

Chapter 2

State of Art and Theory of Submarine Groundwater Discharge (SGD)

2.1 Definition and Drivers of SGD

The water discharge is the most important pathway connecting land and ocean. Surface water inputs (e.g., rivers and streams) are usually easily visible and are typically large point material sources to the coastal ocean (Mulligan and Charette 2009). Hence, the contribution of surface water discharge to the ocean geochemical budgets has been well studied. The hydrodynamics and impact of terrestrial water on geochemical cycles of elements and its influence on the ocean ecosystem has been well recognised.

Another pathway connecting land and ocean is a direct groundwater flow. Groundwater discharge typically has a smaller water flow rate compared to river flow rate although locally it can be an important point source. However, chemical fluxes associated with groundwater discharge can be comparable to river chemical fluxes (Moore 2010). Thus, groundwater flow through coastal sediments to the marine ecosystem can have a significant impact on many processes taking place in the coastal areas and therefore there is a need for the process to be better understood.

Coastal aquifers usually consist of complicated systems described as confined, semi-confined and unconfined (Fig. 2.1). Freshwater can flow through an aquifer forced by hydraulic head and entrain seawater that is diffusing and dispersing up from the salty aquifer that lies underneath. On the other hand, seawater can percolate the seabed driven by a variety of forces. The zone of intermediate salinity extended between fresh water and seawater is called subterranean estuary (Moore 1999).

There are several forces that drive groundwater flow to the coastal ecosystem. The primary terrestrial driving force of fluid flow through coastal aquifers is the hydraulic gradient. Groundwater flows from the upland region of a watershed to unconfined or semi-confined aquifers on the coast where it can meet salty pore water that has infiltrated from the ocean (Burnett et al. 2006; Moore 2009; Mulligan

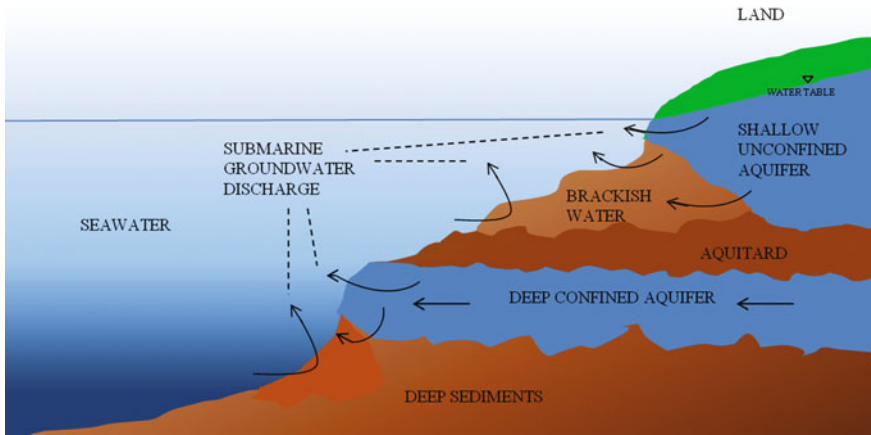


Fig. 2.1 General scheme of SGD. Groundwater located in the shallow, unconfined aquifer can discharge directly to the coastal ocean or can mix with seawater already in the sediment and be discharged as brackish water (seepage water). SGD is determined by both terrestrial and marine forces. Based on Burnett et al. (2006)

and Charette 2009). Usually, there is not one driving force behind SGD but a number of them including terrestrial and marine forces (Moore 2010). The main forces that influence submarine groundwater discharge are: water level differences across a permeable barrier; tidal pumping, wave setup (Taniguchi et al. 2002; Burnett et al. 2003; Massel et al. 2005), storms, current-induced pressure gradients in the coastal zone; upland recharge causing seasonal inflow and outflow of seawater into the aquifer (Michael et al. 2005) and geothermal heating (Kohout 1965).

As there are a number of different forces causing SGD, there are also many modes of SGD. The most modern and cited definition of groundwater is “water that resides within the saturated zone of geologic material” (Burnett et al. 2006; Moore 2010). Hence, pore water that fills space among sediments grains and thus makes sediments saturated like submerged, porous materials, is synonymous with groundwater (Moore 2010). There is considerable confusion regarding groundwater discharge definition, because it occurs as a slow diffuse flow or seepage through sediment and is characterized by substantial temporal and spatial variability (Burnett et al. 2006). Therefore, other definitions are in use. The first one considers only the discharge of terrestrial groundwater and often identify groundwater as rainwater that has infiltrated and percolated to the water table, or put on some similar qualifications, consistent with the applications to freshwater in terrestrial systems (Burnett et al. 2006). The second one characterizes submarine groundwater discharge as “any flow of water from seabed to the coastal ocean, regardless of fluid composition or driving force” (Burnett et al. 2003) and include fresh SGD, saline SGD and brackish SGD. The latter being a mixture of end-members (groundwater end-member and seawater end-member).

There are also definitions characterizing SGD that occurs farther from the shoreline (Fig. 2.1) forced by the advection of water through permeable shelf sediments and rocks. As SGD occurrence on the continental shelf (coming from deeper aquifers) is driven by buoyancy and pressure gradients, it can also be called deep pore water upwelling (DPU) (Piekarek-Jankowska 1996; Moore 2010). When the flow of water is driven by an inland hydraulic head through highly permeable aquifers or by large-scale cyclic movement of water caused by thermal heating, the process is called offshore submarine springs (Moore 2010).

In sandy, coastal areas seafloor currents are strong enough to create ripples (Fig. 2.2). Waves generate pressure gradients that can drive pore water exchange. This is also a type of SGD (Moore 2009). In the ripple troughs water percolates through the sediments and flows on a curved path toward the ripple crests, where pore water is released.

There are pros and cons of each of the groundwater discharge definitions. The advantage of defining groundwater discharge as a flow of water from the seabed to the marine environment (including fresh, saline and brackish SGD) is that it takes into account discharges of both: terrestrial groundwater and recirculated seawater. It is obvious that in the coastal ecosystem the seawater intrusion into the sediment is a common process (Massel et al. 2005). However, the recirculated seawater is not a new source of water and associated material fluxes for the marine environment. Moreover, SGD has been identified as a material pathway from land to the sea and consequently the above mentioned definition does not fulfil the criterion. Hence, for the purpose of this study, SGD is defined as groundwater (terrestrial water) discharge, while groundwater is identified as water which has salinity below 0.5. As a result groundwater is discharged to the coastal ecosystem as sediment porewater. The mixture of groundwater and seawater is referred to seepage water. The main aim of defining SGD as terrestrial groundwater flow is to characterize a new source of chemical substances loads to the study area and the Baltic Sea.

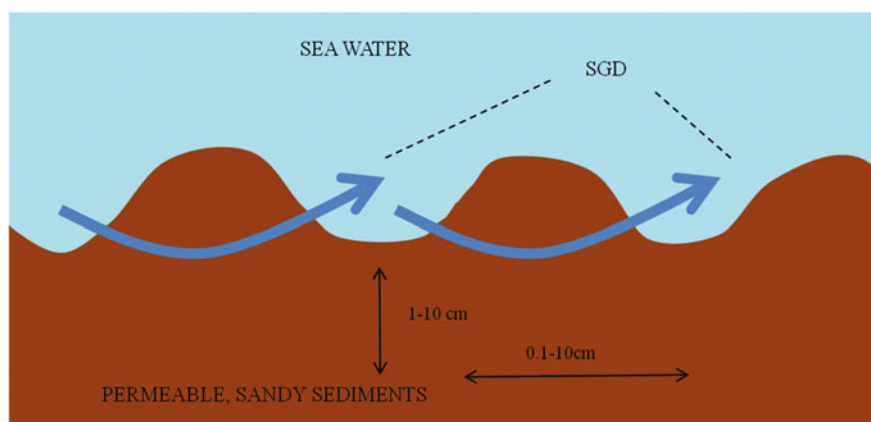


Fig. 2.2 Pore water exchange forced by differential pressure gradients. Based on Moore (2009)

2.2 The Worldwide Studies of SGD

Generally, submarine groundwater discharge into oceans and seas occurs constantly all over the world along coast lines (Peltonen 2002; Moore 2010). Groundwater discharge to the sea has been a topic of interest for many centuries (Burnett et al. 2006). A Roman geographer, Strabo (63BC–21AD) mentioned a submarine spring 4 km offshore from Latakia, Syria in the Mediterranean Sea (Kohout 1966). The spring was used as a source of fresh water which was transported to the town. Pliny the Elder (23–79 AD) described submarine springs in the Black Sea and in the Mediterranean Sea (Kohout 1966).

Later, groundwater hydrologists made efforts to identify drinking groundwater reserves and evaluate the behaviour of freshwater arriving in seawaters. Their studies were also focused on the identification of the groundwater-seawater (freshwater-saltwater) interface in the coastal zone. The first physical formulations of seawater intrusion were made by Badon-Ghyben and Herzberg (Badon-Ghyben 1888–1889; Herzberg 1901 both as cited in Bear et al. 1999), and thus called the Ghyben-Herzberg relationship. The relationship was based on a number of assumptions describing the elevation of the water table and the density difference of fresh water and seawater. The assumptions defined an unrealistic, hydrostatic situation because the idea of freshwater and seawater mixing was not allowed. This hydrostatic process would find saline groundwater everywhere below the sea level (Burnett et al. 2003; Moore 2010). In time scientists recognised that a more sophisticated equation is required to describe freshwater flow. Dupuit (1863 as cited in Freeze and Cherry 1979) identified hydrostatic distribution of fresh groundwater and seawater by making several assumptions: flow of groundwater was entirely horizontal; the seawater-groundwater interface was a no-flow boundary; and that salty groundwater was stationary. The Dupuit-Ghyben-Herzberg relationship leads to the awkward idea that all the groundwater had to escape at the shoreline (Burnett et al. 2003; Moore 2010). This was later improved by Hubbert (1940) who implemented the concept of an outflow interval. As a result seawater-groundwater interface intersected at the sea floor at some distance from the shore, producing a discharge area of intermediate salinity (Moore 2010). This concept was modified by Glover (1964) and Henry (1964). Both of them calculated the size of the interval and the position of the seawater-groundwater interface. Later Vacher (1988) used Herzberg's methodology as a boundary condition in order to calculate the width of the outflow interval.

The development of numerical models allowed for the calculation of more realistic SGD hydrodynamics. The first use of the notion of exponential decrease to estimate the distribution of seepage rates offshore was made by McBride and Pfannkuch (1975). They calculated groundwater discharge rate into lakes. Others scientists used similar models in coastal ecosystems. Models allowed for saline groundwater to circulate in reaction to hydraulic gradient, however flow across the seawater-groundwater interface was forbidden. The improvement in relation to the earlier models was that seawater-groundwater interface itself might change

locations. Currently models allow water to cross seawater-groundwater interface. The density driven circulation on a wide range of time and space is also possible. However, there are still some limitations to the method application (Burnett et al. 2006).

Studies concerning SGD have been neglected for many years because of the difficulty in the valuation of the importance of SGD. However, this perception has changed and scientists have recognized SGD as an important factor influencing coastal zones, thus meriting further study. As a result the Scientific Committee on Oceanic Research (SCOR) created two groups (working groups- WPs) to examine SGD. In 1997 SCOR WG-112 was formed to study more accurately and completely how submarine groundwater discharge impacts chemical and biological processes in the coastal ocean (Burnett 1999). SCOR WG-114 was established in 1999 to determine the fluid flow through permeable sediments and rocks to local and global ocean and SGD contribution to biogeochemical cycling and its impact on the environment (Boudreau et al. 2001). The growing number of publications demonstrates how interest in SGD studies increased over time. According to Web of Science (Thompson Reuters, <https://apps.webofknowledge.com>) in 1980s and 1990s number of published manuscripts per year oscillated from 0 to 4, in 2008 the number of published manuscripts increased to 79 and in 2014 to 123 (Thompson Reuters, <https://apps.webofknowledge.com>). These articles cover many aspects of SGD. The main focus has been on SGD measurements and SGD modelling leading to the development of methods of identifying and quantifying SGD. Recently scientists have started determining SGD influence on the environment and chemical substances fluxes via SGD, however there are still issues that need to be solved as well as a number of unrecognized geographical areas impacted by groundwater discharge. One of the most challenging issues is identifying the effect of chemical substances fluxes via SGD on their concentrations and the reactions taking place in subterranean estuaries. Another outstanding issue would be the recognition of the local and global importance of SGD and its influence on chemical substances budgets (Moore 2010).

2.3 Significance of SGD

Submarine groundwater discharges to the coastal ecosystems have been recognised as a sources of dissolved chemical substances that cause chemical and ecological effects in receiving waters. Groundwater, in many coastal areas, becomes contaminated or at least enriched with a variety of chemical substances (e.g. nutrients, metals, organic compounds) and can have higher concentrations of dissolved solids than river water. As a result SGD makes a larger contribution to the flux of dissolved chemical compounds than river run-off. Additionally, groundwater seeping through the sediments interacts with recirculated seawater and impacts the marine environment.

2.3.1 SGD as a Source of Nutrients and Biological Effects on the Coastal Ocean

Pioneering investigations concerning the biological importance of groundwater seepage into the sea were conducted by Kohout and Kolpinski (1967). They documented an explicit connection between groundwater discharge into the Biscayne Bay, Florida and biological zonation. Marsh (1977) presented SGD as a source of nutrients for coral reefs along the coast of Guam island. Similar phenomena were documented by D'Elia et al. (1981). Valiela et al. (1978, 1992, 2002) suggested that nitrogen fluxes via SGD can be critical to the nutrient economy of salt marshes. The harmful algal blooms in some areas were also related to nutrient supply via SGD (Lapointe and O'Connell 1989; LaRoche et al. 1997; Hwang et al. 2005; Hu et al. 2006; Lee and Kim 2007). A study in Masan Bay, Korea showed that large nutrient fluxes via SGD could lead not only to eutrophication but also to the occurrence of red tides (Lee et al. 2009). McCoy and Corbett (2009) suggested that eutrophication of coastal ecosystems as well as the continental shelf can be related to nutrient loads supplied via SGD.

Numerous studies have proven that the flux of nutrients via SGD is equal or greater than that from surface runoff: along the western Australian coast, North Perth (Johannes 1980); on eastern coast of Florida Bay (Corbett et al. 1999, 2000), in Florida Keys (Lapointe et al. 1990), in the Upper Floridan aquifers (Crotwell and Moore 2003); in Tampa Bay, Florida (Kroeger et al. 2007), in the Tomales Bay, California (Oberdorfer et al. 1990); along the South Carolina coast (Krest et al. 2000); in the Great South Bay, New York (Bokuniewicz 1980; Capone and Bautista 1985; Bokuniewicz and Pavlik 1990; Capone and Slater 1990); on the Georgia Shelf (Simmons 1992); in the Ria Formosa lagoon, Portugal (Leote et al. 2008) and in Hwasung and Bangdu Bay, off the volcanic island of Jeju, Korea (Kim et al. 2011).

Scientists not only tried to estimate nutrient fluxes via SGD but also investigated the sources of groundwater nutrients and processes taking place in the coastal ecosystems. Slomp and Van Cappellen (2004) first addressed the main sources of nutrients in groundwater as both natural loads from organic matter decomposition, mineral dissolution (phosphorous) and anthropogenic input from fertilizers, manure and wastewater. They suggested that the residence time of groundwater and redox conditions strongly determine the transformation, removal and transport of groundwater nitrogen and phosphorous into the coastal marine environment. Waska and Kim (2011) indicated that the nutrient biogeochemistry of SGD was impacted by tidal oscillations, seasonal precipitation changes and switched nutrient regimes. Moreover, they suggested that nutrient fluxes via SGD can be related to primary production dynamics in Hampyeong Bay, Yellow Sea. Ibáñez et al. (2012) reported that a high rate of groundwater seepage can promote the mitigation of nitrate ions whereas a low rate of groundwater seepage can promote net amplification of nitrate ions into the Ria Formosa lagoon throughout the year.

Submarine groundwater discharge and derived nutrient (NO_2^- , NO_3^- , NH_4^+ , PO_4^{3-} , and SiO_2) loadings to the coastal sea were systematically assessed along the coast of Majorca Island (Spain) in a general survey around the island and in three representative coves during 2010. Substantial loads of the investigated nutrients were estimated, first of all DIN and SiO_2 . Seasonal and yearly variations were documented. The study provides evidence that SGD is a major contributor to the dissolved pool of nutrients in the nearshore waters of Majorca (Travor-Sánchez et al. 2014). The conclusion of the study was confirmed by results of investigations carried out in coastal waters of Balearic Islands (Spain) that showed that SGD is a major pathway for delivering DIN ($1900 \text{ mmol m}^{-1} \text{ d}^{-1}$), dissolved Fe ($4.1 \text{ mmol m}^{-1} \text{ d}^{-1}$) and, to a lesser extent, DIP ($16 \text{ mmol m}^{-1} \text{ d}^{-1}$) into the nearshore waters. This allochthonous input may sustain a substantial phytoplankton biomass resulting in an onshore–offshore gradient ($4.7\text{--}7.1 \text{ mg m}^{-3}$ in nearshore seawater as compared with $<1 \text{ mg m}^{-3}$ in offshore stations). Both studies emphasize the relevance of SGD-driven nutrient inputs in the regulation of nearshore phytoplankton communities of oligotrophic areas.

Several recent studies have indicated that loads of nutrients delivered to the coastal zone via SGD exceed those delivered via local river run-off (Wong et al. 2014; Wang et al. 2015; Makings et al. 2014; McAllister et al. 2014). The various nutrients may be delivered to the estuary by different mechanisms (Ji et al. 2013). The intensity of nutrient discharge greatly depends on hydrologic conditions, as established in one subterranean system (Waquoit Bay, MA, USA). More than a doubling of the groundwater-associated nitrogen flux to surface water during the summer as compared to winter was due, primarily, to a reduction in nitrogen attenuation within the subterranean estuary. Because marine groundwater intrusion has been shown to increase during the summer, a greater contribution of recycled nutrients from the coastal ocean to the subterranean estuary was calculated. Also the longer residence times within the subterranean estuary during the winter, which would result from reduced marine groundwater circulation, allow oxygen depletion of the groundwater, creating a favorable environment for important nutrient transformations such as nitrification, denitrification, and anammox (Gonneea et al. 2014). This is supported by results presented by Santos et al. (2013) who, as a result of a four months of daily nutrient and radon (a natural groundwater tracer) observations at the outlet of a heavily drained coastal wetland, illustrated how episodic floods and diffuse groundwater seepage influence the biogeochemistry of a sub-tropical estuary (Richmond River, New South Wales). The authors report significant correlations between radon and ammonium and N/P ratios and between radon and dissolved organic nitrogen (DON) during the post-flood stage. While in this specific event the flood lasted for 14 % of the time of the surface water time series, it accounted for 18 % of NH_4 , 32 % of NO_x , 66 % of DON, 58 % of PO_4 and 55 % of dissolved organic phosphorus (DOP) catchment exports. The groundwater contribution to the total surface water catchment exports was nearly 100 % for ammonium, and <20 % for the other nutrients. Post-flood groundwater seepage shifted the system from a DON to a dissolved inorganic N-dominated one and

doubled N/P ratios in surface waters. It is hypothesized that the Richmond River Estuary N/P ratios may reflect a widespread trend of tidal rivers and estuaries becoming more groundwater-dominated and phosphorus-limited as coastal wetlands are drained for agriculture, grazing and development (Santos et al. 2013). The delivered loads of nutrients can enhance local primary productivity by as much as 50 % (Luo et al. 2014; Makings et al. 2014), however the percentage greatly depends on the nutrient in question (Makings et al. 2014).

The role of submarine groundwater discharge (SGD), the leakage of groundwater from aquifers into coastal waters, in coastal eutrophication has been demonstrated mostly for the North American and European coastlines, but poorly quantified in other regions. Global estimates of N inputs via SGD to coastal waters show that it has increased from about 1.0 to 1.4 Tg of nitrate ($\text{NO}_3\text{-N}$) per year over the second half of the 20th century. Since this increase is not accompanied by an equivalent increase of groundwater phosphorus (P) and silicon (Si), SGD transport of nitrate is an important factor for the development of harmful algal blooms in coastal waters (Beusen et al. 2013).

2.3.2 SGD as a Source of Metals to the Marine Coastal Ecosystems

Submarine groundwater discharge (SGD) and fluxes of several chemical compounds via SGD have received particular attention recently. However, studies of SGD impact on metal fluxes in the coastal ocean are scarce.

Studies on the flux of metals via SGD generally indicate that SGD is a significant source of metals for the marine environment. Barium and strontium, similarly to radium, have higher concentrations in groundwater than seawater. Barium fluxes via SGD were equal or higher than river barium fluxes (Moore 1997; Shaw et al. 1998; Santos et al. 2009) while Strontium fluxes via SGD were estimated to be comparable to its river flux (Basu et al. 2001). A comparison of both barium and strontium distribution in the subterranean estuary showed that concentrations of these elements differ relatively to salinity. Both are released to the estuary, however the extent of release is greater for barium than strontium (Charette and Sholkovitz 2006). Jeong et al. (2012) determined concentrations of selected trace elements (aluminium, manganese, iron, cobalt, nickel and copper) in groundwater and calculated their fluxes via SGD. The budget calculation showed that SGD was responsible for unusually enhanced concentrations of some trace elements in the summer in coastal seawater of the volcanic island Jeju. Charette et al. (2005) found elevated concentrations of dissolved iron and reduced manganese in groundwater in comparison to seawater. On mixing anoxic groundwater with oxic seawater large fractions of dissolved iron and manganese were oxidized and precipitated within the sediments. Thus, it was made clear that subterranean estuaries represent zones of substantial changes in the anoxic and oxic conditions impacting iron and

manganese distribution and co-precipitation with other metals (Charette and Sholkovitz 2002).

Results of some studies suggested that selected metal concentrations in groundwater exhibit nonconservative behaviours upon mixing with seawater (Charette and Sholkovitz 2002; Windom et al. 2006; Beck et al. 2007, 2009). For example dissolved cobalt and nickel showed nonconservative behaviour as oppose to the conservative behaviour of salinity upon the mixing of groundwater and seawater end-members (Beck et al. 2007). The processes that could influence behaviour of selected metals were mineralization of organic matter, manganese oxidation-reduction cycle, forming or dissolution of colloids and organo-metallic complexes (Sañudo-Wilhelmy et al. 2002; Baumann et al. 2006; Beck et al. 2010). On the other hand, there are elements like dissolved copper, lead, silver, aluminium, and manganese that did not show clear dependences in relation to salinity changes.

Submarine groundwater discharge and derived trace element (Cd, Co, Cu, Fe, Mo, Ni, Pb, V and Zn) loadings to the coastal sea were investigated along the coast of Majorca Island, Spain during 2010. It was established that brackish water discharges through the shoreline are important contributors to Fe, and Zn budgets of the near-shore waters. Furthermore the results of the study showed that SGD-derived elements are conditioned by the hydrogeological formations of the aquifer and discharge type. Thus, while rapid discharges through karstic conduits are enriched in SiO_2 and Zn, the large detrital aquifers of the island typically present enhanced concentrations of Fe. The study provides evidence that SGD is a major contributor to the dissolved pool of trace metals in the nearshore waters of Majorca (Travor-Sánchez et al. 2014). Similar study was carried out in the coastal area of Balearic Islands. The results show that SGD is a major pathway for delivering dissolved Fe ($4.1 \text{ mmol m}^{-1} \text{ d}^{-1}$) and nutrients into the nearshore waters. This work emphasizes the relevance of SGD-driven trace metal inputs in the regulation of near-shore phytoplankton communities of oligotrophic areas (Rodellas et al. 2014). The discharge can be modified by red-ox phenomena as concluded by McAllister et al. (2014). However, geochemical cycles occurring at the interface between terrestrial and marine groundwater are not well understood for most elements. This is particularly true of the transition metals, many of which have particular ecological relevance as micronutrients or toxicants. The distribution of nine dissolved metals (Fe, Mn, Mo, V, Co, Ni, Cu, Pb, and Al) was investigated in the Great South Bay, New York, USA accompanied by a simple kinetic and chemical separation of labile and organic-complexed metal species. Dissolved Mn showed marked sub-surface enrichment- suggestive of diagenetic remobilization. Dissolved Fe, however, was higher by more than three orders-of-magnitude in fresh groundwater ($90 \text{ }\mu\text{M}$) as compared to marine groundwater ($0.02 \text{ }\mu\text{M}$), and pH-mediated removal was evident as slightly acidic fresh groundwater (pH 6.8) mixed with marine groundwater (pH ~ 8.0). Dissolved Mo, Co, and Ni were primarily cycled with Mn, and highly elevated concentrations relative to bay surface waters were observed. High levels of dissolved Pb (up to 4250 pM) observed in the fresh groundwater were nearly quantitatively removed within the groundwater-seawater mixing zone. Dissolved Cu exhibited nonconservative removal, and was correlated with the

redox potential of the pore-waters. Substantial percentages (>15 %) of organic-metal species were only observed for Cu and Ni, suggesting that these complexes were not generally very important for the investigated metal cycling in the subterranean estuary. Kinetically labile species were observed for all metals examined except Cu and Pb, and represented an approximately constant proportion (between 10 and 70 %) of the total dissolved pool for each metal, indicating equilibrium between labile and non-labile species throughout the mixing zone. The nonconservative behavior observed for all metals examined in this study suggests that occurring reactions are vastly important to the source/sink function of permeable sediments. Thus studies seeking to quantify SGD-derived trace metal fluxes must take into account biogeochemical processes occurring in the subterranean estuary (Beck et al. 2010). In order to evaluate the role of SGD as a source of rare earth elements (REEs) in the coastal ocean, the SGD associated discharge of REEs were estimated into two semi-enclosed coastal bays in the southern coast of Korean peninsula. The mass balances of REEs proved that the REE fluxes were two to three orders of magnitude higher than those through other sources, such as diffusion from bottom sediments and atmospheric dust fallout. The neodymium (Nd) inputs from the two small coastal bays, Gamak Bay (148 km²) and Hampyeong Bay (85 km²), were estimated to be from 0.7×10^4 to 1.3×10^4 mol y⁻¹, which is 0.06–0.3 % of the total Nd flux from global rivers. In the study area coastal seawater was observed to have a substantially higher middle REE (MREE) due to a large discharge of highly enriched with MREE groundwater. The results suggest that the SGD-driven REE fluxes may contribute considerably to the global budget of REEs in the ocean (Kim and Kim 2014).

2.3.3 SGD as a Source of Mercury to the Marine Coastal Ecosystems

The mercury concentrations in groundwater and mercury flux associated with SGD have been a topic of several studies (Laurier et al. 2007; Bone et al. 2007; Black et al. 2009; Lee et al. 2011; Ganguli et al. 2012; Rahman et al. 2014). Laurier et al. (2007) measured the mercury concentrations not only in groundwater and seawater but also in blue mussels (*Mytilus edulis*) and concluded that high mercury concentrations were associated with strong seepage or long groundwater pathways. They also recognized SGD as a significant source of bioavailable mercury for mussels in the eastern part of the Seine Bay. Bone et al. (2007) observed high mercury release within the subterranean estuary, in the Waquoit Bay. They calculated that mercury flux via SGD is one order of magnitude greater than its atmospheric flux in the area. Black et al. (2009) calculated not only mercury concentrations and fluxes but also monomethylmercury concentrations and fluxes related to SGD on the California coast. They also proved that SGD could be

important source of both mercury and monomethylmercury to the coastal ecosystem similarly to Lee et al. (2011) and Ganguli et al. (2012).

Kwokal et al. (2014) assessed mercury speciation and distribution, for the first time, from the water, sediment, rock, soil and air of anchialine caves. They evaluated the origin and distribution of four mercury species—total (THg), reactive (RHg), dissolved gaseous mercury (DGHg) and monomethylmercury (MeHg) in water from Bjeajka cave and Lenga Pit in the Croatian Adriatic Sea from 2006 to 2011. Concentrations of all mercury species were elevated at both sites compared to adjacent seawater. The vertical distribution of MeHg concentrations followed that of THg, however the ratio of MeHg/THg above the Bjeajka halocline was drastically higher (up to 57 %) compared to MeHg proportion (1–2 %) below the halocline, which was similar to that of surface seawater. In sediment of Bjeajka, THg concentrations were considerably above concentrations in unpolluted Adriatic marine. The highest THg amounts found in soil and air were inside and in close proximity to Bjeajka, while THg in rock ($\leq 0.01 \text{ mg kg}^{-1}$) were below reported values for unaltered carbonates.

Ganguli et al. (2012) evaluated the influence of groundwater-seawater interaction on mercury dynamics in Maunalua Bay, a coral reef ecosystem located on the south shore of O'ahu, (Hawaii), by combining geochemical data with submarine groundwater discharge rates. During a rising tide, unfiltered total mercury (U-Hg_T) concentrations in seawater increase. It was attributed to an increase in suspended particulate matter at high tide. Approximately 90 % of mercury in groundwater was in the filtered ($< 0.45 \text{ }\mu\text{m}$) fraction. Groundwater discharge during a period of amplified SGD appeared to contribute to an increase in total mercury concentrations in filtered seawater and in unfiltered seawater. The larger magnitude of change in F-Hg_T relative to U-Hg_T suggests mercury complexation and/or solubility dynamics in seawater were altered by the addition of groundwater. The site specific Rn-222 derived SGD flux estimates and groundwater F-Hg_T concentrations were used to calculate mercury loadings. A reported weighted average Maunalua Bay groundwater mercury flux of $0.68 \pm 0.67 \text{ mol Year}^{-1}$ was obtained by combining the proportional flux of F-Hg_T from three distinct SGD zones, and place these results into a broader context by comparing and contrasting flux estimates from locations around the world. It was concluded that results from existing SGD studies should be evaluated to develop future sampling strategies. Szymczycha et al. (2013) investigated both groundwater flow and mercury concentrations in pore water and seawater at a seeping site of the Bay of Puck, southern Baltic Sea. Seawater samples were characterized by elevated Hg_{T_D} (total dissolved mercury) concentrations, as compared to concentrations in groundwater. High Hg_{T_D} concentrations in pore water of the uppermost sediment layers were attributed to seawater intrusion into the sediment. The relationship between Hg_{T_D} concentrations and salinity of pore water was nonconservative, indicating removal of dissolved mercury upon mixing seawater with groundwater. The mechanism of dissolved mercury removal was further elucidated by examining its relationships with both dissolved organic

matter, dissolved manganese (Mn II), and redox potential. It was concluded that groundwater is a factor that dilutes the mercury concentrations in pore water.

Rahman et al. (2014) investigated submarine groundwater discharge (SGD) and various solutes released with SGD, including Hg, in the Hampyeong Bay, a coastal embayment in the Yellow Sea, recently. It was established that SGD was the prime input source of Hg in the bay ($12\text{--}18 \text{ mol Year}^{-1}$), contributing 65 % of the total input. Atmospheric deposition was the second dominant source of Hg ($8.5 \pm 2.7 \text{ mol Year}^{-1}$), contributing 31 % to the total input. The results of the current study suggest that SGD can be a significant source of Hg in estuarine/coastal systems; therefore, estimating the coastal mass budgets of Hg must include SGD as a prime source of Hg (Rahman et al. 2014).

2.3.4 SGD as a Source of Dissolved Carbon Species to the Coastal Marine Ecosystems

There are studies documenting that SGD is an important source of both dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) to the marine environment (Cai et al. 2003; Goñi and Gardner 2003; Moore 2003; Santos et al. 2009; Kim et al. 2011; Liu et al. 2012; Smith and Cave 2012; Brodecka et al. 2013). Cai et al. (2003) indicated that DIC concentration in groundwater is few orders of magnitude greater than in local rivers on the South Carolina coast. Goñi and Gardner (2003) estimated DOC fluxes via SGD in the same study area, however these fluxes were smaller in comparison with DIC fluxes. DIC and DOC fluxes via SGD into the Okatee, South Carolina exceeded river inputs to the marsh (Moore 2003). Both Santos et al. (2009) and Smith and Cave (2012) indicated that DOC fluxes via SGD were a source of dissolved organic carbon to the study areas, which were the west coast of Florida, Kinvara and Aughinish Bays, West Ireland respectively. Liu et al. (2012) proved that in spite of small SGD rates and the associated DIC fluxes were high compared to rivers. The DIC flux ranged from 23 to 53 % of the river DIC flux.

Substantial influence of SGD on CO_2 and methane distribution in coastal waters off Australia was reported by Maher et al. (2014), while large CO_2 loads delivered to the coastal sea-water via SGD—by Macklin et al. (2014). The later study proved that melioration of the near-shore swamps for developing housing districts greatly enhanced the loads. In the former study, however the question was not answered whether methane is delivered with SGD or diffuses from subsurface sediments layers, as documented in studies carried out in the southern Baltic Sea (Reindl and Bolalek 2012).

Liu et al. (2014) measured the average SGD flux (marine plus terrestrial groundwater) into the southwest Florida Shelf (SWFS). The terrestrial groundwater flux was of the same order of magnitude as the local river discharge. Shelf-water total alkalinity (TALK) and dissolved inorganic carbon (DIC) concentrations could

not be explained by river inputs alone, suggesting a groundwater source. These T_{Alk} and DIC fluxes exceeded by a factor of 11–71 the combined input of local rivers, suggesting that SGD was the dominant source of T_{Alk} and DIC to the SWFS during 2009. SGD is an important component of the inorganic carbon budget for the coastal ocean.

Porubsky et al. (2014) used multiple techniques, including thermal infrared aerial remote sensing, geophysical and geological data, geochemical characterization and radium isotopes, to evaluate the role of groundwater as a source of dissolved nutrients, carbon, and trace gases to the Okatee River estuary, South Carolina. Thermal infrared aerial remote sensing surveys illustrated the presence of multiple submarine groundwater discharge sites in Okatee headwaters. Significant relationships were observed between groundwater geochemical constituents and ^{226}Ra activity in groundwater with higher ^{226}Ra activity correlated to higher concentrations of organics, dissolved inorganic carbon, nutrients, and trace gases to the Okatee system. A system-level radium mass balance confirmed a substantial submarine groundwater discharge contribution of these constituents to the Okatee River. Diffusive benthic flux measurements and potential denitrification rate assays tracked the fate of constituents in creek bank sediments. Groundwater geochemical data indicated significant differences in groundwater chemical composition and radium activity ratios between the eastern and western sides of the river; these likely arose from the distinct hydrological regimes observed in each area. Groundwater from the western side of the Okatee headwaters was characterized by higher concentrations of dissolved organic and inorganic carbon, dissolved organic nitrogen, inorganic nutrients and reduced metabolites and trace gases, i.e. methane and nitrous oxide, than groundwater from the eastern side. Differences in organic matter supply, and/or groundwater residence time likely contributed to this pattern. The contrasting features of the east and west sub-marsh zones highlight the need for multiple techniques for characterization of submarine groundwater discharge sources and the impact of biogeochemical processes on the delivery of carbon to coastal areas via submarine groundwater discharge.

Intensity of carbon export from some areas seem to be especially intensive. These include mangrove areas. A majority of the global net primary production of mangroves is unaccounted for by current carbon budgets. It has been hypothesized that this “missing carbon” is exported as dissolved inorganic carbon (DIC) from subsurface respiration and groundwater (or pore-water) exchange driven by tidal pumping. Concentrations and $\delta^{13}\text{C}$ values of DIC, dissolved organic carbon (DOC), and particulate organic carbon (POC), along with radon (Rn-222 , a natural submarine groundwater discharge tracer), were measured in a tidal creek in Moreton Bay, Australia. Concentrations and $\delta^{13}\text{C}$ values displayed consistent tidal variations, and mirrored the trend in Rn-222 in summer and winter. DIC and DOC were exported from, and POC was imported to, the mangroves during all tidal cycles. The exported DOC had a similar $\delta^{13}\text{C}$ value in summer and winter (about -30 parts per thousand). The exported $\delta^{13}\text{C}$ -DIC showed no difference between summer and

winter and had a $\delta^{13}\text{C}$ value slightly more enriched (similar to -22.5 parts per thousand) than the exported DOC. The imported POC had differing values in summer (similar to -16 parts per thousand) and winter (about -22 parts per thousand), reflecting a combination of seagrass and estuarine particulate organic matter (POM) in summer and most likely a dominance of estuarine POM in winter. A coupled Rn-222 and carbon model showed that 93–99 % of the DIC and 89–92 % of the DOC exports were driven by groundwater advection. DIC export averaged $3 \text{ g C m}^{-2} \text{ d}^{-1}$ and was an order of magnitude higher than DOC export, and similar to global estimates of the mangrove missing carbon (Maher et al. 2013). Carbon dioxide entering the coastal ecosystem with SGD is likely to influence pH of sea water there.

To better predict how ocean acidification will affect coral reefs, it is important to understand how biogeochemical cycles on reefs alter carbonate chemistry over various temporal and spatial scales. The study that quantifies the contribution of shallow pore-water exchange (as quantified from advective chamber incubations) and fresh groundwater discharge (as traced by Rn-222) to total alkalinity (TA) dynamics was carried out on a fringing coral reef lagoon along the southern Pacific island of Rarotonga over a tidal and diel cycle. Benthic alkalinity fluxes were affected by the advective circulation of water through permeable sediments, depending on the advection rate. Submarine groundwater discharge was a source of total alkalinity (TA) to the lagoon, with the highest flux rates measured at low tide, and an average daily TA flux of $1080 \text{ mmol m}^{-2} \text{ d}^{-1}$ at the sampling site. Both sources of TA were important on a reef-wide basis, although SGD acted solely as a delivery mechanism of TA to the lagoon, while pore water advection was either a sink or source of TA dependent on the time of day. This study describes overlooked sources of TA to coral reef ecosystems that can potentially alter water column carbonate chemistry. The authors suggest that pore-water and groundwater fluxes of TA should be taken into account in ocean acidification models in order to properly address changing carbonate chemistry within coral reef ecosystems (Cyronak et al. 2013). Szymczycha et al. (2014) ascent to the understanding that submarine groundwater discharge is an important yet poorly recognised pathway of material transport to the marine environment. They report on the results of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) concentrations and loads in the groundwater seeping into the southern Baltic Sea. Most of the research was carried out in the Bay of Puck (2009–2010), while in 2013 the study was extended to include several other groundwater seepage impacted areas situated along the Polish coastline. The annual average concentrations of DIC and DOC measured in the groundwater were equal to $64.5 \pm 10.0 \text{ mg C L}^{-1}$ and $5.8 \pm 0.9 \text{ mg C L}^{-1}$ respectively. The carbon specific flux into the Bay of Puck was estimated at $850 \text{ mg m}^{-2} \text{ year}^{-1}$. The loads of carbon via SGD were significant locally yet of limited importance for the entire Baltic Sea. It is concluded that the SGD derived carbon load to the Baltic Sea is an important component of the carbon budget, which gives the sea a firmly heterotrophic status.

Seidel et al. (2014) believes that seawater circulation in permeable coastal sediments is driven by tidal changes in hydraulic gradients. The resulting submarine groundwater discharge is a source of nutrients and dissolved organic matter (DOM) to the water column. Yet, little is known about the cycling of DOM within tidal sediments, because the molecular DOM characterization remains analytically challenging. One technique that can dissect the multitude of molecules in DOM is ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). To aim at a high resolution DOM analysis the authors studied the seasonal turnover and marine and terrestrial sources of DOM in an intertidal creek bank of the southern North Sea down to 3 m depth and link the biogeochemical processes to FT-ICR-MS data and the analyses of inorganic pore water chemistry, $\delta^{13}\text{C}$ of solid-phase extracted dissolved organic carbon (SPE-DOC), dissolved black carbon (DBC) and dissolved carbohydrates (DCHO). Increasing concentrations of dissolved Fe, Mn, P, total alkalinity, dissolved nitrogen, DOC and a concomitant decrease of sulfate along the seawater circulation path from the upper tidal flat to the tidal flat margin indicate continuous microbial activity. The relative increase of Si concentrations, unsaturated aliphatics, peptide molecular formulae and isotopically more ^{13}C -enriched SPE-DOC towards the tidal flat margin suggests that remineralization processes mobilize DOM from buried algal (diatoms) and microbial biomass. Pore water in sediments <100 cm depth contains ^{13}C -depleted SPE-DOC and highly unsaturated compounds which are probably derived from eroded peats, suggesting rapid removal of bioavailable marine DOM such as DCHO from the water column and selective enrichment of terrestrial DOM. DBC concentrations are highest in the discharging pore water close to the tidal creek suggesting that the intertidal flat is an important DBC source to the coastal ocean. Pore water DOM accumulating at the low water line is enriched in N and S. Seidel et al. (2014) hypothesize that this is partly due to DOM reacting with dissolved sulfide and ammonium which may increase the refractory character of the DOM, hence making it less bioavailable for in situ active microbes. Maher et al. (2015) indicated that a majority of the global net primary production of mangroves is unaccounted for by current carbon budgets. The author hypothesized that this “missing carbon” is exported as dissolved inorganic carbon (DIC) from subsurface respiration and groundwater (or pore-water) exchange driven by tidal pumping. They measured $\delta^{13}\text{C}$ of dissolved organic carbon (DOC), and particulate organic carbon (POC), along with radon (Rn-222, a natural submarine groundwater discharge tracer), in a tidal creek in Moreton Bay, Australia. Concentrations and $\delta^{13}\text{C}$ values displayed consistent tidal variations, and mirrored the trend in Rn-222 in summer and winter. DOC was exported from, and POC was imported to, the mangroves during all tidal cycles. The exported DOC had a similar $\delta^{13}\text{C}$ value in summer and winter (equal to -30 parts per thousand). The imported POC had differing values in summer (equal to -16 parts per thousand) and winter (similar to -22 parts per thousand), reflecting a combination of seagrass and estuarine particulate organic matter (POM) in summer and most likely a dominance of estuarine POM in winter. A coupled Rn-222 and carbon model showed that 89–92 % of the DOC exports were driven by groundwater advection. Szymczycha et al. (2014)

measured dissolved organic carbon (DOC) concentrations and loads in the groundwater seeping into the southern Baltic Sea. Most of the research was carried out in the period 2010–2013. The annual average concentrations of DOC in the groundwater ($5.8 \pm 0.9 \text{ mg C L}^{-1}$) were an order of magnitude smaller than DIC.

2.3.5 SGD Impact on Coastal Ecology

The “Olhos de Agua” beach is the only area on the South coast of Portugal where submarine freshwater seepages have been identified. Encarnação et al. (2014) investigated the influence of SGD on benthic community there. According to the authors submarine groundwater discharges have been documented as contributing to the biological productivity of coastal areas, through a bottom-up support to higher trophic levels. Nevertheless, the effects on the bottom levels of the coastal food web, namely the meiofauna, are still very poorly known. In their study, meiofauna assemblages in the area impacted by SGD were compared with the meiofauna from a similar area, but without SGD. Samples were taken in Spring and Summer 2011, under different hydrological regimes, aquifer recharge (after Winter) and dryness (after Spring), respectively. The major changes in the community were recorded at a seasonal level, with higher abundances and number of taxa in Spring, when compared to Summer. This may be explained by better sediment aeration during spring along with higher food availability from the sedimentation of spring phytoplankton blooms. Although no significant differences were detected by multivariate analysis on the meiofauna abundances between Control and Impact areas, pair-wise tests on the interactions between factors in number of taxa (S) and species richness (Margalefs d) suggested that the discharge of groundwater stimulated an increase in meiofauna diversity. Such effect can be observed between the meiofauna assemblages from impacted and control areas and also between periods with different discharge regimes (Spring and Summer) in the impacted area. These findings highlight the role that freshwater discharges from coastal aquifers have on meiofauna assemblages and suggest that SGD contribute to enhance the transfer of energy from the lower levels of the trophic web to upper levels.

Results obtained by Kotwicki et al. (2014) support the findings. The discharge of groundwater into the sea affects surrounding environments by changing the salinity, temperature and nutrient regimes. This should lead to the spatial effects of a submarine groundwater discharge (SGD) on the abundance and structure of the meiofaunal community. The effect was investigated by Kotwicki et al. (2014) in the shallow area of Puck Bay (Baltic Sea). Result of several field expeditions in the years 2009 and 2010 indicated that low-saline groundwater escapes into the bay from permeable, sandy, near-shore sediments. The results provided evidence that the discharge of groundwater has a clear effect on meiofaunal assemblages in the research area. This effect was reflected in a significant decline of certain meiofaunal taxa, mainly Nematodes and Harpacticoids, as well as in altered patterns of temporal distribution and small-scale (vertical) zonation of meiofaunal assemblages.

2.4 Methods Used to Measure SGD

Quantifying groundwater discharge to the seas is a challenging task since groundwater flow is temporally and spatially variable. Submarine groundwater discharge is a part of a complex hydrological and hydrogeological problem of water exchange between land and sea (Zekster and Dzyuba 2014). Subsurface water exchange between land and ocean involves two inter-related processes: submarine discharge into seas and oceans and seawater intrusion into the shore. Quantification of groundwater discharge is a very difficult task as it depends on many factors such as hydrogeological conditions, weather parameters shifts and human management of the coastal ecosystem (McCoy and Corbett 2009). Groundwater discharge to the coastal ecosystem can be estimated by a number of methods. However, each technique has certain limitations because of generalized assumptions and natural variability. Typically researchers address limitations of the implemented method at particular study area or use several techniques to detect and measure SGD. The most popular methods used to quantify SGD are: hydrodynamic method for calculating lateral groundwater flow (Zekster and Dzyuba 2014); methods based on investigation of the coastal drainage area (Pierkarek-Jankowska 1994; Peltonen 2002); methods based on investigation of the sea (Peltonen 2002); modelling (Burnett et al. 2006; Moore 2010), direct measurements (Burnett et al. 2006; Moore 2010) and tracer techniques (Burnett et al. 2001, 2006; Moore 2010).

2.4.1 Seepage Meter

The direct measurement of groundwater seepage rates can be made using manual “seepage meter”. First seepage meter was developed to measure water loss from irrigation canals by Israelsen and Reeve (1944). In 1977 Lee designed a seepage meter consisting of a 55-gallon (208 L) steel drum, fitted with a sample port and plastic collection bag (Fig. 2.3). The drum, in a shape of a chamber, is “open end down” inserted into the sediment. Groundwater seeping through the sediment displace water trapped in the chamber and forces it up through the port into the plastic bag. The actual volume of groundwater can be calculated using the end-member approach (Burnett et al. 2006; Szymczycha et al. 2012). The change in volume of water in the plastic bag over a measured time interval provides submarine groundwater discharge rate (Burnett et al. 2006; Taniguchi et al. 2006). There are several recommendation while using the seepage meter method. Typically, installation of few seepage meters is essential in order to average groundwater seepage rate because of temporal and spatial variability (Shaw and Prepas 1990a, b). The resistance of the tube and bag have to be minimized to prevent artefacts (Fellows and Brezonik 1980; Shaw and Prepas 1989; Belanger and Montgomery 1992). Covering the plastic bag may decrease the effects of surface water movements due to waves, currents or other activities (Libelo and MacIntyre 1994). Corbett and Cable (2000) suggested that

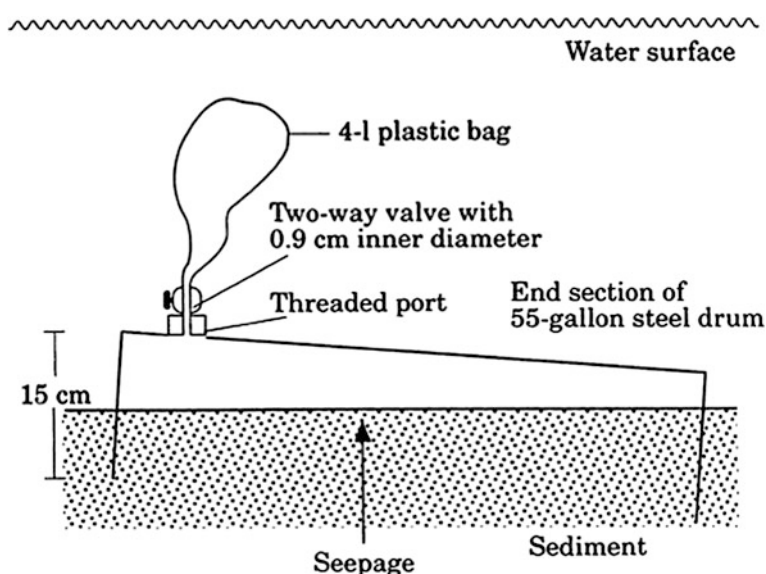


Fig. 2.3 Lee-type, manual seepage meter (Lee 1977). Water seeps through the sediment into the chamber and is forced into a plastic bag attached to a tube in the top of the drum. The change in volume over a measured time interval provides the groundwater seepage rate

seepage meter is a practical device for measuring groundwater rates, however it proves very labor intensive and time consuming.

This was a reason for developing automated seepage meters. Many types of automated seepage meters using different methods of water sensing were constructed (Burnett et al. 2006). Fukuo (1986), Cherkauer and McBride (1998), Boyle (1994) installed remote device from the surface of various water bodies. Others used: hydrothermal vents (Sayles and Dickinson 1990), ultrasonic measurements (Paulsen et al. 2001), heat-pulse devices (Krupa et al. 1998; Taniguchi and Fukuo 1993), continuous heat type automated seepage meters based on Granier method (Taniguchi and Iwakawa 2001) or dye-dilution seepage meters (Sholkovitz et al. 2003). The following conclusions and recommendations were suggested for using the seepage meter method: seepage meters (manual or automated) can give good results of groundwater discharge rates when used in a relatively calm environment (Burnett et al. 2006; Swarzenski and Izbicki 2009). In calm conditions seepage meters provide a direct measure of SGD, however the results are required to evaluate the pattern of SGD. These patterns most often relay on higher seepage at low tide and often, but not always, a decrease in seepage with increasing distance from the shore.

Seepage meters most often collect samples composed of both seeping groundwater and recirculated seawater. Contribution of both fractions can be separated applying the so called ‘end members approach’.

The end-member method is one of the hydrograph separation methods based on the use of geochemical end-member concentrations (Burnett et al. 2006). The end-member approach is based on the mass balance:

$$\begin{aligned} D_S &= D_G + D_{SW} \\ C_S D_S &= C_G D_G + C_{SW} D_{SW} \end{aligned}$$

where: C and D are the geochemical concentrations (C) and discharge rate (D). Subscripts S, G, SW represent respectively: collected sample, groundwater and seawater. Using the above two equations and the measured values of C_S , C_G , C_{SW} , D_S , the two unknowns, namely D_G and D_{SW} can be calculated. When salinity is used as a geochemical tracer, the separation of SGD into the seepage water components, fresh groundwater and recirculated seawater, is possible (Burnett et al. 2006; Szymczycha et al. 2012). Usually the end-member approach is used together with other methods. Good example of the end-member approach usage is described by Luek and Beck (2014). They indicated that the SGD ^{224}Ra end-member activity varied with seasonal pore water salinity fluctuations, representing end-member control on seasonal ^{224}Ra flux. Each Ra isotope suggested a different SGD volume flux, indicating that different nuclide regeneration rates can respond to and reflect different flow mechanisms in the subterranean estuary. The study designates that volume fluxes estimated using geochemical tracers are sensitive to SGD end-member variations and the end-member variability must be well-characterized for reliable SGD flux estimates.

2.4.2 Piezometers

In general, measurements of hydraulic conductivity and gradient of pore water combined with the Darcy Law characterise the principles of the method. Piezometer (usually multi-level piezometer nest) is inserted into the sediment in the groundwater impacted area. The groundwater potential can be measured at few depths (Freeze and Cherry 1979; Povinec et al. 2008) and the Darcian flux (q-groundwater discharge volume per unit area per unit time) can be calculated:

$$q = -Kdh/dL$$

where K is hydraulic conductivity and dh/dL is the hydraulic gradient in which h is the hydraulic head and L is distance.

The serious limitation of the method is the natural variability in seepage fluxes. Because of that obtaining the representative hydraulic conductivity is difficult. However, the problem can be solved by combining the method with seepage meter method in order to estimate hydraulic conductivity from obtained seepage fluxes and the hydraulic gradient (Taniguchi 1995).

Piezometers referred to as groundwater lances (Szymczycha et al. 2012) can be applicative devices for pore water samples collecting, in order to obtain a two dimensional distribution of SGD composition (Charette et al. 2005; Beck et al. 2007). This method allows collecting pore water samples with high resolution and consequently the biogeochemistry of groundwater impacted coastal aquifer can be better characterized (Charette et al. 2005; Charette and Sholkovitz 2006; Beck et al. 2007, 2010; Pempkowiak et al. 2010; Szymczycha et al. 2012).

2.4.3 Natural Tracers

The natural tracers approach has been used over a wide range of scales from estuaries to continental shelves to estimate SGD. Natural tracers present an integrated signal when they enter seawater via different pathways. The selected natural geochemical tracers should be highly enriched or decreased within groundwater of the studied aquifer, compared to other sources of water e.g. rivers or rain (Burnett et al. 2006). To assess SGD by applying the natural tracer approach several others conditions also need to be defined, including concentrations of the tracer, water and tracer sources and sinks, boundary conditions (e.g. the study area, volume) and resistance time of the surface water body. After determining the conditions, simple mass balances or box models for the system can be constructed and SGD can be assessed.

Radium isotopes (^{223}Ra , ^{224}Ra , ^{226}Ra , ^{228}Ra) are highly concentrated in coastal groundwater and show conservative mixing (after radiation decay is considered) in the course of hydrogeological processes. This makes them ideal chemical tracers to quantify SGD and water mass ages in coastal zones (Moore 2010; Luo et al. 2014). Thus, radium isotopes (^{223}Ra , ^{224}Ra , ^{226}Ra) and radon (^{222}Rn) have been fairly frequently exploited for groundwater discharge quantification (Burnett et al. 2006). ^{224}Ra and ^{223}Ra were adopted as tracers to qualify submarine groundwater discharge (SGD) in Tolo Harbor, a highly urbanized embayment in Hong Kong (Luo et al. 2014). SGD was estimated to be $1.2\text{--}3.0\text{ cm d}^{-1}$, lateral SGD was $5.7\text{--}7.9\text{ cm d}^{-1}$ and bottom SGD was $0.3\text{--}2.0\text{ cm d}^{-1}$. Fresh SGD was estimated to be $(2.1\text{--}5.5) \times 10^5\text{ m}^3\text{ d}^{-1}$ from the study area. The results expose that total SGD in this area represents about 1–2.4 % of the total sea water in the harbor and that fresh groundwater discharge is about 1.5–4 times larger than the total river discharge in the area. There is a good reason for radium isotopes and radon to be used to determine SGD. Relatively to the sea, they are highly enriched in salty and fresh coastal groundwater, thus even small fluxes of SGD can be identified through their strong signal.

Methane (CH_4), several natural radioactive isotopes (^3H , ^{14}C , U) and stable isotopes (^2H , ^3He , ^4He , ^{13}C , ^{15}N) have also been used as geochemical tracers in SGD studies (Moore 2010). It has been proven that SGD can be an important source of CH_4 to coastal waters (Bugna et al. 1996). Other studies (Cable et al. 1996) presented that ^{222}Rn and CH_4 concentrations not only show positive relationships with seepage meters measurements but are also closely related to salinity.

Some isotopes, like uranium can be removed from anoxic sediments via saline SGD (Burnett et al. 2006) and therefore can be used as SGD tracers. Basu et al. (2001) recognized SGD as an important supplier of strontium to global oceans based on their studies on Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ in the Bengal basin. Rahaman and Singh (2012) used strontium, $^{87}\text{Sr}/^{86}\text{Sr}$ and an inverse model to characterise SGD (combined freshwater and recycled seawater) with knowledge of seawater and river water end-member composition.

The natural tracer approach renders fine results in cases of big scale studies compared to the seepage meters or piezometers approach, however the challenging objective is identifying not only groundwater tracers but also all the other tracer sources and sinks in the system.

2.4.4 Infrared Imaging

Infrared thermography has been used to detect the location and spatial variability of SGD. The method exploits the temperature difference between surface water and groundwater during certain seasons and the fact that coastal and submarine springs can modify the colour and transparency of seawater (Mejías et al. 2012). The temperature of surface seawater (sea surface temperature-SST) can be detected by several methods like: NOAA-AVHRR, TERRA-MODIS and ARS/ENVISAT-AATSR satellite images (McClain et al. 1985; Reynolds and Smith 1994; Zavody et al. 1995; Mejías et al. 2012) which gives a suitable spatial and temporal resolution for detecting SGD. Infrared imaging is commonly used for SGD identification, but has not been applied to estimating the flux of SGD. Usually single images are not useful for quantifying SGD, they are quite appreciated in guiding field-work such as hydrogeologic and geochemical tracer based studies. The infrared image of the field site helped in planning field-work and in interpreting the hydraulic head data and seepage measurements (Mulligan and Charette 2006).

2.4.5 GIS Topology

Although many researchers agree on the importance of submarine groundwater discharge (SGD), it remains difficult to locate and quantify this process. A groundwater typology was developed based on local digital elevation models and compared to concurrent radon mapping indicative of SGD in the Niantic River, CT, USA (Rapaglia et al. 2015). Areas of high radon activity were located near areas of high flow accumulation lending evidence to the utility of this approach to locate SGD. The benefits of this approach are three-fold: fresh terrestrial SGD may be quickly located through widely-available digital elevation models at little or no cost to the investigator; fresh SGD may also be quantified through the GIS approach by multiplying pixelated flow accumulation with the expected annual recharge; and, as

these data necessarily quantify only fresh SGD, a comparison of these data with SGD, as calculated by Rn activity, may allow for the separation of the fresh and recirculated fractions of SGD. This exercise was completed for the Niantic River where SGD, as calculated by the GIS model, is $1.2 \text{ m}^3/\text{s}$, SGD as calculated by Rn activity is $0.73\text{--}5.5 \text{ m}^3/\text{s}$ while SGD as calculated via a theoretical approach is $1.8\text{--}4.3 \text{ m}^3/\text{s}$. The fresh, terrestrial SGD accounts for 22–100 % of total SGD in the Niantic River.

2.4.6 Hydrologic Approach

The hydrologic approach for determining SGD can be separated into two main methods. The first one is the mass balance method (Piekarek-Jankowska 1994; Peltonen 2002; Burnett et al. 2006) while the second is the Darcy's law calculation.

Simple water balance equation has been proven to be useful in some basins as an estimate of fresh SGD and can be described as:

$$P = E_T + D_S + D_G + dS$$

where P is precipitation, E_T is evapotranspiration, D_S is surface discharge, D_G is groundwater discharge and dS is the change in water storage (Burnett et al. 2006). The method is quite simple, but it has some limitations. First, precipitation, evapotranspiration, surface discharge, and the change in water storage need to be precisely determined. Secondly, the aquifer should be isolated by impermeable layers and discharging directly to the sea (Peltonen 2002). Thirdly, the limitation of the method is its implementation, only to formations, where the value of deep infiltration exceeds the accuracy of other components of the water balance equation (Zekster et al. 1973). It is said that water balance method is suitable to estimate the fresh groundwater discharge (Moore 2010).

The Darcy law is usually used together with other methods like piezometers, though the measurement of soil permeability and hydraulic head at few locations are essential. First, the field data are collected and then, SGD rate can be calculated with Darcy law.

2.4.7 Mathematical Models

Different kinds of models have been developed over the past 50 years and have become an invaluable tool for understanding subsurface flow in coastal aquifers (Li et al. 1999; McCOy and Corbett 2009). The mathematical and numerical simulations represent a form of differential equations for both: the flux and the transport phenomena. Analytical solutions to differential equations can be implemented in a limited number of cases, in which the aquifers are both homogenous and isotropic

and boundary conditions are simple whereas numerical models can be used in heterogeneous, anisotropic aquifers (Peltonen 2002). The benefits of numerical hydrogeologic models are that they provide the opportunity to simplify key features in aquifer systems and enable analysis of groundwater and saltwater movement under varying conditions (pre-pumping, pumping, future) that are not possible to estimate by other methods. Once the hydrogeologic framework has been described and effectively simulated, current and future SGD estimates can be evaluated by simply entering and changing model input parameters as they change with time. In general, hydrogeologic models are limited by the availability of data (e.g. groundwater pumping, hydraulic head, hydrostratigraphic, transmissivity) and must be validated periodically by other independent methods such as direct measurement and/or geochemical tracers.

There are several different model approaches, each characteristic to a certain study area or interactions between surface water, groundwater and seawater (Sadurski 2000; Massel et al. 2005).

The general suggestion for using numerical models to simulate groundwater flow is to implement the complementary numerical approach, in which the salinity distribution in the surface water is simulated by a three dimensional (3D) numerical model in order to determine the location and strength of SGD (Burnett et al. 2006). A good example of such model is PCFLOW3D, a 3D, non-linear baroclinic numerical model which was used in the groundwater impacted area of Donnalucata, Sicily (Burnett et al. 2006). The simulation results were in line with the observations of SGD-rates.

In the Baltic Sea region estimation of groundwater discharge from the territory of Poland was also calculated using analytical and numerical models (Kryza and Kryza 2006). The geological construction and hydrogeological conditions were characterized on the basis of regional elaboration and numerous publications. Then hydrogeological schema was set for area of water supply of the waterside zone of the sea. Four main aquifers were assigned and their parameters were characterized. Along cross-section above 500 km long analytic counts of direct inflow of groundwater to the Baltic Sea were performed. Numeric models for four representative areas were constructed indicating zones of groundwater direct inflow to the Baltic Sea. Calculations based on analytical and numerical models were reported comparable.

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