C.1). Because the sampling campaigns for the different compartments were conducted during different periods, the resulting flux estimates should be interpreted as first-order approximations, here reported as median values and annual ranges (Table C.1).

The flux of electrons supplied during DO reduction in the lagoon water column was then estimated based on the electron equivalents of each chemical reaction (see section C.2 for biogeochemical assumptions details). Since each O_2 molecule accepts four electrons during complete reduction to water, a 1:4 molar ratio was used to convert the electron flux into a DO reduction rate ($\mu M d^{-1}$). To assess the potential impact of SGD on oxygen dynamics in our system, the DO reduction rate was normalized to the water volume of the lagoon ($kmol m^{-3} d^{-1}$).

6.3. Results and discussion

6.3.1. Recirculated SGD is the primary source of oxygen-demanding compounds

Fresh coastal groundwater, saline coastal groundwater, and lagoon porewater exhibited distinct physicochemical characteristics (Table 6.1). Fresh groundwater was relatively oxic, with a median DO of $3.5 mg L^{-1}$ and ORP of 40 mV, while saline coastal groundwater had the lowest median DO concentrations and ORP values ($1.8 mg L^{-1}$ and -190 mV, respectively). Lagoon porewater showed slightly higher median DO ($3.2 mg L^{-1}$) but strongly reducing conditions (-210 mV).

The highest concentrations of NH_4^+ were measured in saline coastal groundwaters ($41 \mu M$), with low concentrations in lagoon porewaters and fresh coastal groundwaters (Fig. C.1). CH_4 showed a similar pattern, being higher in saline groundwater ($1.4 \mu M$) than in fresh groundwater ($0.34 \mu M$). DOC peaked in coastal saline waters and lagoon porewaters ($360 \mu M$ in both water sources), compared to lower concentrations in fresh groundwater ($140 \mu M$). DON and Fe^{2+} showed an opposite behavior to DOC, with the highest concentrations in fresh groundwater ($750 \mu M$ and $0.44 \mu M$, respectively), followed by saline groundwater ($270 \mu M$ and $0.21 \mu M$) and lagoon porewater ($30 \mu M$ and below detection). Lagoon porewater was the main source of H_2S ($590 \mu M$). Overall, fresh groundwater contained generally low concentrations of reduced species (except for DON), saline groundwater was an important source of NH_4^+ and DOC concentrations, and lagoon porewater was mainly enriched in H_2S and DOC. Fe^{2+} and CH_4 were generally low, with fresh and saline coastal groundwaters as their main sources, respectively. These biogeochemical signatures among the

groundwater sources highlight that each SGD pathway might contribute differently to the delivery of solutes into the lagoon. Therefore, an appropriate assessment of the role of SGD on DO depletion cannot be achieved without distinguishing the relative contribution of the different pathways.

Table 6.1. Median and min-max ranges for different physicochemical parameters and dissolved chemical species in fresh coastal groundwater, saline coastal groundwater, and lagoon porewater.

	Fresh groundwater		coastal Saline groundwater		coastal Lagoon porewater	
	median	range	median	range	median	range
Salinity	8.5	2.6–9.3	38	31–47	44	42–46
ORP (mV)	40	-300–98	-190	-360–43	-210	-280–8.0
DO (mg L ⁻¹)	3.5	0.77–6.5	1.8	0.56–4.6	3.2	0.74–7.8
NH ₄ ⁺ (μM)	2.5	0.7–110	41	2.3–210	3.7	0.068–35
H ₂ S (μM)	BDL	BDL	3.6	BDL–7.2	590	0.44–1400
DOC (μM)	140	57–1200	360	190–1400	360	250–490
DON (μM)	750	26–2700	270	27–1600	30	15–45
CH ₄ (μM)	0.34	BDL–99	1.4	0.34–26	0.73	0.13–1.7
Fe ²⁺ (μM)	0.44	-	0.21	0.19–0.23	BDL	BDL–2.7

*BDL=Below detection limit; ND=No data

Solute fluxes into the Mar Menor lagoon, estimated from reported flow rates for each SGD pathway (Rodriguez-Puig et al., 2025), were strongly influenced by both the magnitude of groundwater discharge and the chemical composition of each pathway. Integrating the contributions from the different SGD pathways, total fluxes of reduced compounds entering the lagoon varied annually between (in kmol d⁻¹) 77–110 for NH₄⁺, 230–3700 for H₂S, 130–660 for DOC, 520–630 for DON, 2.8–4.5 for CH₄, and -0.10–2.9 for Fe²⁺. These values indicate that the primary reduced species supplied by SGD in Mar Menor are NH₄⁺, H₂S, DOC, and DON, while Fe²⁺ and CH₄ contribute relatively little. This pattern, which reflects the lower concentrations of these solutes in groundwater, is consistent with observations from Atlantic coastal settings (Moore et al., 2024). Although these figures provide an overview of the flux magnitude, they offer limited insight into the complex dynamics of groundwater discharge, including the preferential input pathways for each solute and the temporal variability of the drivers controlling the magnitude of each SGD component (McAllister et al., 2015; Taniguchi et al., 2019).

Indeed, the magnitude and relative contribution of each pathway to the total input varied markedly across seasons and differed among chemical species (Fig. 6.2). For instance, fresh SGD was a relevant transport mechanism for DON and DOC (up to 98 and 18 kmol d⁻¹, representing 16 and 14% of total inputs, respectively), while being a negligible source of NH₄⁺, H₂S, CH₄, and Fe²⁺. Most of these species are formed as by-products of anaerobic organic matter mineralization, where, after oxygen is consumed, other oxidants are sequentially used based on favorable thermodynamics (reduction of nitrate, manganese, iron, sulfate, and methanogenesis) (Canfield & Thamdrup, 2009; Middelburg & Levin, 2009). Since fresh groundwater in Mar Menor is largely oxic, oxygen remains the most thermodynamically favorable electron acceptor, and anaerobic pathways are not expected to occur. Moving along the coastal aquifer mixing zone, salinity increases while DO concentrations and ORP decrease (Fig. C.2). These conditions favor the formation of NH₄⁺, H₂S, CH₄, and Fe²⁺ in groundwaters from lagoon sediments, as previously observed (Amaral et al., 2023). Indeed, saline SGD was the primary source of NH₄⁺ (up to 93 kmol d⁻¹; >87% of total NH₄⁺ inputs year-round) and DON (up to 580 kmol d⁻¹; >83% of total NH₄⁺ inputs year-round), as previously reported in Mar Menor (Rodríguez-Puig, accepted) and other areas (Gonneea & Charette, 2014). It also supplied DOC with fluxes on the order of 10² kmol d⁻¹, and CH₄ and Fe²⁺ at lower magnitudes, on the order of 10⁻¹-10⁰ kmol d⁻¹, consistent with (Moore et al., 2024). In contrast to Moore's study, saline SGD in Mar Menor delivered comparatively low H₂S inputs (up to 8 kmol d⁻¹), explained by the low concentrations in the coastal saline groundwater endmembers. However, further conclusions are avoided, given the strong spatial variability in both the chemical and microbial composition of Mar Menor groundwaters (Lavergne et al., 2025; Romano-Gude et al., 2025; Rodríguez-Puig, accepted) and the limited number of coastal saline groundwater H₂S endmembers (n=2). Interestingly, H₂S in Mar Menor was mainly supplied by PEX (up to 3700 kmol d⁻¹), consistent with elevated porewater concentrations of this compound observed in reductive environments (Tamborski et al., 2017). This short-scale pathway also contributed to 10–40% of total CH₄, and a negligible contribution to DON budgets, with fluxes on the order of 10⁰-10¹ kmol d⁻¹.

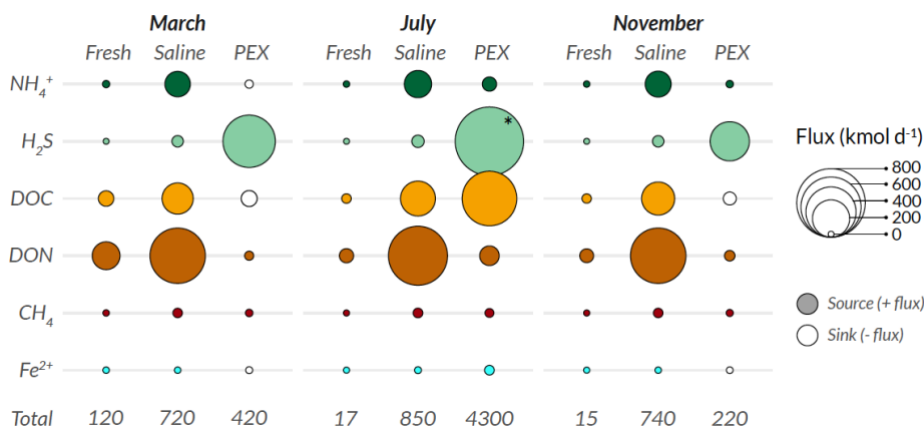


Figure 6.2. Fluxes of NH_4^+ (dark green), H_2S (light green), DOC (orange), DON (brown), CH_4 (red), and Fe^{2+} (light blue) in kmol d^{-1} delivered by each SGD pathway (Fresh, Saline, or PEX) in each season (March, July, and November). The asterisk (*) indicates that bubble size is not proportional (value=3700). Hollow circles represent sinks (negative fluxes) while filled circles represent sources (positive fluxes). Numbers on the total row indicate the pathway-specific total flux considering all chemical species. All values are reported in Table C.1.

The amount of inflowing solutes to a coastal system can also vary seasonally, owing to variations in the relative supply of the different SGD pathways. The commonly overlapping forcings of each pathway determine the resulting flow magnitude (Taniguchi et al., 2019). In Mar Menor, the forces driving fresh SGD and saline recirculation at long timescales are mostly constant throughout the year, owing to the stable piezometric level mainly controlled by infiltration from year-round irrigation of agricultural fields (Martínez-Alvarez et al., 2011). The relatively static freshwater-saltwater interface in the aquifer and the constant concentrations in coastal groundwaters over time (no significant differences among campaigns, $p > 0.05$ for NH_4^+ , DOC, and CH_4) result in relatively small variability in chemical fluxes. In contrast, PEX largely responds to increased bioirrigation processes in the lagoon's bottom in summer (Rodríguez-Puig et al., 2025), exhibiting a 4-fold increase in groundwater flows and between 6- and 16-fold increase in the supply of reduced substances (Fig. 6.2).

Considering the sum of all oxygen-demanding compounds, fresh SGD was the minor contributing pathway year-round (tens to hundreds of kmol d^{-1}), followed by saline SGD (hundreds of kmol d^{-1}), and PEX (generally ranging in the hundreds, but peaking at thousands in summer). The stark contrasts among pathways underscore that SGD definitions excluding processes with spatial scales smaller than 1 m (Moore, 2010) can underestimate total SGD chemical fluxes and/or bias estimations towards certain chemical species. Likewise, studies reporting only

fluxes associated with one SGD pathway (Moore et al., 2024; Sanial et al., 2021) can neglect important preferential pathways (e.g., PEX for H_2S) and underplay the magnitude of chemical inputs. This oversight is particularly critical because these inputs can substantially alter water chemistry and have detrimental biogeochemical effects. For instance, H_2S release can contribute to water acidification (W.-J. Cai et al., 2017) and pose a threat to aquatic organisms such as fish and bacteria (Küster et al., 2005; Lazado et al., 2024). Similarly, shallow coastal areas, where SGD is ubiquitous, dominate global ocean CH_4 emissions (Weber et al., 2019) despite representing a small fraction of the global ocean.

Note that these estimations are based on area-normalized SGD flows derived from whole-lagoon estimates, resulting in Darcy flux rates ranging from 0.01 to 0.10 cm d^{-1} for fresh groundwater discharge, 1.5–1.7 cm d^{-1} for saline recirculation, and 0.4–3.0 cm d^{-1} for PEX. This approach likely underestimates the lineal velocities for fresh and recirculated SGD, as these pathways occur at the freshwater–lagoon water interface near the coastline rather than over the entire lagoon, being primarily driven by hydraulic gradients onshore and pressure gradients in the lagoon, generated by wave pumping or density gradients (Alcolea et al., 2019; Rodriguez-Puig et al., 2025). Assuming that these processes occur within a 500 m nearshore zone, the discharge rate of fresh SGD would rise to 0.11–0.86 cm d^{-1} , while saline recirculation would amount to 13–15 cm d^{-1} .

6.3.2. SGD-driven chemical oxygen demand can contribute to partial bottom-water hypoxia in Mar Menor

The contribution of SGD to coastal DO budgets has only recently been acknowledged. In the coastal waters of Long Bay (USA), in Myrtle Beach (USA), and in the Changjiang River Estuary (China), high radium or radon concentrations (SGD proxies) coincide with low DO concentrations, suggesting a link between SGD and hypoxia (McCoy et al., 2011; Peterson et al., 2016; Guo et al., 2020). Because reduced species supplied by SGD function as electron donors in redox chemical reactions that reduce oxygen, subsequent research has demonstrated that they can lower the concentration of DO in coastal waters (Moore et al., 2024; Sanial et al., 2021). According to these studies, if there is no air invasion, saline SGD can reduce DO concentrations in the Mississippi Bight (USA) bottom waters (Sanial et al., 2021) and even totally deplete seawater DO concentrations over a tidal cycle in the Okatee River basin (Moore et al., 2024). However, little is known about the role of fresh SGD and PEX in reduced substances delivery or their potential impact on coastal lagoons.

In Mar Menor, the potential DO demand rate from SGD inputs was assessed in 2021, which amounted to $3.7 \mu\text{M d}^{-1}$ in winter, $15 \mu\text{M d}^{-1}$ in summer, and $2.8 \mu\text{M d}^{-1}$ in autumn (Fig. 6.3), displaying a similar temporal pattern to the SGD discharge rate. The chemical species that contributed the most to DO reduction in the lagoon were H_2S and DON, which together accounted for over 90% of total DO demand. In summer, H_2S alone contributed to 83% of direct DO consumption. Most of the oxygen demand was due to recirculation pathways, accounting for over 90% of total oxygen demand. In spring and autumn, saline SGD accounted for 52–71% of the total groundwater oxygen demand, whereas PEX drove 84% of the total groundwater-derived oxygen demand in the summer. By connecting sediment porewater to the receiving water column and increasing oxygen demand, the recirculation belt serves as a conduit for reduced species over both short and long timescales. Conversely, fresh SGD was only relatively relevant (9% of total DO demand) in March.

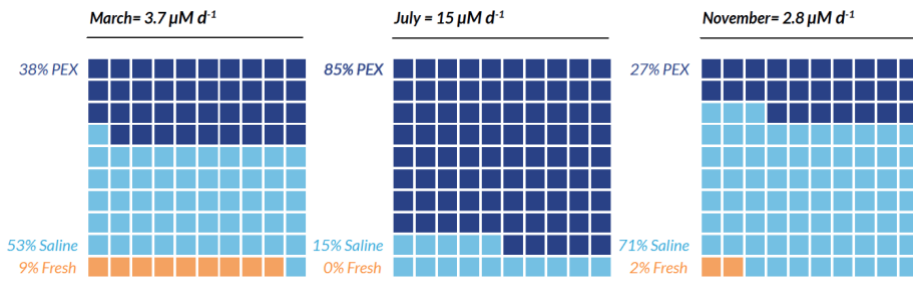


Figure 6.3. Relative contribution (%) from each SGD pathway (Fresh, Saline, and PEX) to the total oxygen consumption rate in Mar Menor ($\mu\text{M d}^{-1}$) in March, July, and November. Captions on top of each plot indicate the total DO consumption rate ($\mu\text{M d}^{-1}$) due to SGD inputs in each season. Each tile represents 1% of DO consumption.

To provide some context, most surface waters exhibit DO concentrations between 6 and 9 mg L^{-1} (190 – $280 \mu\text{M}$) globally. Reported surface concentrations include $\sim 9 \text{ mg L}^{-1}$ in Eckernförde Bay (Steinle et al., 2017), $\sim 8 \text{ mg L}^{-1}$ in San Francisco Bay (Cloern & Jassby, 2012), and 6 – 9 mg L^{-1} in Zhejiang coastal waters (Dong et al., 2024). Mar Menor DO levels also typically fall within these ranges and decrease from winter ($\sim 9 \text{ mg L}^{-1}$) to summer ($\sim 4 \text{ mg L}^{-1}$; UPCT-SDS, 2025 and Fig. C.3) due to reduced solubility from temperature and salinity increase. Oxygen concentrations in coastal areas commonly decrease in summer due to higher temperatures, increased biological demand, and fewer mixing events (i.e., weaker winds and increased stratification; Steinle et al., 2017; Zheng et al., 2023; Zhou et al., 2020). The potential DO demand from SGD in the lagoon can thus only consume $\sim 1\%$ of the available DO in the water column each day during winter and

autumn and up to 12% during summer. These calculations assume a well-mixed water column and rapid oxidation of the SGD-derived substances once they reach the overlying water. Under these conditions, SGD is a minor contributor to potential DO consumption in the Mar Menor coastal lagoon.

Due to the shallowness of the water column, Mar Menor is typically well-mixed; however, large freshwater inputs caused by precipitation can produce saline stratification that lasts longer than a month (Pereira et al., 2025). Additionally, thermal stratification can happen, mostly in the summer, when weak winds prohibit vertical mixing (Y. Ye et al., 2024). In the lagoon, typical low-intensity winds (3.4 m s^{-1}) generate 0.15 m high waves, with very low orbital velocities (0.002 m s^{-1}). As a result, waves barely disturb the bottom waters, and only extreme wind episodes (wave height=0.9 m) generate significant orbital velocity in the bottom (0.1 m s^{-1} ; Morote-Sánchez et al., 2025b). Likewise, current velocity is generally low ($0.00\text{-}0.03 \text{ m s}^{-1}$), with higher velocities along the shore-perpendicular main current paths (Pereira et al., 2025). Water renewal time is also heterogeneous in space, with values ranging from <1 d along the margins to 300 d in the southern region, particularly in bottom waters (Pereira et al., 2025). These hydrodynamic features can promote stratification, with reduced vertical exchange and isolation of the bottom layer from atmospheric invasion. SGD-delivered chemical species undergo fast oxidation that acts as a sink for DO while remaining contained beneath the pycnocline. Our estimates suggest that SGD inputs could consume up to ~50% the total available oxygen in a 1-m bottom layer within a single day. If stratification persists, SGD alone could completely deplete DO in the water column on the order of days. This mechanism is particularly critical during summer in the southern region of the lagoon, which is prone to oxygen depletion due to reduced oxygen solubility, accumulation of organic matter, and nocturnal respiration of *Caulerpa prolifera* meadows and decomposition of phytoplankton blooms, as observed during the August 2021 hypoxic event (López-Castejón et al., 2026). In this context, SGD is a dual driver of hypoxia via direct DO reduction and indirect DO consumption through the delivery of nutrients that enhance primary production (Rodríguez-Puig, accepted), thereby exacerbating hypoxic conditions from eutrophication processes. The combined effects of these processes highlight that SGD is a relevant factor in the lagoon's hypoxia dynamics.

To contextualize the significance of SGD-driven oxygen demand via chemical species, it can be compared with other key oxygen consumption pathways in coastal environments. The main oxygen sinks are water column microbial respiration during organic matter degradation (WCR) and sediment oxygen demand (SOD), which includes benthic fauna respiration and chemical oxidation

of reduced compounds (Pitcher et al., 2021). WCR is usually the dominant oxygen sink (Del Giorgio, 2005), but SOD can dominate in shallow environments due to the higher ratio of sediment area to water column volume (Fennel & Testa, 2019). Reported global ranges for SOD in coastal lagoons (<5 m deep) are between 0.6 and 1.7 g O₂ m⁻² d⁻¹, with strong spatial and temporal variability related to changes in temperature and organic matter availability (Grenz et al., 2019; Leoni et al., 2022; Machado & Knoppers, 1988). Mean areal rates for water column respiration in the coastal ocean and estuaries are 3.5 and 3.7 g O₂ m⁻² d⁻¹, respectively (Del Giorgio, 2005). Microbial activity has been shown to increase with dissolved organic matter inputs (DOM), highly present in Mar Menor due to anthropogenic influence (Amaral et al., 2023; Cerro-Gálvez et al., 2021; Robinson, 2019). In Mar Menor, the areal rate of chemical consumption due to SGD inputs ranged between 0.40 and 2.1 g O₂ m⁻² d⁻¹ for a 4.5 m water column (1.8–9.7 g O₂ m⁻² d⁻¹ for a 1 m water column). These values, which account for 15–60% of the average water column respiration and are comparable to SOD rates in coastal lagoons, demonstrate the significance of SGD oxygen demand in the DO budget in coastal lagoons.

6.3.3. Hydrological, temporal, and chemical controls on SGD-driven oxygen demand across coastal systems

Globally, quantitative estimations of oxygen consumption driven by SGD-derived reduced substances (Moore et al., 2024; Sanial et al., 2021) are very scarce (Fig. 6.4), reporting contrasting impacts across locations. In some systems, SGD can consume all DO in the water column (Moore et al., 2024), while in others, such as the Mar Menor coastal lagoon, its influence seems negligible under well-mixed water-column conditions (~1% of total DO). The magnitude of area-normalized SGD flows varies by 1–2 orders of magnitude, despite similar concentrations of reduced substances in SGD between the current study and those reported by Moore et al. (2024), the magnitude of area-normalized SGD flows differs by 1–2 orders of magnitude. This, combined with the shallower water column at Moore's study sites, results in DO depletion rates that can vary up to two orders of magnitude (Fig. 6.4). This difference highlights the importance of considering the hydrological, chemical, and temporal factors that govern SGD-driven consumption and biogeochemical implications, raising the key question of when and how SGD becomes an important mechanism for DO depletion. This section focuses on three key factors: depth of the mixed layer, water residence time, and chemical

composition, along with the magnitude of SGD water flow, to better understand their influence on biogeochemical impacts.

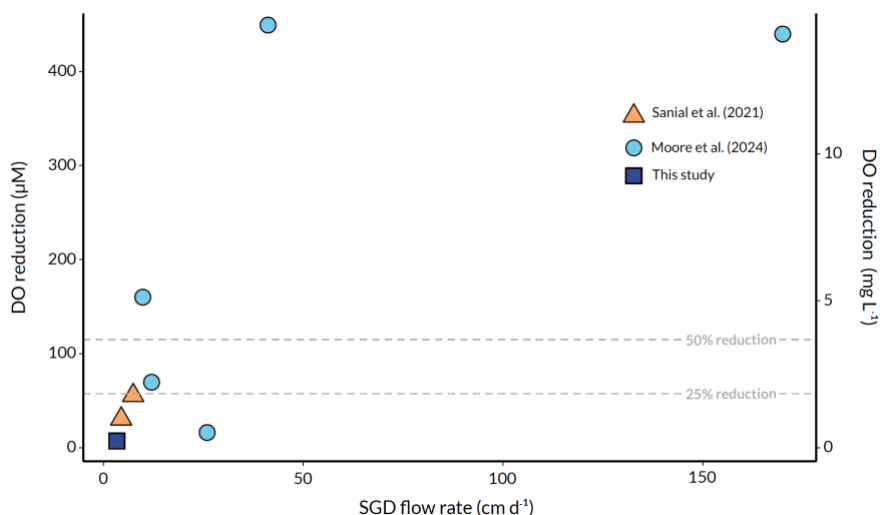


Figure 6.4. Total dissolved oxygen (DO) reduction expressed in μM (left y-axis) and mg L^{-1} (right y-axis) and SGD flow rates (cm d^{-1}) reported across different studies in Myrtle Beach, Okatee River basin, Mississippi Sound, and the Mar Menor lagoon. Water depths or bottom-layer thickness range from 1 to 9 m. DO reduction is reported as a function of tidal cycle, residence time, or daily rates, depending on the study. Dashed grey lines indicate 25% and 50% reductions in DO relative to full saturation at 20°C, salinity 35, and 1 atm.

With comparable SGD flow rates, the influence of SGD on DO depletion is larger in shallow waters than in deep-water columns (Long et al., 2019). Studies included in Fig. 6.4 were conducted in locations with depths ranging from 1 to 9 m, and the differences in observed DO reduction reflect both the magnitude of chemical fluxes (directly linked to SGD flow rates) and the depth of the receiving water body. To illustrate the effect of water depth independently of flow rate, the total DO chemically consumed by SGD was normalized to hypothetical water column depths. For instance, when the locations in Fig. 6.4 are scaled to a 1 m column, SGD can consume at least 50% of the total DO (relative to full DO saturation at 20°C and salinity of 35), even at relatively low flow rates in most systems (Fig. 6.5). In 2 m water columns, the same flux reduces approximately 25% of DO relative to full saturation. This effect is further amplified at higher water temperatures (e.g., 30 °C, typical of summer sea surface temperature in the Mediterranean Sea), because oxygen solubility decreases, thereby reducing the baseline DO inventory. Consequently, the same SGD flux consumes a proportionally larger fraction of the available DO. Based on reported fluxes (Fig. 6.4), SGD can consume ~25% of the DO ($\sim 1.5 \text{ mg L}^{-1}$) in shallow water columns

(<3 m), without considering additional biological demand from nutrient inputs. With increasing sea surface temperatures (IPCC, 2014) and subsequent ocean stratification (Robinson, 2019), an increasing number of systems may be exposed to oxygen depletion.

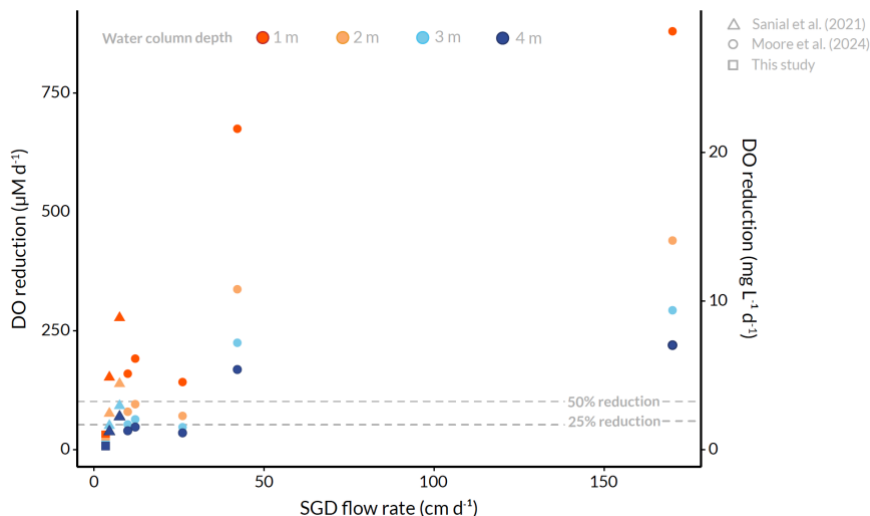
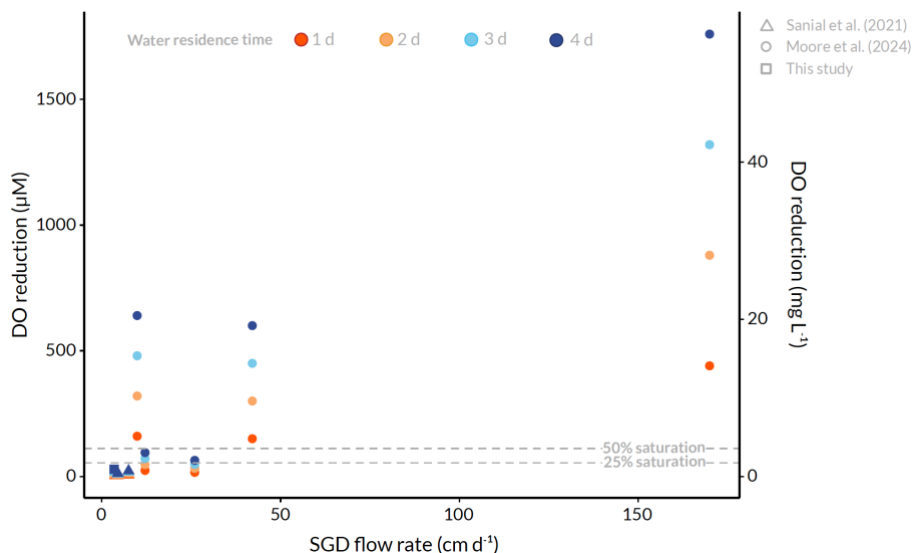


Figure 6.5. Estimated DO reduction expressed in μM (left y-axis) and mg L^{-1} (right y-axis) and SGD flow rates (cm d^{-1}) across different locations normalized to different water column depths (from 1 to 4 m). DO reduction is reported as a function of tidal cycle, residence time, or daily rates, depending on the study. Dashed grey lines indicate a 25% and 50% reduction in DO relative to full saturation at 20°C , salinity 35, and 1 atm.

Extending the analysis to temporal scales, oxygen renewal rate, here defined as the initial DO concentration divided by the water flushing time, also determines the extent of biogeochemical impact on the receiving waters (Fennel & Testa, 2019). Hypoxia vulnerability increases when the rate of SGD-driven DO consumption exceeds this renewal rate. For instance, in a system with an initial DO of 5 mg L^{-1} and a DO consumption of $1 \text{ mg L}^{-1} \text{d}^{-1}$, hypoxia is predicted for flushing times exceeding 5 days (assuming no vertical or lateral exchange). Even in systems with direct ocean connections and relatively rapid flushing times, with residence times on the order of days (e.g., X. Liu et al., 2019; Sakamoto et al., 2024), total oxygen loss can reach up to $500 \mu\text{M}$ (based on data from Mississippi Sound, Myrtle Beach, and the Okatee River basin; Fig. 6.6). This magnitude of consumption represents nearly twice the inventory of a saturated water column at 20°C ($282 \mu\text{M}$), suggesting that without continuous hydrodynamic renewal, these SGD inputs are sufficient to drive the system into a state of permanent anoxia. In semi-enclosed water bodies, long residence times (e.g., 270 days in the

Mar Menor lagoon, Pereira et al., 2025; 180 days in Chesapeake Bay, Du & Shen, 2016; 80 days in Osaka Bay, Sakamoto et al., 2024) substantially extend the contact time between SGD-derived oxygen-demanding compounds and the receiving water mass. In Mar Menor, for instance, isolated water masses require ~80 days to reach hypoxia during most of the year, while only ~9 days are needed in summer. This seasonal acceleration facilitates the development of hypoxic conditions, particularly in zones with limited atmospheric exchange.



of cm d^{-1} to m d^{-1} , consistent with reported observations worldwide (Craddock et al., 2024; Michael et al., 2005), groundwater concentrations as low as $\sim 50 \mu\text{M}$ can still considerably impact DO.

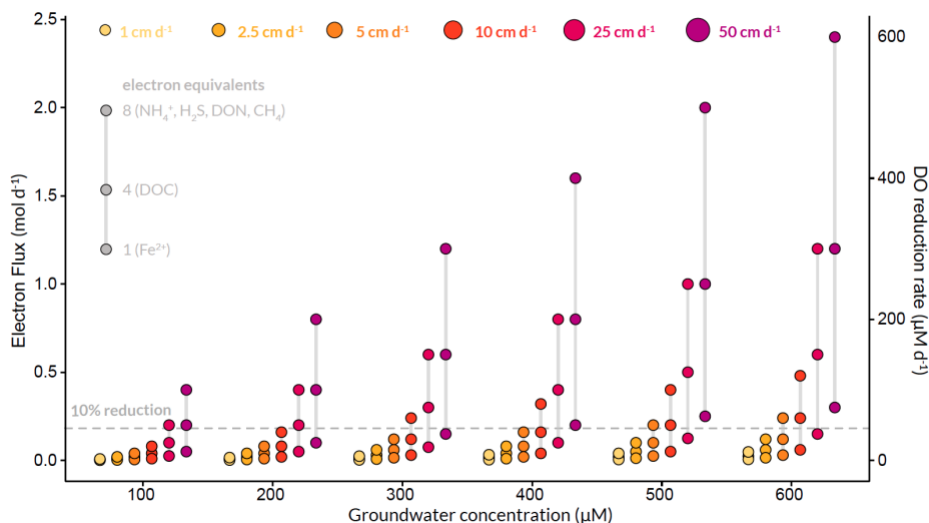


Figure 6.7. Electron flux supplied (mol d^{-1}) and resulting DO reduction rate ($\mu\text{M d}^{-1}$) for different groundwater endmember concentrations of reduced substances (μM) and different flow rates per unit area (cm d^{-1}). The dots within each flow rate category designate the electron equivalents supplied during the oxidation of the different reduced compounds.

Using the results of this simulation, SGD-driven DO consumption can be evaluated in sites where either SGD rates or endmember concentrations are uncertain. For example, in Estero de Punta Banda, Mexico, where depths range from 1 to 10 m, flushing times are ~ 4 days, and reported SGD rates are $\sim 4 \text{ cm d}^{-1}$ (Schubert et al., 2023b), DO reduction can be evaluated based on Fig. 6.7. In this lagoon, SGD-driven DO is likely to be significant (at least 10% of total DO reduced) in shallower zones when groundwater concentrations exceed $\sim 300 \mu\text{M}$ for daily water renewal and may become relevant at concentrations as low as $\sim 100 \mu\text{M}$ when residence time increases to 4 days. Although these estimations consider only a single reduced constituent, a comprehensive assessment of SGD-driven biogeochemical implications requires accounting for total electron donor capacity, which refers to the cumulative concentration of all reduced species weighted by their specific stoichiometric oxygen demand. Including SGD in coastal DO budgets is particularly important under global warming, as salinization of coastal aquifers is expected to affect 80% of coastal areas below 60°N by 2100 (Richardson et al.,

2025), potentially releasing more electron donors and intensifying SGD-driven DO consumption (Moore & Joye, 2021).

This study provides qualitative guidelines to quickly assess the role of SGD in DO depletion. However, deoxygenation is an inherently complex process, arising from the multiple drivers involved (Pitcher et al., 2021), requiring thorough monitoring programs (Cloern & Jassby, 2012) and innovative solutions, such as the development of digital twins (Y. Ye et al., 2024). Furthermore, several challenges across scientific boundaries remain, including identifying and quantifying additional oxygen-demanding species in groundwater, understanding the dominant SGD pathways for DO consumption, integrating the chemical and biological demand from SGD, assessing the ecological impacts of the oxidation by-products in the water column, determining the oxidation kinetics in the water column from the water-sediment interface to the surface, and characterizing benthic biogeochemical zonation to anticipate heterogeneous inputs (G. Chen et al., 2022). Finally, increasing the number of reports of SGD-derived fluxes of reduced substances is essential to establish more robust guidelines for evaluating their impact on coastal oxygen dynamics.

7. Conclusions, knowledge gaps, and future research opportunities

7.1. General conclusions

Current research on submarine groundwater discharge (SGD) is often limited by our ability to accurately **identify and quantify its different pathways**. This is key to determining chemical fluxes, as it requires **pathway-specific assessment of biogeochemical characteristics** and linking them to specific **ecological outcomes**. The present PhD thesis refines the application of radium (Ra) isotopes to better resolve and quantify SGD pathways, which is essential from a hydrological, chemical, ecological, and temporal standpoint. Inaccurate pathway discrimination can result in biased flux estimates, hinder ecological interpretations at annual scales, and misdirect mitigation efforts.

In this thesis, the application of Ra isotopes enabled the quantification of the different SGD pathways inflowing to a coastal lagoon and their seasonality, while addressing common sources of uncertainty and identifying the main driving forces behind each pathway. Because these pathways exhibit different temporal behaviors, an accurate assessment of SGD seasonality requires explicit pathway discrimination. This thesis also integrated the specific biogeochemical processing within each pathway to resolve pathway-specific nutrient fluxes, demonstrating that the inclusion of SGD in coastal biogeochemical budgets and a proper assessment of ecological impacts requires clear pathway discrimination. Finally, this thesis explored oxygen consumption due to SGD by quantifying direct dissolved oxygen (DO) demand from SGD-derived reduced substances. This constitutes the first effort to assess the role of individual pathways in oxygen depletion. Overall, this thesis provides new insights into tracer-based quantification and SGD seasonality and the interplay between chemical cycling in the subterranean estuary (STE), pathway-specific fluxes, and ecological outcomes. Besides providing a general understanding that can be expanded to other systems globally, these results are rooted in the specific framework of the Mar Menor. In this sense, they build on previous knowledge of the Mar Menor ecosystem, contributing to a deeper understanding of its functioning and can inform future management and protection strategies.

Chapters 4 to 6 address these questions, and the conclusions of this work are summarized below.

7.1.1. Chapter 4: Quantification of SGD pathways using radium isotopes

An appropriate understanding of SGD requires constraining the magnitude and composition of its different pathways, but this differentiation is rarely conducted due to methodological limitations. **This work demonstrates how Ra isotopes can be applied to quantify the contribution of different pathways and advances the understanding of SGD processes, including their quantification and seasonality.**

The multi-isotope model developed in this study, which combines transient Ra mass balances (^{224}Ra , ^{226}Ra , and ^{228}Ra) with a 1D advective transport model of radionuclides in the aquifer, can be used to concurrently estimate various SGD pathways while integrating information on their temporal scales. Applied over one year (17 mass balance simulations), the model quantified the magnitude and seasonality of three main SGD pathways in the Mar Menor coastal lagoon: fresh SGD, long-scale recirculation, and porewater exchange (PEX).

Long-scale recirculation dominated the water flow throughout the year, with relatively constant discharge rates approximately one order of magnitude higher than fresh SGD ($10^6 \text{ m}^3 \text{ d}^{-1}$ vs. $10^3\text{--}10^5 \text{ m}^3 \text{ d}^{-1}$, respectively). Fresh SGD was sustained by a high water table elevation driven by agricultural infiltration, with precipitation events also influencing its magnitude. As a result, the salt wedge toe also remained virtually stable throughout the year. In contrast, short-scale flows (PEX) exhibited strong seasonal variability, with summer discharge rates up to four times higher than in winter, reaching $4 \times 10^6 \text{ m}^3 \text{ d}^{-1}$. These seasonal variations could result from the combined influence of multiple drivers, including winds, surface currents, and faunal activity in bottom sediments. Temporal analyses revealed that the increased PEX observed in summer is most likely largely driven by biological changes in the sediments, specifically faunal bioirrigation, which enhances sediment–water exchange across the lagoon. The dominance of recirculation pathways in the lagoon emphasizes their capacity to transport metals, nutrients, and other dissolved substances. However, their contribution to the delivery of these solutes is still mainly disregarded. In addition to anticipating SGD pathway dynamics and their reaction to global change, an understanding of these processes is essential for developing mitigation strategies in the Mar Menor lagoon.

7.1.2. Chapter 5: Biogeochemical transformations and pathway-resolved nutrient fluxes

Current research on SGD-derived nutrient fluxes often overlooks the unique biogeochemical signatures of different SGD pathways, neglecting their differences in biogeochemical transformations and spatiotemporal dynamics. However, the impact of SGD inputs on the coastal environment depends on the magnitude and chemical composition of each SGD pathway. **This study resolves pathway-specific SGD fluxes and integrates their specific biogeochemical processing to assess the ecological impact of SGD.**

The results derived from this work revealed that nutrient concentrations in each SGD pathway were shaped by watershed-scale land use and local redox-driven biogeochemical processes. In Mar Menor, nutrient inputs were strongly shaped by preferential pathways: continental discharge (stream and fresh SGD) primarily governed NO_x inputs, while NH_4^+ , DON, DIP, and DSi inputs were mainly supplied by recirculated SGD (long-scale recirculation and PEX) across seasons. Additionally, by providing extra DIP inputs (24 kmol d^{-1}) in the summer, short-scale recirculation flows can have a significant seasonal impact on nutrient limitation and eutrophication. By distinguishing between these pathways, this study demonstrates that relying on bulk SGD estimates can mask the critical role of internally recycled nutrients, leading to biased flux calculations and misdirection of management efforts.

These findings challenge the prevailing assumption that eutrophication and overall ecological degradation in the Mar Menor are solely driven by continental nitrogen inputs due to human activities. More broadly, this work demonstrates that recirculation groundwater fluxes, often overlooked in coastal studies, can play a central role in nutrient cycling and ecological responses. With the intensification of anthropogenic pressures and salinization of coastal aquifers, a comprehensive understanding of nutrient transport through SGD pathways of different origins and timescales is essential for evaluating and managing the vulnerability of coastal ecosystems.

7.1.3. Chapter 6: Impact of SGD pathways on chemical oxygen demand

Only a limited number of studies have explored the role of SGD in increasing oxygen demand through direct DO reduction, despite the potential biogeochemical implications of this process. **This work represents one of the first efforts to link the supply of reduced compounds via different SGD pathways and direct oxygen reduction and provides qualitative guidelines for its assessment based on groundwater magnitude and composition.**

This study represents the first evaluation of direct DO demand driven by the delivery of reduced compounds (NH_4^+ , H_2S , DOC, DON, CH_4 , and Fe^{2+}) via different SGD pathways. Daily fluxes of reduced species (kmol d^{-1}) were converted into DO reduction rates ($\mu\text{M d}^{-1}$) using stoichiometric electron-transfer ratios. The results indicated that recirculated SGD (both long- and short-scale) was the primary driver of abiotic oxygen demand, accounting for over 90% of the total SGD-driven DO consumption in Mar Menor. This lagoon is frequently affected by hypoxic events, whose underlying causes remain uncertain. Under well-mixed conditions, SGD consumed ~1% of available DO, but this contribution increased to 11% in summer. The seasonal peak was driven by lower DO in the water column and a 6 to 16-fold increase in the delivery of reduced substances via PEX.

The susceptibility of a coastal system to SGD-induced oxygen depletion is governed by three main factors: hydrological (discharge rate and affected volume), temporal (flushing time of the receiving waters), and chemical (groundwater chemical composition). Coastal systems characterized by limited oxygen renewal, small water volumes, high groundwater discharge rates, and SGD enriched in NH_4^+ , H_2S , DON, CH_4 are more vulnerable to direct DO consumption. Within this framework, qualitative guidelines coupling SGD magnitude and groundwater composition can be used to evaluate the potential influence of SGD-derived chemical oxygen demand in coastal systems globally.

7.2. Knowledge gaps and future research opportunities

As a well-recognized component of coastal hydrological and biogeochemical budgets, the study of SGD has advanced substantially over the past 30 years. Nevertheless, SGD often remains an inconspicuous source of contamination, even though its effects on coastal ecosystems are rarely invisible. In this section, the main knowledge gaps and associated research opportunities identified during the development of this thesis are summarized:

Conceptualization and estimation of SGD

▪ Methodological and conceptual fragmentation

Current SGD research is limited by inconsistent terminology and definitions (e.g., the exclusion of small-scale processes, such as PEX). In addition, many studies do not explicitly distinguish between different SGD pathways, often focusing on the fresh component or reporting total SGD flows, which is often linked to the limited ability of single-method approaches to resolve multiple pathways simultaneously. This lack of conceptual consistency can substantially bias estimates of SGD magnitude and its ecological impacts.

Opportunities: Establishing common terminology and conceptual frameworks across disciplines is essential. Future works should adopt multiscale approaches, enabling accurate identification of the main pathways and their drivers. This could be achieved through multi-method approaches, capable of capturing different SGD pathways, shifting from bulk estimations to process-oriented conceptualization.

▪ Spatial scales and sampling biases

The spatial dimension of SGD presents challenges from both the intrinsic heterogeneity of the discharge and methodological biases. On the physical side, high spatial variability driven by hydrogeological heterogeneity and diversity of anthropogenic pressures hinders the extrapolation of point measurements to regional or global scales. As a result, local-scale variability is oversimplified or neglected in large-scale assessments. On the observational side, SGD studies remain unevenly distributed across environments and regions. Research tends to concentrate in regions with high GDP, focuses on known SGD hotspots, and disproportionately samples sandy shorelines compared to muddy

ones (Kretschmer et al., 2025; Taniguchi et al., 2019), biasing global compilations.

Opportunities: Future efforts should prioritize spatially representative samplings across lithologies and socioeconomic contexts. Expanding research into data-poor regions through collaboration with local institutions and leveraging technological advances is key to reducing uncertainties in global SGD estimations.

- **Temporal scales and sampling biases:**

The temporal dimension of SGD also presents inherent challenges linked to the scale of variability of discharge flows and operational biases. Different SGD pathways operate at scales that range from seconds to thousands of years and are subject to different periodicities and disturbances that modulate their magnitude (e.g., semi-diurnal, seasonal, episodic extreme events). The overlap of pathways with differing temporal frequencies challenges the estimation of representative annual fluxes. Currently, most SGD estimations rely on snapshots or seasonal estimates (e.g., wet vs. dry season) that, while useful as a first characterization, fail to capture fluctuations over small timescales. Moreover, field sampling is skewed toward favorable weather, and in some regions, hourly or daily oscillations of driving forces can strongly modify SGD and override seasonal patterns.

Opportunities: Narrowing the temporal gap requires expanding long-term monitoring networks globally and adopting high-resolution temporal measurements to disentangle high-frequency forcings, seasonal variability, and long-term trends (Geng et al., 2026), particularly under global change pressure.

- **Conceptual uncertainties**

Conceptual uncertainties remain a critical, yet frequently under-assessed, challenge in Ra-based SGD studies. They originate from assumptions in mass balance models, including the steady-state approach, and from methodological choices for quantifying sinks and sources, which are rarely systematically reported (Rodellas et al., 2021).

Opportunities: To enhance the reliability and transparency of reported estimates, researchers can: shift from steady-state to transient models that incorporate temporal variability in model inputs and tracer inventories, optimize sample distribution in the field and refine the determination of mean tracer concentrations (e.g., geostatistical

interpolation methods), and implement stochastic uncertainty quantification (e.g., Monte Carlo simulations) (Rapaglia et al., 2012; Rodellas et al., 2021). In addition, performing sensitivity analysis and scenario-based comparisons (e.g., steady-state vs. transient Ra concentrations) allows quantifying the relative conceptual uncertainties (Rodellas et al., 2021; Tamborski et al., 2020a).

- **Use of radium and radon isotopes**

Although Ra isotopes and Rn are the most widely used tracers of SGD, their application is constrained by the appropriate characterization of their distribution and variability in the aquifer. SGD studies often overlook controls on isotopic enrichment in groundwaters, including transit time, lithology, and groundwater chemistry. In addition, selecting the appropriate radionuclides according to the spatiotemporal scale of the process traced, along with a suitable quantification model (e.g., mass balance, eddy diffusivity, or mixing model), is a critical step to ensure a precise quantification.

Opportunities: Improving reactive transport models of radionuclides in the aquifer, developing experimental or in situ assessments of key parameters to better understand Ra distribution in the aquifer, establishing standardized guidelines for tracer selection that explicitly consider decay and production rates in the aquifer (Diego-Feliu, 2022a), and developing reliable marine models to better constrain oceanic drivers are some of the future directions.

The subterranean estuary and environmental effects of SGD

- **Biogeochemical transformations in the STE**

Although Moore (1999) emphasized the biogeochemical role of STEs, many SGD studies still overlook their function as highly reactive zones that modify groundwater composition along its flow path before reaching the coastal ocean. The interaction of chemical composition, residence times, lithology, redox conditions, and microbial communities governs these dynamic environments. As a result, the distribution and concentration of nutrients, carbon, metals, and other solutes are non-conservative. Thus, constraining the endmember composition of discharging waters is a primary challenge when estimating SGD-derived solute inputs.

Opportunities: Recognition of the STE as a driver of ecosystem functioning is essential for accurately assessing SGD-derived solute fluxes. Major frontiers in coastal biogeochemical cycles are inextricably linked to the microbial dimension of SGD, including the integration of metabolic pathways and transformation rates of microbial communities via metagenomics and metatranscriptomics and evaluating the impact of anthropogenic disturbance on microbial communities (Lu et al., 2025; Ruiz-González et al., 2021).

- **Legacy pollution**

Pollutants derived from past land use can accumulate in soils and the aquifer and be slowly released to the ocean via SGD, acting as a major source of legacy pollution. As a result, SGD drives environmental degradation long after surface inputs have been reduced. Current SGD fluxes may reflect historical contamination, increasing the complexity of source attribution and prediction of ecosystem recovery.

Opportunities: Assessing historical pollution and groundwater timescales is key to anticipating future contaminant releases. Water quality evaluations should incorporate time lags between past inputs and present-day fluxes and acknowledge that current pollutant activities may become future legacy pollution (I. R. Santos et al., 2021).

- **Ecological effects**

Despite growing recognition of the ecological impacts of SGD, explicitly linking fluxes with ecological outcomes remains challenging. SGD research is largely focused on nutrient inputs and primary production responses, while other environmental impacts, such as direct DO consumption or metal bioaccumulation within trophic webs, remain poorly constrained. **Opportunities:** Future research should aim to link quantified fluxes to measurable ecological outcomes and broaden the focus beyond nutrients to include multiple stressors, with particular emphasis on understudied pollutants such as contaminants of emerging concern.

Broader implications

- **Global change:**

It is anticipated that anthropogenic stressors and climate change will significantly affect coastal groundwater, especially topography-limited

aquifers. However, little is still known about baseline conditions, controls, and driver interactions. Furthermore, little research has been done on particular effects of climate change, such as changes in wind speed, coastal erosion, and chemical and biological effects (Richardson et al., 2024).

Opportunities: Key opportunities include anticipating the cumulative effects of global change in SGD, evaluating feedbacks among system components, leveraging technological advances such as machine learning-based predictions and remote sensing techniques, and downscaling climatic and oceanographic drivers to SGD spatiotemporal scales (Geng et al., 2026; Richardson et al., 2025).

- **Integrated coastal management**

SGD is often neglected in coastal management plans, which traditionally focus on surface water or consider SGD primarily as a freshwater resource (Douglas & Murgulet, 2025).

Opportunities: Distinguishing external (land-derived) versus internal (remobilized) pollution sources is crucial for guiding mitigation strategies. More broadly, strengthening the cross-talk between scientists and policymakers, or moving from interdisciplinarity to transdisciplinarity, is essential to combine SGD with societal needs and thus incorporate SGD into management frameworks.

- **General praxis:**

The lack of standardized reporting of basic parameters, methodological transparency, and consistent data reporting (e.g., total fluxes versus coastline length-normalized fluxes) limits comparability across SGD studies.

Opportunities: The SGD community should better integrate FAIR data principles (Findability, Accessibility, Interoperability, and Reusability) (Wilkinson et al., 2016). This includes providing standardized metadata (e.g., basic system parameters and normalized fluxes), transparency on decision-making, including negative results and analytical uncertainties, and depositing data in open-access repositories.

Appendices

A. Supplementary material for Chapter 4

A.1. *Radium mass balance model terms: sinks and sources*

The magnitude of SGD into the Mar Menor coastal lagoon was estimated with a transient Ra mass balance approach (see section 2.4 in Methodology). Relevant sources include discharge from streams, diffusion from bottom sediments, and desorption from bottom sediments, while relevant sinks are radioactive decay and exchange with the Mediterranean Sea. All these fluxes are discussed in the following dedicated sections, except for radioactive decay, which is already discussed in the Methodology section.

All sources and sinks have been independently calculated using different approaches, including a Regional Ocean Model System (ROMS) for water exchange between Mediterranean seawater and lagoon water (F_{ex}), experiments for Ra diffusion and desorption (F_{Diff} and F_{Des} , respectively) and the acquisition of data from streamflow monitoring to estimate Ra inputs from streams (F_{Str}). As a result of the different individual approaches used, each term has been estimated with different temporal resolutions. For instance, streamflow and lagoon-sea water exchange can be estimated with daily frequency, while decay fluxes have been estimated for each month.

Discharge from streams, inflow, and outflow rates from and to the Mediterranean Sea were weighted depending on the temporal proximity of each event relative to each sampling campaign (refer to section 3.3 in Results). Analytical uncertainties associated with each of the Ra fluxes were individually estimated by propagating the uncertainties of each term. Relative uncertainties associated with SGD-driven Ra fluxes were estimated to be lower than 36 %. However, this uncertainty assessment neglects all the potential errors associated with the conceptualization of the system and the methods used, the so-called conceptual uncertainties (Rodellas et al., 2021). To account for potential conceptual uncertainties, we report all SGD-driven Ra fluxes derived from the mass balance with an arbitrary relative uncertainty of 50% (see Text S2.5).

A.1.1. Discharge from streams

The flux of radium delivered by stream discharge F_{Str} (dpm d⁻¹) was assessed both as direct input of dissolved radium and as radium released via desorption processes from suspended sediments caused by salinity changes. The latter occurs due to increased ionic strength in the hypersaline environment of the lagoon waters (Hancock et al., 2000; W. Su et al., 2022), as it influences the distribution coefficient between the liquid and solid phases (K_d ; see Text S2.3). In this estimation, only the Rambla del Albuñón stream was considered, as it is the only permanent stream in the area and the steam with the greatest flow. The total contribution of Ra inputs from streams can be solved as:

$$F_{Str} = Q_{Str}A_{i,diss} + Q_{Str}C_{TSS}A_{i,des}, \quad \text{Equation A.1}$$

where Q_{Str} is the discharge rate of the stream (m³ d⁻¹), $A_{i,diss}$ is the dissolved radium activity for each isotope (dpm m⁻³), C_{TSS} is the concentration of Total Suspended Solids in the stream (g m⁻³), and $A_{i,des}$ is the maximum desorbable radium activity for sediments (dpm g⁻¹).

Discharge values for the Rambla del Albuñón stream were retrieved from the Canal Mar Menor streamflow monitoring database (<https://canalmarmenor.carm.es/>). To obtain a daily value, the estimated discharge was calculated using linear interpolation between available data points. The dissolved radium activity for each isotope $A_{i,diss}$ were calculated as an average of Ra activities during the three intensive sampling campaigns. The concentration of Total Suspended Solids (C_{TSS}) was assessed by filtering 3.5 L of stream water through 0.45 µm pre-dried filters. The filter was subsequently dried at 65°C until constant weight was achieved. The maximum desorbable radium activity ($A_{i,des}$) was determined via desorption experiments for ²²³Ra and ²²⁴Ra and via gamma spectrometry for ²²⁶Ra and ²²⁸Ra.

Desorption experiments were performed on 7 different sediment samples from various locations on the coast (Pz1, Pz5, and Pz7) and in the lagoon (L11), all of them potentially influenced by sediment inputs from streams. Before the experiment, between 200 and 400 g of sediment were dried at 65 °C for at least 72 h, until achieving 0% of humidity. The quantity of sediment dried depended on the available amount for each core. The dry sediment was then mixed with different Ra-free water volumes (from 0.2 L to 6.5 L; salinity=42) to reach Ra saturation (i.e., all radium susceptible to

desorb has migrated to the water). As a result, different water/sediment ratios were assessed (from 0.5 to 30) for each core. Sediments were continuously resuspended for >30 min. The water was then filtered at 0.45µm to remove the sediment and filtered three times through an Mn-loaded column to extract all desorbed radium. The sample was rinsed with MilliQ water, dried down to 50 % humidity (Sun & Torgersen, 1998), and measured in a RaDeCC alpha detection system to quantify the desorbed radium activity. The maximum desorbable radium activities were estimated from maximum water/sediment ratios of each sample and reported as an average of all samples. Maximum desorbable activities of ^{226}Ra and ^{228}Ra were based on were based on sediments collected near the stream mouth. The sediment sample was dried at 65 °C until constant weight was achieved and ground with a mortar and pestle. The sediments were then placed in sealed containers for 3 weeks and measured via gamma spectrometry using a high-purity Ge well-type detector. Estimated stream discharge fluxes from March 2021 to May 2022 in dpm d⁻¹ ranged from 3.1×10^6 to 66×10^6 for ^{224}Ra , from 5.9×10^6 to 20×10^6 for ^{226}Ra , and 6.9×10^6 to 25×10^6 for ^{228}Ra .

A.1.2. Diffusion fluxes from bottom sediments

The flux of radium delivered by molecular diffusion from bottom sediments (F_{Diff} ; dpm d⁻¹) is the result of Ra activity gradients between porewater and the overlying water column. Diffusive fluxes were only assessed for ^{223}Ra and ^{224}Ra , as short-lived isotopes are particularly sensitive to internal Ra fluxes because the Ra lost to diffusion is regenerated on timescales comparable to the isotope's half-life. On the other hand, the diffusive flux was considered negligible for long-lived ones due to their long half-lives (Rodellas et al., 2015). Sediment cores were collected at seven locations, including shore (Pz1, Pz5, and Pz7) and lagoon stations (L2, L11, L13, and L17). Before the incubation process, the overlying water of the sediment cores was replaced with Ra-free seawater from the lagoon. Subsequently, the cores were left undisturbed for 1 month to achieve equilibrium between radium porewater activities and the overlying water. Caps were used to prevent evaporation, and physicochemical parameters were measured at the start and end of the experiment. After the incubation period, the overlying water was filtered 3 times through the same Mn-fiber to quantitatively extract the radium, for which we followed the same methodology described in Chapter 3. The Ra diffusive fluxes from sediments were estimated via core incubation experiments performed twice on each

core (n = 14). The radium diffusive flux was estimated as per the following equation:

$$F_{\text{Diff}} = J_{i,\text{Diff}} \cdot S, \quad \text{Equation A.2}$$

where $J_{i,\text{Diff}}$ is the specific radium diffusive flux for each sediment core (dpm $\text{m}^{-2} \text{d}^{-1}$) and S is the surface of the lagoon (m^2). $J_{i,\text{Diff}}$ can be estimated as:

$$J_{i,\text{Diff}} = \frac{I_{i,C} \lambda_i}{A_C}, \quad \text{Equation A.3}$$

where $I_{i,C}$ is the dissolved radium inventory (dpm) in each sediment core after the incubation period, λ_i is the decay constant of each isotope (d^{-1}), and A_C is the core surface area (0.03 m^2). $J_{i,\text{Diff}}$ was estimated separately for each sediment type (i.e., sandy or muddy). The total diffusive radium flux was estimated by multiplying the specific radium diffusive flux by the coverage of each bottom type (m^2) in the lagoon (90% muddy, 10% sandy; Ruiz et al. (2020)). The estimated diffusive flux for ^{224}Ra was $1.4 \times 10^9 \text{ dpm d}^{-1}$. The estimated diffusive fluxes in this study do not account for potential seasonal variations as they are based on a single experiment. However, molecular diffusion and bioirrigation may be influenced by temperature and dissolved oxygen and can enhance radium diffusive fluxes up to 2-fold. To account for this potential temporal variability, we assigned an uncertainty of $\pm 50\%$, as proposed by Garcia-Orellana et al. (2014).

A.1.3. Desorption fluxes from resuspended bottom sediments

The radium flux associated with desorption processes resulting from resuspension of bottom sediments was estimated for ^{224}Ra and considered negligible for long-lived isotopes because their regeneration occurs over a timescale longer than the resuspension events. Resuspension events in Mar Menor are mainly driven by wind-induced waves and currents. The periodicity of wind speed and direction is 12/24 h (Gilabert et al., 2023). Consequently, the frequency of the resuspension events is assumed to be on the order of 1 day. The radium flux due to resuspension of bottom sediment was estimated following Equation A.4:

$$F_{\text{des}} = V f C_{\text{TSS}} A_{i,\text{des}}, \quad \text{Equation A.4}$$

where V is the lagoon volume (m^3), f refers to the frequency of the resuspension events (d^{-1}), C_{TSS} is the concentration of Total Suspended Solids in the lagoon (g m^{-3}), and $A_{i,\text{des}}$ is the maximum desorbable radium activity (dpm g^{-1}). The methodology followed for desorption experiments is

detailed in section A.1.3. C_{TSS} was estimated by filtering a known volume of lagoon water through Whatman GF/F glass microfiber filter papers and weighting the retained solid mass. Assuming that new sediments are resuspended each day (thus, having maximum Ra desorbable activities), we calculated maximum desorption fluxes, thus providing conservative estimates for SGD Ra fluxes. The estimated desorption flux for ^{224}Ra was $2.9 \times 10^8 \pm 1.4 \times 10^8 \text{ dpm d}^{-1}$.

A.1.4. Water exchange with the Mediterranean Sea: Hydrodynamic model

The water exchange between the Mar Menor lagoon and the Mediterranean Sea for the period of analysis was determined through numerical modelling simulations performed by a previously calibrated and validated ROMS (Regional Ocean Model System) hydrodynamic implementation covering the Mar Menor domain and the nearshore Mediterranean (Pereira, F., 2024, unpublished). ROMS is a hydrostatic, free-surface, primitive equation, Boussinesq ocean general circulation model designed primarily for coastal applications. It uses terrain-following vertical coordinates allowing for greater vertical resolution in shallow water and regions with complex bathymetry. The model is widely used by the scientific community for a diverse range of applications. The algorithms that comprise ROMS computational nonlinear kernel are described in detail in Shchepetkin & McWilliams (2003, 2005) and the tangent linear and adjoint kernels and platforms are described in Moore et al. (2004). A simulation was performed covering the period between March 2021 and May 2022. The model oceanic boundary was forced with daily salinity and water temperature data from the Atlantic Iberian Biscay Irish-Ocean Physics Reanalysis (Copernicus Marine Service, 2020) and water level data from a tide gauge moored in the San Pedro del Pinatar port (outside the Mar Menor lagoon), and the atmospheric boundary was forced with air temperature, relative humidity, sea level pressure, wind speed and direction, cloud cover, net solar radiation and longwave radiation from the HARMONIE-AROME atmospheric model (Calvo Sánchez et al., 2018). The model was also fed with freshwater runoff data retrieved from the Canal Mar Menor streamflow monitoring database and groundwater discharge obtained from the hydrogeological model of Alcolea et al. (2019).

The model implementation was validated against water level measured by seven tide gauges located along Mar Menor and current speed measured by five ADCP's moored in the outlets (Las Encañizadas, El Estacio and

Marchamalo). Water level data were then used to calculate the lagoon's volume, while ADCP data were used to estimate the water exchange in each outlet. The area of the cross-sections where the ADCPs were moored was estimated through in-situ depth measurements, and the water exchange occurring in each outlet was calculated through Equation A.5. Note that the Ra exchange with the Mediterranean Sea through La Manga sand bar is negligible (Sánchez-Badorrey & Jalón-Rojas, 2015) and was excluded in this work.

$$Q = v * A_{C-S}, \quad \text{Equation A.5}$$

where Q is the flow ($\text{m}^3 \text{s}^{-1}$) that crosses the cross-section, v is the current speed (m s^{-1}) averaged over the cross-section, and A_{C-S} the cross-section area (m^2). Based on this, the water exchange-associated radium flux (F_{ex}) was estimated as:

$$F_{\text{ex}} = Q_{\text{in}}A_{i,\text{Est}} - Q_{\text{out}}A_i, \quad \text{Equation A.6}$$

where Q_{in} and Q_{out} are the inflow and outflow, respectively, at the cross-sections of the El Estacio and Marchamalo ($\text{m}^3 \text{d}^{-1}$). $A_{i,\text{Est}}$ and A_i are the radium concentrations in El Estacio's mouth (outside the lagoon) and in the lagoon for each isotope (dpm m^{-3}), respectively. Q_{in} and Q_{out} were estimated with daily frequency from 30 s resolution data. $A_{i,\text{Est}}$ was estimated from an average of concentrations in El Estacio's mouth in July and November ($n=2$). $A_{i,\text{lag}}$ was estimated from a three-station average for each sampling campaign. Estimated exchange fluxes from March 2021 to May 2022 in dpm d^{-1} ranged from 0.3×10^8 to 19×10^8 for ^{224}Ra , from 6.6×10^8 to 7.4×10^8 for ^{226}Ra , and 1.4×10^9 to 2.9×10^9 for ^{228}Ra .

A.1.5. *Tracer residence time*

The residence time of each isotope in the system (t_{Ra} ; d) was calculated for each month of the sampling period. It depends on its decay constant and on the flushing time (Eq. 3.2). The flushing time was estimated according to Eq. 8.A (Monsen et al., 2002), and is equivalent to water residence time because the influence of evaporation and dispersion is negligible (Garcia-Orellana et al., 2021):

$$t_f = \frac{V}{Q_{\text{out}}}, \quad \text{Equation A.7}$$

where V is the lagoon's volume (m^3), and Q_{out} is the volumetric outflow rate ($\text{m}^3 \text{d}^{-1}$). The volume of the lagoon was from the ROMS hydrodynamic model

of Mar Menor (see Text S1.4) as a monthly average volume from 30 s resolution data. The average flushing time (t_f) during 2021 is 130 days.

A.2. Estimation of fresh SGD, long-scale recirculated SGD and PEX with an advective transport model of radionuclides in groundwater

The relative contribution of each SGD pathway (i.e., fresh SGD, long-scale recirculation and PEX) to the total SGD-derived radium flux was estimated by combining a hydrogeological model of the Campo de Cartagena aquifer with an advective transport model of radionuclides in groundwater (Eq. 5.8). The quantification of each term is detailed in the following sections.

A.2.1. Hydrogeological model of the Campo de Cartagena Quaternary Aquifer

A three-dimensional (3D) hydrogeological model was developed to integrate a surface water balance model with a groundwater model (Alcolea et al., 2019). The surface water balance was quantified using the SPHY (Spatial Processes in Hydrology (Terink et al., 2015) model, an open-source bucket-type modeling code adapted for the study area by Contreras et al. (2014). SPHY calculates daily water balance components and soil moisture dynamics at discrete soil layers, driven by precipitation inflows and water losses (e.g., interception and evapotranspiration), which depend on vegetation, root depth, water storage, and soil texture. Lateral fluxes in the vadose zone were considered negligible due to the smooth topography over the whole catchment, with most slopes below 1%.

Inputs to SPHY include static inputs (i.e., terrain slope from a Digital Elevation Model and soil hydraulic properties derived from textural maps and pedotransfer functions) and dynamic inputs (i.e., climate data such as precipitation and evapotranspiration and satellite-based vegetation data such as NDVI for vegetation phenology).

The model outputs, including evapotranspiration losses and aquifer recharge, were used as inputs for the 3D variable-density groundwater model simulated with SUTRA (Saturated-Unsaturated TRANsport, Voss & Provost (2010)). Heterogeneous aquifer properties, such as hydraulic conductivity and storativity, were calibrated using the Regularized Pilot Points Method (Alcolea et al., 2006), as implemented in the PEST software (Doherty, 2016). Relevant outputs of the coupled surface water-groundwater flow model include the fresh SGD into the Mar Menor lagoon.

A.2.2. *Ra equilibration experiments for PEX endmember determination*

The Ra equilibrium activity in the interstitial water of permeable sediments of the lagoon used to derive the radium endmember of PEX ($A_{eq.,s,i}$; dpm m⁻³) was assessed with Ra equilibration experiments. They were conducted on sediments collected at four different locations in the lagoon (n = 7). Sediments were placed in beakers and filled up to the sediment upper layer with Ra-free seawater from the Mar Menor lagoon (i.e., full saturation). Caps were used to prevent evaporation, and samples were left undisturbed for at least one month. Physicochemical parameters were measured at the start and end of the experiment. Subsequently, the sediments were centrifuged to separate the interstitial water from the sediments, and 20g of Mn-fiber were soaked for at least 15 minutes. The fibers were treated following the methods described in Chapter 3. ²²⁴Ra equilibrium activities ranged from 620 to 2800 dpm 100 L⁻¹.

The Ra activity in interstitial water derived from the Ra equilibration experiments was validated with a second batch of experiments in cores collected in a posterior campaign. After collection, the overlying water was removed, and the sediment was centrifuged to recover the interstitial water. Sample treatment and measurement is detailed above. Both experiments yielded comparable Ra activities (570–1800 dpm 100 L⁻¹).

A.2.3. *Ra retardation factor*

Solid-solution interaction processes can reduce the velocity of a solute, like radium, relative to groundwater flow velocity in a dynamic system (McKinley & Russell Alexander, 1993). This phenomenon, known as retardation, significantly influences radium distribution in groundwater and solids. Evaluating this process is a key step, as it can determine the specific transit time of each isotope to reach equilibrium in the aquifer (Diego-Feliu et al., 2021). The retardation factor (R) characterizing Ra sorption can be estimated from the distribution coefficient of radium, assuming the ionic exchange as the predominant factor controlling retardation:

$$R = 1 + K_d \frac{\rho_b}{\phi}, \quad \text{Equation A.8}$$

where K_d (m³ kg⁻¹) is the radium distribution coefficient between sediment and water, ρ_b (kg m⁻³) is the dry bulk density, and ϕ (-) is the porosity. Dry bulk density was estimated from core sediments collected in different parts of the lagoon (n=5). Cores were sliced every 1 cm and representative

subsamples were dried at 65 °C until constant weight was achieved. They were then ground with a mortar and pestle (Alorda Montiel et al., 2025). An average of the first 20 cm was estimated for each core. On that basis, an average was calculated separately for coastal and lagoon sediment cores (n=2 and n=3, respectively). Porosity was calculated as:

$$\phi = 1 - \frac{\rho_b}{\rho_p}, \quad \text{Equation A.9}$$

where ρ_b is the dry bulk density of the sediments (kg m^{-3}), and ρ_p is the particle density (kg m^{-3}). Typical particle density values for gravel, sand, silt and clay were retrieved from literature (Blake, 2008). The particle density value for each core was estimated by accounting for the percentage of gravel, sand, silt, and clay in each one cm section based on gran size analysis (Alorda-Montiel et al., 2025). A particle density value was then estimated for coastal and inner lagoon sediment cores (2650 and 2680 kg m^{-3} , respectively). Lastly, K_d was estimated as:

$$K_d = \frac{Ra_s}{Ra_w}, \quad \text{Equation A.10}$$

where Ra_s is the sediment surface-bound radium activity (dpm kg^{-1}), and Ra_w is the dissolved radium in interstitial water (dpm m^3). Exchangeable Ra_s was estimated from lagoon cores from desorption experiments (A.1). Ra_w was calculated with Ra equilibration experiments (section A.1.2). The obtained K_d represents thus the distribution factor in saline interstitial waters (i.e., applied to the PEX Ra endmember). The estimated Ra retardation factor for saline waters in lagoon sediments ranged from 4 to 80.

A.2.4. Radium enrichment and transit times in the aquifer

The evolution of Ra activities in the aquifer not only depends on the isotope's half-life but also on groundwater transit times and the retardation factor (Diego-Feliu et al., 2021). The % of enrichment of Ra isotopes in the groundwater flow relative to the Ra activities in equilibrium with parent (Th) can be estimated as:

$$\% \text{ enrichment} = \frac{A_{eq,i}}{A_{SGD,i}} (1 - e^{-\lambda_i \cdot R \cdot \tau}), \quad \text{Equation A.11}$$

where $A_{eq,i}$ is the Ra equilibrium activity, $A_{SGD,i}$ is the Ra activity in SGD (dpm m^{-3}), λ_i is the decay constant of each isotope (d^{-1}), R is the Ra retardation factor, and τ is the transit time of groundwater in the aquifer (d). For

instance, for $R=50$, ^{224}Ra needs a transit time of 0.3 days to reach 95% enrichment. For the same transit time, ^{228}Ra will achieve 0.5 % enrichment. For the same R values, a transit time of 185 days would be needed to achieve 95 % enrichment in ^{228}Ra .

A.2.5. Model input parameters in the Monte Carlo analysis

Long-scale recirculation (Q_L), PEX (Q_S), and PEX transit times (τ_S) and their associated uncertainties are estimated with a Monte Carlo analysis of the model described in Eq. (9). Values for the total recirculated water Ra flux ($F_{\text{RSGD},i} = F_{\text{SGD},i} - F_{\text{Fresh},i}$) are generated via normally distributed random values based on the mean and 50% uncertainty derived from each isotope mass balance. This ensures accounting for potential conceptual uncertainties inherent to sampling design and methodology choice, amongst others. Ra activity in the lagoon (A_i) values are generated via normally distributed random values based on the mean and standard deviation derived from the averaged Ra activities at stations L2, L11, and L17 (see section 3.3). Ra retardation factor (R) values are generated via uniformly distributed random values based on the estimated range (4–80). Values for $A_{S,228}$ are generated via uniformly distributed random values based on the bulk radioactive equilibrium of the $^{224}\text{Ra}_{\text{gw}}/^{228}\text{Ra}_{\text{gw}}$ AR (1.0-1.2) (Diego-Feliu et al., 2021).

Table A.1. Ra activity ranges for each sample type and isotope. Units in dpm 100 L⁻¹.

Sample type	^{223}Ra	^{224}Ra	^{226}Ra	^{228}Ra
Stream	1.7-25	52-750	13-230	23-630
Well	1.3-7.3	41-440	2.7-58	14-350
Fresh (salinity < 10)	3.2-15	18-460	27-27	110-110
Brackish (salinity 10 – 30)	2.2-9.6	40-230	30-35	23-74
Saline (salinity > 30)	3.0-46	21-840	16-62	23-430
Lagoon	0.7-6.2	5.1-150	16-76	31-120

Table A.2. Lagoon and sea activities for ^{224}Ra , ^{226}Ra , and ^{228}Ra from March 2021 to May 2022. Units in dpm 100 L⁻¹.

Campaign	Sample	Type	^{223}Ra	$\Delta^{223}\text{Ra}$	^{224}Ra	$\Delta^{224}\text{Ra}$	^{226}Ra	$\Delta^{226}\text{Ra}$	^{228}Ra	$\Delta^{228}\text{Ra}$
March 2021	OP2_L1	Lagoon surface	1.3	0.4	23.4	2.6	21.3	1.5	47.5	2.4
March 2021	OP2_L2	Lagoon surface	1.5	0.3	20.2	2.2	21.6	1.5	62.4	2.7
March 2021	OP2_L2D	Lagoon deep	1.9	0.3	21.4	2.4	20.5	1.5	59.4	2.9
March 2021	OP2_L3	Lagoon surface	1.0	0.2	17.2	2.0	21.5	1.4	65.2	2.6
March 2021	OP2_L4	Lagoon surface	1.6	0.3	17.0	1.9	19.1	1.3	66.0	2.8
March 2021	OP2_L5	Lagoon surface	0.9	0.3	17.1	1.9	18.0	1.4	64.2	2.8
March 2021	OP2_L6	Lagoon surface	1.4	0.3	18.9	2.0	19.0	1.3	48.3	2.3
March 2021	OP2_L7	Lagoon surface	1.5	0.3	15.8	1.9	21.1	1.6	66.0	3.5
March 2021	OP2_L8	Lagoon surface	1.6	0.3	17.6	2.0	16.5	1.2	56.6	2.3
March 2021	OP2_L9	Lagoon surface	1.7	0.3	21.2	2.2	16.5	1.6	54.3	2.8
March 2021	OP2_L10	Lagoon surface			15.8	1.8	18.9	1.5	57.4	2.8
March 2021	OP2_L11	Lagoon surface	1.7	0.4	19.6	2.2	19.2	1.3	63.1	2.9
March 2021	OP2_L11D	Lagoon deep	2.0	0.4	34.0	3.8	21.8	1.6	67.1	3.4
March 2021	OP2_L12	Lagoon surface	1.2	0.3	20.7	2.0	22.6	1.4	55.3	2.5
March 2021	OP2_L13	Lagoon surface	1.6	0.3	31.0	3.2	23.7	1.5	59.9	2.8
March 2021	OP2_L14	Lagoon surface	1.1	0.2	15.1	1.7	25.1	1.6	56.5	3.0
March 2021	OP2_L15	Lagoon surface			10.3	1.2	16.0	1.5	30.9	1.9
March 2021	OP2_L16	Lagoon surface	1.7	0.4	20.3	2.2	26.5	1.8	57.7	3.0
March 2021	OP2_L17	Lagoon surface	1.5	0.3	15.4	1.7	18.3	1.5	51.1	3.2
March 2021	OP2_L17D	Lagoon deep	2.4	0.4	19.6	2.4	26.1	1.5	72.4	3.1
March 2021	OP2_L18	Lagoon surface	2.5	0.4	28.4	2.9	34.3	1.5	88.6	3.8
March 2021	OP2_L19	Lagoon surface	1.5	0.3	14.3	1.7	30.0	1.7	71.6	3.2
March 2021	OP2_L20	Lagoon surface	1.8	0.3	19.1	2.1	24.0	1.6	65.8	3.4
March 2021_2	OP_210315_L2	Lagoon surface	1.6	0.3	22.4	2.6	23.6	1.4	54.1	2.7
March 2021_2	OP_210315_L6	Lagoon surface	2.1	0.3	19.4	2.6	24.1	1.4	57.5	2.8
March 2021_2	OP_210315_L11	Lagoon surface	1.7	0.3	18.8	2.4	23.9	1.5	72.5	3.4
March 2021_2	OP_210315_L13	Lagoon surface	1.8	0.3	24.4	2.8	28.5	1.6	74.3	3.7
March 2021_2	OP_210315_L17	Lagoon surface	2.1	0.4	17.2	2.4	22.4	1.6	71.3	3.5
April 2021	OP_210428_L2	Lagoon surface	2.3	0.4	28.3	3.1	19.3	1.4	52.9	2.7
April 2021	OP_210428_L11	Lagoon surface	2.5	0.4	35.9	3.9	18.2	1.4	63.6	3.1

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April 2021	OP_210428_L17	Lagoon surface	3.3	0.5	26.5	2.9	18.0	1.4	66.5	3.2
June 2021	OP3_L2	Lagoon surface	2.7	0.5	43.7	4.7	24.4	2.0	87.1	4.2
June 2021	OP3_L11	Lagoon surface	3.2	0.7	65.3	6.3	21.7	1.5	66.3	3.1
June 2021	OP3_L13	Lagoon surface	4.0	0.6	45.6	4.8	26.6	2.0	72.2	3.5
June 2021	OP3_L17	Lagoon surface	3.6	0.6	52.2	5.2	20.3	1.5	73.2	3.7
July 2021	OP4_L1	Lagoon surface	2.7	0.7	43.6	4.6	22.8	1.8	60.5	6.0
July 2021	OP4_L2	Lagoon surface	2.8	0.7	42.3	4.6	24.6	2.2	55.0	5.7
July 2021	OP4_L2D	Lagoon deep	2.6	0.6	39.1	4.4	24.1	2.1	60.6	4.4
July 2021	OP4_L3	Lagoon surface	2.8	0.7	38.7	4.0	24.3	1.8	56.9	5.9
July 2021	OP4_L4	Lagoon surface	2.5	0.8	52.7	5.4	26.2	2.0	64.2	5.3
July 2021	OP4_L5	Lagoon surface	2.4	0.5	52.1	5.5	22.5	1.6	54.9	2.9
July 2021	OP4_L6	Lagoon surface	3.2	0.8	54.2	5.4	25.5	1.8	58.6	6.8
July 2021	OP4_L7	Lagoon surface	2.7	0.5	55.7	6.0	28.6	2.6	65.9	3.3
July 2021	OP4_L8	Lagoon surface	4.0	0.8	58.2	6.3	27.1	2.3	62.9	4.0
July 2021	OP4_L9	Lagoon surface	3.3	0.9	64.2	6.4	29.2	1.8	57.5	7.0
July 2021	OP4_L10	Lagoon surface	4.9	0.9	76.2	8.1	28.9	2.6	79.4	7.1
July 2021	OP4_L11	Lagoon surface	4.5	0.9	73.3	8.1	23.9	1.6	60.8	6.6
July 2021	OP4_L11D	Lagoon deep			146.2	17.2	26.2	1.6	74.4	6.2
July 2021	OP4_L12	Lagoon surface	4.4	0.9	67.0	7.0	29.3	2.4	72.7	7.0
July 2021	OP4_L13	Lagoon surface			78.8	8.5	30.1	1.8	80.3	4.5
July 2021	OP4_L13D	Lagoon deep	6.2	1.3	93.9	10.3	27.9	1.7	75.9	6.6
July 2021	OP4_L14	Lagoon surface	4.8	0.9	57.7	6.1	27.1	2.3	76.5	3.5
July 2021	OP4_L15	Lagoon surface	4.1	0.8	57.2	6.1	26.1	1.6	66.9	3.5
July 2021	OP4_L15D	Lagoon deep	5.1	1.1	76.6	8.6	29.9	1.9	80.7	7.3
July 2021	OP4_L16	Lagoon surface	4.7	0.9	59.6	6.1	28.5	2.5	75.2	6.6
July 2021	OP4_L17	Lagoon surface	5.0	0.8	54.3	6.1	25.5	2.1	73.5	6.4
July 2021	OP4_L17D	Lagoon deep	4.3	0.7	42.3	4.6	23.7	2.6	71.9	11.7
July 2021	OP4_L18	Lagoon surface	4.0	0.8	59.9	6.5	25.7	2.1	74.7	5.9
July 2021	OP4_L19	Lagoon surface	5.2	0.8	48.7	5.4	30.7	2.5	87.3	7.0
July 2021	OP4_L20	Lagoon surface	5.1	0.8	54.0	5.3	26.9	1.7	68.1	3.3
July 2021	OP4_ESTACIO	Sea	1.6	0.4	23.3	2.3	11.8	1.7	12.2	2.3
August 2021	OP_210818_L2	Lagoon surface	6.9	0.8	26.6	3.4	22.8	1.5	76.7	3.6
August 2021	OP_210818_L11	Lagoon surface	3.4	0.4	16.0	2.8	25.9	2.1	68.1	5.8
August 2021	OP_210818_L17	Lagoon surface	2.3	0.4	14.8	2.6	30.3	2.1	79.8	5.9

September 2021	OP_210920_L2	Lagoon surface			18.3	2.2	23.1	1.9	55.9	5.2
September 2021	OP_210920_L11	Lagoon surface	1.9	0.3	8.5	1.3	28.8	1.6	69.6	5.8
September 2021	OP_210920_L13	Lagoon surface			67.6	7.0	28.9	2.3	74.3	6.0
September 2021	OP_210920_L17	Lagoon surface	2.3	0.4	14.6	1.9	30.0	1.6	73.7	6.0
October 2021	OP_211014_L2	Lagoon surface	2.2	0.4	21.8	3.4	24.0	1.6	55.5	5.4
October 2021	OP_211014_L11	Lagoon surface	1.1	0.3	5.6	1.6	26.3	2.3	62.5	5.7
October 2021	OP_211014_L13	Lagoon surface	1.8	0.4	27.0	3.5	27.0	2.1	67.0	5.6
October 2021	OP_211014_L17	Lagoon surface	3.0	0.5	12.0	2.6	27.0	1.6	65.6	3.2
November 2021	OP5_L1	Lagoon surface	1.9	0.6	22.9	2.4	22.2	2.1	52.9	5.2
November 2021	OP5_L2	Lagoon surface	1.1	0.3	14.9	1.8	21.7	1.6	51.8	4.9
November 2021	OP5_L2D	Lagoon deep			21.7	2.3	23.9	2.1	53.7	5.5
November 2021	OP5_L3	Lagoon surface	0.9	0.3	8.9	1.2	22.2	1.6	53.1	5.3
November 2021	OP5_L4	Lagoon surface	1.0	0.3	13.1	1.7	22.1	2.0	56.3	5.1
November 2021	OP5_L5	Lagoon surface	1.0	0.2	8.8	1.1	18.8	2.2	43.1	4.9
November 2021	OP5_L6	Lagoon surface	1.9	0.4	22.3	2.4	20.4	2.0	51.5	5.1
November 2021	OP5_L7	Lagoon surface	1.2	0.3	7.2	1.1	21.3	2.1	52.1	5.0
November 2021	OP5_L8	Lagoon surface	1.3	0.4	5.6	1.0	21.8	2.0	56.2	5.2
November 2021	OP5_L9	Lagoon surface	1.7	0.5	23.9	2.8	24.4	1.8	55.0	5.8
November 2021	OP5_L10	Lagoon surface	2.0	0.4	23.4	2.5	22.8	1.6	56.3	5.4
November 2021	OP5_L11	Lagoon surface	1.8	0.6	10.6	1.4	21.0	2.2	49.6	5.0
November 2021	OP5_L11D	Lagoon deep			6.3	1.2	24.9	2.2	57.4	5.5
November 2021	OP5_L12	Lagoon surface	1.4	0.4	5.1	1.0	23.7	2.1	59.0	5.0
November 2021	OP5_L13	Lagoon surface	2.1	0.4	19.4	2.2	24.4	2.1	51.7	5.2
November 2021	OP5_L13D	Lagoon deep	2.5	0.5	23.9	2.6	24.0	1.6	52.3	6.0
November 2021	OP5_L14	Lagoon surface	2.1	0.4	17.2	2.1	24.6	2.2	53.8	5.4
November 2021	OP5_L15	Lagoon surface			7.0	1.2	24.8	2.2	56.5	5.5
November 2021	OP5_L16	Lagoon surface			16.8	2.1	25.5	1.6	54.0	4.1
November 2021	OP5_L17	Lagoon surface	0.7	0.3	10.8	1.5	26.6	1.7	56.5	2.9
November 2021	OP5_L17D	Lagoon deep			10.6	1.5	29.1	2.6	63.7	6.3
November 2021	OP5_L18	Lagoon surface	1.7	0.4	13.3	1.8	25.7	1.6	55.4	5.2
November 2021	OP5_L19	Lagoon surface	1.6	0.3	11.7	1.6	28.9	1.9	58.4	5.9
November 2021	OP5_L20	Lagoon surface	1.8	0.4	13.3	1.6	24.4	2.1	49.0	5.7
November 2021	OP5_L21	Lagoon surface	1.6	0.4	19.7	2.2	28.1	2.6	59.4	6.0
November 2021	OP5_ESTACIO	Sea	0.8	0.5	9.8	1.2	12.5	1.5	23.9	2.5

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November 2021_2	OP_211130_L2	Lagoon deep	1.3	0.2	13.5	2.1	25.5	2.5	57.4	2.9
November 2021_2	OP_211130_L11	Lagoon surface	1.2	0.2	5.2	1.5	24.1	2.1	54.1	5.3
November 2021_2	OP_211130_L13	Lagoon surface	1.8	0.3	10.4	1.8	23.9	1.6	50.9	4.9
November 2021_2	OP_211130_L13D	Lagoon deep	1.2	0.2	7.0	1.7	24.2	2.3	52.5	5.4
November 2021_2	OP_211130_L17	Lagoon surface	2.1	0.3	14.5	2.1	27.1	1.8	55.3	5.3
December 2021	OP_211221_L2	Lagoon surface			16.4	2.5	20.9	1.6	46.1	5.3
December 2021	OP_211221_L11	Lagoon surface	1.6	0.3	9.0	1.7	25.0	2.5	56.3	5.9
December 2021	OP_211221_L13	Lagoon surface	2.3	0.4	10.8	1.8	24.7	2.4	50.3	5.9
December 2021	OP_211221_L13D	Lagoon deep			6.8	2.3	22.9	2.2	45.4	5.5
December 2021	OP_211221_L17	Lagoon surface			6.4	1.4	22.1	1.8	50.0	5.7
January 2022	OP_220111_L2	Lagoon surface			12.2	1.7	24.6	1.6	44.1	5.3
January 2022	OP_220111_L11	Lagoon surface			10.0	1.4	23.2	1.8	49.5	3.6
January 2022	OP_220111_L13	Lagoon surface	1.5	0.3	9.8	1.4	19.0	2.1	46.5	5.2
January 2022	OP_220111_L13D	Lagoon deep			16.8	2.1	20.3	1.8	47.1	3.4
January 2022	OP_220111_L17	Lagoon surface			10.3	1.5	21.0	1.6	48.3	2.6
February 2022	OP_220214_L2	Lagoon surface	1.1	0.3	14.9	1.4	20.8	2.1	37.2	4.9
February 2022	OP_220214_L11	Lagoon surface			13.5	2.0	22.4	2.4	46.0	5.7
February 2022	OP_220214_L13	Lagoon surface	2.4	0.4	17.3	2.2	24.6	2.4	48.8	2.5
February 2022	OP_220214_L13D	Lagoon deep			22.9	2.7	24.7	1.8	50.4	3.5
February 2022	OP_220214_L17	Lagoon surface			13.5	2.0	20.4	1.9	43.8	4.5
March 2022	OP_220311_L2	Lagoon surface			15.2	2.4	18.7	2.0	39.9	4.3
March 2022	OP_220311_L11	Lagoon surface			15.1	2.3	19.2	7.8	41.6	2.0
March 2022	OP_220311_L13	Lagoon surface			25.1	3.4	20.9	1.8	42.7	5.1
March 2022	OP_220311_L13D	Lagoon deep	2.2	0.4	19.5	2.6	19.7	1.9	41.1	3.3
March 2022	OP_220311_L17	Lagoon surface	1.9	0.4	20.3	2.5	21.1	2.0	42.8	4.7
March 2022_2	OP_220330_L2	Lagoon surface			17.1	2.7	17.7	1.6	39.8	4.2
March 2022_2	OP_220330_L11	Lagoon surface	1.7	0.3	16.6	2.8	21.8	2.7	47.3	7.0
March 2022_2	OP_220330_L13	Lagoon surface	2.1	0.4	18.1	3.0	20.7	2.1	42.0	4.5
March 2022_2	OP_220330_L13D	Lagoon deep	1.9	0.4	23.8	3.5	19.9	1.9	45.2	3.5
March 2022_2	OP_220330_L17	Lagoon surface	1.8	0.4	19.0	3.0	18.4	1.8	40.3	3.6
April 2022	OP_220419_L2	Lagoon surface	1.7	0.3	22.7	2.4	19.7	2.2	40.7	4.8
April 2022	OP_220419_L11	Lagoon surface	1.6	0.2	16.5	2.0	21.5	2.0	42.6	4.4
April 2022	OP_220419_L13	Lagoon surface	2.7	0.3	27.9	2.8	18.9	1.7	44.1	3.3
April 2022	OP_220419_L13D	Lagoon deep	3.3	0.4	26.4	2.8	22.6	2.5	41.8	5.9

April 2022	OP_220419_L17	Lagoon surface	1.9	0.3	14.4	1.8	18.4	1.7	39.0	2.9
May 2022	OP_220510_L2	Lagoon surface	1.9	0.3	17.8	2.9	17.9	1.8	36.7	5.0
May 2022	OP_220510_L11	Lagoon surface	1.8	0.3	7.1	2.3	16.9	1.5	45.0	3.7
May 2022	OP_220510_L13	Lagoon surface	2.5	0.3	30.9	4.3	17.6	1.6	43.1	3.1
May 2022	OP_220510_L13D	Lagoon deep	2.9	0.5	36.2	5.1	20.0	1.8	47.6	3.4
May 2022	OP_220510_L17	Lagoon surface	2.4	0.3	16.8	2.9	18.4	1.8	44.7	5.2

Table A.3. Definitions and values of the terms used in the ^{224}Ra , ^{226}Ra , and ^{228}Ra mass balance from Eq. 4.2 for March, July, and November 2021.

Term	Definition	March			July			November			Units
V	Lagoon volume	5.73			5.91			6.04			$\times 10^8 \text{ m}^3$
S	Lagoon surface area	1.35			1.35			1.35			$\times 10^8 \text{ m}^2$
τ	Frequency of resuspension events	1			1			1			d
		^{224}Ra	^{226}Ra	^{228}Ra	^{224}Ra	^{226}Ra	^{228}Ra	^{224}Ra	^{226}Ra	^{228}Ra	
A	Lagoon Ra activity	184	197	588	566	250	651	121	230	526	dpm m^{-3}
$\partial \text{AV} / \partial t$	Change of Ra inventory with time	11.8	0	5.11	43.6	0	5.11	-13.2	0	-10.6	$\times 10^8 \text{ dpm d}^{-1}$
Q_{Str}	Weighted stream discharge rate	9.5	2.0	2.0	2.1	2.2	2.2	1.4	1.3	1.3	$\times 10^4 \text{ m}^3 \text{ d}^{-1}$
A_{Str}	Stream Ra activity	612	514	603	612	514	603	612	514	603	dpm m^{-3}
J_{diff}	Ra diffusive flux	10.1	N	N	10.1	N	N	10.1	N	N	$\text{dpm m}^{-2} \text{ d}^{-1}$
A_{Des}	Maximum desorbable Ra activity	0.49	N	N	0.49	N	N	0.49	N	N	dpm m^{-3}
λ	Decay constant	0.19	1.2×10^{-6}	3.3×10^{-4}	0.19	1.2×10^{-6}	3.3×10^{-4}	0.19	1.2×10^{-6}	3.3×10^{-4}	d^{-1}
Q_{In}	Weighted inflow rate from the Mediterranean Sea	2.3	3.8	3.8	3.3	3.9	3.9	4.2	3.8	3.8	$\times 10^6 \text{ m}^3 \text{ d}^{-1}$
A_{EST}	Channel's mouth Ra activity	120	87	130	120	87	130	120	87	130	dpm m^{-3}
Q_{Out}	Weighted outflow rate to the Mediterranean Sea	5.1	4.7	4.7	3.7	4.5	4.5	3.9	4.5	4.5	$\times 10^6 \text{ m}^3 \text{ d}^{-1}$

N = Negligible.

Table A.4. Estimated radium fluxes terms used in the ^{224}Ra , ^{226}Ra , and ^{228}Ra mass balances from Eq. 4.1 for March, July, and November 2021. All fluxes are in dpm d^{-1} .

Term	March			July			November			
	^{224}Ra	^{226}Ra	^{228}Ra	^{224}Ra	^{226}Ra	^{228}Ra	^{224}Ra	^{226}Ra	^{228}Ra	
dAV/dt	12	0	5.1	44	0	5.1	-13	0	-11	$\times 10^8$
F _{SGD}	21 $\pm$ 4	0.71 $\pm$ 0.08	2.9 $\pm$ 0.3	64 $\pm$ 18	0.67 $\pm$ 0.03	3.1 $\pm$ 0.5	12 $\pm$ 3	0.7 $\pm$ 0.1	0.9 $\pm$ 0.3	$\times 10^9$
F _{Str}	5.8 $\pm$ 0.5	1.03 $\pm$ 0.07	1.2 $\pm$ 0.1	1.3 $\pm$ 0.1	1.18 $\pm$ 0.07	1.4 $\pm$ 0.1	8.26 $\pm$ 0.06	7.06 $\pm$ 0.04	8.3 $\pm$ 0.07	$\times 10^7$
F _{Diff}	1.4 $\pm$ 0.5	N	N	1.4 $\pm$ 0.5	N	N	1.4 $\pm$ 0.5	N	N	$\times 10^9$
F _{Des}	2.9 $\pm$ 1.4	N	N	2.9 $\pm$ 1.4	N	N	2.9 $\pm$ 1.4	N	N	$\times 10^8$
F _{λ}	2100 $\pm$ 300	0.016 $\pm$ 0.001	12 $\pm$ 1	6400 $\pm$ 180	0.0158 $\pm$ 0.0003	13 $\pm$ 2	1400 $\pm$ 270	0.0158 $\pm$ 0.002	10.3 $\pm$ 0.7	$\times 10^7$
F _{ex}	7 $\pm$ 2	7.2 $\pm$ 0.8	22.6 $\pm$ 0.8	17 $\pm$ 6	6.8 $\pm$ 0.2	25 $\pm$ 5	0.3* $\pm$ 3.0	7 $\pm$ 1	19 $\pm$ 3	$\times 10^8$

* indicates Ra inflow flux > Ra outflow flux (i.e., negative net exchange)

dAV/dt = Change of inventory over time; F_{Str} = Stream flux; F_{Diff} = Diffusion flux; F_{Des} = Sediment desorption flux; F _{λ} = Decay flux; F_{ex} = Mar Menor–Mediterranean exchange flux, F_{SGD} = SGD flux. N = Negligible.

Table A.5. Selected values for radium endmember concentrations in fresh groundwater discharge, long-scale recirculation, and porewater exchange for ^{224}Ra , ^{226}Ra and ^{228}Ra . Units in dpm m^{-3} .

Fresh groundwater discharge (A_F)			Long-scale recirculation (A_L)			Porewater Exchange (A_S)
^{224}Ra	^{226}Ra	^{228}Ra	^{224}Ra	^{226}Ra	^{228}Ra	^{224}Ra
617	538	499	884	475	757	10001
478	567	908	1112	211	597	22105
443	236	803	1937	289	720	14088
854	354	369	3738	574	4272	6218
638	283	923	226	483	872	27805
1056	302	851	1671	553	2251	15433
2691	429	1104	709	475	757	13859
586	274	483	8447	587	1107	
1558	462		1813	618		
4568	399		1787			
918			3735			
1230			807			
1706						
450						

*Values for $A_{S,228}$ (n=100,000) are generated via uniformly distributed random values based on ^{224}Ra activities. Refer to Text A.2.5 for detailed information.

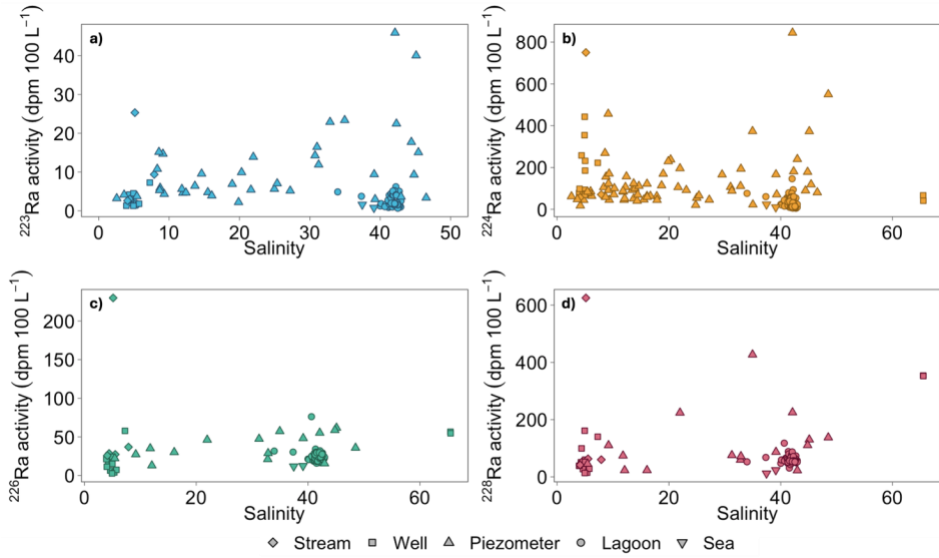


Figure A.1. Ra activities (dpm 100L⁻¹) vs salinity for stream, well, piezometer, lagoon, and sea samples for a) ²²³Ra, b) ²²⁴Ra, c) ²²⁶Ra, and d) ²²⁸Ra.

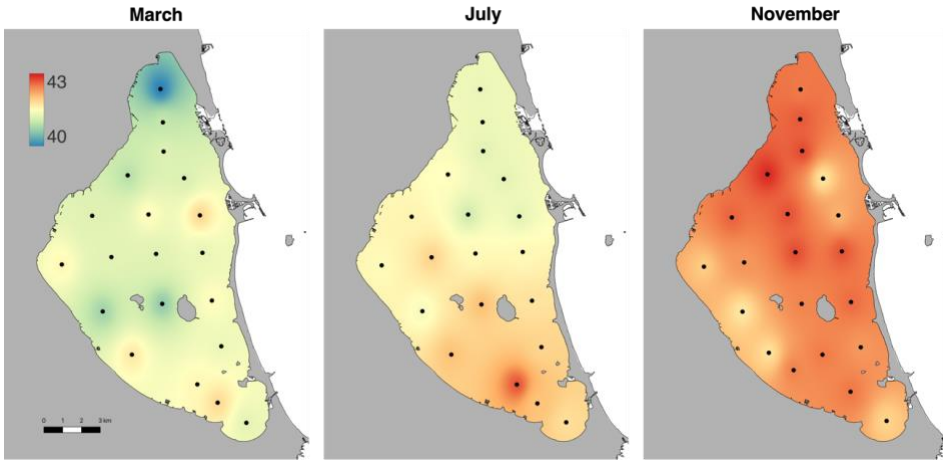


Figure A.2 Seasonal surface salinity distribution in the Mar Menor lagoon in March, July, and November 2021. Dots represent sampling points used to derive the Inverse Distance Weight (IDW) interpolation.

B. Supplementary material for Chapter 5

B.1. Statistical analysis and spatial interpolation

To test for significant differences in nutrient concentrations among different sample types, a one-way Analysis of Variance (ANOVA) was first performed using the `aov()` function from the `stats` package in R (v.4.2.2). Prior to conducting ANOVA, assumptions of normality and homogeneity of variance were tested using Shapiro-Wilk test and Levene's test, respectively. In cases where these assumptions were violated, a Kruskal-Wallis (K-W) test was performed using the `kruskal.test()` function (`stats` package from R). If the K-W test indicated significant differences, post-hoc pairwise comparisons were conducted using Dunn's test with Benjamini-Hochberg correction with the `dunnTest` function of the `FSA` package. All statistical tests were considered significant at $p < 0.05$.

To visualize nutrient distributions across the lagoon surface and estimate mean concentrations, we used geostatistical interpolation methods through ordinary kriging. Empirical variograms were computed for each nutrient and season, and theoretical models (spherical or exponential) were fitted using the `fit.variogram()` function from the `gstat` R package. This function estimates the nugget, sill, and range parameters by minimizing the sum of squared errors (SSE) between empirical variogram points and the theoretical model. The model with the lowest SSE was selected for interpolation. Kriging was performed with the `krige()` function to estimate nutrient concentrations at a regular grid resolution of 75 m. The resulting predictions were converted to raster layers, from which mean nutrient concentrations for each season were calculated. To assess potential uncertainties associated with this method, Inverse Distance Weight interpolation was also performed. The mean concentrations derived from IDW were highly consistent with those from kriging, with differences falling within the reported standard deviations. These results indicate that the choice of interpolation method does not significantly influence the mean nutrient values.

B.2. Determination of nutrient endmember concentrations and Monte Carlo simulation to estimate nutrient fluxes

The complex and spatially variable processes in the subterranean estuary and the non-conservative behavior of nutrients challenge the accurate

determination of the endmember nutrient concentration in each SGD pathway, which is a key step to determining SGD-derived nutrient fluxes. This step is particularly relevant when isolating contributions from different SGD pathways because each one is characterized by a unique biogeochemical signature (I. R. Santos et al., 2021). As a result, oversimplifying the system's conceptual model or designing inadequate sampling strategies can lead to substantial inaccuracies in nutrient flux quantification (Rodellas et al., 2021). Several approaches have been proposed to better constrain endmember values, including increasing the number of samples (Charette, 2007), collecting nearshore water after all biogeochemical processes have occurred (Santos et al., 2008), or performing numerical simulations (Zhu et al., 2025). In this study, we combined the aforementioned strategies to improve the robustness of nutrient flux estimates. Specifically, we collected a total of 72 coastal groundwater samples, distributed from 80 m inland to 44 m seawards and 14 lagoon porewater samples. The main hydrological pathways, including stream discharge, fresh groundwater discharge, long-scale recirculation, and porewater exchange, have been previously described in detail in by Rodríguez-Puig et al. (2025).

To assign samples to the specific SGD pathways, we used a dual-criteria approach, combining biogeochemical information with spatial context. As a first-order classification, samples were grouped according to salinity, a primary indicator of freshwater-seawater mixing regimes in coastal aquifers, consistent with previous SGD publications (e.g., Zhu et al., 2025). Three salinity classes were defined: fresh (salinity <10), brackish (salinity 10–30), and saline (salinity >30). Spatial integration was subsequently included, accounting for proximity to the shoreline or lagoon location, and known hydrological features, enabling the distinction between inland-derived fresh groundwater, nearshore mixing zones, saline recirculated groundwater, and lagoon porewaters. Based on the combined salinity and spatial criteria, four main sample groups were identified: fresh coastal groundwater, brackish coastal groundwater, saline coastal groundwater, and lagoon porewater. These groups were then used to define representative nutrient endmember concentrations for each SGD pathway. As an independent validation of this classification, a principal component analysis (PCA) was conducted with physicochemical variables (e.g., salinity, ORP, concentration of nutrient species), revealing distinct and coherent clusters aligned along the salinity gradient and corresponding to the four sample

groups, with each cluster exhibiting characteristic nutrient compositions (Fig. B.4).

Lagoon porewater samples were collected in 2024–2025, three years after the initial coastal groundwater endmember sampling in 2021. While this temporal gap could introduce potential variability in nutrient concentrations, bottom sediments in the lagoon remain persistently saturated by lagoon water, which stabilizes solute concentrations in the porewater. Moreover, porewater chemistry is largely controlled by sediment biogeochemistry and hydrodynamics, with relatively minor interannual variation when sampling occurs under comparable seasonal and hydrodynamic conditions (Ahrens et al., 2020; Krask et al., 2022). In this study, salinity, water level, temperature, and dissolved oxygen were similar between the 2021 and 2024–2025 campaigns, supporting the assumption that porewater nutrient composition remained broadly stable. Future work should investigate the spatial and temporal drivers of lagoon porewater composition in Mar Menor, including intra- and interannual variability, to fully quantify potential changes.

The flux of each nutrient associated with the different water pathways was estimated as:

$$F_{nut,i} = Q_i \cdot C_{nut,i}, \quad \text{Equation B.1}$$

where F_{nut} is the flux of the target nutrient species ($\mu\text{mol d}^{-1}$), i denotes each water pathway or endmember type (e.g., fresh or saline), Q is the water flow (L d^{-1}), and C_{nut} (μM) represents the net nutrient concentration in the discharging waters (i.e., nutrient endmember concentrations). For recirculation pathways (i.e., long-scale recirculation and porewater exchange), C_{nut} is defined as the difference between nutrient concentrations in groundwater and lagoon waters. This allows for the correction of nutrients originally present in the infiltrating lagoon water (Cook et al., 2018a).

Based on the selected endmembers, we performed a Monte Carlo analysis with 100,000 numerical simulations to constrain the most probable nutrient flux associated with each SGD pathway. By using a wide range of endmember values and reporting interquartile ranges (Q1–Q3), we ensure that our estimates reflect the most likely flux scenarios while accounting for inherent uncertainties. The Monte Carlo parametrization included values for Q_{str} (stream discharge), Q_F (fresh groundwater discharge), Q_L (long-scale

recirculation), and Q_S (porewater exchange). Values for $C_{nut, str}$ were estimated as the mean of stream samples (R1 and R2) in each seasonal survey. For each SGD pathway, a pool of groundwater concentration values ($C_{nut, gw}$) was derived from coastal groundwater samples or lagoon porewater samples, as previously described. For each simulation, $C_{nut, gw}$ values from each endmember pool ($n=12-16$), were randomly selected via deterministic combinational analysis, excluding values based on Tukey's method for outlier detection. This allowed for including the full range of observed variability in the nutrient endmember samples. For Q_{Str} and Q_F , 100,000 random values were generated from normal distributions based on the mean, with a standard deviation (sd) corresponding to 50% uncertainty. Q_L and Q_S followed a lognormal distribution, and their mean and sd were derived from their log-scale parameters (μ and σ values). Lagoon surface nutrient concentrations ($C_{nut, sw}$) in each season were derived from kriging-based interpolations, as described in Text S2. Mean and sd concentrations were generated following a normal distribution. Sampling stations were evenly distributed across the lagoon ($n=20-21$ per season), minimizing spatial bias.

B.2.1. *Alternative approach to estimate nutrient fluxes from SGD pathways*

To further validate our Monte Carlo results, we performed a cross-check analysis in which recirculation-driven nutrient fluxes were estimated by multiplying the SGD Ra flux by the excess ratio of nutrient over Ra concentrations in each pathway (e.g., Cho et al., 2018). This approach was based on the Ra model for quantifying SGD flows described in Chapter 4, following Eqs. B.2 and B.3 for long-scale recirculation and PEX nutrient fluxes, respectively:

$$F_{nut, long} = F_{226, long} \cdot \frac{C_{nut, long}}{A_{226, long}}, \quad \text{Equation B.2}$$

$$F_{nut, PEX} = F_{224, PEX} \cdot \frac{C_{nut, PEX}}{A_{224, PEX}}, \quad \text{Equation B.3}$$

Where i denotes the SGD pathway, $F_{nut, i}$ is the nutrient flux supplied by long-scale recirculation or PEX, $F_{Ra, i}$ is the radium flux supplied by a specific SGD pathway (^{226}Ra flux for long-scale and ^{224}Ra for PEX), $C_{nut, i}$ and $A_{Ra, i}$ are the net nutrient concentrations and Ra activities in that pathway (i.e., groundwater measured concentration/activity minus lagoon water concentration/activity). This cross-check yielded results consistent with

those reported in the manuscript, with differences between methods falling within the associated uncertainties.

B.3. Nutrient distribution along the land–lagoon continuum

Large differences in dissolved nutrient concentrations were also observed across sampled compartments (Fig. 2), with different relationships between salinity and nutrient enrichment (Fig. B.5). Seasonal variation in concentrations was negligible within each compartment, except streams, where strong variability was observed across seasons and depending on the nutrient species.

The $\text{NO}_3^- / \text{NH}_4^+$ ratio exhibited variations with salinity, with the median ratio values of 100 in streams, 600 in inland groundwater, 300 in fresh coastal groundwaters, and <1 in brackish, saline, lagoon porewater, and lagoon samples (Fig. B.2). The nitrogen speciation also varied across compartments (Fig. B.6).

Dissolved nutrient concentrations also varied according to ORP values in the coastal aquifer, particularly nitrogen species and DIP (Fig. B.7). We observed strongly reducing environments in the coastal aquifer, with ORP values as low as -400 mV. Groundwater samples from reducing environments featured NO_x concentrations (median= $2 \mu\text{M}$) remarkably lower than those collected in oxidizing environments (median= $600 \mu\text{M}$). An opposite trend was observed for NH_4^+ , with the highest concentrations found in reducing conditions (median= $50 \mu\text{M}$) and negligible concentrations in oxidizing environments (median= $3 \mu\text{M}$). DIP followed the same pattern, with elevated concentrations in samples with negative ORP (median= $0.4 \mu\text{M}$), although relatively high concentrations were also found in samples with positive ORP (median= $0.2 \mu\text{M}$). DON and DSi concentrations did not correlate with ORP.

B.4. Estimation of nutrient sources to the lagoon

The contribution of different nutrient sources to the Mar Menor lagoon was estimated to assess the relative importance of SGD as a vector of nutrients. Relevant sources included diffusion from the sediments, atmospheric deposition, inflow from the Mediterranean Sea through the inlets, stream discharge, and SGD.

Diffusion from the sediments to the overlying water column was estimated using Fick's first law of diffusion, following Equation B.4:

$$J = \frac{\phi \cdot D_{s,i} \cdot dC}{dz}, \quad \text{Equation B.4}$$

where ϕ is porosity of the lagoon's bottom sediments, estimated as $1 - (\rho - P)$, where ρ is the dry bulk density (kg m^{-3}) and P is the particle density (kg m^{-3}). Dry bulk density was estimated from lagoon sediment cores, as described in (Alorda-Montiel et al., 2025), and typical particle density values for gravel, sand, silt and clay were retrieved from literature (Blake, 2008) based on gran size analysis. D_s is the bulk sediment diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) for chemical species i . $D_{s,i}$ was corrected for tortuosity (θ^2) according to ($D_{0,i}/\theta^2$). θ^2 was estimated following (Ullman & Aller, 1982) and D_0 was estimated from (Yuan-Hui & Gregory, 1974). The concentration gradient (dC/dz) was calculated as the difference between the median concentration in bottom waters at stations L2, L11, L13, and L17 (1 m above the sediment) in different seasons and the median concentration in porewaters at 30 cm. The diffusive flux ($\text{mmol m}^{-2} \text{d}^{-1}$) was subsequently extrapolated to the total Mar Menor area (135 km^2).

Atmospheric deposition fluxes were retrieved from literature for different sites in the Mediterranean Sea (Marín Beltrán, 2017), with the exception of NO_2^- due to the lack of data. As a result, atmospheric deposition fluxes for NO_x might be underestimated, although NO_3^- constitutes the main nitrogen species within NO_x . The deposition fluxes were averaged and extrapolated to the Mar Menor area.

Mediterranean Sea inflow was estimated using the average water inflow in 2021 based daily estimates from a Regional Ocean Model System (ROMS) (Gilabert et al., 2020; Pereira et al., 2025). Annual mean concentrations measured at the main channel mouth on the Mediterranean side in July and November were multiplied by the water flow to obtain the nutrient influx.

B.5. Land use and biogeochemical transformations in the subterranean estuary control nutrient concentrations in discharging groundwaters

The extensive dataset produced in this study allowed a comprehensive characterization of the potential sources delivering nutrients to the Mar Menor. At the basin scale, differences in land use among hydrological sub-basins (Figs. 1.8 and B.8) strongly influence nutrient distributions in the Mar

Menor coastal aquifer (Table B.4). For instance, higher NO_x concentrations occur in agriculturally dominated basins, while elevated NH_4^+ levels are associated with more urbanized basins (Fig. B.9). The influence of anthropogenic activities on nutrient concentrations in groundwaters has also been observed in subterranean estuaries worldwide (S. J. Wilson et al., 2024a).

At the sub-basin scale, geochemical processes occurring in the subterranean estuary result in different nutrient signatures across and within sampling sites. The subterranean estuaries act as biogeochemical hotspots, where nutrient composition is controlled by different factors, including nutrient origin, redox conditions, organic matter content, microbial communities present, and groundwater transit times (Slomp & Van Cappellen, 2004).

The studied coastal groundwaters showed a clear transition from terrestrially influenced groundwater samples, characterized by fresh waters, oxidative conditions, agriculturally dominated basins and enriched in “new” nutrients (i.e., NO_x), to lagoon-influenced groundwater, characterized by more saline waters, reducing conditions and enriched in recycled nutrients (e.g., NH_4^+ , PO_4^{3-}) (Fig. 6.B). This change in nutrient composition along the subterranean estuary is likely influenced by highly diverse and heterogeneous microbial communities found in Mar Menor coastal groundwaters (Romano-Gude et al., 2025), which occupy the wide variety of ecological niches hidden within pores and sediment interfaces of this transition zone. Transit time further modulates these groundwater transformations by determining the contact time between groundwater and the biogeochemical matrix (Devol, 2015). In coastal aquifers, seawater recirculation flows may have transit times ranging from several days to years (Robinson et al., 2018). Long transit times could promote reducing conditions that drive anaerobic nitrogen transformations, including NO_3^- loss due to denitrification and dissimilatory nitrate reduction to ammonium. The latter process, together with organic matter decomposition, contributes to NH_4^+ production (Heiss et al., 2017; Slomp & Van Cappellen, 2004; S. J. Wilson et al., 2024b). These dynamics are particularly evident in the long-scale recirculation pathway in Mar Menor, as we observed elevated enrichment of NH_4^+ and DSi.

Assessing elemental ratios essential for primary production is critical to understanding potential ecological responses to nutrient inputs driven by SGD (Robinson et al., 2018). We show that in Mar Menor, median N/P ratios of potential nutrient sources decrease markedly along the hydrological

continuum, from extremely high values in inland groundwater ($\sim 10,000$) to very low values in lagoon porewaters (<5), indicating a shift from N to P dominance toward the coast (Fig. B.2). The high N/P ratios in inland groundwater reflect the agricultural nitrogen inputs in the basin, which enrich freshwater sources, and have been observed in highly anthropized regions (Zhu et al., 2025). In addition, oxic conditions allow for conservative transport of N relative to P, which is more easily removed by adsorption on sediments, supporting high N/P ratios in fresh water (Slomp & Van Cappellen, 2004). As groundwater flows towards the coast, redox conditions become more reducing, promoting the release of PO_4^{3-} from the mineralization of organic matter and/or the reduction of Fe-oxides. Simultaneously, nitrogen species composition shifts as NO_3^- is lost mainly due to denitrification and NH_4^+ is released from organic matter decomposition and dissimilatory nitrate reduction to ammonium (DNRA) (Slomp & Van Cappellen, 2004), thus lowering $\text{NO}_3^-/\text{NH}_4^+$ ratios along the land-lagoon continuum (Fig. B.2a). Hence, the relative contribution of different groundwater pathways determines the chemical form and stoichiometry of nutrient inputs, which can favor different groups of primary producers, and ultimately impact primary productivity and ecosystem functioning (Lecher & Mackey, 2018).

Seasonal N/P dynamics in the lagoon, and their impact on Mediterranean waters, are largely governed by biogeochemical processes along the land-lagoon continuum. N/P ratios in the adjacent Mediterranean Sea are ~ 40 . In spring (March), inflow from the sea combined with internal lagoon processes such as enhanced primary productivity contribute to diluting the extremely high N/P ratios of continental inputs (~ 1000), with the average lagoon ratio reaching 275. In July, however, average N/P ratios in the lagoon drop to 15. The higher average concentrations of DIP in the lagoon ($0.1 \mu\text{M}$) compared to Mediterranean Sea waters ($0.04 \mu\text{M}$) suggest that the lagoon becomes a net source of P to the Mediterranean in summer, potentially influencing nutrient dynamics and primary production in the adjacent Mediterranean Sea waters (Jiménez-Casero et al., 2025).

Appendices

Table B.1. Nutrient concentrations (μM) used as endmembers for each SGD pathway in the Monte Carlo simulation. F = fresh SGD, S = long-scale recirculation, P = PEX.

NO _x			NH ₄ ⁺			DIN			DON			DSi			DIP		
F	S	P	F	S	P	F	S	P	F	S	P	F	S	P	F	S	P
1300	0.51	3.7	0.70	46	4.0	1300	47	7.0	890	480	910	110	87	100	0.28	3.0	9.9
240	1.7	4.0	0.68	200	3.3	240	200	8.5	220	90	360	97	120	38	0.33	1.4	9.7
1500	0.76	3.6	3.9	21	4.5	1500	22	8.7	1000	120	400	110	65	98	0.29	1.0	9.0
490	1.5	2.6	9.7	2.3	5.1	500	35	4.9	1300	420	140	96	60	100	0.12	0.37	9.3
430	2.6	2.1	2.5	11	2.3	430	180	9.5	2700	222	100	85	43	11	0.52	0.087	9.6
20	1.5	0.12	0.65	180	7.4	72	210	16	600	30	150	130	82	120	0.23	0.21	6.2
520	3.5	0.24	1.5	210	16	520	45	7.6	2500	30	430	59	100	51	0.15	0.28	0.68
0.28	0.15	1.5	2.0	44	7.4	54	38	26	60	310	170	98	49	60	0.26	2.3	1.3
1500	0.44	1.2	10	35	24	1500	26	19	57	30	67	110	78	19	0.17	0.20	8.1
1200	0.058	1.0	1.4	25	17	1200	52	14	30	510	93	110	52	17	0.86	3.1	4.6
340	0.59	2.3	1.6	52	13	450	140	13	1800	850			96	47	0.080	3.3	6.8
1200	1.0	1.1		140	11	1200	66	7.2	1400	27			85	56	0.37	0.12	7.4
430		1.2		66	6.1	430	39	7.9	350				89	39	0.57		6.3
610		0.91		38	6.7	610		5.0	26				40	40			5.9
		0			4.1			5.2						27			2.2
		0.19			5.0									36			2.0

Table B.2. Concentration ranges (μM) of each nutrient by sample type.

Sample type	NO_x	NH_4^+	DIN	DON	DIP	DSi
Stream	1670 – 1960	2.4 – 15.8	1700 – 2000 200	180 – 1340	1.81 – 3.92	97 – 141
Inland GW	2.12 – 3830	0.4 – 46.9	– 3800	20 – 3200	0.09 – 2.34	47 – 439
Fresh coastal GW	0.07 – 1530	0.7 – 108	54 – 1500	12 – 2690	0.08 – 0.99	38 – 445
Brackish coastal GW	0.25 – 1430	0.5 – 1720	11 – 1700	BDL – 295	0.06 – 19.42	36 – 250
Saline coastal GW	0.06 – 380	2.3 – 278	22 – 382	BDL – 1710	0.09 – 13.50	15 – 123
Lagoon porewater	0.12 – 4.0	2.3 – 24	4.9 – 26	70 – 430	0.68 – 9.7	11 – 120
Lagoon water	0.03 – 12.2	0.1 – 10.6	0.46 – 14	18 – 56	BDL – 0.23	1 – 24

Note. BDL = Below Detection Limit. BDL = 0.006 μM for NO_x , 0.003 μM for NH_4^+ , 0.071 μM for DON, 0.010 μM for DIP, and 0.016 μM for DSi.

Table B.3. Nutrient fluxes supplied to Mar Menor by stream, fresh SGD, long-scale recirculated SGD, and PEX in March, July, and November 2021. All units in kmol d⁻¹

	Pathway	NO _x		NH ₄ ⁺		DIN		DON		DIP		DSi	
		Median	Q1 - Q3	Median	Q1 - Q3	Median	Q1 - Q3	Median	Q1 - Q3	Median	Q1 - Q3	Median	Q1 - Q3
March	Stream	150	92 - 210	0.60	0.38 - 0.85	150	90 - 210	15	9.7 - 22	0.16	0.099 - 0.22	12	7.7 - 17
	Fresh	66	27 - 130	0.21	0.10 - 0.44	70	29-95	68	8.4 - 190	0.033	0.017 - 0.043	13	8.2 - 13
	Long-scale	-1.3	-6.1 - 1.1	98	7.8 - 280	120	32 - 300	150	-8500 1100	0.92	0.017 - 5.7	190	54 - 360
	PEX	-0.20	-2.5 - 1.4	2.0	-1.3 - 11	2.3	-1.5 - 12	200	31 - 550	6.8	0.85 - 18	54	8.3 - 140
	Total	210		100		340		430		7.9		270	
July	Stream	32	20 - 46	0.040	0.025 0.057	32	20 - 46	18	12 - 26	0.065	0.041 - 0.092	1.6	1.0 - 2.3
	Fresh	9.5	3.9 - 20	0.030	0.015 0.065	9.9	4.1 - 19	9.8	1.2 - 27	0.047	0.0025 - 0.0081	1.8	1.2 - 1.9
	Long-scale	1.1	-0.18 4.9	130	10 - 360	170	39 - 400	160	18 - 1300	0.82	0.016 - 6.6	170	38 - 350
	PEX	4.4	-0.19 12	27	6.7 - 60	39	11 - 78	740	190 - 1900	24	4.5 - 60	110	-0.61 - 310
	Total	47		160		250		930		25		280	
November	Stream	21	13 - 30	0.20	0.12 - 0.28	21	13 - 30	17	11 - 24	0.032	0.020 - 0.046	1.2	0.78 - 1.8
	Fresh	8.7	3.6 - 18	0.028	0.014 0.059	9.1	3.7 - 18	8.8	1.1 - 24	0.0043	0.0023 - 0.0074	1.7	1.1 - 2.3
	Long-scale	-3.0	-12 - 1.7	99	16 - 250	120	38 - 270	160	13 - 960	0.64	0.040 - 3.0	170	61 - 310
	PEX	-0.50	-3.7 - 1.2	4.3	0.50 - 10	2.4	-0.53 - 9.5	110	13 - 300	3.5	0.32 - 9.8	30	3.4 - 75
	Total	26		100		150		300		4.2		200.0	

Table B.4. Land use composition (%) in each hydrological basin (see Fig. B.9) where coastal groundwater samples were collected.

Coastal GW site	Hydrological basin	Agriculture	Urban	Vegetated areas	Mining	Others
Pz1	38, 18	81.55	2.89	14.51	1.00	0.04
Pz2	40	38.97	39.35	21.68	0.00	0.00
Pz3	19	84.36	6.01	9.53	0.10	0.00
Pz4	41	36.39	63.61	0.00	0.00	0.00
Pz5	44	48.53	28.39	7.39	0.00	15.70
Pz6	36	24.68	40.98	34.34	0.00	0.00
Pz7	33, 12	45.80	10.40	42.89	0.91	0.00
Pz8	32	57.33	22.95	19.72	0.00	0.00
Pz9	NA	0.00	100.00	0.00	0.00	0.00

Note. Sites assigned to two basins (e.g., Pz1 and Pz7) are located within a few meters of a neighboring basin boundary, and the land use composition reflects combined area of the two basins. Sites Pz9 and Pz10, located in La Manga sandbar, are not associated with any hydrological basin and are excluded from further analysis.

Table B.5. Nutrient fluxes supplied to Mar Menor by each potential source. All units in kmol d^{-1} .

Nutrient source	NO_x	NH_4^+	DIP	DSi
Sediment diffusion	0.38	0.87	0.16	9.64
Mediterranean Sea inflow	6.6	3.5	0.4	5.1
Atmospheric deposition	8.2	10.8	0.3	66.1
Stream discharge	66.5	0.3	0.1	5.0
Total SGD	28.2	180	12	250

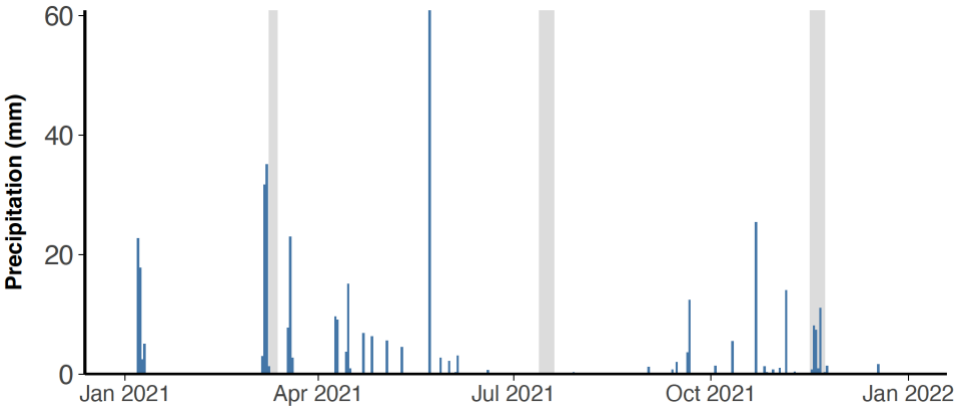


Figure B.1. Precipitation in San Javier meteorological station in 2021. Data retrieved from the Agroclimatical Information System of the region.

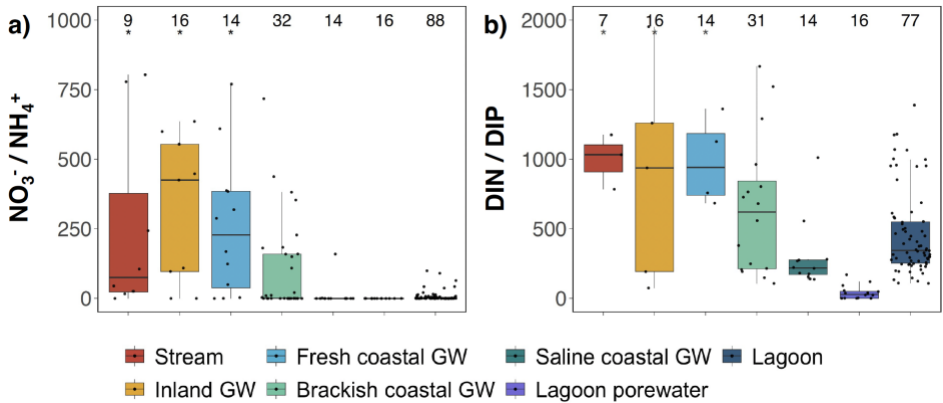


Figure B.2. Nutrient ratios in stream, inland groundwater (i.e., wells), fresh (<10), brackish (10 - 30), and saline (>30) coastal groundwater, lagoon porewater, and lagoon water for a) $\text{NO}_3^- / \text{NH}_4^+$ and b) DIN / DIP . Asterisks (*) indicate that one or more samples exceeded the activity range of the plot and are therefore not displayed. Numbers on top indicate the number of samples in each category.

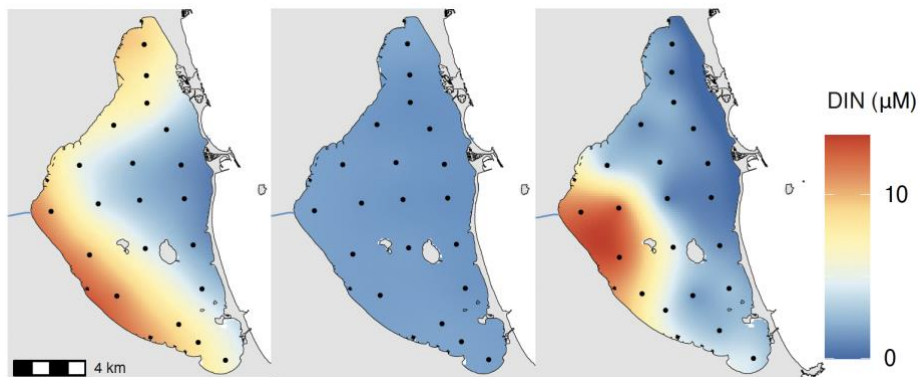


Figure B.3. Seasonal surface distribution of DIN concentrations (μM) in the Mar Menor lagoon in March, July, and November 2021 (from left to right). Dots represent sampling stations used to derive the kriging spatial interpolation.

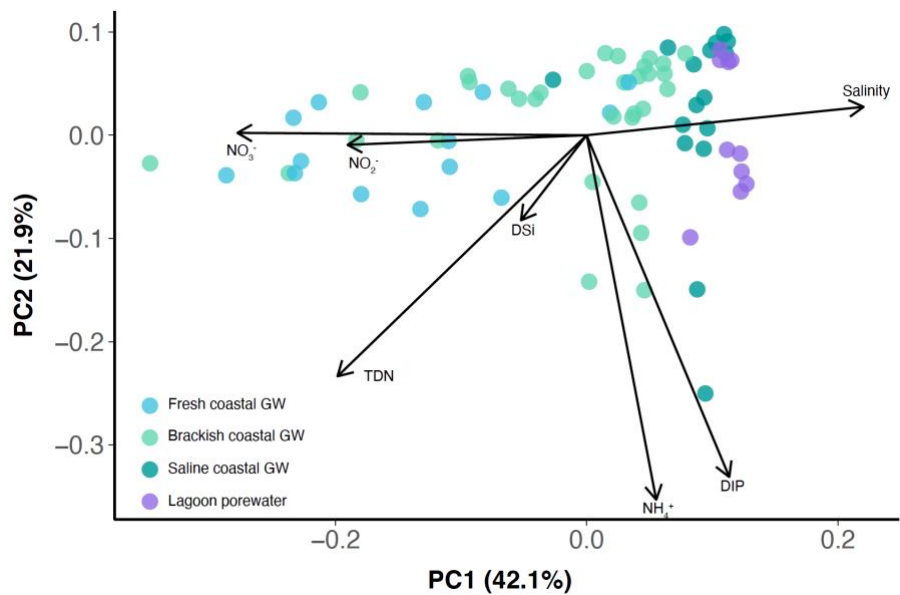


Figure B.4. Principal Component Analysis biplot showing the first two principal components (PC1 = 42.1 % variance, horizontal) and PC2 (21.9 % variance, vertical) for environmental variables in coastal groundwaters. Dot color denotes sample type.

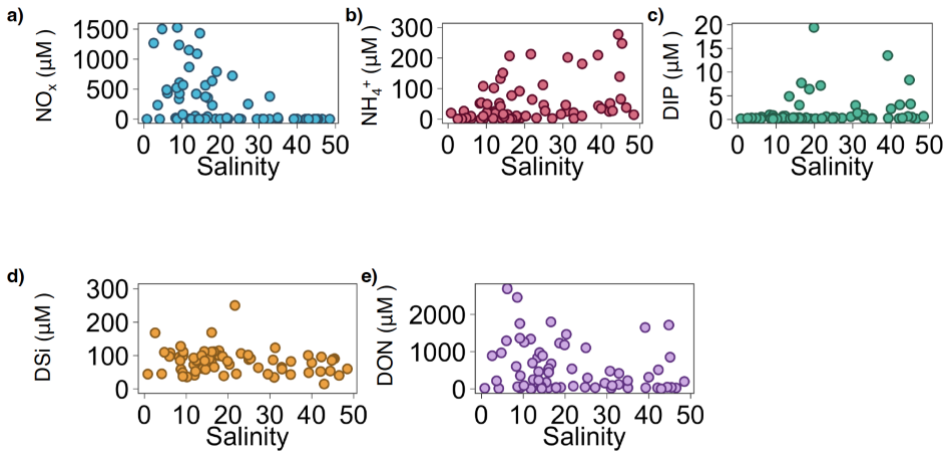


Figure B.5. Relationship between nutrient concentrations (μM) and salinity values in coastal groundwaters (fresh, brackish, and saline) for **a)** NO_x , **b)** NH_4^+ , **c)** DIP, **d)** DSi, and **e)** DON.

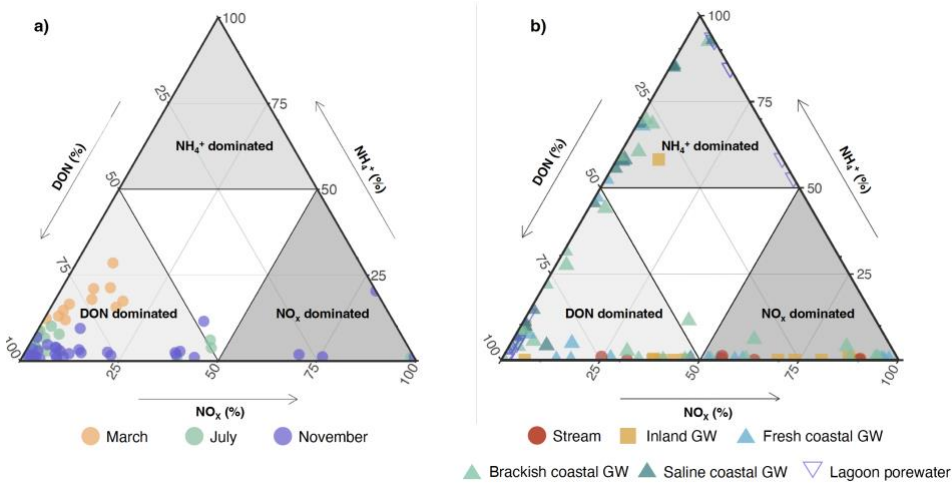


Figure B.6 Nitrogen speciation expressed as the percentage of NO_x , NH_4^+ , and DON, shown on ternary plots. **a)** Samples from lagoon waters colored by season: orange (March), turquoise (July), and purple (November). **b)** Samples colored by water source: stream (red circle), inland groundwater (yellow square), fresh coastal groundwater (blue triangle), brackish coastal groundwater (turquoise triangle), saline coastal groundwater (teal triangle), and lagoon porewater (inverted triangle with purple outline).

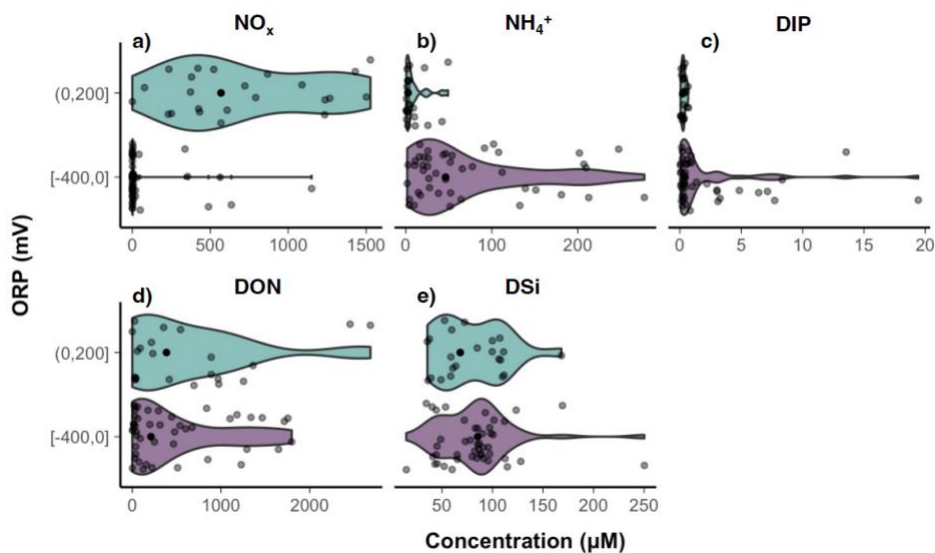


Figure B.7. Relationship between nutrient concentrations (μM) and Oxidation-Reduction Potential (ORP; mV) values in coastal groundwaters for **a)** NO_x , **b)** NH_4^+ , **c)** DIP, **d)** DON, and **e)** DSi.

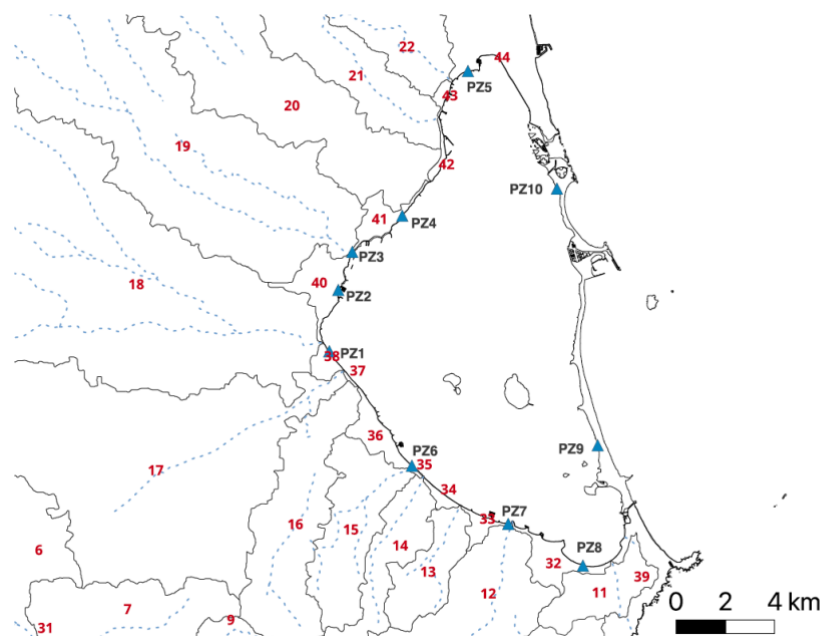


Figure B.8. Hydrological basins in the area surrounding Mar Menor, with coastal groundwater sampling locations indicated by blue triangles. Ephemeral streams are shown in dashed blue lines.

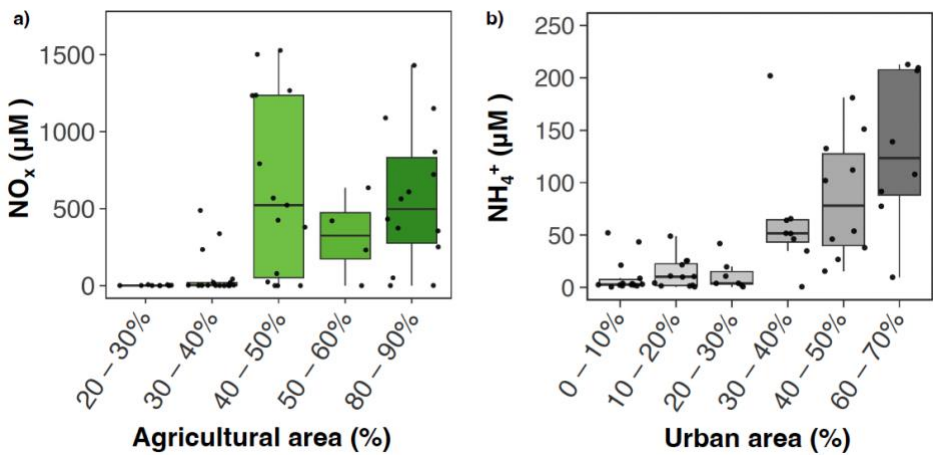


Figure B.9. Boxplots of nutrient concentrations in different hydrological sub-basins in relation to the main land use areas. **a)** NO_x concentrations (μM) as a function of agricultural area (%). **b)** NH_4^+ concentrations as a function of urban area (%).

C. Supplementary information for Chapter 6

C.1. Determination and considerations of groundwater endmember concentrations

Fresh coastal groundwater, saline coastal groundwater, and lagoon porewater samples were used to estimate the concentration of NH_4^+ , H_2S , DOC, DON, CH_4 , and Fe^{2+} in each groundwater pathway (fresh discharge, lagoon water recirculation, and PEX, respectively) to estimate the flux of each reducing agent in March, July, and November 2021. The number of samples to estimate each endmember varied across pathways and chemical species (see Table B.2).

Fresh and saline coastal groundwater samples, representative of fresh SGD and recirculated SGD, respectively, were collected in July, March, and November 2021 and July 2025. The concentrations of the analyzed chemical species showed no significant temporal variation, with the exception of fresh DON samples, which appeared lower in March compared to July. However, this observation is based on only three samples in March, and such a small pool could bias the results, given the natural variability in the STE. In addition, although efforts were made to sample the same locations, exact replication of sampling points across seasons was not possible. Thus, the observed variability in DON is more likely linked to these factors rather than true seasonal changes. To ensure robust estimates and maintain consistency with other solutes, median concentrations across all field surveys were used to define endmember concentrations. Temporal data for H_2S and Fe^{2+} were not available (see Table B.2). Consequently, their concentrations were also assumed to be constant. In contrast, lagoon porewater concentrations, representative of PEX, showed strong variability across seasons. Accordingly, the median endmember concentrations were determined individually for each season when seasonal data were available. For DON and CH_4 in lagoon porewaters, constant concentrations were assumed due to limited temporal coverage.

Water column concentrations, used to determine the net flux for recirculated SGD and PEX (groundwater concentrations minus lagoon concentrations), were estimated as the average of lagoon surface water samples collected during each survey (March, July, and November 2021; $n=21$ per season). For H_2S and Fe^{2+} , overlying water concentrations from sediment cores were used.

Water fluxes were calculated for the 2021 field campaigns, whereas groundwater endmember concentrations were derived from samples collected in 2021 as well as additional campaigns in 2024 and 2025. This approach assumes that

groundwater endmember chemistry is relatively stable over time compared to the more variable water fluxes. Indeed, variability in groundwater concentrations of NH_4 , DOC, and DON in 2021, 2024, and 2025 falls within the expected biogeochemical variability in the subterranean estuary. The only notable variability was observed in lagoon porewater concentrations, likely driven by intra-annual climatic factors (Rodriguez-Puig et al., 2025), suggesting that samples collected in similar climatic conditions are representative across years.

C.2. Biogeochemical considerations

Upon entering the water column, the reduced agents delivered by SGD undergo aerobic oxidation, where these compounds are electron donors, and oxygen is the terminal electron acceptor. The reduction of each mole of oxygen requires four moles of electrons. Conversely, each solute releases a given number of electrons during oxidation: NH_4^+ , H_2S , labile DON, and CH_4 transfer eight electrons per mol when oxidized to NO_3^- , SO_4^{2-} , NO_3^- , and CO_2 , respectively; DOC releases four electrons per mol C during oxidation to CO_2 , and Fe^{2+} transfers one electron per mol when oxidized to Fe^{3+} . Thus, SGD fluxes can be converted to electron equivalents, and NH_4^+ , H_2S , DON, and CH_4 are the compounds with the highest oxygen demand because each mole can consume two moles of O_2 .

All solutes were assumed to be fully oxidized over one day, except for CH_4 and DON. CH_4 was assumed to be oxidized only 40%, following Moore et al. (2024) and consistent with observations in mangrove waters and the Baltic Sea (Henriksson et al., 2026; Yau et al., 2024). Protein-like compounds account for over 60% of total DOM in Mar Menor porewaters (Amaral et al., 2023), suggesting that a large fraction of DON is potentially labile and subject to quick microbial oxidation. To provide conservative estimates, we assumed 15% oxidation of DON over one day, following Moore et al. (2024). However, we acknowledge that both the composition and oxidation rates of DON likely vary seasonally due to changes in DOM sources and physicochemical conditions, such as temperature (Amaral et al., 2023).

Table C.1. Median fluxes of dissolved reduced compounds delivered by Fresh SGD, Saline SGD, and PEX in March, July, and November 2021. All units in kmol d⁻¹.

		NH₄⁺	H₂S	DOC	DON	CH₄	Fe²⁺
March	Fresh SGD	0.33	BDL	18	98	0.044	0.058
	Saline SGD	78	6.1	130	500	2.5	0.055
	PEX	-1.1	440	-19	2.0	0.47	-0.21
	Total	77	450	130	600	3.0	-0.10
July	Fresh SGD	0.048	BDL	2.7	14	0.0064	0.0083
	Saline SGD	93	8.4	170	580	2.8	0.19
	PEX	14	3700	490	38	1.7	2.8
	Total	107	3700	660	630	4.5	2.9
November	Fresh SGD	0.044	BDL	2.4	13	0.0058	0.0076
	Saline SGD	82	6.0	150	500	2.5	0.054
	PEX	0.42	230	-10	4.3	0.3	-0.1
	Total	82	230	140	520	2.8	-0.047

Table C.2. Sampling period, number of samples and groundwater endmember data treatment for each solute and pathway.

NH₄⁺	Fresh	Saline	PEX
Sampling period	Jul, Mar, Nov 2021 & Jul 2025	Jul, Mar, Nov 2021 & Jul 2025	Nov 24, Jul 24, Mar 25 & Jul 25
N° of samples	15	16	4-8
Endmember choice	Pool	Pool	Seasonally dependent
H₂S			
Sampling period	Jul 25	Jul 25	Mar 25 & Jul 25
N° of samples	1	2	4
Endmember choice	Single measurement	Pool	Seasonally dependent (winter-summer)
DOC			
Sampling period	Jul, Mar, Nov 2021 & Jul 2025	Jul, Mar, Nov 2021 & Jul 2025	Mar 25 & Jul 25
N° of samples	12	12	4
Endmember choice	Pool	Pool	Seasonally dependent (winter-summer)
DON			
Sampling period	Jul, Mar, Nov 2021	Jul, Mar, Nov 2021	May 24 & March 25
N° of samples	14	14	10
Endmember choice	Pool	Pool	Pool
CH₄			
Sampling period	Jul, Mar, Nov 2021, Jul 25	Jul, Mar, Nov 2021, Jul 25	Jul 25
N° of samples	14	14	4
Endmember choice	Pool	Pool	Pool
Fe²⁺			
Sampling period	Jul 25	Jul 25	Mar 25 & Jul 25
N° of samples	1	2	4
Endmember choice	Single measurement	Pool	Seasonally dependent (winter-summer)

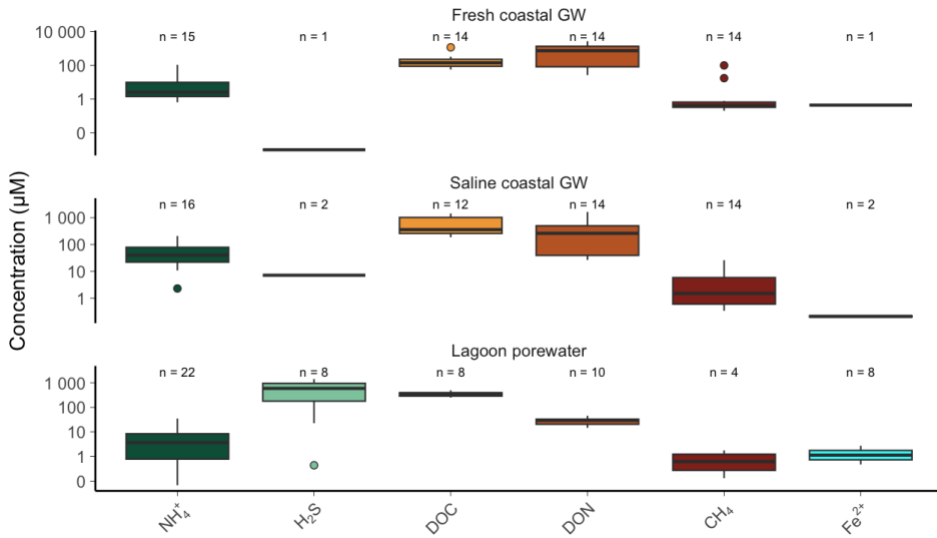


Figure C.1. Concentration (μM) of reduced compounds in fresh groundwater (top), saline groundwater (middle), and lagoon porewater (bottom) in Mar Menor. From left to right: NH_4^+ , H_2S , DOC, DON, CH_4 , and Fe^{2+} . The number of samples per solute is indicated above each box.

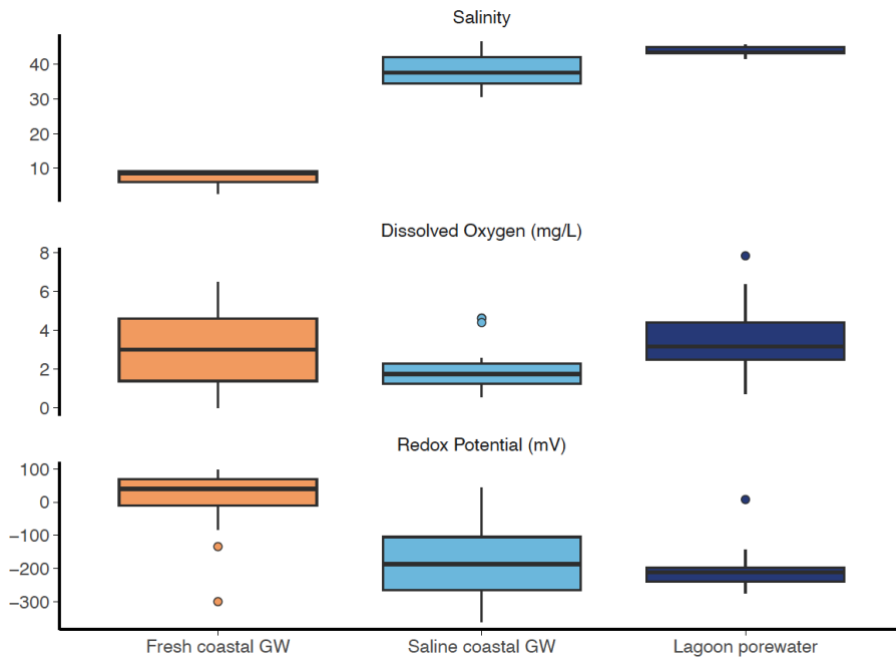


Figure C.2. Salinity, dissolved oxygen (mg L⁻¹), and ORP (mV) in fresh coastal groundwater, saline coastal groundwater, and lagoon porewater in Mar Menor.

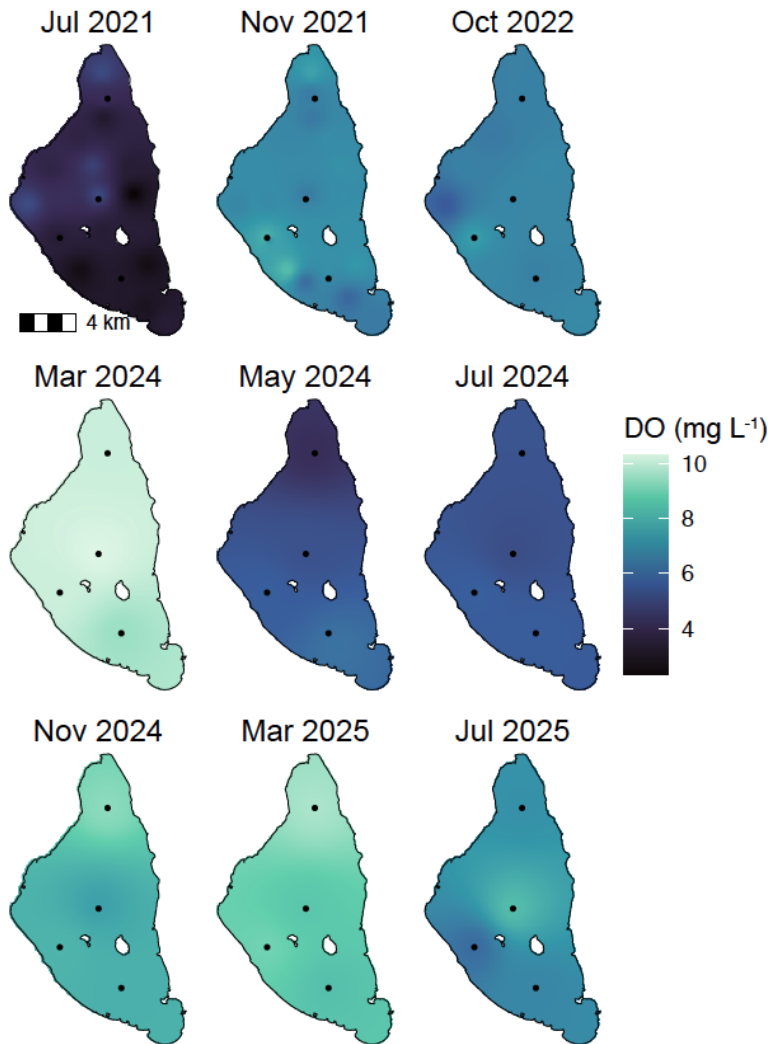


Figure C.3. Dissolved oxygen (mg L^{-1}) concentrations in Mar Menor surface waters across different seasons and years. Data points represent measured values, and the interpolated surface was generated using inverse distance weighting.

References

- Abualtayef, M., Rahman, G. A., Snounu, I., Qahman, K., Sirhan, H., & Seif, A. K. (2017). Evaluation of the effect of water management interventions on water level of Gaza coastal aquifer. *Arabian Journal of Geosciences*, 10(24), 555. <https://doi.org/10.1007/s12517-017-3329-x>
- Adyasari, D., Dimova, N. T., Dulai, H., Gilfedder, B. S., Cartwright, I., McKenzie, T., & Fuleky, P. (2023). Radon-222 as a groundwater discharge tracer to surface waters. *Earth-Science Reviews*, 238, 104321. <https://doi.org/10.1016/j.earscirev.2023.104321>
- Águila, J. F., McDonnell, M. C., Flynn, R., Hamill, G. A., Ruffell, A., Benner, E. M., Etsias, G., & Donohue, S. (2022). Characterizing groundwater salinity patterns in a coastal sand aquifer at Magilligan, Northern Ireland, using geophysical and geotechnical methods. *Environmental Earth Sciences*, 81(8), 231. <https://doi.org/10.1007/s12665-022-10357-1>
- Ahrens, J., Beck, M., Marchant, H. K., Ahmerkamp, S., Schnetger, B., & Brumsack, H.-J. (2020). Seasonality of Organic Matter Degradation Regulates Nutrient and Metal Net Fluxes in a High Energy Sandy Beach. *Journal of Geophysical Research: Biogeosciences*, 125(2), e2019JG005399. <https://doi.org/10.1029/2019JG005399>
- Alcaraz, M. N. G., Ceacero-Moreno, M., Álvarez-Rogel, J., Alcaraz, M. N. G., Ceacero-Moreno, M., & Álvarez-Rogel, J. (2024). La situación actual de contaminación en las ramblas de la Sierra Minera de Cartagena-La Unión. *Remediación y restauración ecológica de emplazamientos degradados por la minería: Marco de Actuaciones Prioritarias para recuperar el Mar Menor*, 108–129. <https://portalinvestigacion.upct.es/documentos/67ab21216e765f0ccc69cd1a?lang=ca>
- Alcaraz, M., Polo, M. J., Hornero, J., Jiménez-Martínez, J., Alcolea, A., & Manzano, M. (2024). Cálculo de la evolución espacio-temporal de la recarga al acuífero cuaternario del Campo de Cartagena (SE España) desde 1970 a 2022. *Ingeniería del Agua*, 28(3), 198–212. <https://doi.org/10.4995/ia.2024.21733>
- Alcolea, A., Carrera, J., & Medina, A. (2006). Pilot points method incorporating prior information for solving the groundwater flow inverse problem. *Advances in Water Resources*, 29(11), 1678–1689. <https://doi.org/10.1016/j.advwatres.2005.12.009>
- Alcolea, A., Contreras, S., Hunink, J. E., García-Aróstegui, J. L., & Jiménez-Martínez, J. (2019). Hydrogeological modelling for the watershed management of the Mar Menor coastal lagoon (Spain). *Science of The Total Environment*, 663, 901–914. <https://doi.org/10.1016/j.scitotenv.2019.01.375>
- Alongi, D. M. (1997). *Coastal Ecosystem Processes*. CRC Press. <https://doi.org/10.1201/9781003057864>

- 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., & Canals, M. (2019). Remobilization of dissolved metals from a coastal mine tailing deposit driven by groundwater discharge and porewater exchange. *Science of The Total Environment*, 688, 1359–1372. <https://doi.org/10.1016/j.scitotenv.2019.06.224>
- Alorda-Kleinglass, A., Ruiz-Mallén, I., Diego-Feliu, M., Rodellas, V., Bruach-Menchén, J. M., & Garcia-Orellana, J. (2021). The social implications of Submarine Groundwater Discharge from an Ecosystem Services perspective: A systematic review. *Earth-Science Reviews*, 221, 103742. <https://doi.org/10.1016/j.earscirev.2021.103742>
- Alorda-Kleinglass, A., Rodellas, V., Diego-Feliu, M., Marbà, N., Morell, C., & Garcia-Orellana, J. (2024). The connection between Submarine Groundwater Discharge and seawater quality: The threat of treated wastewater injected into coastal aquifers. *Science of The Total Environment*, 922, 170940. <https://doi.org/10.1016/j.scitotenv.2024.170940>
- Alorda-Montiel, I., Rodellas, V., Arias-Ortiz, A., Palanques, A., Bravo, A. G., Rodríguez-Puig, J., Alorda-Kleinglass, A., Green-Ruiz, C., Diego-Feliu, M., Masqué, P., Gilabert, J., & Garcia-Orellana, J. (2025). A century of sediment metal contamination of Mar Menor, Europe's largest saltwater lagoon. *Marine Pollution Bulletin*, 220, 118347. <https://doi.org/10.1016/j.marpolbul.2025.118347>
- Álvarez-Rogel, J., Jiménez-Cárceles, F. J., & Nicolás, C. E. (2006). Phosphorus and Nitrogen Content in the Water of a Coastal Wetland in the Mar Menor Lagoon (Se Spain): Relationships With Effluents From Urban and Agricultural Areas. *Water, Air, and Soil Pollution*, 173(1–4), 21–38. <https://doi.org/10.1007/s11270-005-9020-y>
- Álvarez-Rogel, J., Barberá, G. G., Maxwell, B., Guerrero-Brotons, M., Díaz-García, C., Martínez-Sánchez, J. J., Sallent, A., Martínez-Ródenas, J., González-Alcaraz, M. N., Jiménez-Cárceles, F. J., Tercero, C., & Gómez, R. (2020). The case of Mar Menor eutrophication: State of the art and description of tested Nature-Based Solutions. *Ecological Engineering*, 158, 106086. <https://doi.org/10.1016/j.ecoleng.2020.106086>
- Amaral, V., Santos-Echeandía, J., Ortega, T., Álvarez-Salgado, X. A., & Forja, J. (2023). Dissolved organic matter distribution in the water column and sediment pore water in a highly anthropized coastal lagoon (Mar Menor, Spain): Characteristics, sources, and benthic fluxes. *Science of The Total Environment*, 896, 165264. <https://doi.org/10.1016/j.scitotenv.2023.165264>
- Amato, D. W., Bishop, J. M., Glenn, C. R., Dulai, H., & Smith, C. M. (2016). Impact of Submarine Groundwater Discharge on Marine Water Quality and Reef Biota of Maui. *PLOS ONE*, 11(11), e0165825. <https://doi.org/10.1371/journal.pone.0165825>
- Anderson, M. P. (2005). Heat as a Ground Water Tracer. *Groundwater*, 43(6), 951–968. <https://doi.org/10.1111/j.1745-6584.2005.00052.x>
- Andrisoa, A., Lartaud, F., Rodellas, V., Neveu, I., & Stieglitz, T. C. (2019a). Enhanced Growth Rates of the Mediterranean Mussel in a Coastal Lagoon Driven

- by Groundwater Inflow. *Frontiers in Marine Science*, 6. <https://doi.org/10.3389/fmars.2019.00753>
- Andrisoa, A., Stieglitz, T. C., Rodellas, V., & Raimbault, P. (2019b). Primary production in coastal lagoons supported by groundwater discharge and porewater fluxes inferred from nitrogen and carbon isotope signatures. *Marine Chemistry*, 210, 48–60. <https://doi.org/10.1016/j.marchem.2019.03.003>
- Anthony, A., Atwood, J., August, P., Byron, C., Cobb, S., Foster, C., Fry, C., Gold, A., Hagos, K., Heffner, L., Kellogg, D. Q., Lellis-Dibble, K., Opaluch, J. J., Oviatt, C., Pfeiffer-Herbert, A., Rohr, N., Smith, L., Smythe, T., Swift, J., & Vinhateiro, N. (2009). Coastal Lagoons and Climate Change: Ecological and Social Ramifications in U.S. Atlantic and Gulf Coast Ecosystems. *Ecology and Society*, 14(1), art8. <https://doi.org/10.5751/ES-02719-140108>
- Arauzo, M., Valladolid Martín, M., & Andries, D. M. (2024). Contaminación por nitrato en las aguas subterráneas de la Demarcación Hidrológica del Segura (España) y su particular incidencia en el área de captación del Mar Menor. *Estudios Geológicos*, 80(1), 1071. <https://doi.org/10.3989/egeol.45105.1071>
- Ayari, S., Gabtni, H., & Zouhri, L. (2023). Imaging seawater flow in porous media under climate change water stress using geophysics: A case study of Menzel Horr coastline in Northeastern Tunisia, Mediterranean basin. *Environmental Earth Sciences*, 82(21), 499. <https://doi.org/10.1007/s12665-023-11199-1>
- Aydogdu, A., Miraglio, P., Escudier, R., Clementi, E., & Masina, S. (2023). The dynamical role of upper layer salinity in the Mediterranean Sea. *State of the Planet*, 1-osr7, 1–9. <https://doi.org/10.5194/sp-1-osr7-6-2023>
- Baudron, P., Cockenpot, S., Lopez-Castejon, F., Radakovitch, O., Gilabert, J., Mayer, A., Garcia-Arostegui, J. L., Martinez-Vicente, D., Leduc, C., & Claude, C. (2015). Combining radon, short-lived radium isotopes and hydrodynamic modeling to assess submarine groundwater discharge from an anthropized semiarid watershed to a Mediterranean lagoon (Mar Menor, SE Spain). *Journal of Hydrology*, 525, 55–71. <https://doi.org/10.1016/j.jhydrol.2015.03.015>
- Bishop, J. M., Glenn, C. R., Amato, D. W., & Dulai, H. (2017). Effect of land use and groundwater flow path on submarine groundwater discharge nutrient flux. *Journal of Hydrology: Regional Studies, Water, Energy, and Food Nexus in the Asia-Pacific Region*, 11, 194–218. <https://doi.org/10.1016/j.ejrh.2015.10.008>
- Blake, G. R. (2008). Particle density. In *Encyclopedia of Soil Science* (pp. 504–505). Springer, Dordrecht. https://doi.org/10.1007/978-1-4020-3995-9_406
- Boatman, C. D., & Murray, J. W. (1982). Modeling exchangeable NH₄⁺ adsorption in marine sediments: Process and controls of adsorption. *Limnology and Oceanography*, 27(1), 99–110. <https://doi.org/10.4319/lo.1982.27.1.0099>
- Breitbart, D.; Levin, L. A.; Oschlies, A.; Grégoire, M.; Chavez, F. P.; Conley, D. J.; Garçon, V.; Gilbert, D.; Gutiérrez, D.; Isensee, K.; Jacinto, G. S.; Limburg,

- K. E.; Montes, I.; Naqvi, S. W. A.; Pitcher, G. C.; Rabalais, N. N.; Roman, M. R.; Rose, K. A.; Seibel, B. A.; Telszewski, M.; Yasuhara, M.; Zhang, J. (2018). Declining Oxygen in the Global Ocean and Coastal Waters. *Science*, 359 (6371), eaam7240. <https://doi.org/10.1126/science.aam7240>.
- Bullock, E. J., Schaal, I. V., Cardenas, M. B., McClelland, J. W., Henderson, P. B., & Charette, M. A. (2024). Seasonality of submarine groundwater discharge to an Arctic coastal lagoon. *Limnology and Oceanography*, 69(6), 1429–1438. <https://doi.org/10.1002/lno.12585>
- Burnett, W. C., Taniguchi, M., & Oberdorfer, J. (2001). Measurement and significance of the direct discharge of groundwater into the coastal zone. *Journal of Sea Research, Land-Ocean Interactions in the Coastal Zone*, 46(2), 109–116. [https://doi.org/10.1016/S1385-1101\(01\)00075-2](https://doi.org/10.1016/S1385-1101(01)00075-2)
- Burnett, W. C., Bokuniewicz, H., Huettel, M., Moore, W. S., & Taniguchi, M. (2003a). Groundwater and pore water inputs to the coastal zone. *Biogeochemistry*, 66(1/2), 3–33. <https://doi.org/10.1023/B:BIOG.0000006066.21240.53>
- Burnett, W. C., & Dulaiova, H. (2003b). Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. *Journal of Environmental Radioactivity, 2001: An Ocean Odyssey*, 69(1), 21–35. [https://doi.org/10.1016/S0265-931X\(03\)00084-5](https://doi.org/10.1016/S0265-931X(03)00084-5)
- Burnett, W. C., Aggarwal, P. K., Aureli, A., Bokuniewicz, H., Cable, J. E., Charette, M. A., Kontar, E., Krupa, S., Kulkarni, K. M., Loveless, A., Moore, W. S., Oberdorfer, J. A., Oliveira, J., Ozyurt, N., Povinec, P., Privitera, A. M. G., Rajar, R., Ramessur, R. T., Scholten, J., ... Turner, J. V. (2006). Quantifying submarine groundwater discharge in the coastal zone via multiple methods. *Science of The Total Environment*, 367(2–3), 498–543. <https://doi.org/10.1016/j.scitotenv.2006.05.009>
- Cabello, V., & Brugnach, M. (2023). Whose waters, whose nutrients? Knowledge, uncertainty, and controversy over eutrophication in the Mar Menor. *Ambio*, 52(6), 1112–1124. <https://doi.org/10.1007/s13280-023-01846-z>
- Cable, J. E., Corbett, D. R., & Walsh, M. M. (2002). Phosphate Uptake in Coastal Limestone Aquifers: A Fresh Look at Wastewater Management. *Limnology and Oceanography Bulletin*, 11(2), 29–32. <https://doi.org/10.1002/lob.200211229>
- Cable, J. E., & Martin, J. B. (2008). In situ evaluation of nearshore marine and fresh pore water transport into Flamengo Bay, Brazil. *Estuarine, Coastal and Shelf Science, Submarine Groundwater Discharge Studies along the Ubatuba Coastal Area in South-Eastern Brazil*, 76(3), 473–483. <https://doi.org/10.1016/j.ecss.2007.07.045>
- Cabral, A., Sugimoto, R., Taniguchi, M., Tait, D., Nakajima, T., Honda, H., & Santos, I. R. (2023). Fresh and saline submarine groundwater discharge as sources of carbon and nutrients to the Japan Sea. *Marine Chemistry*, 249, 104209. <https://doi.org/10.1016/j.marchem.2023.104209>
- Cai, P., Shi, X., Moore, W. S., & Dai, M. (2012). Measurement of ^{224}Ra : ^{228}Th disequilibrium in coastal sediments using a delayed coincidence counter.

- Marine Chemistry*, 138–139, 1–6.
<https://doi.org/10.1016/j.marchem.2012.05.004>
- Cai, P., Shi, X., Moore, W. S., Peng, S., Wang, G., & Dai, M. (2014). 224Ra:228Th disequilibrium in coastal sediments: Implications for solute transfer across the sediment–water interface. *Geochimica et Cosmochimica Acta*, 125, 68–84. <https://doi.org/10.1016/j.gca.2013.09.029>
- Cai, W.-J.; Huang, W.-J.; Luther, G. W.; Pierrot, D.; Li, M.; Testa, J.; Xue, M.; Joesoef, A.; Mann, R.; Brodeur, J.; Xu, Y.-Y.; Chen, B.; Hussain, N.; Waldbusser, G. G.; Cornwell, J.; Kemp, W. M. (2017). Redox Reactions and Weak Buffering Capacity Lead to Acidification in the Chesapeake Bay. *Nat. Commun.* 8 (1), 369. <https://doi.org/10.1038/s41467-017-00417-7>.
- Calvo Sánchez, J., Martín Pérez, D., Morales Martín, G., & Viana Jimenez, S. (2018). HARMONIE-AROME, modelo operativo de escala convectiva de AEMET. Parte I: Modelo de predicción y validación. *Acta de Las Jornadas Científicas de La Asociación Meteorológica Española*, 1(35), 117–125. <https://doi.org/10.30859/ameJrCn35p117>
- Canfield, D. E.; Thamdrup, B. (2009). Towards a Consistent Classification Scheme for Geochemical Environments, or, Why We Wish the Term ‘Suboxic’ Would Go Away. *Geobiology* 2009, 7 (4), 385–392. <https://doi.org/10.1111/j.1472-4669.2009.00214.x>.
- Cardenas, M. B., Bennett, P. C., Zamora, P. B., Befus, K. M., Rodolfo, R. S., Cabria, H. B., & Lapus, M. R. (2015). Devastation of aquifers from tsunami-like storm surge by Supertyphoon Haiyan. *Geophysical Research Letters*, 42(8), 2844–2851. <https://doi.org/10.1002/2015GL063418>
- Cardenas, M. B., Rodolfo, R. S., Lapus, M. R., Cabria, H. B., Fullon, J., Gojunco, G. R., Breecker, D. O., Cantarero, D. M., Evaristo, J., Siringan, F. P., & Zhang, T. (2020). Submarine Groundwater and Vent Discharge in a Volcanic Area Associated With Coastal Acidification. *Geophysical Research Letters*, 47(1), e2019GL085730. <https://doi.org/10.1029/2019GL085730>
- Carlson, D. A., Van Biersel, T. P., & Milner, L. R. (2008). Storm-Damaged Saline-Contaminated Boreholes as a Means of Aquifer Contamination. *Groundwater*, 46(1), 69–79. <https://doi.org/10.1111/j.1745-6584.2007.00380.x>
- Carratalá, A., Moreno-González, R., & León, V. M. (2017). Occurrence and seasonal distribution of polycyclic aromatic hydrocarbons and legacy and current-use pesticides in air from a Mediterranean coastal lagoon (Mar Menor, SE Spain). *Chemosphere*, 167, 382–395. <https://doi.org/10.1016/j.chemosphere.2016.09.157>
- Cataudella, S., Crosetti, D., Ciccotti, E., & Massa, F. (2015). 2. SUSTAINABLE MANAGEMENT IN MEDITERRANEAN COASTAL LAGOONS: INTERACTIONS AMONG CAPTURE FISHERIES, AQUACULTURE AND THE ENVIRONMENT.
- Cave, R. R., & Henry, T. (2011). Intertidal and submarine groundwater discharge on the west coast of Ireland. *Estuarine, Coastal and Shelf Science*, 92(3), 415–423. <https://doi.org/10.1016/j.ecss.2011.01.019>
- Cerro-Gálvez, E.; Dachs, J.; Lundin, D.; Fernández-Pinos, M.-C.; Sebastián, M.; Vila-Costa, M. (2021). Responses of Coastal Marine Microbiomes

- Exposed to Anthropogenic Dissolved Organic Carbon. *Environ. Sci. Technol.*, 55 (14), 9609–9621. <https://doi.org/10.1021/acs.est.0c07262>.
- Charette, M. A., Buesseler, K. O., & Andrews, J. E. (2001). Utility of radium isotopes for evaluating the input and transport of groundwater-derived nitrogen to a Cape Cod estuary. *Limnology and Oceanography*, 46(2), 465–470. <https://doi.org/10.4319/lo.2001.46.2.0465>
- Charette, M. A., & Sholkovitz, E. R. (2002). Oxidative precipitation of groundwater-derived ferrous iron in the subterranean estuary of a coastal bay. *Geophysical Research Letters*, 29(10), 85-1-85-4. <https://doi.org/10.1029/2001GL014512>
- Charette, M. A. (2007). Hydrologic forcing of submarine groundwater discharge: Insight from a seasonal study of radium isotopes in a groundwater-dominated salt marsh estuary. *Limnology and Oceanography*, 52(1), 230–239. <https://doi.org/10.4319/lo.2007.52.1.0230>
- Chen, G.; Xu, B.; Zhao, S.; Yang, D.; Burnett, W. C.; Diao, S.; Gao, M.; Xu, X.; Wang, L. (2022). Submarine Groundwater Discharge and Benthic Biogeochemical Zonation in the Huanghe River Estuary. *Acta Oceanol. Sin.*, 41 (1), 11–20. <https://doi.org/10.1007/s13131-021-1882-3>.
- Chen, X., Zhang, F., Lao, Y., Wang, X., Du, J., & Santos, I. R. (2018). Submarine Groundwater Discharge-Derived Carbon Fluxes in Mangroves: An Important Component of Blue Carbon Budgets? *Journal of Geophysical Research: Oceans*, 123(9), 6962–6979. <https://doi.org/10.1029/2018JC014448>
- Chen, Y., Liu, J., Cukrov, N., Sun, S., Chen, X., Yu, X., Zhu, X., Zhang, F., & Du, J. (2025). Groundwater carbon exports dominate dissolved carbon budgets in a seagrass meadow karstic bay (Adriatic Sea, Croatia). *Journal of Hydrology*, 133391. <https://doi.org/10.1016/j.jhydrol.2025.133391>
- Cho, H.-M., Kim, G., Kwon, E. Y., Moosdorf, N., Garcia-Orellana, J., & Santos, I. R. (2018). Radium tracing nutrient inputs through submarine groundwater discharge in the global ocean. *Scientific Reports*, 8(1), 2439. <https://doi.org/10.1038/s41598-018-20806-2>
- Cline, J. D. (1969). Spectrophotometric Determination of Hydrogen Sulfide in Natural Waters. *Limnology and Oceanography*, 14(3), 454–458. <https://doi.org/10.4319/lo.1969.14.3.0454>
- Cloern, J. E.; Jassby, A. D. (2012). Drivers of Change in Estuarine-Coastal Ecosystems: Discoveries from Four Decades of Study in San Francisco Bay. *Rev. Geophys.*, 50 (4). <https://doi.org/10.1029/2012RG000397>.
- Cojean, A. N. Y., Lehmann, M. F., Robertson, E. K., Thamdrup, B., & Zopfi, J. (2020). Controls of H₂S, Fe²⁺, and Mn²⁺ on Microbial NO₃⁻-Reducing Processes in Sediments of an Eutrophic Lake. *Frontiers in Microbiology*, 11. <https://doi.org/10.3389/fmicb.2020.01158>
- Comité de asesoramiento científico del Mar Menor. (2017). *INFORME INTEGRAL SOBRE EL ESTADO ECOLÓGICO DEL MAR MENOR* (5. Depuración y Descontaminación de Aguas, p. 125). Región de Murcia.
- Condon, L. E., & Maxwell, R. M. (2015). Evaluating the relationship between topography and groundwater using outputs from a continental-scale

- integrated hydrology model. *Water Resources Research*, 51(8), 6602–6621. <https://doi.org/10.1002/2014WR016774>
- Conesa, H. M., & Jiménez-Cárceles, F. J. (2007). The Mar Menor lagoon (SE Spain): A singular natural ecosystem threatened by human activities. *Marine Pollution Bulletin*, 54(7), 839–849. <https://doi.org/10.1016/j.marpolbul.2007.05.007>
- Contreras, S., Hunink, J. E., & Baille, A. (2014). *Building a Watershed Information System for the Campo de Cartagena basin (Spain) integrating hydrological modeling and remote sensing*. January 2015, 59. <https://doi.org/10.13140/2.1.2032.9281>
- Cook, P. G., Rodellas, V., & Stieglitz, T. C. (2018a). Quantifying Surface Water, Porewater, and Groundwater Interactions Using Tracers: Tracer Fluxes, Water Fluxes, and End-member Concentrations. *Water Resources Research*, 54(3), 2452–2465. <https://doi.org/10.1002/2017WR021780>
- Cook, P. G., Rodellas, V., Andrisoa, A., & Stieglitz, T. C. (2018b). Exchange across the sediment-water interface quantified from porewater radon profiles. *Journal of Hydrology*, 559, 873–883. <https://doi.org/10.1016/j.jhydrol.2018.02.070>
- Copernicus Marine Service. (2020). *Atlantic-Iberian Biscay Irish- Ocean Physics Reanalysis*. <https://doi.org/10.48670/moi-00029>
- Corman, J. R. (2025). Calcium carbonate and phosphorus interactions in inland waters. *Limnology and Oceanography Letters*, 10(2), 158–178. <https://doi.org/10.1002/lol2.10452>
- Corson-Dosch, H. R., Nell, C. S., Volentine, R. E., Archer, A. A., Bechtel, E., Bruce, J. L., Felts, N., Gross, T. A., Lopez-Trujillo, D., Riggs, C. E., & Read, E. (2023). The water cycle. In *General Information Product* (No. 221). U.S. Geological Survey. <https://doi.org/10.3133/gip221>
- Cosby, A. G., Lebakula, V., Smith, C. N., Wanik, D. W., Bergene, K., Rose, A. N., Swanson, D., & Bloom, D. E. (2024). Accelerating growth of human coastal populations at the global and continent levels: 2000–2018. *Scientific Reports*, 14(1), 22489. <https://doi.org/10.1038/s41598-024-73287-x>
- Cossa, D., Knoery, J., Bănanu, D., Harmelin-Vivien, M., Sonke, J. E., Hedgecock, I. M., Bravo, A. G., Rosati, G., Canu, D., Horvat, M., Sprovieri, F., Pirrone, N., & Heimbürger-Boavida, L.-E. (2022). Mediterranean Mercury Assessment 2022: An Updated Budget, Health Consequences, and Research Perspectives. *Environmental Science & Technology*, 56(7), 3840–3862. <https://doi.org/10.1021/acs.est.1c03044>
- Costall, A., Harris, B., & Pigois, J. P. (2018). Electrical Resistivity Imaging and the Saline Water Interface in High-Quality Coastal Aquifers. *Surveys in Geophysics*, 39(4), 753–816. <https://doi.org/10.1007/s10712-018-9468-0>
- Craddock, R. D., Mohammed, A. A., Tamborski, J. J., & Kurylyk, B. L. (2024). Submarine Groundwater Discharge at a Mega-Tidal Beach. *Hydrological Processes*, 38(11), e15319. <https://doi.org/10.1002/hyp.15319>
- Davis, R. A., & FitzGerald, D. M. (2019). *Beaches and Coasts* (1st ed.). Wiley. <https://doi.org/10.1002/9781119334491>

- Devol, A. H. (2015). Denitrification, Anammox, and N₂ Production in Marine Sediments. *Annual Review of Marine Science*, 7(Volume 7, 2015), 403–423. <https://doi.org/10.1146/annurev-marine-010213-135040>
- Diaz, R. J.; Rosenberg, R. (2008). Spreading Dead Zones and Consequences for Marine Ecosystems. *Science*, 321 (5891), 926–929.
- Diego-Feliu, M., Rodellas, V., Alorda-Kleinglass, A., Tamborski, J., Van Beek, P., Heins, L., Bruach, J. M., Arnold, R., & Garcia-Orellana, J. (2020). Guidelines and Limits for the Quantification of Ra Isotopes and Related Radionuclides With the Radium Delayed Coincidence Counter (RaDeCC). *Journal of Geophysical Research: Oceans*, 125(4), e2019JC015544. <https://doi.org/10.1029/2019JC015544>
- Diego-Feliu, M., Rodellas, V., Saaltink, M. W., Alorda-Kleinglass, A., Goyetche, T., Martínez-Pérez, L., Folch, A., & Garcia-Orellana, J. (2021). New perspectives on the use of ²²⁴Ra/²²⁸Ra and ²²²Rn/²²⁶Ra activity ratios in groundwater studies. *Journal of Hydrology*, 596, 126043. <https://doi.org/10.1016/J.JHYDROL.2021.126043>
- Diego-Feliu, M. (2022a). *IMPROVING THE USE OF RADIUM ISOTOPES AND RADON AS TRACERS OF SUBMARINE GROUNDWATER DISCHARGE*.
- Diego-Feliu, M., Rodellas, V., Alorda-Kleinglass, A., Saaltink, M., Folch, A., & Garcia-Orellana, J. (2022b). Extreme precipitation events induce high fluxes of groundwater and associated nutrients to coastal ocean. *Hydrology and Earth System Sciences*, 26(18), 4619–4635. <https://doi.org/10.5194/hess-26-4619-2022>
- Diego-Feliu, M., Munoz-Pinyol, M., Tur-Piedra, J., Trabucchi, M., Alorda-Kleinglass, A., González-Fernández, R., Ferrer, N., Almillategui, B., Sawyer, A., Green-Ruiz, C. R., Ledo, J., Rodellas, V., & Folch, A. (2025). Combining seepage meters and amphibious electric resistivity tomography to investigate pathways of submarine groundwater discharge. *Science of The Total Environment*, 968, 178831. <https://doi.org/10.1016/j.scitotenv.2025.178831>
- Doherty, J. (2016). *PEST-model-independent Parameter Estimation. User Manual Part I* (6th ed.). Watermark Numerical Computing.
- Domingo-Pinillos, J. C., Senent-Aparicio, J., García-Aróstegui, J. L., & Baudron, P. (2018). Long Term Hydrodynamic Effects in a Semi-Arid Mediterranean Multilayer Aquifer: Campo de Cartagena in South-Eastern Spain. *Water*, 10(10), 1320. <https://doi.org/10.3390/w10101320>
- Dong, L.; Wang, D.; Song, L.; Gong, F.; Chen, S.; Huang, J.; He, X. (2024). Monitoring Dissolved Oxygen Concentrations in the Coastal Waters of Zhejiang Using Landsat-8/9 Imagery. *Remote Sens.* 16 (11), 1951. <https://doi.org/10.3390/rs16111951>.
- Douglas, A. R., Murgulet, D., & Montagna, P. A. (2021). Hydroclimatic variability drives submarine groundwater discharge and nutrient fluxes in an anthropogenically disturbed, semi-arid estuary. *Science of The Total Environment*, 755, 142574. <https://doi.org/10.1016/j.scitotenv.2020.142574>
- Douglas, A. R., & Murgulet, D. (2025). Groundwater-Surface Water Interactions in the Coastal Zone. In P. A. Montagna & A. R. Douglas (Eds.), *Freshwater*

- Inflows to Texas Bays and Estuaries: A Regional-Scale Review, Synthesis, and Recommendations* (pp. 143–172). Springer Nature Switzerland. https://doi.org/10.1007/978-3-031-70882-4_5
- Du, J. & Shen, J. (2016). Water Residence Time in Chesapeake Bay for 1980–2012. *J. Mar. Syst.*, 164, 101–111. <https://doi.org/10.1016/j.jmarsys.2016.08.011>.
- Dulaiova, H., & Burnett, W. C. (2004). An efficient method for γ -spectrometric determination of radium-226,228 via manganese fibers. *Limnology and Oceanography: Methods*, 2(8), 256–261. <https://doi.org/10.4319/lom.2004.2.256>
- Duque, C., Jessen, S., Tirado-Conde, J., Karan, S., & Engesgaard, P. (2019a). Application of Stable Isotopes of Water to Study Coupled Submarine Groundwater Discharge and Nutrient Delivery. *Water*, 11(9). <https://doi.org/10.3390/w11091842>
- Duque, C., Knee, K. L., Russoniello, C. J., Sherif, M., Abu Risha, U. A., Sturchio, N. C., & Michael, H. A. (2019b). Hydrogeological processes and near shore spatial variability of radium and radon isotopes for the characterization of submarine groundwater discharge. *Journal of Hydrology*, 579, 124192. <https://doi.org/10.1016/j.jhydrol.2019.124192>
- Duque, C., Michael, H. A., & Wilson, A. M. (2020a). The Subterranean Estuary: Technical Term, Simple Analogy, or Source of Confusion? *Water Resources Research*, 56(2), e2019WR026554. <https://doi.org/10.1029/2019WR026554>
- Duque, C., Russoniello, C. J., & Rosenberry, D. O. (2020b). History and evolution of seepage meters for quantifying flow between groundwater and surface water: Part 2 – Marine settings and submarine groundwater discharge. *Earth-Science Reviews*, 204, 103168. <https://doi.org/10.1016/j.earscirev.2020.103168>
- Dwyer, I. P., Swenson Perger, D. A., Graffam, M., Aller, R. C., Wehrmann, L. M., & Volkenborn, N. (2024). Seasonality of bioirrigation by the maldanid polychaete *Clymenella torquata* and related oxygen dynamics in permeable sediments. *Journal of Experimental Marine Biology and Ecology*, 572, 151987. <https://doi.org/10.1016/j.jembe.2024.151987>
- Ekau, W.; Auel, H.; Pörtner, H.-O.; Gilbert, D. (2010). Impacts of Hypoxia on the Structure and Processes in Pelagic Communities (Zooplankton, Macro-Invertebrates and Fish). *Biogeosciences*, 7 (5), 1669–1699. <https://doi.org/10.5194/bg-7-1669-2010>.
- Emili, A., Koron, N., Covelli, S., Faganeli, J., Acquavita, A., Predonzani, S., & Vittor, C. D. (2011). Does anoxia affect mercury cycling at the sediment–water interface in the Gulf of Trieste (northern Adriatic Sea)? Incubation experiments using benthic flux chambers. *Applied Geochemistry, Mercury Biogeochemical Cycling in Mercury Contaminated Environments*, 26(2), 194–204. <https://doi.org/10.1016/j.apgeochem.2010.11.019>
- Erkul, E., Wunderlich, T., Wilken, D., Igel, J., Müller-Petke, M., Ronczka, M., Splith, T., Fischer, S., Gilfedder, B., Böttcher, M. E., Ehlert von Ahn, C. M., Gründling, R., Hoffmann, J., Jenner, A.-K., Lu, E., Oehler, T., Rabbel, W., Sander, L., Scholten, J., ... Mallast, U. (2025). Submarine groundwater

- discharge into a temperate tidal basin: Mapping and characterization by a multi-method and multi-scale approach. *Estuarine, Coastal and Shelf Science*, 324, 109445. <https://doi.org/10.1016/j.ecss.2025.109445>
- Erostate, M., Huneau, F., Garel, E., Ghiotti, S., Vystavna, Y., Garrido, M., & Pasqualini, V. (2020). Groundwater dependent ecosystems in coastal Mediterranean regions: Characterization, challenges and management for their protection. *Water Research*, 172, 115461. <https://doi.org/10.1016/j.watres.2019.115461>
- Esteve, M. A., Carreño, M. F., Robledano, F., Martínez-Fernández, J., & Miñano, J. (2008). Dynamics of Coastal Wetlands and Land Use Changes in the Watershed: Implications for the Biodiversity. In *Wetlands Ecology Conservation and Restoration* (pp. 133–175) Nova science publishers.
- Fang, L., Kim, H., Kim, J., Cheng, P., Ryu, Y., Kim, G., & Kim, M. (2025). Preliminary study on tracing ^{14}C in groundwater-derived dissolved organic carbon: Transport, transformation, and seawater recirculation in Jeju Island, South Korea. *Frontiers in Marine Science*, 12. <https://doi.org/10.3389/fmars.2025.1719001>
- Fennel, K.; Testa, J. M. (2019). Biogeochemical Controls on Coastal Hypoxia. *Annu. Rev. Mar. Sci.*, 11 (Volume 11, 2019), 105–130. <https://doi.org/10.1146/annurev-marine-010318-095138>.
- Fernández-Alías, A., Montaña-Barroso, T., Conde-Caño, M.-R., Manchado-Pérez, S., López-Galindo, C., Quispe-Becerra, J.-I., Marcos, C., & Pérez-Ruzafa, A. (2022). Nutrient overload promotes the transition from top-down to bottom-up control and triggers dystrophic crises in a Mediterranean coastal lagoon. *Science of The Total Environment*, 846, 157388. <https://doi.org/10.1016/j.scitotenv.2022.157388>
- Ferrarin, C., Rapaglia, J., Zaggia, L., Umgiesser, G., & Zuppi, G. M. (2008). Coincident application of a mass balance of radium and a hydrodynamic model for the seasonal quantification of groundwater flux into the Venice Lagoon, Italy. *Marine Chemistry*, 112(3–4), 179–188. <https://doi.org/10.1016/j.marchem.2008.08.008>
- Forster, S., Khalili, A., & Kitlar, J. (2003). Variation of nonlocal irrigation in a subtidal benthic community. *Journal of Marine Research*, 61(3), 335–357. <https://doi.org/10.1357/002224003322201223>
- Fraile-Nuez, E., Machín, F., Santana-Casiano, J. M., González-Dávila, M., Domínguez-Yanes, J. F., Mercado, J., Gómez-Ballesteros, M., García-Muñoz, R., Ramos-Segura, A., Bernardeau Esteller, J., Peran-Acosta, J., Garrido-Faustino, S., Vergara-Mañas, E., Conde-Caño, R.M., & Ruíz-Fernández, J. M. (2016). *Estudio oceanográfico integral de alta resolución de la laguna costera del Mar Menor, Murcia*.
- Furnas, M., Alongi, D., McKinnon, D., Trott, L., & Skuza, M. (2011). Regional-scale nitrogen and phosphorus budgets for the northern (14°S) and central (17°S) Great Barrier Reef shelf ecosystem. *Continental Shelf Research*, 31(19), 1967–1990. <https://doi.org/10.1016/j.csr.2011.09.007>
- Futch, J. C., Griffin, D. W., & Lipp, E. K. (2010). Human enteric viruses in groundwater indicate offshore transport of human sewage to coral reefs

- of the Upper Florida Keys. *Environmental Microbiology*, 12(4), 964–974. <https://doi.org/10.1111/j.1462-2920.2010.02141.x>
- Gao, D., Liu, C., Li, X., Zheng, Y., Dong, H., Liang, X., Niu, Y., Yin, G., Liu, M., & Hou, L. (2022). High importance of coupled nitrification-denitrification for nitrogen removal in a large periodically low-oxygen estuary. *Science of The Total Environment*, 846, 157516. <https://doi.org/10.1016/j.scitotenv.2022.157516>
- Garcés, E., Basterretxea, G., & Tovar-Sanchez, A. (2011). Changes in microbial communities in response to submarine groundwater input. *Marine Ecology Progress Series*, 438, 47–58. <https://doi.org/10.3354/meps09311>
- García-Aróstegui, J. L. (2018). *Asesoramiento hidrogeológico sobre el acuífero del campo de Cartagena en contacto con el Mar Menor. Informe de asesoramiento para la puesta en marcha de la investigación y seguimiento hidrogeológico de las actuaciones en marcha durante 2018* (No. Expediente CARM: N-75/17). Instituto Geológico y Minero de España. Ministerio de Ciencia, Innovación y Universidades. https://canalmarmenor.carm.es/wp-content/uploads/2020/07/Informe-2-asesoramiento-del-IGME-a-la-CARM_Campo-Cartagena-Mar-Menor.pdf
- García-Ayllón, S. (2018). Predictive Diagnosis of Agricultural Periurban Areas Based on Territorial Indicators: Comparative Landscape Trends of the So-Called “Orchard of Europe.” *Sustainability*, 10 (6), 1820. <https://doi.org/10.3390/su10061820>.
- García-Oliva, M., Pérez-Ruzafa, Á., Umgieser, G., McKiver, W., Ghezzi, M., De Pascalis, F., & Marcos, C. (2018). Assessing the Hydrodynamic Response of the Mar Menor Lagoon to Dredging Inlets Interventions through Numerical Modelling. *Water*, 10(7), 959. <https://doi.org/10.3390/w10070959>
- García-Orellana, J., Cochran, J. K., Bokuniewicz, H., Daniel, J. W. R., Rodellas, V., & Heilbrun, C. (2014). Evaluation of ²²⁴Ra as a tracer for submarine groundwater discharge in Long Island Sound (NY). *Geochimica et Cosmochimica Acta*, 141, 314–330. <https://doi.org/10.1016/j.gca.2014.05.009>
- García-Orellana, J., López-Castillo, E., Casacuberta, N., Rodellas, V., Masqué, P., Carmona-Catot, G., Vilarrasa, M., & García-Berthou, E. (2016). Influence of submarine groundwater discharge on (210)Po and (210)Pb bioaccumulation in fish tissues. *Journal of Environmental Radioactivity*, 155–156, 46–54. <https://doi.org/10.1016/j.jenvrad.2016.02.005>
- García-Orellana, J., Rodellas, V., Tamborski, J., Diego-Feliu, M., van Beek, P., Weinstein, Y., Charette, M., Alorda-Kleinglass, A., Michael, H. A., Stieglitz, T., & Scholten, J. (2021). Radium isotopes as submarine groundwater discharge (SGD) tracers: Review and recommendations. *Earth-Science Reviews*, 220, 103681. <https://doi.org/10.1016/J.EARSCIREV.2021.103681>
- García-Pintado, J., Martínez-Mena, M., Barberá, G. G., Albaladejo, J., & Castillo, V. M. (2007). Anthropogenic nutrient sources and loads from a Mediterranean catchment into a coastal lagoon: Mar Menor, Spain.

- Science of The Total Environment*, 373(1), 220–239.
<https://doi.org/10.1016/j.scitotenv.2006.10.046>
- García-Solsona, E., García-Orellana, J., Masqué, P., Rodellas, V., Mejías, M., Ballesteros, B., & Domínguez, J. A. (2010). Groundwater and nutrient discharge through karstic coastal springs (Castelló, Spain). *Biogeosciences*, 7(9), 2625–2638. <https://doi.org/10.5194/bg-7-2625-2010>
- Geng, X., & Boufadel, M. C. (2017). The influence of evaporation and rainfall on supratidal groundwater dynamics and salinity structure in a sandy beach. *Water Resources Research*, 53(7), 6218–6238. <https://doi.org/10.1002/2016WR020344>
- Geng, X., Haroon, A., Zhang, X., Zhang, H., & Kanoa, H. (2026). From pores to coastlines: Multiscale perspectives on submarine groundwater discharge and coastal ecosystems. *Frontiers in Marine Science*, 13. <https://doi.org/10.3389/fmars.2026.1753663>
- Gilabert, J. (2001). Seasonal plankton dynamics in a Mediterranean hypersaline coastal lagoon: The Mar Menor. *Journal of Plankton Research*, 23(2), 207–218. <https://doi.org/10.1093/plankt/23.2.207>
- Gilabert, J., López Castejón, F., Tudela-Meroño, D., & Rodríguez de Mesas, C. (2020). *Modelado Hidrodinámico de Alta Resolución del Mar Menor. Estudio del intercambio de agua entre el Mar Menor y el Mediterráneo*. Región de Murcia.
- Gilabert, J., Duarte Pereira, F., Oliveira Cecilio, R., Moroté Sánchez, B., García Steinebronn, D. P., Carballo Lafuente, G., López Castejón, F., & Rodríguez de Mesas, C. (2023). *Estudio hidrodinámica del Mar Menor (Gastos corrientes)* (p. 400). Región de Murcia. Consejería de Medio Ambiente, Universidades, Investigación y Mar Menor.
- Gilbert, D.; Rabalais, N. N.; Díaz, R. J.; Zhang, J. (2010). Evidence for Greater Oxygen Decline Rates in the Coastal Ocean than in the Open Ocean. *Biogeosciences*, 7 (7), 2283–2296. <https://doi.org/10.5194/bg-7-2283-2010>.
- Girault, F., Perrier, F., & Przylibski, T. A. (2018). Radon-222 and radium-226 occurrence in water: A review. *Geological Society, London, Special Publications*, 451(1), 131–154. <https://doi.org/10.1144/SP451.3>
- Gleick, P. (1993). *Water in crisis: A guide to the world's fresh water resources*. Oxford University Press.
<https://unesdoc.unesco.org/ark:/48223/pf0000096389>
- Gómez-Ballesteros, M., Bruque Carmona, G., Rioja, L. M., Fraile-Nuez, E., Ramos-Segura, A., Bermejo, J. I., García-Muñoz, R., Bernardeau-Esteller, J., Belando Torrente, M., González, A., Bardisa, E., Arrese, B., & Ruiz-Fernández. (2017). *ESTUDIO DEL FONDO MARINO DE LA LAGUNA COSTERA DEL MAR MENOR, MURCIA Informe Final (Abril-Junio 2017)*. Instituto Español de Oceanografía. Ministerio de Economía y Competitividad.
- Gonneea, M. E., Mulligan, A. E., & Charette, M. A. (2013). Climate-driven sea level anomalies modulate coastal groundwater dynamics and discharge. *Geophysical Research Letters*, 40(11), 2701–2706. <https://doi.org/10.1002/grl.50192>

- Gonneea, M. E.; Charette, M. A. (2014). Hydrologic Controls on Nutrient Cycling in an Unconfined Coastal Aquifer. *Environ. Sci. Technol.*, 48 (24), 14178–14185. <https://doi.org/10.1021/es503313t>.
- Grenz, C.; Moreno, M. O.; Soetaert, K.; Denis, L.; Douillet, P.; Fichez, R. (2019). Spatio-Temporal Variability in Benthic Exchanges at the Sediment-Water Interface of a Shallow Tropical Coastal Lagoon (South Coast of Gulf of Mexico). *Estuar. Coast. Shelf Sci.*, 218, 368–380. <https://doi.org/10.1016/j.ecss.2019.01.012>.
- Greskowiak, J., & Holtappels, M. (2026). Tide- and wave-induced recirculation flux in sandy beach aquifers – Semi-analytical approximation and uncertainty assessment. *Estuarine, Coastal and Shelf Science*, 332, 109742. <https://doi.org/10.1016/j.ecss.2026.109742>
- Guimond, J. A., Demir, C., Kurylyk, B. L., Walvoord, M. A., McClelland, J. W., & Cardenas, M. B. (2023). Wind-modulated groundwater discharge along a microtidal Arctic coastline. *Environmental Research Letters*, 18(9), 094042. <https://doi.org/10.1088/1748-9326/acf0d8>
- Guldin, J. A., Schutte, C. A., & Kipp, L. E. (2026). Groundwater-derived nutrient fluxes and offshore mixing rates along the New Jersey coast. *Estuarine, Coastal and Shelf Science*, 332, 109766. <https://doi.org/10.1016/j.ecss.2026.109766>
- Guo, X.; Xu, B.; Burnett, W. C.; Wei, Q.; Nan, H.; Zhao, S.; Charette, M. A.; Lian, E.; Chen, G.; Yu, Z. (2020). Does Submarine Groundwater Discharge Contribute to Summer Hypoxia in the Changjiang (Yangtze) River Estuary? *Sci. Total Environ.*, 719, 137450. <https://doi.org/10.1016/j.scitotenv.2020.137450>.
- Gutiérrez-Martín, D., Gil-Solsona, R., Saaltink, M. W., Rodellas, V., López-Serna, R., Folch, A., Carrera, J., & Gago-Ferrero, P. (2023). Chemicals of emerging concern in coastal aquifers: Assessment along the land-ocean interface. *Journal of Hazardous Materials*, 448, 130876. <https://doi.org/10.1016/j.jhazmat.2023.130876>
- Hagedorn, B., Becker, M. W., & Silbiger, N. J. (2020). Evidence of freshened groundwater below a tropical fringing reef. *Hydrogeology Journal*, 28(7), 2501–2517. <https://doi.org/10.1007/s10040-020-02191-1>
- Hancock, G. J., Webster, I. T., Ford, P. W., & Moore, W. S. (2000). Using Ra isotopes to examine transport processes controlling benthic fluxes into a shallow estuarine lagoon. *Geochimica et Cosmochimica Acta*, 64(21), 3685–3699. [https://doi.org/10.1016/S0016-7037\(00\)00469-5](https://doi.org/10.1016/S0016-7037(00)00469-5)
- Hare, D. K., Briggs, M. A., Rosenberry, D. O., Boutt, D. F., & Lane, J. W. (2015). A comparison of thermal infrared to fiber-optic distributed temperature sensing for evaluation of groundwater discharge to surface water. *Journal of Hydrology*, 530, 153–166. <https://doi.org/10.1016/j.jhydrol.2015.09.059>
- Heiss, J. W., Post, V. E. A., Laattoe, T., Russoniello, C. J., & Michael, H. A. (2017). Physical Controls on Biogeochemical Processes in Intertidal Zones of Beach Aquifers. *Water Resources Research*, 53(11), 9225–9244. <https://doi.org/10.1002/2017WR021110>

- Henriksson, L.; McKenzie, T.; Yau, Y. Y. Y.; Cheung, H. L. S.; Majtényi-Hill, C.; Ljungberg, W.; Tomer, A. S.; Bonaglia, S.; Santos, I. R. (2026). Large Methane Oxidation across an Oxygen Gradient in Baltic Sea Deep Waters. *Limnology and Oceanography Letters*, 11 (1), <https://doi.org/10.1002/lol2.70081>.
- Hersbach, H., Bell, B., Berrisford, P., Hirahara, S., Horányi, A., Muñoz-Sabater, J., Nicolas, J., Peubey, C., Radu, R., Schepers, D., Simmons, A., Soci, C., Abdalla, S., Abellan, X., Balsamo, G., Bechtold, P., Biavati, G., Bidlot, J., Bonavita, M., ... Thépaut, J. (2020). The ERA5 global reanalysis. *Quarterly Journal of the Royal Meteorological Society*, 146(730), 1999–2049. <https://doi.org/10.1002/qj.3803>
- Hoffmann, J. J. L., Erkul, E., Fischer, S., Yolcubal, I., Yogeshwar, P., Rabbel, W., Haroon, A., Bariş, Ş., Şener, A., Schneider Von Deimling, J., Kaplanvural, I., Tezkan, B., Şen, E., Gross, F., Pekşen, E., Gasimov, E., & Micallef, A. (2025). Bridging Land and Sea: Geophysical insights into coastal karstic groundwater dynamics, freshwater plumes and saltwater intrusions in the urban regions of Antalya (Türkiye). *Journal of Hydrology: Regional Studies*, 57, 102145. <https://doi.org/10.1016/j.ejrh.2024.102145>
- Hondula, K. L., Martin, R. E., & Asner, G. P. (2025). Variability in contamination of submarine groundwater discharge into West Hawai'i coral reefs. *Frontiers in Marine Science*, 12. <https://doi.org/10.3389/fmars.2025.1634234>
- Honfo, K. J., Chaigneau, A., Morel, Y., Duhaut, T., Marsaleix, P., Okpeitcha, O. V., Stieglitz, T., Ouillon, S., Baloitcha, E., & Rétif, F. (2024). Water mass circulation and residence time using Eulerian approach in a large coastal lagoon (Nokoué Lagoon, Benin, West Africa). *Ocean Modelling*, 190, 102388. <https://doi.org/10.1016/j.ocemod.2024.102388>
- Howarth, R. W. (2008). Coastal Nitrogen Pollution: A Review of Sources and Trends Globally and Regionally. *Harmful Algae*, 8 (1), 14–20. <https://doi.org/10.1016/j.hal.2008.08.015>.
- Huettel, M., Berg, P., & Kostka, J. E. (2014). Benthic Exchange and Biogeochemical Cycling in Permeable Sediments. *Annual Review of Marine Science*, 6(1), 23–51. <https://doi.org/10.1146/annurev-marine-051413-012706>
- Hughes, A. L. H., Wilson, A. M., & Moore, W. S. (2015). Groundwater transport and radium variability in coastal porewaters. *Estuarine, Coastal and Shelf Science*, 164, 94–104. <https://doi.org/10.1016/j.ecss.2015.06.005>
- Hughes, B. B.; Levey, M. D.; Fountain, M. C.; Carlisle, A. B.; Chavez, F. P.; Gleason, M. G. (2015). Climate Mediates Hypoxic Stress on Fish Diversity and Nursery Function at the Land–Sea Interface. *Proc. Natl. Acad. Sci.*, 112 (26), 8025–8030. <https://doi.org/10.1073/pnas.1505815112>.
- IPCC. (2014). *Climate Change 2013: The Physical Science Basis*; Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change; Cambridge University Press.
- IPCC. (2023). *IPCC, 2023: Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, H. Lee and J. Romero (eds.)]. IPCC, Geneva, Switzerland. (First). Intergovernmental*

- Panel on Climate Change (IPCC). <https://doi.org/10.59327/IPCC/AR6-9789291691647>
- Jafari, H., Sudegi, A., & Bagheri, R. (2019). Contribution of rainfall and agricultural returns to groundwater recharge in arid areas. *Journal of Hydrology*, 575, 1230–1238. <https://doi.org/10.1016/j.jhydrol.2019.06.029>
- Jeen, S.-W., Kang, J., Jung, H., & Lee, J. (2021). Review of Seawater Intrusion in Western Coastal Regions of South Korea. *Water*, 13(6). <https://doi.org/10.3390/w13060761>
- Jensen, H. S., Mortensen, P. B., Andersen, F. ., Rasmussen, E., & Jensen, A. (1995). Phosphorus cycling in a coastal marine sediment, Aarhus Bay, Denmark. *Limnology and Oceanography*, 40(5), 908–917. <https://doi.org/10.4319/lo.1995.40.5.0908>
- Ji, T., Du, J., Moore, W. S., Zhang, G., Su, N., & Zhang, J. (2013). Nutrient inputs to a Lagoon through submarine groundwater discharge: The case of Laoye Lagoon, Hainan, China. *Journal of Marine Systems*, 111–112, 253–262. <https://doi.org/10.1016/j.jmarsys.2012.11.007>
- Jiménez-Casero, J., Ruiz, J. M., Bernardeau-Esteller, J., García-Muñoz, R., Sánchez-Lizaso, J. L., Marín-Guirao, L., & Belando, M. D. (2025). Cascading ecological impacts: From eutrophic coastal lagoon collapse to decline of *Posidonia oceanica* meadows in the Mediterranean. *Marine Pollution Bulletin*, 221, 118536. <https://doi.org/10.1016/j.marpolbul.2025.118536>
- Jiménez-Martínez, J., Aravena, R., & Candela, L. (2011). The Role of Leaky Boreholes in the Contamination of a Regional Confined Aquifer. A Case Study: The Campo de Cartagena Region, Spain. *Water, Air, & Soil Pollution*, 215(1–4), 311–327. <https://doi.org/10.1007/s11270-010-0480-3>
- Jiménez-Martínez, J., Candela, L., García-Aróstegui, J. L., & Aragón, R. (2012). A 3D geological model of Campo de Cartagena, SE Spain: Hydrogeological implications. *Geologica Acta*, 10(1), 1–14. <https://doi.org/10.1344/105.000001703>
- Jiménez-Martínez, J., García-Aróstegui, J. L., Hunink, J. E., Contreras, S., Baudron, P., & Candela, L. (2016). The role of groundwater in highly human-modified hydrosystems: A review of impacts and mitigation options in the Campo de Cartagena-Mar Menor coastal plain (SE Spain). *Environmental Reviews*, 24(4), 377–392. <https://doi.org/10.1139/er-2015-0089>
- Joshi, S. R., Kukkadapu, R. K., Burdige, D. J., Bowden, M. E., Sparks, D. L., & Jaisi, D. P. (2015). Organic Matter Remineralization Predominates Phosphorus Cycling in the Mid-Bay Sediments in the Chesapeake Bay. *Environmental Science & Technology*, 49(10), 5887–5896. <https://doi.org/10.1021/es5059617>
- Jou-Claus, S., Folch, A., & Garcia-Orellana, J. (2021). Applicability of Landsat 8 thermal infrared sensor for identifying submarine groundwater discharge springs in the Mediterranean Sea basin. *Hydrology and Earth System Sciences*, 25(9), 4789–4805. <https://doi.org/10.5194/hess-25-4789-2021>
- Jung, H. C., & Yoon, Y. (2025). Climate change effects on submarine groundwater discharge and regional variations along the Korean Peninsula.

- Communications Earth & Environment*, 6(1), 1–10.
<https://doi.org/10.1038/s43247-025-02084-9>
- Kasonga, T. K., Coetzee, M. A. A., Kamika, I., Ngole-Jeme, V. M., & Benteke Momba, M. N. (2021). Endocrine-disruptive chemicals as contaminants of emerging concern in wastewater and surface water: A review. *Journal of Environmental Management*, 277, 111485.
<https://doi.org/10.1016/j.jenvman.2020.111485>
- Kennish, M. J., & Paerl, H. W. (Eds.). (2010). *Coastal Lagoons: Critical Habitats of Environmental Change*. CRC Press.
<https://doi.org/10.1201/EBK1420088304>
- Khant, N. A., & Kim, H. (2022). Review of Current Issues and Management Strategies of Microplastics in Groundwater Environments. *Water*, 14(7).
<https://doi.org/10.3390/w14071020>
- Kim, I., & Kim, G. (2014). Submarine groundwater discharge as a main source of rare earth elements in coastal waters. *Marine Chemistry*, 160, 11–17.
<https://doi.org/10.1016/j.marchem.2014.01.003>
- King, J. N., Mehta, A. J., & Dean, R. G. (2009). Generalized analytical model for benthic water flux forced by surface gravity waves. *Journal of Geophysical Research: Oceans*, 114(C4), 2008JC005116.
<https://doi.org/10.1029/2008JC005116>
- Kirkegaard, C., Sonnenborg, T. O., Auken, E., & Jørgensen, F. (2011). Salinity Distribution in Heterogeneous Coastal Aquifers Mapped by Airborne Electromagnetics. *Vadose Zone Journal*, 10(1), 125–135.
<https://doi.org/10.2136/vzj2010.0038>
- Kiro, Y., Yechieli, Y., Voss, C. I., Starinsky, A., & Weinstein, Y. (2012). Modeling radium distribution in coastal aquifers during sea level changes: The Dead Sea case. *Geochimica et Cosmochimica Acta*, 88, 237–254.
<https://doi.org/10.1016/j.gca.2012.03.022>
- Kiro, Y. (2025). Coastal aquifers key contributors to ocean chemistry through solute fluxes. *Nature Communications*, 16(1), 7082.
<https://doi.org/10.1038/s41467-025-62411-8>
- Kjerfve, B., & Magill, K. E. (1989). Geographic and hydrodynamic characteristics of shallow coastal lagoons. *Marine Geology*, 88(3–4), 187–199.
[https://doi.org/10.1016/0025-3227\(89\)90097-2](https://doi.org/10.1016/0025-3227(89)90097-2)
- Kjerfve, B. (1994). Coastal lagoon processes. *Coastal Lagoon Processes*, 60, 1–8.
- Koné, Y. J.-M., Van De Vijver, B., & Schoelynck, J. (2019). The Role of Macrophytes in Biogenic Silica Storage in Ivory Coast Lagoons. *Frontiers in Earth Science*, 7, 248. <https://doi.org/10.3389/feart.2019.00248>
- Kotwicki, L., Grzelak, K., Czub, M., Dellwig, O., Gentz, T., Szymczycha, B., & Böttcher, M. E. (2014). Submarine groundwater discharge to the Baltic coastal zone: Impacts on the meiofaunal community. *Journal of Marine Systems*, 129, 118–126. <https://doi.org/10.1016/j.jmarsys.2013.06.009>
- Krask, J. L., Buck, T. L., Dunn, R. P., & Smith, E. M. (2022). Increasing tidal inundation corresponds to rising porewater nutrient concentrations in a southeastern U.S. salt marsh. *PLOS ONE*, 17(11), e0278215.
<https://doi.org/10.1371/journal.pone.0278215>

- Kretschmer, D. V., Michael, H. A., Moosdorf, N., Oude Essink, G. H. P., Bierkens, M. F. P., Wagener, T., & Reinecke, R. (2025). A Perceptual Model of Drivers and Limiters of Coastal Groundwater Dynamics. *Hydrological Processes*, 39(1), e70058. <https://doi.org/10.1002/hyp.70058>
- Kroeger, K. D., & Charette, M. A. (2008). Nitrogen biogeochemistry of submarine groundwater discharge. *Limnology and Oceanography*, 53(3), 1025–1039. <https://doi.org/10.4319/lo.2008.53.3.1025>
- Küster, E.; Dorusch, F.; Altenburger, R. (2005). Effects of Hydrogen Sulfide to *Vibrio Fischeri*, *Scenedesmus Vacuolatus*, and *Daphnia Magna*. *Environ. Toxicol. Chem.*, 24 (10), 2621–2629. <https://doi.org/10.1897/04-546R.1>
- Kwon, E. Y., Kim, G., Primeau, F., Moore, W. S., Cho, H., DeVries, T., Sarmiento, J. L., Charette, M. A., & Cho, Y. (2014). Global estimate of submarine groundwater discharge based on an observationally constrained radium isotope model. *Geophysical Research Letters*, 41(23), 8438–8444. <https://doi.org/10.1002/2014GL061574>
- Kwon, H. K., Kang, H., Oh, Y. H., Park, S. R., & Kim, G. (2017). Green tide development associated with submarine groundwater discharge in a coastal harbor, Jeju, Korea. *Scientific Reports*, 7(1), 6325. <https://doi.org/10.1038/s41598-017-06711-0>
- Lavergne, C., Rodriguez-Puig, J., Ruiz-González, C., Montero-Curiel, M., Casas, G., Romano-Gude, D., Alorda-Montiel, I., Dordal-Soriano, J., Alorda-Kleinglass, A., Diego-Feliu, M., Gilabert, J., Campillo-de La Maza, A., Romera-Castillo, C., Torres-Rodriguez, N., Heimbürger-Boavida, L.-E., García-Orellana, J., Rodellas, V., & G. Bravo, A. (2025). Unveiling Hidden Mercury and Methylmercury Sources: The Role of Submarine Groundwater Discharge in Coastal Lagoons. *Environmental Science & Technology*. <https://doi.org/10.1021/acs.est.5c07191>
- Lazado, C. C.; Stiller, K. T.; Timmerhaus, G.; Megård Reiten, B. K.; Nicolaysen, I. L.; Carletto, D.; Alipio, H. R. D.; Bergstedt, J. H.; Andersen, Ø. (2024). Mucosal and Systemic Physiological Changes Underscore the Welfare Risks of Environmental Hydrogen Sulphide in Post-Smolt Atlantic Salmon (*Salmo Salar*). *Ecotoxicol. Environ. Saf.*, 270, 115897. <https://doi.org/10.1016/j.ecoenv.2023.115897>
- LeRoux, N. K., Kurylyk, B. L., Briggs, M. A., Irvine, D. J., Tamborski, J. J., & Bense, V. F. (2021). Using Heat to Trace Vertical Water Fluxes in Sediment Experiencing Concurrent Tidal Pumping and Groundwater Discharge. *Water Resources Research*, 57(2), e2020WR027904. <https://doi.org/10.1029/2020WR027904>
- Lecher, A. L., Kessler, J., Sparrow, K., Garcia-Tigreros Kodovska, F., Dimova, N., Murray, J., Tulaczyk, S., & Paytan, A. (2016). Methane transport through submarine groundwater discharge to the North Pacific and Arctic Ocean at two Alaskan sites. *Limnology and Oceanography*, 61(S1), S344–S355. <https://doi.org/10.1002/lno.10118>
- Lecher, A. L., & Mackey, K. R. M. (2018). Synthesizing the Effects of Submarine Groundwater Discharge on Marine Biota. *Hydrology*, 5(4), 60. <https://doi.org/10.3390/hydrology5040060>

- Lee, D. R. (1977). A device for measuring seepage flux in lakes and estuaries. *Limnology and Oceanography*, 22(1), 140–147. <https://doi.org/10.4319/lo.1977.22.1.0140>
- Lee, E., Yoon, H., Hyun, S. P., Burnett, W. C., Koh, D.-C., Ha, K., Kim, D., Kim, Y., & Kang, K. (2016). Unmanned aerial vehicles (UAVs)-based thermal infrared (TIR) mapping, a novel approach to assess groundwater discharge into the coastal zone. *Limnology and Oceanography: Methods*, 14(11), 725–735. <https://doi.org/10.1002/lom3.10132>
- León, V. M., & Bellido, J. M. (2016). *Mar Menor. Una laguna singular y sensible. Evaluación científica de su estado*. Instituto Español de Oceanografía. Ministerio de Economía y Competitividad.
- Leoni, S.; Dominik, J.; Cassin, D.; Manfè, G.; Tagliapietra, D.; Acri, F.; Zonta, R. (2022). Sediment Oxygen Demand Rate in a Flow Regulated Lagoon (Venice, Italy). *Front. Environ. Sci.*, 10. <https://doi.org/10.3389/fenvs.2022.1000665>.
- Li, D., Zhao, Y., & Liu, Z. (2025). Nitrogen transformation and drivers in response to hydrological variability in the Yangtze subterranean estuary. *Journal of Environmental Management*, 391, 126474. <https://doi.org/10.1016/j.jenvman.2025.126474>
- Li, Y., Šimůnek, J., Wang, S., Zhang, W., & Yuan, J. (2017). Simulating the Effects of Lake Wind Waves on Water and Solute Exchange across the Lakeshore Using Hydrus-2D. *Water*, 9(8), 566. <https://doi.org/10.3390/w9080566>
- Liefer, J. D., MacIntyre, H. L., Su, N., & Burnett, W. C. (2014). Seasonal Alternation Between Groundwater Discharge and Benthic Coupling as Nutrient Sources in a Shallow Coastal Lagoon. *Estuaries and Coasts*, 37(4), 925–940. <https://doi.org/10.1007/s12237-013-9739-4>
- Lino, Y., Udayashankar, H. N., Suresh Babu, D. S., Ramasamy, M., & Balakrishna, K. (2023). Large submarine groundwater discharges to the Arabian Sea from tropical southwestern Indian Coast: Measurements from seepage meters deployed during the low tide. *Journal of Hydrology*, 620, 129394. <https://doi.org/10.1016/j.jhydrol.2023.129394>
- Liu, J., Du, J., & Yu, X. (2021). Submarine groundwater discharge enhances primary productivity in the Yellow Sea, China: Insight from the separation of fresh and recirculated components. *Geoscience Frontiers*, 12(6), 101204. <https://doi.org/10.1016/j.gsf.2021.101204>
- Liu, J., Lin, L., Yu, X., Chen, X., Peng, T., Lin, X., Zhu, X., & Du, J. (2025). Submarine groundwater discharge governs dissolved carbon cycling: Multi-scale evidence from a large river-dominated groundwater-saltmarsh-estuary system. *Marine Pollution Bulletin*, 220, 118474. <https://doi.org/10.1016/j.marpolbul.2025.118474>
- Liu, W., Zhao, S., Santos, I. R., Dimova, N. T., Zhu, T., Xu, H., Zhang, M., Lian, E., Liu, P., Yu, Z., & Xu, B. (2026). Radium and radon isotopes reveal multi-scale porewater and groundwater nutrient sources in a macrotidal embayment. *Geochimica et Cosmochimica Acta*, 418, 212–223. <https://doi.org/10.1016/j.gca.2026.02.014>
- Liu, X.; Dunne, J. P.; Stock, C. A.; Harrison, M. J.; Adcroft, A.; Resplandy, L. (2019). Simulating Water Residence Time in the Coastal Ocean: A Global

- Perspective. *Geophys. Res. Lett.*, 46 (23), 13910–13919. <https://doi.org/10.1029/2019GL085097>.
- Liu, Y., Jiao, J. J., Liang, W., & Luo, X. (2018). Using Tidal Fluctuation-Induced Dynamics of Radium Isotopes (^{224}Ra , ^{223}Ra , and ^{228}Ra) to Trace the Hydrodynamics and Geochemical Reactions in a Coastal Groundwater Mixing Zone. *Water Resources Research*, 54(4), 2909–2930. <https://doi.org/10.1002/2017WR022456>
- Liu, Y., Mao, R., Yu, S., & Jiao, J. J. (2025). Seasonality of Radium Isotopes in an Intertidal Aquifer. *Journal of Geophysical Research: Oceans*, 130(4), e2024JC022059. <https://doi.org/10.1029/2024JC022059>
- Long, M. H.; Rheuban, J. E.; McCorkle, D. C.; Burdige, D. J.; Zimmerman, R. C. (2019). Closing the Oxygen Mass Balance in Shallow Coastal Ecosystems. *Limnol. Oceanogr.*, 64 (6), 2694–2708. <https://doi.org/10.1002/lno.11248>.
- López-Andreu, F. J., López-Morales, J. A., Hernández-Guillen, Z., Carrero-Rodrigo, J. A., Sánchez-Alcaraz, M., Atenza-Juárez, J. F., & Erena, M. (2023). Deep Learning-Based Time Series Forecasting Models Evaluation for the Forecast of Chlorophyll a and Dissolved Oxygen in the Mar Menor. *Journal of Marine Science and Engineering*, 11(7), 1473. <https://doi.org/10.3390/jmse11071473>
- López-Castejón, F. (2017). *Caracterización de la hidrodinámica del Mar Menor y los flujos de intercambio con el Mediterráneo mediante datos in situ y modelado numérico*. <http://hdl.handle.net/10317/6361>
- López-Castejón, F., Pereira, F., & Gilabert, J. (2026). Hydrodynamics of Mar Menor through field observations and numerical modeling: A wind-forced coastal lagoon. *Journal of Sea Research*, 102689. <https://doi.org/10.1016/j.seares.2026.102689>
- Lu, K., Zhang, Z., Zhu, X., Ibánhez, J. S. P., Yang, B., & Jiang, S. (2025). Coastal rest during the COVID-19 pandemic enhances microbial community stability and metabolic potential in a subterranean estuary. *Npj Biofilms and Microbiomes*, 12(1), 7. <https://doi.org/10.1038/s41522-025-00873-w>
- Luek, J. L., & Beck, A. J. (2014). Radium budget of the York River estuary (VA, USA) dominated by submarine groundwater discharge with a seasonally variable groundwater end-member. *Marine Chemistry*, 165, 55–65. <https://doi.org/10.1016/j.marchem.2014.08.001>
- Luijendijk, A., Hagenaars, G., Ranasinghe, R., Baart, F., Donchyts, G., & Aarninkhof, S. (2018). The State of the World's Beaches. *Scientific Reports*, 8(1), 6641. <https://doi.org/10.1038/s41598-018-24630-6>
- Luijendijk, E., Gleeson, T., & Moosdorf, N. (2020). Fresh groundwater discharge insignificant for the world's oceans but important for coastal ecosystems. *Nature Communications*, 11(1), 1260. <https://doi.org/10.1038/s41467-020-15064-8>
- Luo, M., Zhang, Y., Xiao, K., Wang, X., Zhang, X., Li, G., & Li, H. (2023). Effect of submarine groundwater discharge on nutrient distribution and eutrophication in Liaodong Bay, China. *Water Research*, 247, 120732. <https://doi.org/10.1016/j.watres.2023.120732>

- Ma, Q., & Zhang, Y. (2020). Global Research Trends and Hotspots on Submarine Groundwater Discharge (SGD): A Bibliometric Analysis. *International Journal of Environmental Research and Public Health*, 17(3), 830. <https://doi.org/10.3390/ijerph17030830>
- Machado, E. C.; Knoppers, B. A. (1988). Sediment Oxygen Consumption in an Organic-Rich, Subtropical Lagoon, Brazil. *Sci. Total Environ.*, 75 (2), 341–349. [https://doi.org/10.1016/0048-9697\(88\)90045-9](https://doi.org/10.1016/0048-9697(88)90045-9).
- Maher, D. T., Call, M., Macklin, P., Webb, J. R., & Santos, I. R. (2019). Hydrological Versus Biological Drivers of Nutrient and Carbon Dioxide Dynamics in a Coastal Lagoon. *Estuaries and Coasts*, 42(4), 1015–1031. <https://doi.org/10.1007/s12237-019-00532-2>
- Mar Menor Scientific Data Server. <https://marmenor.upct.es/> (accessed 2025-11-17).
- Marín Beltrán, I. (2017). *Effects of atmospheric deposition on microbial dynamics and composition in two anthropogenically-influenced contrasted coastal sites* [Universitat Politècnica de Catalunya]. <https://doi.org/10.5821/dissertation-2117-121983>
- Martin, J. B., Cable, J. E., Jaeger, J., Hartl, K., & Smith, C. G. (2006). Thermal and chemical evidence for rapid water exchange across the sediment-water interface by bioirrigation in the Indian River Lagoon, Florida. *Limnology and Oceanography*, 51(3), 1332–1341. <https://doi.org/10.4319/lo.2006.51.3.1332>
- Martínez-Alvarez, V., Gallego-Elvira, B., Maestre-Valero, J. F., & Tanguy, M. (2011). Simultaneous solution for water, heat and salt balances in a Mediterranean coastal lagoon (Mar Menor, Spain). *Estuarine, Coastal and Shelf Science*, 91(2), 250–261. <https://doi.org/10.1016/j.ecss.2010.10.030>
- Martínez-Fernández, J., & Esteve-Selma, M. A. (2020). *El colapso ecológico de la laguna del Mar Menor*. <https://doi.org/10.13140/RG.2.2.25577.85601>
- Martínez-Pérez, L., Luquot, L., Carrera, J., Marazuela, M. A., Goyetche, T., Pool, M., Palacios, A., Bellmunt, F., Ledo, J., Ferrer, N., del Val, L., Pezard, P. A., García-Orellana, J., Diego-Feliu, M., Rodellas, V., Saaltink, M. W., Vázquez-Suñé, E., & Folch, A. (2022). A multidisciplinary approach to characterizing coastal alluvial aquifers to improve understanding of seawater intrusion and submarine groundwater discharge. *Journal of Hydrology*, 607, 127510. <https://doi.org/10.1016/j.jhydrol.2022.127510>
- McAllister, S. M.; Barnett, J. M.; Heiss, J. W.; Findlay, A. J.; MacDonald, D. J.; Dow, C. L.; Luther III, G. W.; Michael, H. A.; Chan, C. S. (2015). Dynamic Hydrologic and Biogeochemical Processes Drive Microbially Enhanced Iron and Sulfur Cycling within the Intertidal Mixing Zone of a Beach Aquifer. *Limnol. Oceanogr.*, 60 (1), 329–345. <https://doi.org/10.1002/lno.10029>.
- McCormack, T., Gill, L. W., Naughton, O., & Johnston, P. M. (2014). Quantification of submarine/intertidal groundwater discharge and nutrient loading from a lowland karst catchment. *Journal of Hydrology*, 519, 2318–2330. <https://doi.org/10.1016/j.jhydrol.2014.09.086>

- McCoy, C.; Viso, R.; Peterson, R. N.; Libes, S.; Lewis, B.; Ledoux, J.; Voulgaris, G.; Smith, E.; Sanger, D. (2011). Radon as an Indicator of Limited Cross-Shelf Mixing of Submarine Groundwater Discharge along an Open Ocean Beach in the South Atlantic Bight during Observed Hypoxia. *Cont. Shelf Res.*, 31 (12), 1306–1317. <https://doi.org/10.1016/j.csr.2011.05.009>.
- McDermid, K. J., Martin, K. J., & Haws, M. C. (2019). Seaweed resources of the Hawaiian Islands. *Botanica Marina*, 62(5), 443–462. <https://doi.org/10.1515/bot-2018-0091>
- McKenzie, T., Holloway, C., Dulai, H., Tucker, J. P., Sugimoto, R., Nakajima, T., Harada, K., & Santos, I. R. (2020). Submarine groundwater discharge: A previously undocumented source of contaminants of emerging concern to the coastal ocean (Sydney, Australia). *Marine Pollution Bulletin*, 160, 111519. <https://doi.org/10.1016/j.marpolbul.2020.111519>
- McKenzie, T., Dulai, H., & Fuleky, P. (2021). Traditional and novel time-series approaches reveal submarine groundwater discharge dynamics under baseline and extreme event conditions. *Scientific Reports*, 11(1), 22570. <https://doi.org/10.1038/s41598-021-01920-0>
- McKenzie, T., Moody, A., Barreira, J., Guo, X., Cohen, A., Wilson, S. J., & Ramasamy, M. (2024). Metals in coastal groundwater systems under anthropogenic pressure: A synthesis of behavior, drivers, and emerging threats. *Limnology and Oceanography Letters*, 9(4), 388–410. <https://doi.org/10.1002/lol2.10413>
- McKinley, I. G., & Russell Alexander, W. (1993). Assessment of radionuclide retardation: uses and abuses of natural analogue studies. *Journal of Contaminant Hydrology*, 13(1–4), 249–259. [https://doi.org/10.1016/0169-7722\(93\)90060-6](https://doi.org/10.1016/0169-7722(93)90060-6)
- Meire, L.; Soetaert, K. E. R.; Meysman, F. J. R. (2013). Impact of Global Change on Coastal Oxygen Dynamics and Risk of Hypoxia. *Biogeosciences*, 10 (4), 2633–2653. <https://doi.org/10.5194/bg-10-2633-2013>.
- Meli, P., Ellison, D., Ferraz, S. F. de B., Filoso, S., & Brancalion, P. H. S. (2024). On the unique value of forests for water: Hydrologic impacts of forest disturbances, conversion, and restoration. *Global Change Biology*, 30(2), e17162. <https://doi.org/10.1111/gcb.17162>
- Micallef, A., Person, M., Haroon, A., Weymer, B. A., Jegen, M., Schwalenberg, K., Faghih, Z., Duan, S., Cohen, D., Mountjoy, J. J., Woelz, S., Gable, C. W., Aweres, T., & Kumar Tiwari, A. (2020). 3D characterisation and quantification of an offshore freshened groundwater system in the Canterbury Bight. *Nature Communications*, 11(1), 1372. <https://doi.org/10.1038/s41467-020-14770-7>
- Michael, H. A., Mulligan, A. E., & Harvey, C. F. (2005). Seasonal oscillations in water exchange between aquifers and the coastal ocean. *Nature*, 436(7054), 1145–1148. <https://doi.org/10.1038/nature03935>
- Michael, H. A., Charette, M. A., & Harvey, C. F. (2011). Patterns and variability of groundwater flow and radium activity at the coast: A case study from Waquoit Bay, Massachusetts. *Marine Chemistry*, 127(1–4), 100–114. <https://doi.org/10.1016/j.marchem.2011.08.001>

- Middelburg, J. J.; Levin, L. A. (2009). Coastal Hypoxia and Sediment Biogeochemistry.
- Mondal, M., Mukherjee, A., Kumar, P., Ismaeel, N. M., & Das, K. (2024). A process-based impact of tropical cyclone and hurricane on surface water-groundwater interaction and contaminant mobilization of coastal aquifers. *Progress in Disaster Science*, 22, 100318. <https://doi.org/10.1016/j.pdisas.2024.100318>
- Monsen, N. E., Cloern, J. E., Lucas, L. V., & Monismith, S. G. (2002). A comment on the use of flushing time, residence time, and age as transport time scales. *Limnology and Oceanography*, 47(5), 1545–1553. <https://doi.org/10.4319/lo.2002.47.5.1545>
- Montiel, D., Lamore, A., Stewart, J., & Dimova, N. (2019). Is Submarine Groundwater Discharge (SGD) Important for the Historical Fish Kills and Harmful Algal Bloom Events of Mobile Bay? *Estuaries and Coasts*, 42(2), 470–493. <https://doi.org/10.1007/s12237-018-0485-5>
- Moody, A., Moore, W. S., Pierce, T., & Shiller, A. M. (2024). The effects of submarine groundwater discharge and the Bonnet Carré Spillway on nutrient dynamics in the western Mississippi Sound. *Science of The Total Environment*, 953, 176080. <https://doi.org/10.1016/j.scitotenv.2024.176080>
- Moore, A. M., Arango, H. G., Di Lorenzo, E., Cornuelle, B. D., Miller, A. J., & Neilson, D. J. (2004). A comprehensive ocean prediction and analysis system based on the tangent linear and adjoint of a regional ocean model. *Ocean Modelling*, 7(1–2), 227–258. <https://doi.org/10.1016/j.ocemod.2003.11.001>
- Moore, A. M., Arango, H. G., Broquet, G., Powell, B. S., Weaver, A. T., & Zavala-Garay, J. (2011). The Regional Ocean Modeling System (ROMS) 4-dimensional variational data assimilation systems: Part I – System overview and formulation. *Progress in Oceanography*, 91(1), 34–49. <https://doi.org/10.1016/j.pocean.2011.05.004>
- Moore, W. S., & Reid, D. F. (1973). Extraction of Radium from Natural Waters Using Manganese-Impregnated Acrylic Fibers. *Journal of Geophysical Research*, 78(36).
- Moore, W. S., & Arnold, R. (1996). Measurement of ^{223}Ra and ^{224}Ra in coastal waters using a delayed coincidence counter. *Journal of Geophysical Research: Oceans*, 101(C1), 1321–1329. <https://doi.org/10.1029/95JC03139>
- Moore, W. S. (1999). The subterranean estuary: A reaction zone of ground water and sea water. *Marine Chemistry*, 65(1–2), 111–125. [https://doi.org/10.1016/S0304-4203\(99\)00014-6](https://doi.org/10.1016/S0304-4203(99)00014-6)
- Moore, W. S., Blanton, J. O., & Joye, S. B. (2006). Estimates of flushing times, submarine groundwater discharge, and nutrient fluxes to Okatee Estuary, South Carolina. *Journal of Geophysical Research: Oceans*, 111(C9), 2005JC003041. <https://doi.org/10.1029/2005JC003041>
- Moore, W. S. (2008). Fifteen years experience in measuring ^{224}Ra and ^{223}Ra by delayed-coincidence counting. *Marine Chemistry*, 109(3–4), 188–197. <https://doi.org/10.1016/j.marchem.2007.06.015>

- Moore, W. S. (2010). The Effect of Submarine Groundwater Discharge on the Ocean. *Annual Review of Marine Science*, 2(1), 59–88. <https://doi.org/10.1146/annurev-marine-120308-081019>
- Moore, W. S.; Joye, S. B. (2021). Saltwater Intrusion and Submarine Groundwater Discharge: Acceleration of Biogeochemical Reactions in Changing Coastal Aquifers. *Front. Earth Sci.*, 9, 600710. <https://doi.org/10.3389/feart.2021.600710>.
- Moore, W. S., Benitez-Nelson, C., Schutte, C., Moody, A., Shiller, A., Sibert, R. J., & Joye, S. (2024). SGD-OD: Investigating the potential oxygen demand of submarine groundwater discharge in coastal systems. *Scientific Reports*, 14(1), 9249. <https://doi.org/10.1038/s41598-024-59229-7>
- Moosdorf, N., & Oehler, T. (2017). Societal use of fresh submarine groundwater discharge: An overlooked water resource. *Earth-Science Reviews*, 171, 338–348. <https://doi.org/10.1016/j.earscirev.2017.06.006>
- Moreno-González, R., & León, V. M. (2017). Presence and distribution of current-use pesticides in surface marine sediments from a Mediterranean coastal lagoon (SE Spain). *Environmental Science and Pollution Research*, 24(9), 8033–8048. <https://doi.org/10.1007/s11356-017-8456-0>
- Morote-Sánchez, B., Colomer, J., Soler, M., Gilabert, J., Rodellas, V., Garcia-Orellana, J., & Serra, T. (2025a). Aquatic deoxygenation associated with resuspension of anthropogenic organic matter. *Water Research*, 278, 123327. <https://doi.org/10.1016/j.watres.2025.123327>
- Morote-Sánchez, B., López-Castejón, F., & Gilabert, J. (2025b). Waves in a temperate, microtidal and restricted Mediterranean coastal lagoon. *Ocean Modelling*, 197, 102578. <https://doi.org/10.1016/j.ocemod.2025.102578>
- Muratoglu, A., & Wassar, F. (2024). Water at the intersection of human rights and conflict: A case study of Palestine. *Frontiers in Water*, 6. <https://doi.org/10.3389/frwa.2024.1470201>
- Murdoch, L. C., & Kelly, S. E. (2003). Factors affecting the performance of conventional seepage meters. *Water Resources Research*, 39(6). <https://doi.org/10.1029/2002WR001347>
- Murphy, G. E. P., Romanuk, T. N., & Worm, B. (2020). Cascading effects of climate change on plankton community structure. *Ecology and Evolution*, 10(4), 2170–2181. <https://doi.org/10.1002/ece3.6055>
- Nazari, S., Kruse, I. L., & Moosdorf, N. (2025). Spatiotemporal dynamics of global rain-fed groundwater recharge from 2001 to 2020. *Journal of Hydrology*, 650, 132490. <https://doi.org/10.1016/j.jhydrol.2024.132490>
- Newton, A., Carruthers, T. J. B., & Icely, J. (2012). The coastal syndromes and hotspots on the coast. *Estuarine, Coastal and Shelf Science*, 96, 39–47. <https://doi.org/10.1016/j.ecss.2011.07.012>
- Newton, A., Icely, J., Cristina, S., Brito, A., Cardoso, A. C., Colijn, F., Riva, S. D., Gertz, F., Hansen, J. W., Holmer, M., Ivanova, K., Leppäkoski, E., Canu, D. M., Mocenni, C., Mudge, S., Murray, N., Pejrup, M., Razinkovas, A., Reizopoulou, S., ... Zaldívar, J.-M. (2014). An overview of ecological status, vulnerability and future perspectives of European large shallow, semi-enclosed coastal systems, lagoons and transitional waters. *Estuarine*,

- Coastal and Shelf Science*, 140, 95–122.
<https://doi.org/10.1016/j.ecss.2013.05.023>
- Oehler, T., Eiche, E., Putra, D., Adyasari, D., Hennig, H., Mallast, U., & Moosdorf, N. (2018). Seasonal variability of land-ocean groundwater nutrient fluxes from a tropical karstic region (southern Java, Indonesia). *Journal of Hydrology*, 565, 662–671. <https://doi.org/10.1016/j.jhydrol.2018.08.077>
- Oehler, T., Bakti, H., Lubis, R. F., Purwoarminta, A., Delinom, R., & Moosdorf, N. (2019a). Nutrient dynamics in submarine groundwater discharge through a coral reef (western Lombok, Indonesia). *Limnology and Oceanography*, 64(6), 2646–2661. <https://doi.org/10.1002/lno.11240>
- Oehler, T., Tamborski, J., Rahman, S., Moosdorf, N., Ahrens, J., Mori, C., Neuholz, R., Schnetger, B., & Beck, M. (2019b). DSI as a Tracer for Submarine Groundwater Discharge. *Frontiers in Marine Science*, 6. <https://doi.org/10.3389/fmars.2019.00563>
- Ouaissa, S., Gómez-Jakobsen, F., Yebra, L., Ferrera, I., Moreno-Ostos, E., Belando, M. D., Ruiz, J. M., & Mercado, J. M. (2023). Phytoplankton dynamics in the Mar Menor, a Mediterranean coastal lagoon strongly impacted by eutrophication. *Marine Pollution Bulletin*, 192, 115074. <https://doi.org/10.1016/j.marpolbul.2023.115074>
- Pacheco, J. P.; López-Ballesteros, A.; Mesman, J. P.; Aznarez, C.; Pierson, D.; Trolle, D.; Nielsen, A.; Senent-Aparicio, J. (2025). Coupling SWAT+ and GOTM-WET Models to Assess Agricultural Management Practices for Mitigating Harmful Algal Blooms in Mar Menor, Spain. *J. Environ. Manage.*, 380, 125033. <https://doi.org/10.1016/j.jenvman.2025.125033>.
- Paepen, M., Hanssens, D., De Smedt, P., Walraevens, K., & Hermans, T. (2020). Combining resistivity and frequency domain electromagnetic methods to investigate submarine groundwater discharge in the littoral zone. *Hydrology and Earth System Sciences*, 24(7), 3539–3555. <https://doi.org/10.5194/hess-24-3539-2020>
- Pain, A. J., Martin, J. B., & Young, C. R. (2021). Biogeochemical and Hydrological Drivers of Heterogeneous Nutrient Exports From Subterranean Estuaries. *Frontiers in Marine Science*, 8, 699916. <https://doi.org/10.3389/fmars.2021.699916>
- Palacios, A., Ledo, J. J., Linde, N., Luquot, L., Bellmund, F., Folch, A., Marcuello, A., Queralt, P., Pezard, P. A., Martínez, L., del Val, L., Bosch, D., & Carrera, J. (2020). Time-lapse cross-hole electrical resistivity tomography (CHERT) for monitoring seawater intrusion dynamics in a Mediterranean aquifer. *Hydrology and Earth System Sciences*, 24(4), 2121–2139. <https://doi.org/10.5194/hess-24-2121-2020>
- Pereira, F., López-Castejón, F., Francés, F., Alcolea, A., Jiménez-Martínez, J., Dias, J. M., & Gilabert, J. (2025). Linking ROMS with watershed models for simulating hydrodynamics and thermohaline dynamics in a coastal lagoon affected by extreme weather events. *Ocean Modelling*, 102673. <https://doi.org/10.1016/j.ocemod.2025.102673>
- Pérez-Martín, M. Á. (2023). Understanding Nutrient Loads from Catchment and Eutrophication in a Salt Lagoon: The Mar Menor Case. *Water*, 15(20), 3569. <https://doi.org/10.3390/w15203569>

- Pérez-Ruzafa, A., Fernández, A. I., Marcos, C., Gilabert, J., Quispe, J. I., & García-Charton, J. A. (2005a). Spatial and temporal variations of hydrological conditions, nutrients and chlorophyll a in a Mediterranean coastal lagoon (Mar Menor, Spain). *Hydrobiologia*, 550(1), 11–27. <https://doi.org/10.1007/s10750-005-4356-2>
- Pérez-Ruzafa, Á., Marcos, C., & Gilabert, J. (2005b). 9.3 The ecology of the Mar Menor coastal lagoon: A fast changing ecosystem under human pressure. In *Coastal lagoons. Ecosystem processes and modeling for sustainable use and development*. (pp. 392–422). CRC Press Boca Raton.
- Pérez-Ruzafa, A., Campillo, S., Fernández-Palacios, J. M., García-Lacunza, A., García-Oliva, M., Ibañez, H., Navarro-Martínez, P. C., Pérez-Marcos, M., Pérez-Ruzafa, I. M., Quispe-Becerra, J. I., Sala-Mirete, A., Sánchez, O., & Marcos, C. (2019). Long-Term Dynamic in Nutrients, Chlorophyll a, and Water Quality Parameters in a Coastal Lagoon During a Process of Eutrophication for Decades, a Sudden Break and a Relatively Rapid Recovery. *Frontiers in Marine Science*, 6, 26. <https://doi.org/10.3389/fmars.2019.00026>
- Pérez-Ruzafa, A., Morkune, R., Marcos, C., Pérez-Ruzafa, I. M., & Razinkovas-Baziukas, A. (2020a). Can an oligotrophic coastal lagoon support high biological productivity? Sources and pathways of primary production. *Marine Environmental Research*, 153, 104824. <https://doi.org/10.1016/j.marenvres.2019.104824>
- Pérez-Ruzafa, A., Pérez-Marcos, M., & Marcos, C. (2020b). Coastal lagoons in focus: Their environmental and socioeconomic importance. *Journal for Nature Conservation*, 57, 125886. <https://doi.org/10.1016/j.jnc.2020.125886>
- Pérez-Ruzafa, A., Dezileau, L., Martínez-Sánchez, M. J., Pérez-Sirvent, C., Pérez-Marcos, M., Von Grafenstein, U., & Marcos, C. (2023). Long-term sediment records reveal over three thousand years of heavy metal inputs in the Mar Menor coastal lagoon (SE Spain). *Science of The Total Environment*, 902, 166417. <https://doi.org/10.1016/j.scitotenv.2023.166417>
- Pérez-Ruzafa, A., Molina-Cuberos, G. J., García-Oliva, M., Umgieser, G., & Marcos, C. (2024). Why coastal lagoons are so productive? Physical bases of fishing productivity in coastal lagoons. *Science of The Total Environment*, 922, 171264. <https://doi.org/10.1016/j.scitotenv.2024.171264>
- Petelet-Giraud, E., Cary, L., Cary, P., Bertrand, G., Giglio-Jacquemot, A., Hirata, R., Aquilina, L., Alves, L. M., Martins, V., Melo, A. M., Montenegro, S., Chatton, E., Franzen, M., & Aurouet, A. (2018). Multi-layered water resources, management, and uses under the impacts of global changes in a southern coastal metropolis: When will it be already too late? Crossed analysis in Recife, NE Brazil. *Science of The Total Environment*, 618, 645–657. <https://doi.org/10.1016/j.scitotenv.2017.07.228>
- Peters, C. N., Kimsal, C., Frederiks, R. S., Paldor, A., McQuiggan, R., & Michael, H. A. (2022). Groundwater pumping causes salinization of coastal streams due to baseflow depletion: Analytical framework and application to

- Savannah River, GA. *Journal of Hydrology*, 604, 127238. <https://doi.org/10.1016/j.jhydrol.2021.127238>
- Peterson, R. N.; Moore, W. S.; Chappel, S. L.; Viso, R. F.; Libes, S. M.; Peterson, L. E. (2016). A New Perspective on Coastal Hypoxia: The Role of Saline Groundwater. *Mar. Chem.*, 179, 1–11. <https://doi.org/10.1016/j.marchem.2015.12.005>.
- Piló, D., Barbosa, A. B., Teodósio, M. A., Encarnação, J., Leitão, F., Range, P., Krug, L. A., Cruz, J., & Chícharo, L. (2018). Are submarine groundwater discharges affecting the structure and physiological status of rocky intertidal communities? *Marine Environmental Research*, 136, 158–173. <https://doi.org/10.1016/j.marenvres.2018.02.013>
- Pitcher, G. C.; Aguirre-Velarde, A.; Breitburg, D.; Cardich, J.; Carstensen, J.; Conley, D. J.; Dewitte, B.; Engel, A.; Espinoza-Morriberón, D.; Flores, G.; Garçon, V.; Graco, M.; Grégoire, M.; Gutiérrez, D.; Hernandez-Ayon, J. M.; Huang, H.-H. M.; Isensee, K.; Jacinto, M. E.; Levin, L.; Lorenzo, A.; Machu, E.; Merma, L.; Montes, I.; Swa, N.; Paulmier, A.; Roman, M.; Rose, K.; Hood, R.; Rabalais, N. N.; Salvanes, A. G. V.; Salvattecí, R.; Sánchez, S.; Sifeddine, A.; Tall, A. W.; Plas, A. K. van der; Yasuhara, M.; Zhang, J.; Zhu, Z. (2021). System Controls of Coastal and Open Ocean Oxygen Depletion. *Prog. Oceanogr.*, 197, 102613. <https://doi.org/10.1016/j.pocean.2021.102613>.
- Porubsky, W. P., Weston, N. B., Moore, W. S., Ruppel, C., & Joye, S. B. (2014). Dynamics of submarine groundwater discharge and associated fluxes of dissolved nutrients, carbon, and trace gases to the coastal zone (Okatee River estuary, South Carolina). *Geochimica et Cosmochimica Acta*, 131, 81–97. <https://doi.org/10.1016/j.gca.2013.12.030>
- Precht, E., & Huettel, M. (2003). Advective pore-water exchange driven by surface gravity waves and its ecological implications. *Limnology and Oceanography*, 48(4), 1674–1684. <https://doi.org/10.4319/lo.2003.48.4.1674>
- Purushothaman, A., Vishnudattan, N. K., Nehala, S. P., Meghamol, M. D., Neethu, K. V., Joseph, J., Nandan, S. B., Padmakumar, K. B., & Thomas, L. C. (2023). Patterns and variability in the microplastic contamination along the southwest coast of India with emphasis on submarine groundwater discharge sites. *Marine Pollution Bulletin*, 194, 115432. <https://doi.org/10.1016/j.marpolbul.2023.115432>
- Qu, W., Wang, C., Luo, M., Zheng, C., & Li, H. (2020). Distributions, quality assessments and fluxes of heavy metals carried by submarine groundwater discharge in different types of wetlands in Jiaozhou Bay, China. *Marine Pollution Bulletin*, 157, 111310. <https://doi.org/10.1016/j.marpolbul.2020.111310>
- Rahman, S., Tamborski, J. J., Charette, M. A., & Cochran, J. K. (2019). Dissolved silica in the subterranean estuary and the impact of submarine groundwater discharge on the global marine silica budget. *Marine Chemistry*, 208, 29–42. <https://doi.org/10.1016/j.marchem.2018.11.006>
- Rapaglia, J., Ferrarin, C., Zaggia, L., Moore, W. S., Umgiesser, G., Garcia-Solsona, E., Garcia-Orellana, J., & Masqué, P. (2010). Investigation of residence

- time and groundwater flux in Venice Lagoon: Comparing radium isotope and hydrodynamical models. *Journal of Environmental Radioactivity*, 101(7), 571–581. <https://doi.org/10.1016/j.jenvrad.2009.08.010>
- Rapaglia, J., Koukoulas, S., Zaggia, L., Lichter, M., Manfé, G., & Vafeidis, A. T. (2012). Quantification of submarine groundwater discharge and optimal radium sampling distribution in the Lesina Lagoon, Italy. *Journal of Marine Systems*, 91(1), 11–19. <https://doi.org/10.1016/j.jmarsys.2011.09.003>
- Reading, M. J., Tait, D. R., Maher, D. T., Jeffrey, L. C., Correa, R. E., Tucker, J. P., Shishaye, H. A., & Santos, I. R. (2021). Submarine groundwater discharge drives nitrous oxide source/sink dynamics in a metropolitan estuary. *Limnology and Oceanography*, 66(5), 1665–1686. <https://doi.org/10.1002/lno.11710>
- Del Giorgio, P. A., (2005). *Respiration in Aquatic Ecosystems*, 1. publ.; Ed.; Oxford biology; Oxford Univ. Press: Oxford.
- Richardson, C. M., Davis, K. L., Ruiz-González, C., Guimond, J. A., Michael, H. A., Paldor, A., Moosdorf, N., & Paytan, A. (2024). The impacts of climate change on coastal groundwater. *Nature Reviews Earth & Environment*, 5(2), 100–119. <https://doi.org/10.1038/s43017-023-00500-2>
- Richardson, C. M.; Peucker-Ehrenbrink, B.; Wyatt, S.; Bourbonnais, A.; Hatje, V.; Frey, C.; Sanders, T.; Varela, D. E.; Paytan, A (2025). Effects of Climate Change on River and Groundwater Nutrient Inputs to the Coastal Ocean. *Commun. Earth Environ.* 2025, 6 (1), 761. <https://doi.org/10.1038/s43247-025-02594-6>.
- Robinson, C., Gibbes, B., & Li, L. (2006). Driving mechanisms for groundwater flow and salt transport in a subterranean estuary. *Geophysical Research Letters*, 33(3). <https://doi.org/10.1029/2005GL025247>
- Robinson, C. E., Xin, P., Santos, I. R., Charette, M. A., Li, L., & Barry, D. A. (2018). Groundwater dynamics in subterranean estuaries of coastal unconfined aquifers: Controls on submarine groundwater discharge and chemical inputs to the ocean. *Advances in Water Resources*, 115, 315–331. <https://doi.org/10.1016/j.advwatres.2017.10.041>
- Robinson, C. (2019). Microbial Respiration, the Engine of Ocean Deoxygenation. *Front. Mar. Sci.*, 5. <https://doi.org/10.3389/fmars.2018.00533>.
- Rocha, C., Veiga-Pires, C., Scholten, J., Knoeller, K., Gröcke, D. R., Carvalho, L., Anibal, J., & Wilson, J. (2016). Assessing land–ocean connectivity via submarine groundwater discharge (SGD) in the Ria Formosa Lagoon (Portugal): Combining radon measurements and stable isotope hydrology. *Hydrology and Earth System Sciences*, 20(8), 3077–3098. <https://doi.org/10.5194/hess-20-3077-2016>
- Rocha, C., Robinson, C. E., Santos, I. R., Waska, H., Michael, H. A., & Bokuniewicz, H. J. (2021). A place for subterranean estuaries in the coastal zone. *Estuarine, Coastal and Shelf Science*, 250, 107167. <https://doi.org/10.1016/j.ecss.2021.107167>
- Rocha, C., Jiang, S., Ibáñez, J. S. P., Yang, Q., Mazi, K., & Koussis, A. D. (2022). The effects of subterranean estuary dynamics on nutrient resource ratio availability to microphytobenthos in a coastal lagoon. *Science of The Total*

- Environment*, 851, 157522.
<https://doi.org/10.1016/j.scitotenv.2022.157522>
- Rodellas, V. (2014). *Evaluating Submarine Groundwater Discharge to the Mediterranean Sea by using radium isotopes*. Universitat Autònoma de Barcelona.
- Rodellas, V.; Garcia-Orellana, J.; Tovar-Sánchez, A.; Basterretxea, G.; López-García, J. M.; Sánchez-Quiles, D.; Garcia-Solsona, E.; Masqué, P. (2014) Submarine Groundwater Discharge as a Source of Nutrients and Trace Metals in a Mediterranean Bay (Palma Beach, Balearic Islands). *Mar. Chem.*, 160, 56–66. <https://doi.org/10.1016/j.marchem.2014.01.007>.
- Rodellas, V., Garcia-Orellana, J., Masqué, P., & Font-Muñoz, J. S. (2015). The influence of sediment sources on radium-derived estimates of Submarine Groundwater Discharge. *Marine Chemistry*, 171, 107–117. <https://doi.org/10.1016/J.MARCHEM.2015.02.010>
- Rodellas, V., Garcia-Orellana, J., Trezzi, G., Masqué, P., Stieglitz, T. C., Bokuniewicz, H., Cochran, J. K., & Berdalet, E. (2017). Using the radium quartet to quantify submarine groundwater discharge and porewater exchange. *Geochimica et Cosmochimica Acta*, 196, 58–73. <https://doi.org/10.1016/j.gca.2016.09.016>
- Rodellas, V., Stieglitz, T. C., Andrisoa, A., Cook, P. G., Raimbault, P., Tamborski, J. J., Van Beek, P., & Radakovitch, O. (2018). Groundwater-driven nutrient inputs to coastal lagoons: The relevance of lagoon water recirculation as a conveyor of dissolved nutrients. *Science of The Total Environment*, 642, 764–780. <https://doi.org/10.1016/j.scitotenv.2018.06.095>
- Rodellas, V., Cook, P. G., McCallum, J., Andrisoa, A., Meulé, S., & Stieglitz, T. C. (2020). Temporal variations in porewater fluxes to a coastal lagoon driven by wind waves and changes in lagoon water depths. *Journal of Hydrology*, 581, 124363. <https://doi.org/10.1016/j.jhydrol.2019.124363>
- Rodellas, V., Stieglitz, T. C., Tamborski, J. J., Van Beek, P., Andrisoa, A., & Cook, P. G. (2021). Conceptual uncertainties in groundwater and porewater fluxes estimated by radon and radium mass balances. *Limnology and Oceanography*, 66(4), 1237–1255. <https://doi.org/10.1002/lno.11678>
- Rodellas, V., Roca-Martí, M., Puigcorbó, V., Castrillejo, M., & Casacuberta, N. (2023). Radionuclides as Ocean Tracers. In J. Blasco & A. Tovar-Sánchez (Eds.), *Marine Analytical Chemistry* (pp. 199–273). Springer International Publishing. https://doi.org/10.1007/978-3-031-14486-8_4
- Rodrigues-Filho, J. L., Macêdo, R. L., Sarmiento, H., Pimenta, V. R. A., Alonso, C., Teixeira, C. R., Pagliosa, P. R., Netto, S. A., Santos, N. C. L., Daura-Jorge, F. G., Rocha, O., Horta, P., Branco, J. O., Sartor, R., Muller, J., & Cionek, V. M. (2023). From ecological functions to ecosystem services: Linking coastal lagoons biodiversity with human well-being. *Hydrobiologia*, 850(12), 2611–2653. <https://doi.org/10.1007/s10750-023-05171-0>
- Rodriguez-Puig, J.; Rodellas, V.; Diego-Feliu, M.; Alcolea, A.; Jiménez-Martínez, J.; Alorda-Montiel, I.; Alorda-Kleinglass, A.; Pereira, F.; Manzano, M.; Gilabert, J.; Garcia-Orellana, J. (2025). Seasonality of Submarine Groundwater Discharge Pathways in a Coastal Lagoon Revealed by Radium Isotopes: The Importance of Porewater Exchange in Summer.

- Journal of Hydrology*, 661, 133616.
<https://doi.org/10.1016/j.jhydrol.2025.133616>.
- Roman, M. R.; Brandt, S. B.; Houde, E. D.; Pierson, J. J. (2019). Interactive Effects of Hypoxia and Temperature on Coastal Pelagic Zooplankton and Fish. *Front. Mar. Sci.*, 6. <https://doi.org/10.3389/fmars.2019.00139>.
- Romano-Gude, D., Dordal-Soriano, J., Rodríguez-Puig, J., Bravo, A. G., Alorda-Montiel, I., Alorda-Kleinglass, A., Diego-Feliu, M., Romera-Castillo, C., Mallenco-Fornies, R., Gilabert, J., García-Orellana, J., Rodellas, V., & Ruiz-González, C. (2025). Impact of Submarine Groundwater Discharge on Microbial Communities in a Highly Anthropized Coastal Lagoon (Mar Menor, SE Spain). *Molecular Ecology*, 34, e70201. <https://doi.org/10.1111/mec.70201>
- Rosenberry, D. O. (2005). Integrating seepage heterogeneity with the use of ganged seepage meters: Gangseep. *Limnology and Oceanography: Methods*, 3(2), 131–142. <https://doi.org/10.4319/lom.2005.3.131>
- Roskosch, A., Hette, N., Hupfer, M., & Lewandowski, J. (2012). Alteration of *Chironomus plumosus* ventilation activity and bioirrigation-mediated benthic fluxes by changes in temperature, oxygen concentration, and seasonal variations. *Freshwater Science*, 31(2), 269–281. <https://doi.org/10.1899/11-043.1>
- Ruiz Fernández, J. M., León, V. M., Marín Guirao, L., Giménez Casalduero, F., Alvarez-Rogel, J., Esteve-Selma, M. A., Gómez Cerezo, R., Robledano Aymerich, F., González barberá, G., & Martínez-Fernández, J. (2019). *Informe de síntesis sobre el estado actual del Mar Menor y sus causas en relación a los contenidos de nutrientes*.
- Ruiz-González, C., Rodellas, V., & Garcia-Orellana, J. (2021). The microbial dimension of submarine groundwater discharge: Current challenges and future directions. *FEMS Microbiology Reviews*, 45(5), fuab010. <https://doi.org/10.1093/femsre/fuab010>
- Ruiz, J. M., Albentosa, M., Aldegue, B., Álvarez- Rogel, J., Antón, J., Belando, M. D., Bernardeau, J., Campillo, J. A., Domínguez, J. F., Ferrera, I., Fraile-Nuez, E., García, R., Gómez-Ballesteros, M., Gómez, F., González- Barberá, G., & Gómez-Jakobsen, F. (2020). *Informe de evolución y estado actual del Mar Menor en relación al proceso de eutrofización y sus causas*. (Vol. 2020).
- Rukundo, E., & Doğan, A. (2019). Dominant Influencing Factors of Groundwater Recharge Spatial Patterns in Ergene River Catchment, Turkey. *Water*, 11(4). <https://doi.org/10.3390/w11040653>
- Russoniello, C. J., & Michael, H. A. (2015). Investigation of Seepage Meter Measurements in Steady Flow and Wave Conditions. *Groundwater*, 53(6), 959–966. <https://doi.org/10.1111/gwat.12302>
- Sadat-Noori, M., Santos, I. R., Tait, D. R., & Maher, D. T. (2016). Fresh meteoric versus recirculated saline groundwater nutrient inputs into a subtropical estuary. *Science of The Total Environment*, 566–567, 1440–1453. <https://doi.org/10.1016/j.scitotenv.2016.06.008>
- Sakamoto, K.; Nakano, H.; Toyoda, T.; Urakawa, L. S.; Tsujino, H. (2024). Average Coastal Residence Time Distribution Estimated by a 2-Km Resolution

- Japanese Coastal Model. *J. Oceanogr.*, 80 (1), 45–58. <https://doi.org/10.1007/s10872-023-00704-6>.
- Sánchez-Badorrey, E., & Jalón-Rojas, I. (2015). A new method for zoning of coastal barriers based on hydro-geomorphological and climate criteria. *International Journal of Environmental Research*, 9(1), 351–362.
- Sandonnini, J., Del Pilar-Ruso, Y., Valverde-Urrea, M., & Giménez-Casaldueiro, F. (2024). Infauna evolution of the invertebrate community after a severe eutrophic crisis in the coastal lagoon of the Mar Menor (W Mediterranean). *Regional Studies in Marine Science*, 79, 103824. <https://doi.org/10.1016/j.rsma.2024.103824>
- Sanial, V., Moore, W. S., & Shiller, A. M. (2021). Does a bottom-up mechanism promote hypoxia in the Mississippi Bight? *Marine Chemistry*, 235, 104007. <https://doi.org/10.1016/j.marchem.2021.104007>
- Santos-Echeandía, J., Bernárdez, P., & Sánchez-Marín, P. (2023). Trace metal level variation under strong wind conditions and sediment resuspension in the waters of a coastal lagoon highly impacted by mining activities. *Science of The Total Environment*, 905, 167806. <https://doi.org/10.1016/j.scitotenv.2023.167806>
- Santos, I. R. S., Burnett, W. C., Chanton, J., Mwashote, B., Suryaputra, I. G. N. A., & Dittmar, T. (2008). Nutrient biogeochemistry in a Gulf of Mexico subterranean estuary and groundwater-derived fluxes to the coastal ocean. *Limnology and Oceanography*, 53(2), 705–718. <https://doi.org/10.4319/lo.2008.53.2.0705>
- Santos, I. R., Cook, P. L. M., Rogers, L., Weys, J. D., & Eyre, B. D. (2012a). The “salt wedge pump”: Convection-driven pore-water exchange as a source of dissolved organic and inorganic carbon and nitrogen to an estuary. *Limnology and Oceanography*, 57(5), 1415–1426. <https://doi.org/10.4319/lo.2012.57.5.1415>
- Santos, I. R., Eyre, B. D., & Huettel, M. (2012b). The driving forces of porewater and groundwater flow in permeable coastal sediments: A review. *Estuarine, Coastal and Shelf Science*, 98, 1–15. <https://doi.org/10.1016/j.ecss.2011.10.024>
- Santos, I. R., Chen, X., Lecher, A. L., Sawyer, A. H., Moosdorf, N., Rodellas, V., Tamborski, J., Cho, H.-M., Dimova, N., Sugimoto, R., Bonaglia, S., Li, H., Hajati, M.-C., & Li, L. (2021). Submarine groundwater discharge impacts on coastal nutrient biogeochemistry. *Nature Reviews Earth & Environment*, 2(5), 307–323. <https://doi.org/10.1038/s43017-021-00152-0>
- Savatier, M., Morrissey, P., Gill, L., & Rocha, C. (2023). Intercomparison of marine tracer and catchment-based submarine groundwater discharge estimates for a karst aquifer. *Journal of Hydrology*, 627, 130358. <https://doi.org/10.1016/j.jhydrol.2023.130358>
- Sawyer, A. H., Shi, F., Kirby, J. T., & Michael, H. A. (2013). Dynamic response of surface water-groundwater exchange to currents, tides, and waves in a shallow estuary. *Journal of Geophysical Research: Oceans*, 118(4), 1749–1758. <https://doi.org/10.1002/jgrc.20154>
- Schipanski, M. E., & Bennett, E. M. (2021). Chapter 9—The Phosphorus Cycle. In K. C. Weathers, D. L. Strayer, & G. E. Likens (Eds.), *Fundamentals of*

- Ecosystem Science (Second Edition)* (pp. 189–213). Academic Press. <https://doi.org/10.1016/B978-0-12-812762-9.00009-5>
- Scholten, J. C., Pham, M. K., Blinova, O., Charette, M. A., Dulaiova, H., & Eriksson, M. (2010). Preparation of Mn-fiber standards for the efficiency calibration of the delayed coincidence counting system (RaDeCC). *Marine Chemistry*, 121(1), 206–214. <https://doi.org/10.1016/j.marchem.2010.04.009>
- Schubert, M., Petermann, E., Stollberg, R., Gebel, M., Scholten, J., Knöller, K., Lorz, C., Glück, F., Riemann, K., & Weiß, H. (2019). Improved Approach for the Investigation of Submarine Groundwater Discharge by Means of Radon Mapping and Radon Mass Balancing. *Water*, 11(4), 749. <https://doi.org/10.3390/w11040749>
- Schubert, M., Knoeller, K., Scholten, J., Daesslé, L. W., Bravo, M. M. R., & Solís, E. M. C. (2023). Quantification of groundwater discharge into a shallow coastal lagoon applying a multi-tracer approach. *Environmental Monitoring and Assessment*, 195(5), 601. <https://doi.org/10.1007/s10661-023-11244-3>
- Schutte, C. A., Moore, W. S., Wilson, A. M., & Joye, S. B. (2020). Groundwater-Driven Methane Export Reduces Salt Marsh Blue Carbon Potential. *Global Biogeochemical Cycles*, 34(10), e2020GB006587. <https://doi.org/10.1029/2020GB006587>
- Senent-Aparicio, J., López-Ballesteros, A., Nielsen, A., & Trolle, D. (2021). A holistic approach for determining the hydrology of the mar menor coastal lagoon by combining hydrological & hydrodynamic models. *Journal of Hydrology*, 603, 127150. <https://doi.org/10.1016/j.jhydrol.2021.127150>
- Shchepetkin, A. F., & McWilliams, J. C. (2003). A method for computing horizontal pressure-gradient force in an oceanic model with a nonaligned vertical coordinate. *Journal of Geophysical Research: Oceans*, 108(C3). <https://doi.org/10.1029/2001JC001047>
- Shchepetkin, A. F., & McWilliams, J. C. (2005). The regional oceanic modeling system (ROMS): a split-explicit, free-surface, topography-following-coordinate oceanic model. *Ocean Modelling*, 9(4), 347–404. <https://doi.org/10.1016/j.ocemod.2004.08.002>
- Shinn, E. A., Reich, C. D., & Hickey, T. D. (2002). Seepage meters and Bernoulli's revenge. *Estuaries*, 25(1), 126–132. <https://doi.org/10.1007/BF02696056>
- Simonetti, I.; Lubello, C.; Cappiotti, L. On the Use of Hydrodynamic Modelling and Random Forest Classifiers for the Prediction of Hypoxia in Coastal Lagoons. *Sci. Total Environ.* 2024, 951, 175424. <https://doi.org/10.1016/j.scitotenv.2024.175424>.
- Slomp, C. P., & Van Cappellen, P. (2004). Nutrient inputs to the coastal ocean through submarine groundwater discharge: Controls and potential impact. *Journal of Hydrology*, 295(1–4), 64–86. <https://doi.org/10.1016/j.jhydrol.2004.02.018>
- Smith, C. G., Cable, J. E., Martin, J. B., & Roy, M. (2008). Evaluating the source and seasonality of submarine groundwater discharge using a radon-222 pore water transport model. *Earth and Planetary Science Letters*, 273(3–4), 312–322. <https://doi.org/10.1016/j.epsl.2008.06.043>

- Snyder, M., Taillefert, M., & Ruppel, C. (2004). Redox zonation at the saline-influenced boundaries of a permeable surficial aquifer: Effects of physical forcing on the biogeochemical cycling of iron and manganese. *Journal of Hydrology*, 296(1), 164–178. <https://doi.org/10.1016/j.jhydrol.2004.03.019>
- Soria, J., Vera-Herrera, L., Calvo, S., Romo, S., Vicente, E., Sahuquillo, M., & Sòria-Pepinyà, X. (2021). Residence Time Analysis in the Albufera of Valencia, a Mediterranean Coastal Lagoon, Spain. *Hydrology*, 8(1). <https://doi.org/10.3390/hydrology8010037>
- Soria, J., Pérez, R., & Sòria-Pepinyà, X. (2022). Mediterranean Coastal Lagoons Review: Sites to Visit before Disappearance. *Journal of Marine Science and Engineering*, 10(3). <https://doi.org/10.3390/jmse10030347>
- Starke, C., Ekau, W., & Moosdorf, N. (2020). Enhanced Productivity and Fish Abundance at a Submarine Spring in a Coastal Lagoon on Tahiti, French Polynesia. *Frontiers in Marine Science*, 6. <https://doi.org/10.3389/fmars.2019.00809>
- Steffen, W., Sanderson, A., Tyson, P., Jäger, J., Matson, P., Moore, B., Oldfield, F., Richardson, K., Schellnhuber, H. J., Turner, B. L., & Wasson, R. J. (2005). *Global Change and the Earth System: A Planet Under Pressure*. Springer. <https://doi.org/10.1007/b137870>
- Steinle, L.; Maltby, J.; Treude, T.; Kock, A.; Bange, H. W.; Engbersen, N.; Zopfi, J.; Lehmann, M. F.; Niemann, H. (2017). Effects of Low Oxygen Concentrations on Aerobic Methane Oxidation in Seasonally Hypoxic Coastal Waters. *Biogeosciences*, 14 (6), 1631–1645. <https://doi.org/10.5194/bg-14-1631-2017>.
- Stieglitz, T. C., Van Beek, P., Souhaut, M., & Cook, P. G. (2013). Karstic groundwater discharge and seawater recirculation through sediments in shallow coastal Mediterranean lagoons, determined from water, salt and radon budgets. *Marine Chemistry*, 156, 73–84. <https://doi.org/10.1016/j.marchem.2013.05.005>
- Stookey, L. L. (1970). Ferrozine—A new spectrophotometric reagent for iron. *Analytical Chemistry*, 42(7), 779–781. <https://doi.org/10.1021/ac60289a016>
- Striegl, R. G., Dornblaser, M. M., McDonald, C. P., Rover, J. A., & Stets, E. G. (2012). Carbon dioxide and methane emissions from the Yukon River system. *Global Biogeochemical Cycles*, 26(4). <https://doi.org/10.1029/2012GB004306>
- Su, N., Burnett, W. C., MacIntyre, H. L., Liefer, J. D., Peterson, R. N., & Viso, R. (2014). Natural Radon and Radium Isotopes for Assessing Groundwater Discharge into Little Lagoon, AL: Implications for Harmful Algal Blooms. *Estuaries and Coasts*, 37(4), 893–910. <https://doi.org/10.1007/s12237-013-9734-9>
- Su, W., Ma, Y., Wang, Q., Yan, Q., Lu, X., Ma, Z., Yi, L., Liu, X., Chen, F., Han, F., & Xu, Z. (2022). Effects of salinity and particle size on radium desorption from river sediments in the Qinghai-Tibet Plateau. *Journal of Environmental Radioactivity*, 241, 106771. <https://doi.org/10.1016/J.JENVRAD.2021.106771>

- Su, X., Liu, T., Beheshti, M., & Prigiobbe, V. (2020). Relationship between infiltration, sewer rehabilitation, and groundwater flooding in coastal urban areas. *Environmental Science and Pollution Research*, 27(13), 14288–14298. <https://doi.org/10.1007/s11356-019-06513-z>
- Sun, Y., & Torgersen, T. (1998). The effects of water content and Mn-fiber surface conditions on 224 Ra measurement by 220 Rn emanation. In *Marine Chemistry* (Vol. 62).
- Szymczycha, B., Borecka, M., Białk-Bielińska, A., Siedlewicz, G., & Pazdro, K. (2020). Submarine groundwater discharge as a source of pharmaceutical and caffeine residues in coastal ecosystem: Bay of Puck, southern Baltic Sea case study. *Science of The Total Environment*, 713, 136522. <https://doi.org/10.1016/j.scitotenv.2020.136522>
- Tait, D. R., Santos, I. R., Lamontagne, S., Sippo, J. Z., McMahon, A., Jeffrey, L. C., & Maher, D. T. (2023). Submarine Groundwater Discharge Exceeds River Inputs as a Source of Nutrients to the Great Barrier Reef. *Environmental Science & Technology*, 57(41), 15627–15634. <https://doi.org/10.1021/acs.est.3c03725>
- Tamborski, J., Rogers, A. D., Bokuniewicz, H. J., Cochran, J. K., & Young, C. R. (2015). Identification and quantification of diffuse fresh submarine groundwater discharge via airborne thermal infrared remote sensing. *Remote Sensing of Environment*, 171, 202–217. <https://doi.org/10.1016/j.rse.2015.10.010>
- Tamborski, J., Van Beek, P., Rodellas, V., Monnin, C., Bergsma, E., Stieglitz, T., Heilbrun, C., Cochran, J. K., Charbonnier, C., Anschutz, P., Bejannin, S., & Beck, A. (2019). Temporal variability of lagoon–sea water exchange and seawater circulation through a Mediterranean barrier beach. *Limnology and Oceanography*, 64(5), 2059–2080. <https://doi.org/10.1002/lno.11169>
- Tamborski, J., Cochran, J. K., Bokuniewicz, H., Heilbrun, C., Garcia-Orellana, J., Rodellas, V., & Wilson, R. (2020a). Radium Mass Balance Sensitivity Analysis for Submarine Groundwater Discharge Estimation in Semi-Enclosed Basins: The Case Study of Long Island Sound. *Frontiers in Environmental Science*, 8. <https://doi.org/10.3389/fenvs.2020.00108>
- Tamborski, J., Van Beek, P., Conan, P., Pujo-Pay, M., Odobel, C., Ghiglione, J.-F., Seidel, J.-L., Arfib, B., Diego-Feliu, M., Garcia-Orellana, J., Szafran, A., & Souhaut, M. (2020b). Submarine karstic springs as a source of nutrients and bioactive trace metals for the oligotrophic Northwest Mediterranean Sea. *Science of The Total Environment*, 732, 139106. <https://doi.org/10.1016/j.scitotenv.2020.139106>
- Tamborski, J., Eagle, M. J., Thorpe, M. T., Charette, M. A., Kurylyk, B. L., Rahman, S., Kroeger, K. D., O’Keefe Suttles, J., Mann, A. G., Brooks, T. W., & Wang, Z. A. (2025). Evidence of Mineral Alteration in a Salt Marsh Subterranean Estuary: Implications for Carbon and Trace Element Cycling. *Journal of Geophysical Research: Biogeosciences*, 130(5), e2025JG008758. <https://doi.org/10.1029/2025JG008758>

- Taniguchi, M., Burnett, W. C., Cable, J. E., & Turner, J. V. (2002). Investigation of submarine groundwater discharge. *Hydrological Processes*, 16(11), 2115–2129. <https://doi.org/10.1002/hyp.1145>
- Taniguchi, M., Uchida, S., & Kinoshita, M. (2003). Periodical changes of submarine fluid discharge from a deep seafloor, Suiyo Sea Mountain, Japan. *Geophysical Research Letters*, 30(18). <https://doi.org/10.1029/2003GL017924>
- Taniguchi, M., Dulai, H., Burnett, K. M., Santos, I. R., Sugimoto, R., Stieglitz, T., Kim, G., Moosdorf, N., & Burnett, W. C. (2019). Submarine Groundwater Discharge: Updates on Its Measurement Techniques, Geophysical Drivers, Magnitudes, and Effects. *Frontiers in Environmental Science*, 7, 141. <https://doi.org/10.3389/fenvs.2019.00141>
- Tapia González, F. U., Herrera-Silveira, J. A., & Aguirre-Macedo, M. L. (2008). Water quality variability and eutrophic trends in karstic tropical coastal lagoons of the Yucatán Peninsula. *Estuarine, Coastal and Shelf Science*, 76(2), 418–430. <https://doi.org/10.1016/j.ecss.2007.07.025>
- Ten Hietbrink, S., Patton, H., Dugan, B., Szymczycha, B., Sen, A., Lepland, A., Knies, J., Kim, J.-H., Chen, N.-C., & Hong, W.-L. (2025). Deglaciation drove seawater infiltration and slowed submarine groundwater discharge. *Nature Geoscience*, 18(8), 779–786. <https://doi.org/10.1038/s41561-025-01750-z>
- Terink, W., Lutz, a. F., & Immerzeel, W. W. (2015). *SPHY v2.0: Spatial Processes in Hydrology: Model theory, installation, and data preparation*. 31(October), 71.
- Tomer, A. S., McKenzie, T., Majtényi-Hill, C., Cabral, A., Yau, Y. Y. Y., Call, M., Chen, X., Correa, R. E., Davis, K., Jeffrey, L., Sadat-Noori, M., Tait, D., Webb, J., Maher, D. T., Henriksson, L., Bonaglia, S., Zhao, S., Cardenas, M. B., & Santos, I. R. (2025). Groundwater releases CO₂ to diverse global coastal ecosystems. *Science Advances*, 11(2), eadr3240. <https://doi.org/10.1126/sciadv.adr3240>
- Tovar-Sánchez, A., Basterretxea, G., Rodellas, V., Sánchez-Quiles, D., García-Orellana, J., Masqué, P., Jordi, A., López, J. M., & Garcia-Solsona, E. (2014). Contribution of Groundwater Discharge to the Coastal Dissolved Nutrients and Trace Metal Concentrations in Majorca Island: Karstic vs Detrital Systems. *Environmental Science & Technology*, 48(20), 11819–11827. <https://doi.org/10.1021/es502958t>
- Tragsatec. (2020). *Cuantificación, control de la calidad y seguimiento piezométrico de la descarga de agua subterránea del acuífero Cuaternario del Campo de Cartagena al Mar Menor*. (p. 66).
- Trezzi, G., Garcia-Orellana, J., Rodellas, V., Santos-Echeandia, J., Tovar-Sánchez, A., Garcia-Solsona, E., & Masqué, P. (2016). Submarine groundwater discharge: A significant source of dissolved trace metals to the North Western Mediterranean Sea. *Marine Chemistry*, 186, 90–100. <https://doi.org/10.1016/j.marchem.2016.08.004>
- Tur-Piedra, J., Ledo, J., Diego-Feliu, M., Queralt, P., Marcuello, A., Rodellas, V., & Folch, A. (2024). Spatial and seasonal fluctuations in fresh submarine groundwater discharge revealed by marine continuous resistivity

- profiling. *Scientific Reports*, 14(1), 24854. <https://doi.org/10.1038/s41598-024-75984-z>
- Ullman, W. J., & Aller, R. C. (1982). Diffusion coefficients in nearshore marine sediments. *Limnology and Oceanography*, 27(3), 552–556. <https://doi.org/10.4319/lo.1982.27.3.0552>
- UN Water (Ed.). (2022). *Groundwater making the invisible visible*. UNESCO.
- Utsunomiya, T., Hata, M., Sugimoto, R., Honda, H., Kobayashi, S., Miyata, Y., Yamada, M., Tominaga, O., Shoji, J., & Taniguchi, M. (2017). Higher species richness and abundance of fish and benthic invertebrates around submarine groundwater discharge in Obama Bay, Japan. *Journal of Hydrology: Regional Studies, Water, Energy, and Food Nexus in the Asia-Pacific Region*, 11, 139–146. <https://doi.org/10.1016/j.ejrh.2015.11.012>
- Valsan, G., Warriar, A. K., Amrutha, K., Anusree, S., & Rangel-Buitrago, N. (2023). Exploring the presence and distribution of microplastics in subterranean estuaries from southwest India. *Marine Pollution Bulletin*, 190, 114820. <https://doi.org/10.1016/j.marpolbul.2023.114820>
- Vaquer-Sunyer, R.; Duarte, C. M. (2008). Thresholds of Hypoxia for Marine Biodiversity. *Proc. Natl. Acad. Sci.*, 105 (40), 15452–15457. <https://doi.org/10.1073/pnas.0803833105>.
- Velasco, A. M., Pérez-Ruzafa, A., Martínez-Paz, J. M., & Marcos, C. (2018). Ecosystem services and main environmental risks in a coastal lagoon (Mar Menor, Murcia, SE Spain): The public perception. *Journal for Nature Conservation*, 43, 180–189. <https://doi.org/10.1016/j.jnc.2017.11.002>
- Velasco, J., Lloret, J., Millan, A., Marin, A., Barahona, J., Abellan, P., & Sanchez-Fernandez, D. (2006). Nutrient And Particulate Inputs Into The Mar Menor Lagoon (Se Spain) From An Intensive Agricultural Watershed. *Water, Air, and Soil Pollution*, 176(1–4), 37–56. <https://doi.org/10.1007/s11270-006-2859-8>
- Viollier, E., Inglett, P. W., Hunter, K., Roychoudhury, A. N., & Van Cappellen, P. (2000). The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. *Applied Geochemistry*, 15(6), 785–790. [https://doi.org/10.1016/S0883-2927\(99\)00097-9](https://doi.org/10.1016/S0883-2927(99)00097-9)
- Virtanen, E. A.; Norkko, A.; Nyström Sandman, A.; Viitasalo, M. (2019). Identifying Areas Prone to Coastal Hypoxia – the Role of Topography. *Biogeosciences*, 16 (16), 3183–3195. <https://doi.org/10.5194/bg-16-3183-2019>.
- Volkenborn, N., Polerecky, L., Hedtkamp, S. I. C., Van Beusekom, J. E. E., & De Beer, D. (2007). Bioturbation and bioirrigation extend the open exchange regions in permeable sediments. *Limnology and Oceanography*, 52(5), 1898–1909. <https://doi.org/10.4319/lo.2007.52.5.1898>
- Voss, C. I., & Provost, A. M. (2010). *SUTRA, a model for saturated-unsaturated variable-density ground-water flow with solute or energy transport*. <https://doi.org/02-4231>
- Wang, Q., Cai, P., Jiang, S., Wang, X., Li, G., Liu, Z., Wang, F., & Li, H. (2023). Using 224Ra/228Th disequilibrium to quantify carbon transformation and export from intertidal sandy and muddy sediments. *Geochimica et Cosmochimica Acta*, 355, 222–234. <https://doi.org/10.1016/j.gca.2023.06.024>

- Wang, Wang, Q., Michael, H. A., Liu, Z., Wang, Z., Wang, T., Gao, Y., Luo, M., & Li, H. (2025). Seasonal Submarine Groundwater Discharge Drives Coastal Carbon Cycling and Modulates Buffering Capacity. *Global Biogeochemical Cycles*, 39(8), e2025GB008629. <https://doi.org/10.1029/2025GB008629>
- Wang, X., Baskaran, M., Su, K., & Du, J. (2018). The important role of submarine groundwater discharge (SGD) to derive nutrient fluxes into River dominated Ocean Margins – The East China Sea. *Marine Chemistry*, 204, 121–132. <https://doi.org/10.1016/j.marchem.2018.05.010>
- Waska, H., Kim, S., Kim, G., Peterson, R. N., & Burnett, W. C. (2008). An efficient and simple method for measuring ^{226}Ra using the scintillation cell in a delayed coincidence counting system (RaDeCC). *Journal of Environmental Radioactivity*, 99(12), 1859–1862. <https://doi.org/10.1016/j.jenvrad.2008.08.008>
- Webb, J. R.; Santos, I. R.; Maher, D. T.; Tait, D. R.; Cyronak, T.; Sadat-Noori, M.; Macklin, P.; Jeffrey, L. C. (2019). Groundwater as a Source of Dissolved Organic Matter to Coastal Waters: Insights from Radon and CDOM Observations in 12 Shallow Coastal Systems. *Limnol. Oceanogr.*, 64 (1), 182–196. <https://doi.org/10.1002/lno.11028>.
- Weber, T.; Wiseman, N. A.; Kock, A. (2019). Global Ocean Methane Emissions Dominated by Shallow Coastal Waters. *Nat. Commun.*, 10 (1), 4584. <https://doi.org/10.1038/s41467-019-12541-7>.
- Wei, L., Cai, P., Hong, Q., Wu, T., Liu, W., Cheng, Y., & Mi, P. (2026). Rapid nitrogen removal in sandy beaches driven by periodic tidal inundations. *Limnology and Oceanography*, 71(1), e70314. <https://doi.org/10.1002/lno.70314>
- Weinstein, Y., Yechieli, Y., Shalem, Y., Burnett, W. C., Swarzenski, P. W., & Herut, B. (2011). What Is the Role of Fresh Groundwater and Recirculated Seawater in Conveying Nutrients to the Coastal Ocean? *Environmental Science & Technology*, 45(12), 5195–5200. <https://doi.org/10.1021/es104394r>
- Weng, Q., & Fu, P. (2014). Modeling annual parameters of clear-sky land surface temperature variations and evaluating the impact of cloud cover using time series of Landsat TIR data. *Remote Sensing of Environment*, 140, 267–278. <https://doi.org/10.1016/j.rse.2013.09.002>
- Werner, A. D., Bakker, M., Post, V. E. A., Vandenbohede, A., Lu, C., Ataie-Ashtiani, B., Simmons, C. T., & Barry, D. A. (2013). Seawater intrusion processes, investigation and management: Recent advances and future challenges. *Advances in Water Resources*, 35th Year Anniversary Issue, 51, 3–26. <https://doi.org/10.1016/j.advwatres.2012.03.004>
- Wilkinson, M. D., Dumontier, M., Aalbersberg, I. J., Appleton, G., Axton, M., Baak, A., Blomberg, N., Boiten, J.-W., da Silva Santos, L. B., Bourne, P. E., Bouwman, J., Brookes, A. J., Clark, T., Crosas, M., Dillo, I., Dumon, O., Edmunds, S., Evelo, C. T., Finkers, R., ... Mons, B. (2016). The FAIR Guiding Principles for scientific data management and stewardship. *Scientific Data*, 3(1), 160018. <https://doi.org/10.1038/sdata.2016.18>
- Williams, E. L., Kratt, C. B., Rodolfo, R. S., Lapus, M. R., Lardizabal, R. R., Bangun, A. S., Nguyen, A. T., Tyler, S. W., & Cardenas, M. B. (2024). Multi-Scale

- Thermal Mapping of Submarine Groundwater Discharge in Coastal Ecosystems of a Volcanic Area. *Geophysical Research Letters*, 51(22), e2024GL111857. <https://doi.org/10.1029/2024GL111857>
- Wilson, A. M., Evans, T. B., Moore, W. S., Schutte, C. A., & Joye, S. B. (2015). What time scales are important for monitoring tidally influenced submarine groundwater discharge? Insights from a salt marsh. *Water Resources Research*, 51(6), 4198–4207. <https://doi.org/10.1002/2014WR015984>
- Wilson, S. J., Moody, A., McKenzie, T., Cardenas, M. B., Luijendijk, E., Sawyer, A. H., Wilson, A., Michael, H. A., Xu, B., Knee, K. L., Cho, H., Weinstein, Y., Paytan, A., Moosdorf, N., Chen, C. A., Beck, M., Lopez, C., Murgulet, D., Kim, G., ... Santos, I. R. (2024a). Global subterranean estuaries modify groundwater nutrient loading to the ocean. *Limnology and Oceanography Letters*, 9(4), 411–422. <https://doi.org/10.1002/lol2.10390>
- Wilson, S. J., Song, B., Anderson, I. C., & Tobias, C. R. (2024b). Nitrification in a Subterranean Estuary: An Ex Situ and In Situ Method Comparison Determines Nitrate Is Available for Discharge. *Journal of Geophysical Research: Biogeosciences*, 129(6), e2023JG007876. <https://doi.org/10.1029/2023JG007876>
- Wilson, S. J., Tamborski, J. J., Song, B., Bernhardt, P., & Mulholland, M. R. (2024c). Submarine groundwater discharge as a major nutrient source in river-fed vs. Tidally dominated estuaries. *Limnology and Oceanography*, Ino.12772. <https://doi.org/10.1002/lno.12772>
- Wu, B., & Liu, S. (2020). Dissolution kinetics of biogenic silica and the recalculated silicon balance of the East China Sea. *Science of The Total Environment*, 743, 140552. <https://doi.org/10.1016/j.scitotenv.2020.140552>
- Xin, P., Robinson, C., Li, L., Barry, D. A., & Bakhtyar, R. (2010). Effects of wave forcing on a subterranean estuary. *Water Resources Research*, 46(12), 2010WR009632. <https://doi.org/10.1029/2010WR009632>
- Xiong, G., Geng, H., Zhu, X., Liu, M., Chen, G., Wang, Y., Yang, Y., Xu, X., Wu, J., Wang, J., & Wu, J. (2025). Microplastics act as biogeochemical amplifiers of nitrogen cycling in coastal groundwater: Differential effects under palaeo and modern seawater intrusion regimes. *Journal of Hydrology*, 134871. <https://doi.org/10.1016/j.jhydrol.2025.134871>
- Xu, C., Wang, X., Zhang, F., Lao, Y., Liu, J., & Du, J. (2024). Potential Linkages Between Submarine Groundwater (Fresh and Saline) Nutrient Inputs and Eutrophication in a Coastal Aquaculture Bay. *Journal of Geophysical Research: Oceans*, 129(10), e2024JC021501. <https://doi.org/10.1029/2024JC021501>
- Xu, H., Xu, B., Yu, H., Zhao, S., Burnett, W. C., Yao, Q., Dimova, N. T., Song, S., Guo, X., Chen, X., Zhang, H., & Yu, Z. (2024). Deciphering Multi-Scale Submarine Groundwater Discharge in a Typical Eutrophic Bay. *Journal of Geophysical Research: Oceans*, 129(6), e2024JC021042. <https://doi.org/10.1029/2024JC021042>
- Xue, Y., Zhang, Y., Zhang, M., Wang, X., Xiao, K., Luo, M., & Li, H. (2023). Submarine groundwater discharge and associated metal elements into an urbanized bay. *Marine Pollution Bulletin*, 192, 115092. <https://doi.org/10.1016/j.marpolbul.2023.115092>

- Yau, Y. Y. Y.; Cabral, A.; Reithmaier, G.; Cotovicz Jr, L. C.; Barreira, J.; Abril, G.; Morana, C.; Borges, A. V.; Machado, W.; Godoy, J. M.; Bonaglia, S.; Santos, I. R. (2024). Efficient Oxidation Attenuates Porewater-Derived Methane Fluxes in Mangrove Waters. *Limnology and Oceanography*, 69 (9), 1997–2014. <https://doi.org/10.1002/lno.12639>.
- Ye, K., Dai, Z., Zhang, X., Zhan, C., Ma, Y., Wang, D., Thanh, H. V., & Soltanian, M. R. (2025). Characterizing seasonal submarine groundwater discharge patterns in Daya Bay, China using thermal infrared remote sensing. *Marine Pollution Bulletin*, 218, 118188. <https://doi.org/10.1016/j.marpolbul.2025.118188>
- Ye, Y.; González-Vidal, A.; Cisterna-García, A.; Pérez-Ruzafa, A.; Izquierdo, M. A. Z.; Skarmeta, A. F. (2024). Advancing Towards a Marine Digital Twin Platform: Modeling the Mar Menor Coastal Lagoon Ecosystem in the South Western Mediterranean. *arXiv* September 16. <https://doi.org/10.48550/arXiv.2409.10134>.
- Yeo, M.-H., Kim, Y. S., Houk, P., Chang, A., & Lugwid, A. (2026). Ridge-to-reef linkages in Apra Harbor, Guam describe spatial and temporal variation in water quality and coral reef assemblages. *Marine Pollution Bulletin*, 223, 119026. <https://doi.org/10.1016/j.marpolbul.2025.119026>
- Young, K. S. R., & Pradhanang, S. M. (2021). Small Unmanned Aircraft (sUAS)-Deployed Thermal Infrared (TIR) Imaging for Environmental Surveys with Implications in Submarine Groundwater Discharge (SGD): Methods, Challenges, and Novel Opportunities. *Remote Sensing*, 13(7). <https://doi.org/10.3390/rs13071331>
- Yu, X., Liu, J., Chen, X., Yu, H., & Du, J. (2024). Fresh and saline groundwater nutrient inputs and their impacts on the nutrient budgets in a human-affected bay. *Marine Pollution Bulletin*, 199, 116026. <https://doi.org/10.1016/j.marpolbul.2024.116026>
- Yuan-Hui, L., & Gregory, S. (1974). Diffusion of ions in sea water and in deep-sea sediments. *Geochimica et Cosmochimica Acta*, 38(5), 703–714. [https://doi.org/10.1016/0016-7037\(74\)90145-8](https://doi.org/10.1016/0016-7037(74)90145-8)
- Zamora-López, A.; Guerrero-Gómez, A.; Torralva, M.; Zamora-Marín, J. M.; Oliva-Paterna, F. J. (2025). Eutrophication-Induced Shifts in Fish Assemblages from a Mediterranean Coastal Lagoon. *Sci. Total Environ.*, 1004, 180765. <https://doi.org/10.1016/j.scitotenv.2025.180765>.
- Zhang, B., Chen, X., Du, J., Wang, X., Rozaimi, M., Wang, Y., Wu, D., & Zhang, F. (2025). Mangrove-Derived Dissolved Organic Carbon and Allochthonous Refractory Subsidies via Submarine Groundwater Discharge at Regional and Global Scales. *Water Research*, 124853. <https://doi.org/10.1016/j.watres.2025.124853>
- Zhang, J., Lu, C., Wang, K., & Luo, J. (2025). Multi-timescale dynamic behavior of flow and transport in coastal leakage-influenced aquifer systems over tidal, spring-neap, and seasonal cycles. *Journal of Hydrology*, 134158. <https://doi.org/10.1016/j.jhydrol.2025.134158>
- Zhang, Y., Li, L., Erler, D. V., Santos, I., & Lockington, D. (2017). Effects of beach slope breaks on nearshore groundwater dynamics. *Hydrological Processes*, 31(14), 2530–2540. <https://doi.org/10.1002/hyp.11196>

- Zhang, Z., Yi, L., Hu, Y., Liu, N., & Ren, L. (2024). Submarine groundwater discharge and ocean acidification: Implications from China's coastal waters. *Marine Pollution Bulletin*, 201, 116252. <https://doi.org/10.1016/j.marpolbul.2024.116252>
- Zhao, M., Zhang, Y., Wilson, A. M., Moore, W. S., Smith, E., Lang, S. Q., Sheng, C., Zheng, C., Li, H., Xu, B., Han, G., & Xiao, K. (2026). Large Blue Carbon Export Through Submarine Groundwater Discharge: Insights From a Marsh-Creek Basin System. *Global Biogeochemical Cycles*, 40(2), e2025GB008781. <https://doi.org/10.1029/2025GB008781>
- Zhao, S., Li, M., Burnett, W. C., Cheng, K., Li, C., Guo, J., Yu, S., Liu, W., Yang, T., Dimova, N. T., Chen, G., Yu, Z., & Xu, B. (2022). In-situ radon-in-water detection for high resolution submarine groundwater discharge assessment. *Frontiers in Marine Science*, 9. <https://doi.org/10.3389/fmars.2022.1001554>
- Zhao, W., Bao, H., Peng, L., Du, M., Li, K., Zhan, X., Li, S., Tian, L., Huang, D., Zou, W., Yang, J.-Y. T., & Kao, S.-J. (2025). Transport of Dissolved Black Carbon in Three Estuaries in China: Roles of Flood-Ebb Tides and Submarine Groundwater Discharge. *Global Biogeochemical Cycles*, 39(6), e2025GB008532. <https://doi.org/10.1029/2025GB008532>
- Zheng, Q.; Zhao, H.; Shi, Y.; Duan, M. (2023). Distribution Characteristics of Dissolved Oxygen in Spring in the Northern Coastal Beibu Gulf, a Typical Subtropical Bay. *Water*, 15 (5), 970. <https://doi.org/10.3390/w15050970>.
- Zhou, F.; Lu, X.; Chen, F.; Zhu, Q.; Meng, Y.; Chen, C.; Lao, Q.; Zhang, S. (2020). Spatial-Monthly Variations and Influencing Factors of Dissolved Oxygen in Surface Water of Zhanjiang Bay, China. *J. Mar. Sci. Eng.*, 8 (6), 403. <https://doi.org/10.3390/jmse8060403>.
- Zhou, Y., Befus, K. M., Sawyer, A. H., & David, C. H. (2018). Opportunities and Challenges in Computing Fresh Groundwater Discharge to Continental Coastlines: A Multimodel Comparison for the United States Gulf and Atlantic Coasts. *Water Resources Research*, 54(10), 8363–8380. <https://doi.org/10.1029/2018WR023126>
- Zhou, Y., Sawyer, A. H., David, C. H., & Famiglietti, J. S. (2019). Fresh Submarine Groundwater Discharge to the Near-Global Coast. *Geophysical Research Letters*, 46(11), 5855–5863. <https://doi.org/10.1029/2019GL082749>
- Zhu, T., Zhao, S., Xu, B., Liu, D., Cardenas, M. B., Yu, H., Zhang, Y., Chen, X., Xiao, K., Yi, L., Cho, H.-M., Liu, S., Zhang, Z., Lian, E., Burnett, W. C., Chen, G., Yu, Z., & Santos, I. R. (2025). Large scale submarine groundwater discharge dominates nutrient inputs to China's coast. *Nature Communications*, 16(1), 2932. <https://doi.org/10.1038/s41467-025-58103-y>
- Żogała, B., Stan-Kłeczek, I., & Waligóra, J. (2025). The electrical resistivity tomography as a tool for groundwater prospecting in the flysch lithologies: A case study from Poland. *Acta Geophysica*, 74(1), 6. <https://doi.org/10.1007/s11600-025-01746-8>