The Effect of Submarine Groundwater Discharge on the Ocean

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Key Words

nutrients, trace metals, carbon, limestone, river, estuary, radium

Abstract

The exchange of groundwater between land and sea is a major component of the hydrological cycle. This exchange, called submarine groundwater discharge (SGD), is comprised of terrestrial water mixed with sea water that has infiltrated coastal aquifers. The composition of SGD differs from that predicted by simple mixing because biogeochemical reactions in the aquifer modify its chemistry. To emphasize the importance of mixing and chemical reaction, these coastal aquifers are called subterranean estuaries. Geologists recognize this mixing zone as a site of carbonate diagenesis and dolomite formation. Biologists have recognized that terrestrial inputs of nutrients to the coastal ocean may occur through subterranean processes. Further evidence of SGD comes from the distribution of chemical tracers in the coastal ocean. These tracers originate within coastal aquifers and reach the ocean through SGD. Tracer studies reveal that SGD provides globally important fluxes of nutrients, carbon, and metals to coastal waters.

1. WHAT IS SUBMARINE GROUNDWATER DISCHARGE?

Submarine groundwater discharge (SGD) includes any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force (Burnett et al. 2003) (**Figure 1*a*,*b***). Where sediments are saturated, as expected in submerged materials, groundwater is synonymous with pore water; thus, advective pore water exchange falls under

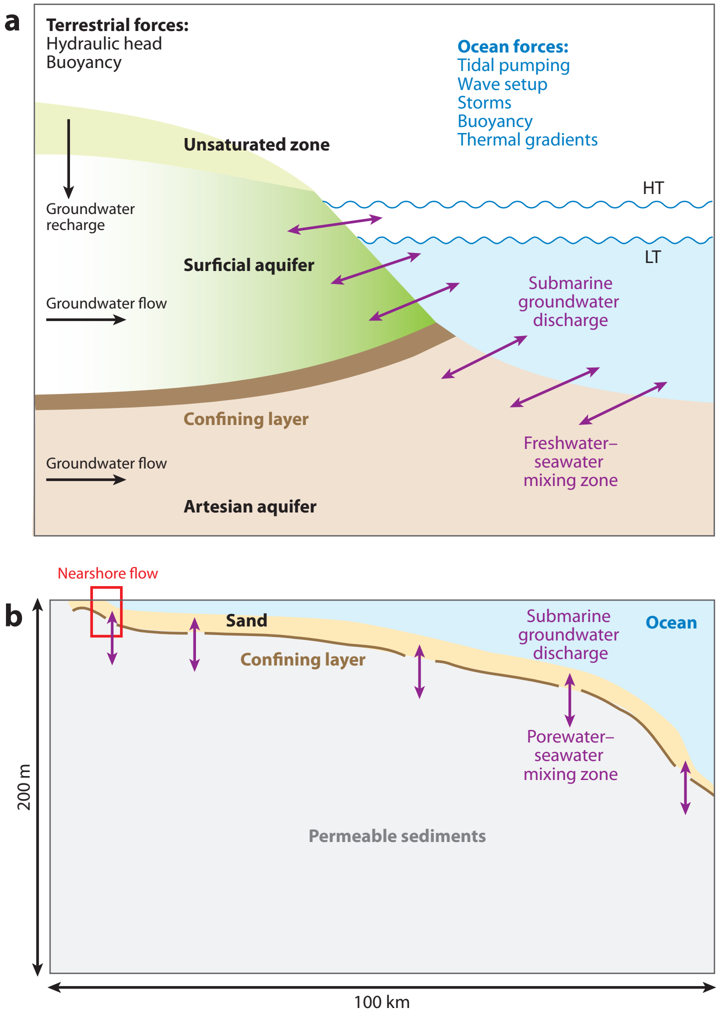


Figure 1

(*a*) Near the shoreline SGD is driven by a combination of terrestrial and ocean physical forces operating in a complex geological environment. The coastline may consist of fractured rocks, limestone, or clastic deposits. Sediments may be deposited in layers that have high hydraulic conductivity, such as coarse gravel and karstic limestone, or low hydraulic conductivity, such as mudstones. The latter are called confining layers. The interplay of the physical forces with the geology produces zones of mixing of terrestrial and sea water. These mixing zones are temporally and spatially variable due to the variety of forces, with each having different time and space scales. (*b*) Submarine groundwater discharge extends from the red box (labeled "Nearshore flow" and representing **Figure 1*a***) throughout the continental shelf. Here flow is driven by interactions of ocean forces with geothermal heating and overpressurized zones beneath discontinuous confining layers.

this definition of SGD. The definition of SGD does not include such processes as deep-sea hydrothermal circulation, deep fluid expulsion at convergent margins, and density-driven cold seeps on continental slopes.

Submarine groundwater discharge (SGD): the flow of water through continental margins from the seabed to the coastal ocean, with scale lengths of meters to kilometers, regardless of fluid composition or driving force

Advective flow: mass flow

Aquifer: permeable geological material saturated with water

An important aspect of SGD is the chemical reactions, often mediated by bacteria, occurring in coastal aquifers. The reactions include (1) desorption of ions from adsorbed sites due to increases in ionic strength, (2) dissolution and precipitation of carbonates, (3) remineralization of organic matter leading to carbon, nutrient, and metal release, and (4) oxidation-reduction reactions that produce and consume metal oxides, which may release or sequester other ions. The direct flow of groundwater into the ocean and the chemical reactions of meteoric and sea water mixtures within coastal aquifers are processes that have been largely ignored in estimating material fluxes between the land and the sea.

Processes associated with SGD have been slow to receive attention from mainstream hydrologists, oceanographers, and geochemists. Early workers recognized that these processes may be important in the formation of dolomite (Hanshaw et al. 1971, Badiozamani 1973) and could constitute a source of nutrients for coral reefs and coastal communities (Johannes 1980), but there was little appreciation of the process in other settings or of its global significance.

Two issues must be considered: (1) What is the flux of freshwater due to SGD? (2) What are the material fluxes due to chemical reactions of sea water and meteoric water with aquifer solids? Hydrologists are primarily concerned with the first question as it relates directly to the freshwater reserve in coastal aquifers and salinization of these aquifers through sea water intrusion. Oceanographers are also interested in this question because there may be buoyancy effects on the coastal ocean associated with direct input of freshwater from the bottom. Chemical, biological, and geological oceanographers are more concerned with the second question as it relates directly to alteration of coastal aquifers and nutrient, metal, and carbon inputs to the ocean (and in some cases removal from the ocean).

We now recognize that SGD is an important component of the hydrological cycle. The total flux of SGD to the Atlantic Ocean is similar in volume to the riverine flux (Moore et al. 2008). Because SGD often contains higher concentrations of nutrients, carbon, and metals than river water (**Table 1**), the high fluxes suggest SGD is probably more important than rivers in the oceanic budgets of these materials. Local studies have found that SGD provides a major source of nutrients to salt marshes, estuaries, coral reefs, and other communities near the shoreline and on the continental shelf. For example, it is estimated that the fluxes of nitrogen and phosphorus to the South Carolina shelf from SGD exceed fluxes from local rivers (Crotwell & Moore 2003, Krest et al. 2000, Moore et al. 2002). Offshore Patos Lagoon, Brazil, SGD may represent as much as 55% of the total nitrogen flux to the adjacent shelf environment (Niencheski et al. 2007). Similar results have been obtained in South Korea (Kim et al. 2003), the Philippines (Taniguchi et al. 2008), and Thailand, where Burnett et al. (2007) estimated that SGD to the upper Gulf of Thailand carries more nitrogen to the Gulf than the Chao Phraya River, the largest source of surface water, which is heavily polluted during its passage through Bangkok. Bacteria are also components of SGD. Boehm et al. (2004, 2006) measured high levels of fecal indicator bacteria in SGD along California beaches.

2. SGD LITERATURE

The SGD literature has grown rapidly in the current decade. A search for the term "submarine groundwater discharge" on the Web of Science in March 2009 (Thompson Reuters, **http://apps.isiknowledge.com**) found 0–4 papers per year during the 1980s and 1990s and 79 in 2008 (**Figure 2**). Admittedly, such a search is not quantitative because the term submarine

Table 1 Examples of the composition of submarine groundwater discharge (SGD) from monitoring wells

Location	Sediment type	Depth (m)	Salinity	NO_x (μM)	NH_4 (μM)	PO_4 (μM)	DIC (mM)	DOC (μM)	Fe (μM)	^{226}Ra (dpm L^{-1})	^{228}Ra (dpm L^{-1})	Reference
Okatee, South Carolina	Marsh	5 4	34.0 35.0	1.8 1.4	108 198	6.1 39	3.51 22.7	381 1890	71 127	1.9 6.4	14.9 17.3	Moore et al. 2006
North Inlet, South Carolina	Marsh	1.2 3.7 0.6	0.2 26.7 34.1	—	34 70 92	0.5 2.7 1.3	2 12	—	—	0.4 17.4 7.7	0.4 5.6 9.0	Krest et al. 2000, Cai et al. 2003
Sapelo Island, Georgia	Hammock	4 1.5	22.0 23.5	—	32 61	—	2.96 7.85	853 676	—	15.5 10.0	4.7 16.4	W.P. Porubsky, S.B. Joye, W.S. Moore, K. Tunca, C. Meile, unpublished paper
Patos Lagoon, Brazil	Sand	1 1	2.3 30.7	1.7 1.1	8 12	8.0 4.2	—	—	6.8 81	0.1 0.7	0.6 2.6	Windom et al. 2006, Niencheski et al. 2007
Long Bay, North Carolina	Sand, mud	4	35.0	0.5	91	6.3	—	250	—	5.5	8.7	Moore et al. 2002
Hilton Head, South Carolina	Floridan aquifer limestone	37 70	0.1 21.2	—	32 154	3.9 2.7	—	—	—	0.2 2.1	0.1 2.3	Crotwell & Moore 2003

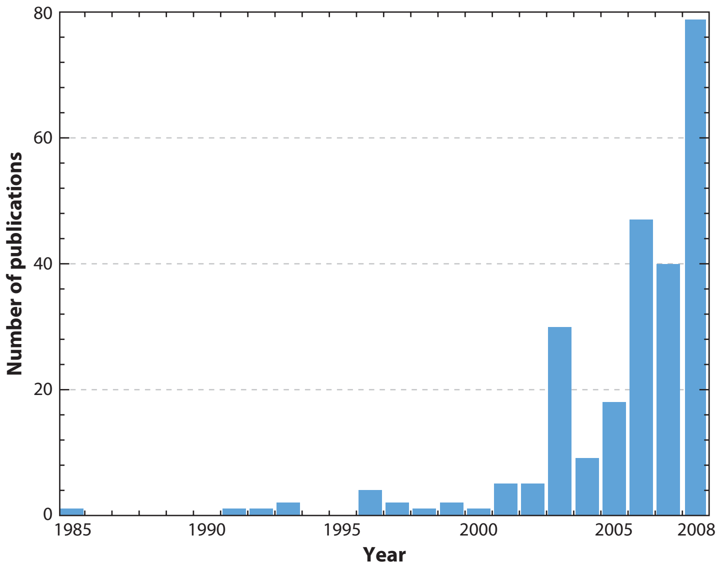


Figure 2

There has been an explosion of the SGD literature in the past 10 years. This is a record of published articles that use the key word "submarine groundwater discharge" as indexed by the Web of Science.

groundwater discharge may not appear in the indexing of all relevant papers. Nevertheless, this search illustrates the rapid emergence of this field.

These papers include numerous studies reporting measurements and measurement techniques at sites worldwide, studies of modeling SGD, inferences of the importance of SGD in current and past times, and reviews of the topic. This interest in SGD derives primarily from the recognition of its importance in delivering not only freshwater to the ocean but also nutrients, metals, carbon, and bacteria.

A recent editor's note in the *Hydrogeology Journal* (Kazemi 2008) points to the "absence of hydrogeologists" in SGD studies. He notes that the recent literature explosion contains few papers written by hydrogeologists and urges them to become more involved in this emerging topic.

There is a recent book (Zektser et al. 2007), several recent review articles (Burnett et al. 2003, 2006; Slomp & Van Cappellen 2004; Swarzenski 2007; Charette et al. 2008), and three recent journal special issues (*Biogeochemistry* 66, pp. 1–202, 2003; *Marine Chemistry* 109, pp. 250–408, 2008; *Estuarine Coastal and Shelf Science* 76, pp. 455–552, 2008) that focus on this topic. Discussion of each paper in the entire SGD literature base is impossible in this review. Instead, I shall focus on studies that represent particular regions and processes and discuss selected papers in detail. I will emphasize some processes that are not well represented in the current literature.

3. HISTORICAL ACCOUNTS OF SGD

3.1. Mediterranean Region

People in ancient times recognized SGD and used it as a source of freshwater. Kohout (1966) noted that in *Natural History*, Pliny, the elder (23 to 79 A.D.) provided an extensive list of submarine springs in the Black Sea and in the Mediterranean Sea from Greece to Spain. Also according to Kohout (1966), the Roman geographer Strabo (63 B.C. to 21 A.D.) described a submarine spring

4 km offshore from Latakia, Syria, where spring water was collected from a boat by lowering a lead funnel attached to a leather tube. Buoyant freshwater flowed up through the tube where it was collected and utilized as a source of freshwater.

Artesian flow: mass flow from a confined aquifer to the subareal or submarine ground surface

3.2. Hawaiian Fish Ponds

Fish ponds on the Hawaiian Islands are an early example of the influence of SGD on coastal populations. As early as the fourteenth century, ancient Hawaiians constructed walls of sand and coral fragments to partially enclose areas on the coast for raising fish. As Kikuchi (1976) describes these structures, called loko pu'uone:

> The permeability of the walls allowed seawater to percolate through, while freshwater springs along the shore provided internal seepage. Because of their proximity to the sea and because of their water salinity, loko pu'uone resembled natural estuarine habitats. Their fish were preferred as delicacies because the native Hawaiians believed that brackish to salt water produced a more savory fish than did freshwater.

Kikuchi (1976) noted that although the groundwater seepage carried nutrients to the ponds, the quantity of fish raised could not provide a substantial source for the general population. Instead, this aquacultural system symbolized the chiefly right to conspicuous consumption and was a manifestation of the chief's political power and his ability to control and tap his resources.

3.3. Southeastern Coast of North America

The Upper Floridan aquifer (UFA) in SE South Carolina and adjacent Georgia is a confined artesian aquifer composed of highly permeable limestone. Prior to the initiation of pumping from the aquifer, which began in about 1885, the flow paths in the UFA are thought to have been generally eastward, converging around Port Royal Sound (Smith 1988). Discharge from the UFA was thought to occur under Port Royal Sound and the coastal Atlantic Ocean in this region. Indeed, sixteenth-century settlers drew freshwater from shallow "barrel wells" along shorelines, where only full strength sea water exists today (DePratter & South 1995).

4. WHAT DRIVES SGD?

4.1 Early Studies of Drivers

Early attempts to evaluate the behavior of freshwater encountering sea water in coastal aquifers relied on the classic Ghyben–Herzberg relationship (Badon-Ghyben 1888, Herzberg 1901). This relationship was based on the elevation of the water table and the density difference of fresh and sea water. It predicted the position of the interface between freshwater and sea water in coastal aquifers; mixing of fresh and salt water was not allowed. Later workers recognized that this relationship represented an unrealistic hydrostatic situation, because a truly stable hydrostatic distribution would lead to saline groundwater everywhere below sea level (Burnett et al. 2003). Dupuit (1863) recognized that there must be a dynamic equilibrium supported by freshwater recharge. He approximated the hydrostatic distribution of fresh and salt water by assuming the flow of groundwater was entirely horizontal and the saltwater/freshwater interface was a no-flow boundary, which intersected the shoreline, and the salty groundwater was stationary. The Dupuit–Ghyben–Herzberg relationship led to the awkward conclusion that all the freshwater recharge had to escape exactly at the shoreline (Burnett et al. 2003). Hubbert (1940) introduced the concept of an outflow gap that allowed the interface to intersect the sea floor at some distance from shore, producing a discharge zone of intermediate salinity. Refinements of this concept by Glover (1959) and Henry (1964) led to techniques to calculate the size of this gap and the position of the saltwater/freshwater interface; however, they led to the mistaken impression that SGD is entirely freshwater derived from land (Burnett et al. 2003).

Cooper et al. (1964) developed a hypothesis to explain the mixing zone of fresh and salt water, or zone of dispersion, and the continuous circulation of seawater observed in various field studies, and attempted to quantify the amount of mixing due to tidal fluctuations. Henry (1964) advanced the concepts further by quantitatively corroborating Cooper's hypothesis and used an advection-diffusion equation to account for hydrodynamic dispersion.

These early studies made assumptions that simplified the computational techniques but led to unrealistic situations. In an estimate of groundwater flow using Darcy's law, aquifer permeability is assumed constant. However, coastal aquifers consist of various mixtures of interbedded sand, silt, and clay or of fractured rocks that are rarely homogenous. Thus, vertical and horizontal permeability may vary by orders of magnitude. Freshwater recharge is rarely stable and may lead to considerable lags between recharge and discharge (Michael et al. 2005). Perhaps most important, ocean forces were rarely considered in these early studies. We use the term sea level, but the sea is rarely level. Waves, tides, winds, and seasonal changes in the wind field and ocean heat budget cause short- and long-term changes of sea level. These changes may be amplified during storm events. Most hydrologists working from land failed to recognize the important effects of the ocean.

4.2. Numerical Methods

Numerical models enabled more realistic hydrodynamics to be studied. The early models allowed the saline groundwater to circulate in response to hydraulic gradients but still prohibited flow across the moving interface. Modern, two-phase models recognize that water can cross isohalines; these models allow density-driven circulation as well as flows driven by other hydraulic gradients onshore (Li et al. 1999, Bear et al. 1999, Wilson 2005). There remains a serious lack of data, especially aquifer permeability, to calibrate and verify these models. In addition, salt dispersion is usually incorporated in a single parameter, although it is recognized that numerous processes can cause dispersion on a wide range of time and space scales (Burnett et al. 2003). Ocean forces continue to be simplified in these models.

4.3. Other Approaches

An entirely different approach to submarine groundwater discharge was pioneered by Kohout (1965), who recognized that geothermal heating could drive cyclic flow of sea water through coastal aquifers. He postulated that at depths of 500–1000 m, the highly-permeable Floridan aquifer in western Florida was in hydraulic contact with the Gulf of Mexico. Cool sea water (5–10°C) entering the deep aquifer would be heated as it penetrated toward the interior of the platform. The warm water would rise through fractures or solution channels, mix with fresh groundwater, and emerge as warm springs along the Florida coast (**Figure 3**). Kohout (1967) presented temperature profiles in deep (~1000 m) wells that revealed a negative horizontal gradient from the interior of the Florida platform (40°C) to the margin (16°C), where sea water penetration was hypothesized. Wells near the margin displayed negative vertical temperature gradients at depths of 500–1000 m; i.e., in some cases temperature decreased with depth. These observations were consistent with the proposed large-scale cycling of sea water–groundwater mixtures through the aquifer.

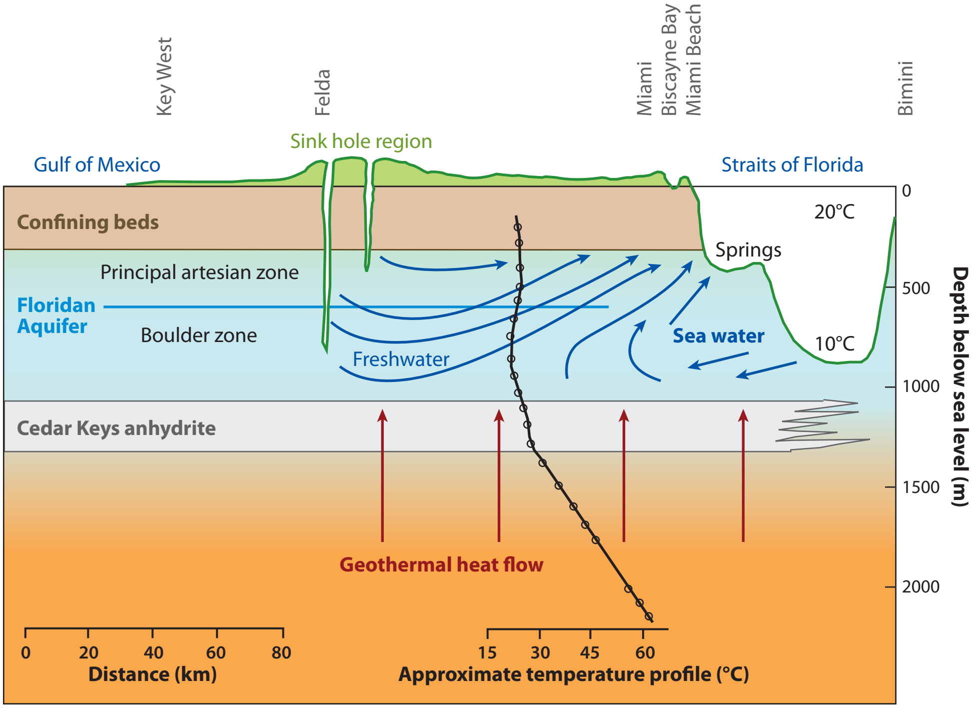


Figure 3

Kohout (1965) envisioned a flow system below the Florida platform where the Floridan aquifer was in contact with cold water in the Florida Straits. As this water entered the aquifer, it would become buoyant due to geothermal heating. The rising sea water would meet freshwater derived from the central platform. The mixed waters should discharge as submarine springs at the platform margin. Redrawn from Kohout (1965).

5. METHODS TO ASSESS AND MEASURE SGD

Attempts to detect and quantify SGD have focused on several approaches: (1) thermal images to detect SGD, (2) electromagnetic techniques to discern subsurface porosity and/or pore water salinity, (3) seepage meters to directly measure discharge, (4) tracer techniques to integrate SGD signals on a regional scale, and (5) groundwater flow modeling. There is an extensive review article on methods to measure SGD (Burnett et al. 2006); therefore, I will provide only a synopsis.

5.1. Thermal Imaging

You have probably encountered SGD walking along the beach barefooted. Cold wet sand on a warm day may represent a site of SGD, where cool water is discharging from an aquifer having a temperature lower than the ocean. The same principle may be applied to aerial surveys using infrared images. In the summer at low tide, sites of SGD appear as colder regions (e.g., Roxburgh 1985). These images provide an excellent view of the coastal area affected by SGD. Johnson et al. (2008) determined correlations between temperature, salinity and nutrients in water samples and used these correlations to translate infrared images of the thermal field to distributions of silica, nitrate and phosphate in Hawaii coastal waters. The area imaged included ancient fish ponds, where cool, nutrient-rich waters emerged.

5.2. Electromagnetic Techniques

The electrical resistivity of sediments is a function of porosity and fluid conductivity. On beaches the resistivity is measured by driving conductivity probes into the sediment at various distances from electrodes attached to an electric generator. The ratio of current applied to induced voltage in the conductivity probes is a measure of the bulk ground conductivity, the inverse of resistivity (Stieglitz et al. 2008). This method may also be used in coastal waters, where a generator and receivers are towed near the sea bed (Hoefel & Evans 2001). Permeable sediments containing sea water have low resistivity. As salinity decreases, resistivity increases. This method is very useful in mapping subsurface zones of brackish or freshwater.

Tracer (of water flow): chemical component with large concentration difference between source and receiving waters

5.3. Direct Measurement by Seepage Meter

Seepage meters are designed to sample SGD as it emerges from the bottom sediment. The simplest seepage meters are 0.25 m^2 benthic chambers with a small plastic bag attached to a port on the top to collect the SGD (Lee 1977). Initially, the bag is partially filled with sea water. The bags are replaced at hourly or longer intervals; volume changes in the bags represent fluxes of water out of or into the sediment. More advanced seepage meters are based on heat pulse (Taniguchi & Fukuo 1993) and acoustic Doppler (Paulsen et al. 2001) technologies or dye dilution (Sholkovitz et al. 2003). These meters can record SGD over tidal cycles or longer.

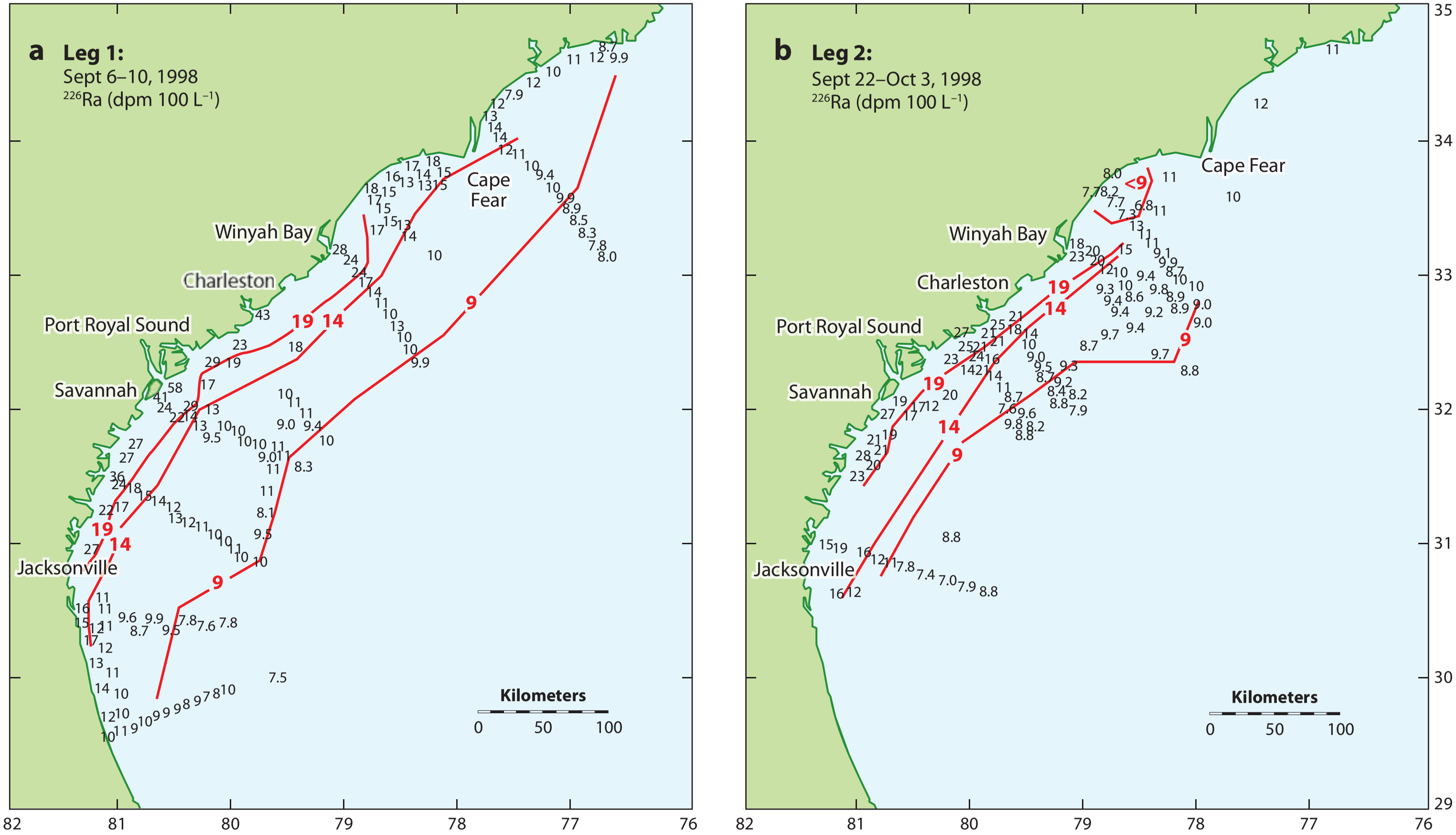
In calm conditions seepage meters provide a direct measure of SGD. Discharge rates from numerous meters are required to evaluate the pattern of SGD. These patterns often, but not always, include higher seepage at low tide and a decrease in seepage with increasing distance from the shoreline. Caution is required in using seepage meters during rough conditions when they may be dislodged or biased by currents and waves (Shinn et al. 2002, 2003; Cable et al. 2006).

5.4. Tracer Techniques

Measurement of a range of tracers at the aquifer–marine interface and in the coastal ocean provides integrated flux estimates of discharge not possible by other means. Temperature is one tracer. Other tracer techniques utilize chemicals (often naturally occurring radionuclides in the uranium and thorium decay series) that have high concentrations in groundwater relative to coastal waters and low reactivity in the coastal ocean. These techniques require evaluation of other sources of the tracer and measurements of the residence time of the coastal water. With this information, an inventory of the tracer in coastal waters is converted to an offshore flux of the tracer. This tracer flux must be replaced by new inputs of the tracer from SGD. To convert the tracer flux to a flux of SGD, the concentration of the tracer in SGD must be known. Swarzenski (2007) and Charette et al. (2008) provide recent reviews of this topic for U-Th series nuclides.

The discovery of high activities of ^{226}Ra (half life = 1600 years) in the coastal ocean (Moore 1996) that could not be explained by input from rivers or sediments, coupled with high ^{226}Ra measurements in salty coastal aquifers, led to the hypothesis that SGD was responsible for the elevated activities in the coastal ocean. These elevated ^{226}Ra activities, which have now been measured along many coasts, provide the primary evidence for large SGD fluxes to the coastal ocean. These distributions may change seasonally, indicating differences in SGD fluxes (Moore 2007) (**Figure 4**).

There are good reasons why radium isotopes are closely linked to SGD studies. Because radium is highly enriched in salty coastal groundwater relative to the ocean, small inputs of SGD can be recognized as a strong signal. In many cases this signal can be separated into different SGD


a Leg 1:
Sept 6–10, 1998
226Ra (dpm 100 L−1)
b Leg 2:
Sept 22–Oct 3, 1998
226Ra (dpm 100 L−1)
Cape Fear
Winyah Bay
Charleston
Port Royal Sound
Savannah
Jacksonville
Kilometers
0 50 100
82 81 80 79 78 77 76
35 34 33 32 31 30 29

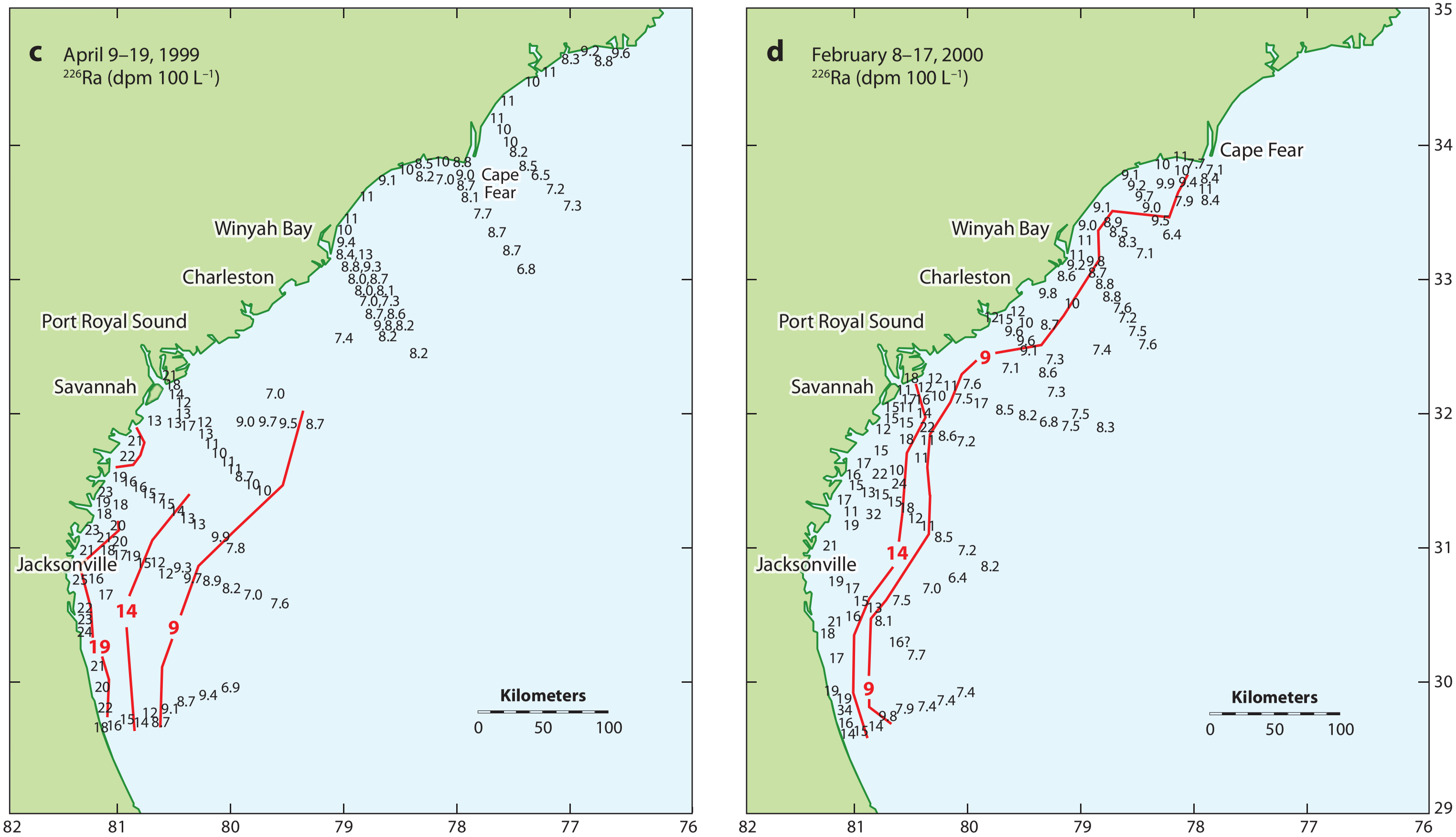


Figure 4

The distribution of ^{226}Ra in South Atlantic Bight surface waters shows a strong seasonality. (*a*) The distribution during early September was similar to prior studies in the summer with high enrichments (>14 dpm 100 L^{-1}) throughout the inner shelf. (*b*) By late September the high activities measured in Long Bay (between Cape Fear and Winyah Bay) had diminished to open ocean values, but high values prevailed to the south. (*c*) In April the distribution was similar to late September. (*d*) Slightly higher values than in April were present in Long Bay in February. From Moore (2007).

components using ^{228}Ra (half life = 5.7 years) and ^{226}Ra, the two long-lived Ra isotopes (Moore 2003). The short-lived Ra isotopes, ^{223}Ra (half life = 11 days) and ^{224}Ra (half life = 3.66 days) are useful in evaluating the residence time or mixing rate of estuaries and coastal waters (Moore 2000a, 2000b; Moore et al. 2006) and estimating radium fluxes. At steady state these fluxes must be balanced by fresh inputs of Ra to the system. If other sources of Ra can be evaluated, the Ra flux that must be sustained by SGD can be evaluated. By measuring the Ra content of water in the coastal aquifers, the amount of SGD necessary to supply the Ra is determined. SGD fluxes of other components are determined by measuring their concentrations in the coastal aquifer or by determining relationships between the component and Ra and multiplying the component/Ra ratio by the Ra flux (Moore et al. 2002).

Other radiotracers also provide evidence of SGD and means to estimate the fluxes. The immediate daughter of ^{226}Ra, ^{222}Rn (half life = 3.8 days), is highly enriched in fresh and salty groundwater. Cable et al. (1996) reported high ^{222}Rn and ^{226}Ra activities in subsurface coastal waters in the Gulf of Mexico. They modeled the measured ^{222}Rn and ^{226}Ra distributions and water residence times to derive fluxes of ^{222}Rn and ^{226}Ra. They estimated that the fluid flux to this 620 km^2 area was comparable to the flow of the largest river in Florida. They also pointed out that the distribution of high ^{222}Rn activities in Florida shelf waters is closely related to the distribution of known submarine springs.

High ^{222}Rn activities in coastal waters reveal sites of significant SGD input (Fanning et al. 1982; Burnett & Dulaiova 2003, 2006; Stieglitz 2005). Because ^{222}Rn can be measured continuously in situ, patterns of SGD through tidal cycles may be evaluated and compared to results from seepage meters (Taniguchi et al. 2008). To estimate SGD fluxes via ^{222}Rn, losses to the atmosphere must also be considered. In addition, other tracers such as methane (Bugna et al. 1996), helium (Top et al. 2001), and Si (Hwang et al. 2005) have been applied to SGD studies.

5.5. Hydrologic Models

Simple water balance calculations have been useful in some situations as an estimate of the fresh groundwater discharge. Hydrogeologic, dual-density, groundwater modeling can also be conducted as simple steady-state (annual average flux) or non-steady-state (requires real-time boundary conditions) methods (Wilson 2005). A lack of data of sediment permeability seriously affects the models. Unfortunately, at present neither approach generally compares well with seepage meter and tracer measurements, often because of differences in scaling in both time and space (Burnett et al. 2006). Apparent inconsistencies between modeling and direct measurement approaches may arise because different components of SGD (fresh and salt water) are being evaluated or the models do not include transient terrestrial (e.g., recharge cycles) or marine processes (e.g., tidal pumping, wave set up, storms, thermal gradients, seasonal sea level changes) that drive part or all of the SGD.

6. MODES OF SGD

6.1. Shoreline Flow, the Subterranean Estuary

In the simplest case, fresh groundwater flows through an aquifer driven by an inland hydraulic head to the sea. As it nears the sea it encounters salty groundwater that has infiltrated from the ocean (**Figure 1*a***). Because the density of fresh groundwater is lower than salt water, it tends to flow above the salt water. Simple models predict that the discharge of such mixtures will be restricted to a few hundred meters from shore in such homogenous unconfined aquifers.

However, coastal sediments often comprise a complex assemblage of confined, semiconfined (e.g., subterranean estuary), and unconfined aquifers. Simple models do not consider the anisotropic nature of the coastal sediments, dynamic processes of dispersion, tidal pumping, wave set-up, thermal gradients, inverted density stratification, and sea level change, or the non-steady-state nature of coastal aquifers due to groundwater mining (Moore 1999). Flow through these systems represents both terrestrial and marine forces and components. Because the timescales of these forcing functions vary over a wide range, SGD may appear to be out of phase with expected forces (Michael et al. 2005).

Subterranean estuary: a semiconfined coastal aquifer that has a clear connection to the sea and within which sea water is diluted with meteoric water

Shear flow: mass flow through submarine sediments driven by currents and waves with scale lengths of cm

In the real world, fresh groundwater flowing toward the sea encounters an irregular interface where mixing of the fluids is driven by diffusion and dispersion augmented by ocean forces. This pattern of two-layer circulation and mixing is similar to that observed in many surface estuaries, leading to the term subterranean estuaries (Moore 1999). Dispersion along the interface may be enhanced by tidal forces operating in an anisotropic medium. The permeability and preferential flow paths may be changed by chemical reactions within the aquifer. Precipitation of solids can restrict or seal some paths, while dissolution will enlarge existing paths or open new ones (Hanshaw et al. 1971). The fluid expelled to the sea may be quite different chemically from the freshwater or sea water that entered.

Viewed from the ocean side, the coastline appears dominated by waves and tides. These effects were recognized by Riedl et al. (1972), who coined the term "subtidal pump." This pump, driven by swash and tidal water level changes, flushes water through permeable sediments. Riedl and his colleagues estimated that 1.2×10^{12} m^3 y^{-1} (equivalent to 3% of world river flow) moves through the sandy beaches of the world.

6.2. Shear Flow

In sandy sediments where bottom currents are sufficiently strong to create ripples, wave-generated pressure gradients may drive pore water exchange, technically a type of SGD. In the ripple troughs, water penetrates into the sediment and flows on a curved path toward the ripple crests, where the pore water is released (Huettel & Gust 1992). The ocean water carries organic matter and oxygen into the sediment, creates horizontal concentration gradients that can be as strong as the vertical gradients, and increases the flux of pore water constituents across the sediment–water interface (Huettel et al. 1998). The depth of the sediment layer that is affected by this advective exchange, sometimes called skin flow, is related to the size and spacing of the ripples and, in homogenous sediment, reaches down to approximately two times the ripple wavelength, but usually no more than 5–10 cm depth. It has been estimated that, worldwide, waves filter a volume of 97×10^{12} m^3 y^{-1} through the permeable shelf sediments (Riedl et al. 1972, Riedl & Machan 1972).

Although shear flow falls within the current technical definition of SGD, I think this process should be considered separately. The conventional techniques that quantify SGD do not recognize shear flow because seepage meters block waves and currents, concentrations of SGD tracers released by shear flow are expected to be low, and current SGD models do not consider this process. Instead of being a type of SGD, I think the fluxes due to shear flow are better understood as a component of benthic respiration (Jahnke et al. 2000, Rao et al. 2008). Therefore, I propose that we change the definition of SGD to the following:

> SGD is the flow of water through continental margins from the seabed to the coastal ocean, with scale lengths of meters to kilometers, regardless of fluid composition or driving force.

This new definition eliminates shallow bioturbation and bioirrigation as well as shear flow.

6.3. Deep Pore Water Upwelling

DPU: deep pore water upwelling

Confining layer: a low-permeability layer in an aquifer

Piezometric head (of an aquifer): the height to which a column of water will rise in a tightly cased well drilled into the aquifer

Most studies of SGD have focused on sites near the shoreline (**Figure 1*a***). Section 6.3 will address processes farther from shore that are not well represented in the recent SGD literature.

Beyond the shoreline, advection of water through permeable shelf sediments and rocks is also submarine groundwater discharge, even if it contains no recognizable meteoric water (**Figure 1*b***). On the continental shelf this advection from deeper permeable sediments and rocks, driven by buoyancy and pressure gradients, can be called deep pore water upwelling (DPU). Offshore submarine springs are one example of this phenomenon. In this case, the flow may be driven by an inland hydraulic head through highly permeable formations or by the large-scale cyclic movement of water due to thermal gradients as envisioned by Kohout (1965, 1967). Other examples that leave visible signs include pockmarks on the sea bed where more buoyant fluids have risen through the sediments (Kaleris et al. 2002) and collapsed sink holes, an example of substantial episodic flow (W. Burnett, pers. comm.).

Off the SE coast of North America, where SGD has been studied extensively, fresh to brackish water within the continental shelf extends as much as 120 km from shore to depths exceeding 600 m (Hathaway et al. 1979, Manheim & Paull 1981). A test hole drilled 40 km offshore from Jacksonville, Florida, tapped an aquifer that produced a flow of freshwater to a height of 10 m above sea level (Kohout et al. 1988). The presence of abundant freshwater within the continental shelf provides a potential mechanism of DPU through leaks or breaches of the confining layers.

6.3.1. Kohout cycles. In one of the earliest scientific studies of SGD, Kohout (1965, 1967) recognized that geothermal heating could drive cyclic flow of sea water through coastal aquifers (see section 4.3). Wilson (2003, 2005) extended the Kohout cycle to mature continental margins in general. She produced model simulations of DPU flow beneath sloping continental shelves driven by geothermal heat flow. Using various permeabilities of the sediments, she produced fluid flow lines throughout the shelf. Her estimates of flow off North Carolina associated with geothermal convection were 740–74,000 m^3 per km of shoreline per year, depending on the permeability selected and on the ratio of horizontal to vertical hydraulic conductivity. She noted that although data on these parameters were sparse, especially from deeper regions of the shelf, deep upwelling must be a significant component of SGD.

6.3.2. Evidence of DPU. Direct evidence of SGD on the continental shelf has been provided by the presence of submarine springs, seepage meters deployed on the shelf, thermal signals in shelf aquifers that indicate water exchange, and chemical signals in bottom water on the shelf.

6.3.2.1. Evidence from submarine springs. Compelling evidence of deep pore water upwelling comes from submarine springs. These features are found along coasts where an inland hydraulic head drives artesian flow through rock and sediment formations. Submarine springs were recorded in ancient times (see section 3.1); in fact, they were probably much more prevalent before coastal development lowered piezometric heads in coastal aquifers (see section 3.3). Some remaining springs have been studied in the context of SGD.

A spectacular submarine spring is located about 4 km east of Crescent Beach, Florida, at a depth of 18 m in the Atlantic Ocean. Confining strata have been eroded to a depth of 38 m at the mouth of the vent, enabling direct hydrologic communication of groundwater with coastal bottom waters. Crescent Beach Spring is considered a first-order magnitude spring with a flow rate of >40 m^3 s^{-1} (Brooks 1961). During a sampling trip to the vent by divers, emerging water had a salinity of 6.02 and was enriched in nutrients and metals compared to ambient ocean water (Swarzenski et al. 2001).

A much deeper feature is located about 42 km off Crescent Beach. The so-called Red Snapper Sink (Spechler & Wilson 1997) is incised about 127 m into the shelf at a water depth of 28 m. Divers investigating the site in 1991 found that water in the bottom of the hole was similar in salinity and sulfate to ambient seawater. They noted that sea water was flowing into small caves at the base of the hole, indicating possible recharge into the Floridan aquifer. Several sampling trips to this feature on a surface vessel have failed to find tracer evidence for SGD in bottom water at this site (W.S. Moore, unpublished data, based on observations from 1998–2000). It is probable that the Red Snapper Sink was similar to Crescent Beach Spring before the piezometric head was lowered along this coast. Preservation of the feature in spite of sedimentation suggests that a spring was active at this site in the recent past.

Other examples of deep springs are the blue holes of the Bahamas. The blue holes, which reach depths exceeding 100 m, are entrances to underwater caves along offshore fracture systems. Whitaker & Smart (1990) investigated groundwater–sea water circulation in 19 blue holes offshore of Andros Island. They found that tidal pumping mixes high-pCO_2 freshwater with sea water within the caves. The brackish mixture dissolves aragonite but not calcite to produce secondary porosity, which enhances groundwater flow. The brackish water is enriched in calcium and strontium. The saline groundwater is depleted in calcium, indicating the precipitation of calcite cement.

6.3.2.2. Evidence from seepage meter studies. Simmons & Love (1987) used seepage meters in Key Largo, Florida, to measure SGD from water depths of 10–35 m. The meters collected water samples of low salinity and high metal and nutrient concentrations. Based on several hundred measurements of SGD at this location, they calculated a mean discharge rate for all deep (27–39 m) measurements of 15 L m^{-2} day^{-1} (N = 261), while the mean of all shallow (10–20 m) values was 19 L m^{-2} day^{-1} (N = 344) (Simmons 1992). An important observation at the deep reef site was an inverse relationship between discharge rate and tidal height. The seepage meters were used in conjunction with submarine minipiezometers described by Lee & Cherry (1978). They also developed an underwater manometer to measure hydraulic heads in seepage meters and piezometers (Simmons & Netherton 1987).

Later studies extended these measurements to the coast of North Carolina at depths of 10–33 m (Simmons 1992). Here researchers occupied a station in 20 m water depth, where the hydraulic head was negative and the seepage meter consistently recorded a flux entering the sediments at a rate of 11 L m^{-2} day^{-1}. By contrast, the hydraulic head at 10 m depth was consistently positive and flow was into the seepage meter (6 L $m^{-2}d^{-1}$). At 37 km offshore and 33 m depth, they encountered the highest flow of 20 L m^{-2} day^{-1}, clearly contradicting the assertion that SGD must decrease away from land.

Semidiurnal variations of fluid flow were measured at a water depth of 1360 m off Ogasawara, Japan, using automated seepage meters (Taniguchi et al. 2003). A temperature depth profile of the pore water under the seabed also suggested heat transport due to advection by the upward fluid flow. Although this study was well below the continental shelf, it illustrates that deep DPU is an important process.

6.3.2.3. Evidence from thermal signals. Moore & Wilson (2005) analyzed pressure, temperature, and radium isotope data obtained from three offshore monitoring wells. These wells were installed at a water depth of 15 m in the seafloor 15–20 km offshore North Carolina. The signals in these wells provide evidence for significant flushing of the seafloor aquifer to depths exceeding 3.5 m. Thermal data from Well 1 showed a consistent pattern of flushing during tidal fluctuations (Moore et al. 2002) (**Figure 5**). Wells 1 and A showed significant thermal perturbations associated with 1999 Hurricanes Dennis and Floyd. Heat flow models based on Well A confirmed that significant pore fluid advection was required to explain these thermal profiles (Moore & Wilson 2005).

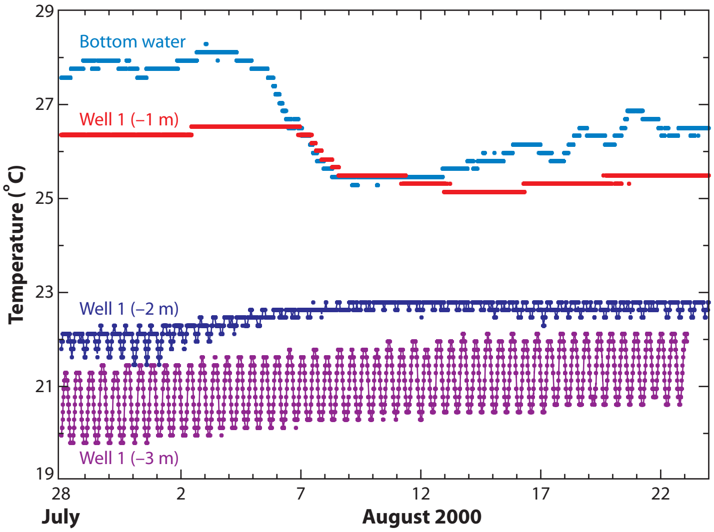


Figure 5

Temperature records in a monitoring well 20 km off North Carolina in 15 m water depth. The deepest recorder below a partial confining layer shows a cyclic pattern exactly in phase with the tide, indicating tidal water exchange. The upper (−1 m) recorder in sand shows a constant temperature followed by an abrupt decrease on 7 August. The decrease is coincident with rapid cooling of bottom water due to upwelling of offshore water. The simultaneous drop in temperature in the well and bottom water on 7 August must represent pore water exchange with ocean water. Similar records are in Moore & Wilson (2005).

Thermal profiles and radium data from the wells also indicated that density gradients between pore fluids and bottom water likely drive significant buoyancy-driven overturn of the pore water in seafloor sediments (**Figure 5**). In addition to indicating new mechanisms for deep pore fluid migration in sandy seafloor sediments, this work clearly demonstrated the value of heat and radium as tracers for deep pore water flushing in permeable coastal environments.

6.3.2.4. Evidence for chemical signals of DPU. Moore & Shaw (1998) reported unambiguous signals of episodic SGD on the continental shelf 30–80 km off the coast of South Carolina in water depths of 20–45 m. Barium, ^{226}Ra, and ^{228}Ra were enriched above ambient ocean concentrations by factors of 3 to 4; ^{223}Ra and ^{224}Ra were enriched by over an order of magnitude. Moore & Shaw (1998) eliminated upwelling of deep water and sediments as Ba and Ra sources and concluded that the source was the discharge of submarine fluids enriched in Ra and Ba. The region of Ra-Ba enrichment was also characterized by a strong fluorescence signal, indicating high concentrations of chlorophyll in the water. It is probable that the leaking fluids supplied nutrients that stimulated productivity in the sediments or bottom waters, which were within the photic zone. Moore & Shaw (1998) estimated that the fluid fluxes necessary to produce the enrichments were of the order of 300–2000 $m^3\ s^{-1}$ from this 80 km long segment of the outer shelf.

Moore & Shaw (1998) noted that the strong enrichment in Ba and Ra measured in August 1995 had not been present during July 1994. Additional surveys of this area in June 1997, September and October 1998, April 1999, and February 2000 did not find the strong subsurface enrichments of Ba and Ra (Moore 2007). The finding in 1995 was clearly an episodic event. A closer look at the meteorological record before the 1995 cruise reveals that a strong storm with 4.5 m waves passed over the area 10 days before the first sampling. It is reasonable to conclude that an episodic SGD flux was initiated by this storm, given the understanding we now have regarding the effect of pore water flushing from sediments by storms on the continental shelf (section 6.3.2.3).

7. ASSESSMENT OF GLOBAL SGD

I have often told my students that it is much easier to make an estimate than it is to know the uncertainty of that estimate. This is certainly the case with global SGD estimates.

7.1. Water Balance

There have been numerous attempts to estimate the total subterranean flux of freshwater to the ocean. Such studies are often based on a water budget that attempts to reconcile precipitation with evapotranspiration and river runoff. Excess freshwater in these budgets is assumed to enter the ocean as fresh SGD. This straightforward approach must include the propagation of errors inherent in each term.

Although most major rivers are gauged, the gauging stations are located upstream of the tidal influences. Changes below gauging stations and completely ungauged rivers lead to uncertainty in estimating world river discharge (e.g., Destouni et al. 2008). Most estimates of world river discharge (R) are between (35–40) $\times$ 10^{12} m^3 $year^{-1}$ (e.g., Berner & Berner 1996, Alley et al. 2002). Dai & Trenbeth (2002) combined flow data from gauged rivers with river transport and water balance models to estimate an average flow of (37.3 $\pm$ 0.7) $\times$ 10^{12} m^3 $year^{-1}$; however, their analysis did not include groundwater discharge, which might bias their water balance model.

Estimates of worldwide precipitation (P) and evapotranspiration (ET) (including evaporation from soil and surface water bodies and transpiration through plant tissues) are uncertain. There are many estimates of these terms, but few that discuss overall errors. Consider this example.

$$\text{Fresh SGD} = P - ET - R$$

Estimates of average annual precipitation over land range from (95–115) $\times$ 10^{12} m^3 $year^{-1}$; average evapotranspiration estimates range from (60–75) $\times$ 10^{12} m^3 $year^{-1}$; and annual river flow estimates range from (35–40) $\times$ 10^{12} m^3 $year^{-1}$ (e.g., Alley et al. 2002, Burnett et al. 2003). If we only consider the difference of the means, the flux of fresh SGD would be zero. But each of the terms on the right of the equation has a range of about $\pm$10%. Propagating the errors yields a fresh SGD flux of (0 $\pm$ 13) $\times$ 10^{12} m^3 $year^{-1}$. At a 2 sigma uncertainty, the upper error of the SGD term approaches the river term.

7.2. Integrated Hydrologic-Hydrogeologic Approach

Zektser et al. (2007) estimated fluxes of fresh groundwater into the ocean using what they call an integrated hydrologic-hydrogeologic approach. This approach assumes that the groundwater input to rivers (m^3 km^{-1} $year^{-1}$) that drain specific hydrogeologic provinces is similar to groundwater discharge to the ocean (m^3 km^{-1} $year^{-1}$) from these provinces. They estimated the groundwater input to the rivers based on published studies and scaled the expected discharge per kilometer of river with the shoreline length of each province to provide groundwater fluxes from each province to the ocean. They noted that this approach only includes fluxes from the upper zones of the provinces (the same zones that drain into rivers) and may miss fluxes from deeper zones (i.e., confined aquifers) that drain into the ocean. Zektser et al. (2007) provided a detailed list of discharge and water composition from each province into individual ocean basins. The water compositions were in almost all cases <1 g L^{-1} total dissolved solids. Zektser et al. (2007) estimated a flux of fresh groundwater to the ocean of (2.2–2.4) $\times$ 10^{12} m^3 $year^{-1}$. Compared to their estimate of the world river flow (40 $\times$ 10^{12} m^3 $year^{-1}$), the fresh SGD component was 5–6%, similar to other estimates (Burnett et al. 2003).

7.3. Local and Regional Tracer Studies

dpm: decay per minute

In contrast to methods that attempt to estimate the freshwater component of SGD, most tracer techniques estimate total SGD. Charette et al. (2008) provide a summary of local and regional studies of SGD fluxes from tracers. Local studies (scale lengths of ∼1 km) have estimated SGD fluxes from 10^3 to 2×10^5 m^3 km^{-1} day^{-1}. Regional studies (10–300 km) have estimated SGD fluxes of 10^5 to 6×10^6 m^3 km^{-1} day^{-1}. It is likely that the regional study estimates are greater because they capture discharge that occurs beyond the shoreline, and includes the inner shelf.

7.4. Integrated Tracer Approach

Although most tracer studies have been local or regional (see section 5.3), the concept is also applicable to entire ocean basins. Almost all ^{228}Ra enters the upper ocean from the continent. Its half life of 5.7 years allows penetration throughout the upper ocean to depths reaching 1 km. Twelve percent of the ocean inventory of ^{228}Ra is lost each year by decay; therefore, if we know the inventory of ^{228}Ra, we know how much must be supplied each year to balance decay.

Moore et al. (2008) mapped the distribution of ^{228}Ra in the upper 1000 m of the Atlantic Ocean. **Figure 6** shows this inventory map. It is clear that the Southern Ocean and South Atlantic contain considerably less ^{228}Ra than the North Atlantic. The south to north increase in inventory tracks the pattern of the surface ocean conveyor. The northward moving surface water receives ^{228}Ra from the continents at a rate greater than the ^{228}Ra decay rate, causing the inventory to increase. Reflecting its continental source, inventories in the North and South Atlantic are generally greater in the boxes intersecting coastal regions. Interestingly, the inventory in the box intersecting the Amazon River mouth is not significantly greater than in boxes intersecting other parts of the South American continent. This supports the conclusion (Moore et al. 2008) that SGD dominates riverine and sedimentary input of ^{228}Ra.

With this knowledge of the inventory of ^{228}Ra in the Atlantic (6.7×10^{17} dpm), we know that 8×10^{16} dpm $year^{-1}$ must be supplied to maintain steady state. Moore et al. (2008) estimated known ^{228}Ra fluxes to the Atlantic from rivers, atmospheric dust, and regeneration and release from coastal and shelf sediments by diffusion and bioturbation. These sources could supply less than half the ^{228}Ra that decayed each year. They assumed the remainder was derived from SGD. Using data from 226 monitoring wells and piezometers (with many sampled multiple times), they estimated the mean activity of ^{228}Ra in coastal groundwater (1.8 dpm L^{-1}). Dividing the flux of ^{228}Ra by the concentration of ^{228}Ra in the coastal groundwater yielded a total SGD flux of $(2–4) \times 10^{13}$ m^3 $year^{-1}$, or 80–160% of the Atlantic river flux. Normalized to the Atlantic shoreline of 85,000 km, the flux is 10^6 m^3 km^{-1} day^{-1}, at the high end of the regional studies. They emphasized that this is not a freshwater flux but a flux of terrestrial and sea water that has penetrated permeable coastal aquifers, reacted to increase radium concentrations 100-fold, and then discharged into the ocean.

8. CHEMICAL EFFECTS OF SGD ON THE OCEAN

8.1. Early Studies of the Chemistry of SGD

What controls the chemical composition of sea water? This is a fundamental question that engaged early philosophers and led to the science of chemical oceanography. The concept of the hydrological cycle explained the source of water for rivers and explained how the ocean could become salty. Early estimates of the age of the ocean were based on the time required to bring the ocean salinity to its present level (e.g., Rubey 1951).

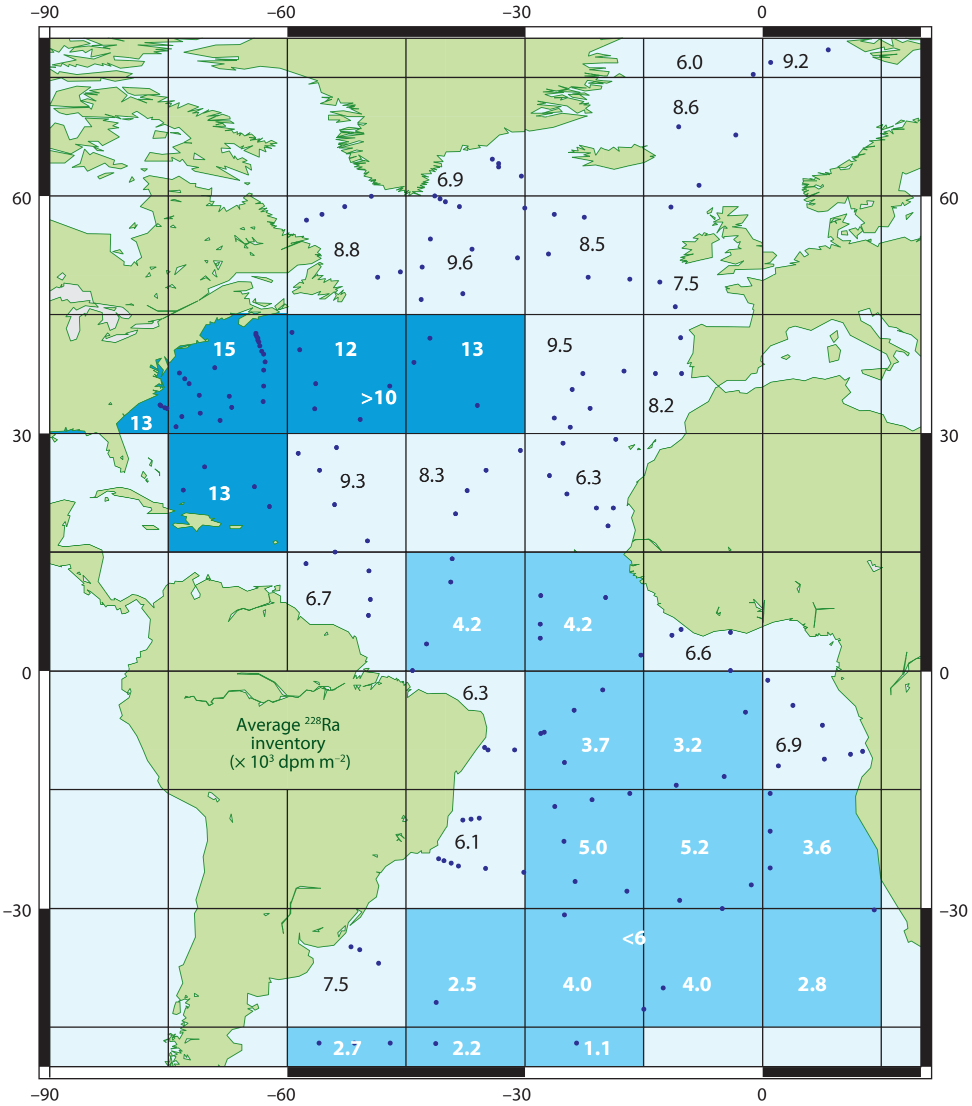


Figure 6

Inventory of ^{228}Ra ($\times 10^3$ dpm m^{-2}) in the upper 1000 m of the Atlantic Ocean. The points show the distribution of stations that were used to calculate ^{228}Ra inventories. All stations within each 15° × 15° box were averaged to yield a bin average, shown as a number in each box. Data from Moore et al. (2008).

The concept of chemical residence time that focused on processes of removal as well as addition (Barth 1952) led to a better understanding of the dynamic nature of chemicals in the sea and to a realization that certain elements were out of balance; i.e., their outputs did not match their inputs. Discovery of deep-sea hydrothermal systems in the 1970s caused a revolution in our understanding of these inputs and outputs (Edmond et al. 1979). Through the latter part of the twentieth century additional input and removal mechanisms were discovered and investigated, including warm circulation through mid-ocean ridge flanks, cold seeps on the continental rise, and submarine groundwater discharge.

Historically, geochemists assumed that the primary flux of materials across the sea bed was driven by diffusion and bioturbation (often modeled as a diffusive process using a bioturbation constant instead of a diffusion constant in Fick's laws). To estimate fluxes, pore waters were extracted from cores of fine-grained sediments and components of interest were measured. Concentration gradients of these components were modeled using diffusion theory to indicate fluxes out of or into the sediments. In some cases cores were recovered intact and changes in concentration of overlying waters were used to indicate fluxes. Such experiments were also carried out on the sea bed using benthic chambers to capture the chemical signals that crossed the water-sediment interface (Jahnke & Christiansen 1989). Berner (1980) provided an excellent summary of theory and case studies in *Early Diagenesis: A Theoretical Approach*.

Although Berner (1980) developed equations that could be applied to bulk flow or advection between pore water and overlying water, the advective process, except for sediment compaction, was not considered important for chemical fluxes. Large-scale advection of pore water required permeable sediments. It was thought that permeable sediments, which were usually composed of relict sands, would not contain significant concentrations of substances of interest. Geochemists sought soupy, smelly mud because they reasoned that this was where the action was.

Other geologists and geochemists working in coastal aquifers had long recognized the importance of chemical reactions between aquifer solids and a mixture of sea water and fresh groundwater. For example, mixing of sea water supersaturated with respect to calcite, with fresh groundwater saturated with respect to calcite, can result in solutions that are either supersaturated or undersaturated with respect to calcite (Plummer 1975). The undersaturated solutions result primarily from the nonlinear dependence of activity coefficients on ionic strength and on changes in the distribution of inorganic carbon species as a result of mixing. Thus, solutions containing a high proportion of sea water relative to fresh groundwater may precipitate calcite and decrease the porosity of coastal aquifers, while at lower sea water–groundwater mixing ratios, the solution may dissolve calcite and increase porosity. Back et al. (1979) proposed this mechanism to explain the excessive secondary porosity of limestone along the east coast of the Yucatan Peninsula.

Sea water–groundwater mixing has also been invoked to explain the formation of dolomite in coastal limestone. Surface sea water is supersaturated with respect to calcite and dolomite, yet the inorganic precipitation of these minerals from sea water is rarely observed. Hanshaw et al. (1971) and Badiozamani (1973) proposed that a mixture of sea water and groundwater could be undersaturated with respect to calcite yet remain supersaturated with respect to dolomite. They suggested that this solution would lead to the replacement of calcite by dolomite. Baker & Kastner (1981) demonstrated that dolomite formation is inhibited by the presence of sulfate ions. Thus, bacterial sulfate reduction in sea water–groundwater mixtures could further favor the formation of dolomite.

Fanning et al. (1981) reported chemical analyses of submerged springs on the west Florida shelf. Mud Hole submarine spring (MHSS) is a 2–3 m depression on a 12 m deep shelf. Warm water (39°C) emerges with a salinity identical to the Gulf of Mexico at a depth of 1000 m. Fanning et al. (1981) estimated its flow at 12 L s^{-1}. They measured significant depletions of magnesium and enrichments of calcium and deduced that the warm water was actively converting calcite to dolomite within the aquifer. They estimated that over 140 m^3 of dolomite could be produced by this single vent each year. The dolomite production would be accompanied by over 2×10^6 moles of Mg^{2+} removal each year. Water from MHSS was depleted in uranium but enriched in silica, radium, and radon.

8.2. Early Investigations of SGD Nutrient Inputs and Potential Biological Effects

Kohout (1964) and Kohout & Kolipinski (1967) published early investigations of the biological importance of groundwater discharge into the sea. Their studies along the shore of Biscayne Bay, Florida, showed a definite relationship between biological zonation and groundwater discharge into the bay.

Other biologists recognized the importance of advective flow through permeable sediments. Without constant input of oxygenated seawater, sediments would become reduced and inhabitable only by organisms that did not require oxygen. The fact that permeable sediments on the continental shelf are generally oxidized indicates that circulation is occurring (Riedl & Machan 1972). Other early workers demonstrated that remineralization of nutrients on or in the sea bed is important in sustaining pelagic primary productivity (Rowe 1975).

Marsh (1977) directly linked SGD with nutrient fluxes to coral reefs on the island of Guam. Johannes (1980) found that the SGD flux of nitrate along the western Australian coast north of Perth was three times greater than from surface runoff. At Discovery Bay, Jamaica, D'Elia et al. (1981) found a strong negative correlation between salinity and nitrate near subsurface springs. They concluded that considerable mixing of meteoric water and sea water was occurring within the coastal aquifer because even at the mouths of the springs the salinity was no lower than 5. From these measurements they interpolated a freshwater end-member of 120 μM NO_3^-; this was similar to values they measured in freshwater coastal wells (60–160 μM NO_3^-). The authors assumed that the nitrate flux was natural in origin because there were no strong sources of anthropogenic input to the aquifer. These papers emphasized the importance of the nitrogen flux to coastal productivity: lagoon macrophytes in the case of Perth and coral reef ecosystems in Discovery Bay.

8.3. Modern Investigations of the Effects of SGD

During the past 10 years there have been over 100 papers detailing the chemical effects of SGD on the coastal ocean (see section 2). Clearly, I cannot discuss each of these. Instead, I will focus on papers that describe different aspects of the process.

8.3.1. Nutrient fluxes. Studies of nutrient fluxes related to SGD comprise a quarter of the papers referenced in **Figure 2**. Slomp & van Cappellen (2004) reviewed the topic, developed a global model to assess nutrient inputs, and concluded that SGD was an important source of nutrients to coastal waters. They pointed out that because phosphorus is removed from groundwater more easily than nitrogen, SGD often has N/P ratios greater than the Redfield ratio of 16. Studies published since this review support the conclusions of Slomp & van Cappellen (2004) and reinforce the importance of SGD. Many early studies found SGD to be an important source of nutrients to coral reefs (section 8.2). Paytan et al. (2006) evaluated nutrient input via SGD to six coral reef sites in the Indian, Atlantic and Pacific oceans, and Gulf of Aqaba and confirmed that SGD was an important source of new nutrients to these coral reef ecosystems.

Because nutrient concentrations in coastal groundwater may reach several orders of magnitude greater than surface waters, groundwater input may be a significant factor in the eutrophication of coastal waters (Paerl 1997). Some studies have linked the nutrients supplied by SGD to harmful algal blooms (Hu et al. 2006, Lee & Kim 2007). These studies emphasize that the N/P ratios delivered by SGD may differ significantly from the Redfield ratio.

8.3.2. Metal fluxes. Barium, like radium, is usually enriched in SGD. Moore (1997) estimated Ba fluxes from SGD near the mouth of the Ganges–Brahmaputra rivers that exceeded river inputs during low river flow. Shaw et al. (1998) estimated barium fluxes from SGD to be about four times the river flux to the SE coast of North America. They found that barium concentration in subsurface fluids could exceed saturation with respect to barite by a factor of 6.

Basu et al. (2001) used strontium concentration and isotopic ratios in groundwater wells in the Bengal delta to estimate fluxes from the Ganges–Brahmaputra River basin to the Bay of Bengal. They suggested that the SGD flux of strontium was similar to the river flux, making the basin a more significant contributer to the rise in $^{87}Sr/^{86}Sr$ ratio in sea water than had been thought. The SGD flux was questioned by Harvey (2002), leading to further discussion by Basu et al. (2002).

Studies of trace metal fluxes associated with SGD have shown that many metals exhibit non-conservative behavior along the flow path from land to sea. Depending on the location and depth of monitoring wells at a field site, very different metal concentrations are obtained (Charette & Sholkovitz 2002, Beck et al. 2007). Thus, estimates of metal fluxes obtained from only a few measurements of groundwater concentrations are quite uncertain. The few studies that focus on SGD as a source of trace metals to coastal waters generally conclude that the SGD source is as large as or greater than river or atmospheric fluxes, but other sources must also be considered. Charette & Buesseler (2004) found that SGD provided an important source of nutrients to the Elizabeth River, Virginia, but the SGD flux of copper was small compared to that derived from antifouling paints on boats. Duncan & Shaw (2003) suggested that the degradation of relic organic carbon in coastal aquifers resulted in the export of dissolved rare earth elements equal to or greater than river inputs along the SE US coast. Bone et al. (2007) investigated the input of mercury associated with SGD into Waquoit Bay, Massachusetts. They estimated that SGD Hg fluxes to the bay were ten times greater than atmospheric fluxes, previously considered to be the major contributor. Laurier et al. (2007) compared Hg input by SGD into the Pays de Cayx on the southern coast of the English Channel with the input to the Seine estuary. They found concentrations in the Pays de Cayx to be higher than in the Seine estuary due to particulate removal in the Seine. Additionally, they found higher concentrations in mussel tissue in the Pays de Cayx than in the Seine, suggesting that mercury was more bioavailable in the Pays de Cayx.

The input of iron to the ocean has become an important topic since it was recognized as an essential micronutrient for plankton in the subarctic Pacific (Martin & Fitzwater 1988). The atmosphere has been considered the primary source of Fe to the surface ocean (Duce & Tindale 1991). Recently this has been challenged by studies on the SE coast of Brazil, where Windom et al. (2006) reported a large SGD flux of Fe to the coastal ocean. Using radium tracers, they estimated that the cross-shelf flux of iron from a 240 km stretch of coastline was equivalent to 10% of the atmospheric flux to the entire South Atlantic Ocean. Considering that similar SGD Fe fluxes are likely throughout this coastal region, the SGD source of Fe could dominate the atmospheric source. Other groups have reported high concentrations of Fe in SGD, which is not surprising considering that SGD is often suboxic or anoxic. Charette & Sholkovitz (2002) considered the consequences of oxidation of iron within the subterranean estuary. They described this oxidation zone as an "iron curtain," where other metals and phosphorus were scavenged before SGD discharged them to the coastal water.

Because the subterranean estuary is often anoxic, metals that are precipitated under reducing conditions are removed when sea water enters such aquifers. Uranium is an example of a metal that is soluble in oxidized sea water but insoluble under reducing conditions. Church et al. (1996) found that salt marsh sediments were an important sink for dissolved uranium. Windom & Niencheski (2003) recognized uranium removal in the freshwater–sea water mixing zone of permeable sediments along the coast of southern Brazil. Moore & Shaw (2008) used the depletion of uranium at the mouths of rivers on the SE coast of North America to estimate the amount of sea water entering anoxic portions of the subterranean estuary. This subterranean removal process should be considered when estimating a global budget for uranium and other redox-sensitive metals.

In some cases, authors have speculated that SGD may be an important component of ocean metal cycles because other processes seem inadequate to achieve mass balances. Milliman (1993) proposed that groundwater inputs of calcium could be an important source of this metal to the ocean that would help resolve inconsistencies in the budget. Johannesson & Burdige (2007) used existing estimates of fresh SGD fluxes to the ocean and measurements of neodymium in fresh coastal groundwater to propose that SGD could supply a component of the Nd flux missing from current estimates.

8.3.3. Carbon fluxes. There are only a few papers that link carbon fluxes to SGD. These conclude that SGD fluxes of both dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) are important pathways from land to sea for carbon. Cai et al. (2003) measured DIC and pCO_2 in fresh and salty coastal wells on the South Carolina coast at North Inlet. They found concentrations orders of magnitude greater than in river or ocean water and estimated DIC fluxes of 0.17 mol m^{-2} day^{-1}. Cai et al. (2003) concluded that SGD fluxes of DIC to these coastal waters exceeded river inputs and recommended that the global importance of DIC fluxes via SGD to the ocean be evaluated. Goñi & Gardner (2003) estimated DOC fluxes from North Inlet, South Carolina, to be 50 mmol m^{-2} day^{-1}. Moore et al. (2006) used radium fluxes and DIC/Ra and DOC/Ra ratios in groundwater to estimate SGD fluxes of DIC and DOC from the Okatee, South Carolina, marsh of 2 mol m^{-2} day^{-1} and 170 mmol m^{-2} day^{-1}, respectively; these greatly exceeded river inputs to the marsh. The strong correlation of carbon and radium in these waters implies that a simple stoichiometric ratio determines the release of these elements during diagenesis. Santos et al. (2009) estimated DOC fluxes via SGD of 19–27 mmol m^{-2} day^{-1} from the west coast of Florida, with the larger fluxes occurring in the summer. Although the data are sparse, it is clear that SGD must be considered in land–sea budgets of carbon cycles.

8.3.4. SGD and hypoxia? SGD containing H_2S, NH_4, CH_4, DOC, and reduced metals is a potential source of reducing fluids to coastal waters that could contribute to hypoxia. These reduced fluids may accumulate in coastal sediments to be released in an episodic event (see section 6.3.2.4). A possible example is outbreaks of H_2S on the Namibian shelf near Walvis Bay, which have been shown to occur after periods of inland rains (Weeks et al. 2004). SGD was one hypothesis offered by Emeis et al. (2004) to explain the H_2S outbreaks. They speculated that the Kuiseb River, which disappears into sand dunes near Walvis Bay, may continue underground through drowned valleys filled with sand and gravel and transmit a hydraulic pressure signal of a rising water table after rain storms. This signal could trigger the release of trapped gasses in the organic-rich coastal sediments.

9. SGD IN THE PAST AND FUTURE

Like surface estuaries, subterranean estuaries are affected strongly by sea level changes. The occurrence of both systems today is due to the drowning of coastlines by the last transgression of the sea. Twenty thousand years ago, SGD was probably concentrated at the shelf edge and in shelf springs, where channel cutting breached overlying confining units, resulting in artesian flow. If these channels were filled with coarse clastics during sea level rise, the channel fill may currently serve as an effective conduit for shallow groundwater flow across the shelf, and the breaches may provide communication between the surficial and deeper confined aquifers (Mulligan et al. 2007).

As the rising sea approached its current level, both surface and subterranean estuaries developed as sea water infiltrated into river basins and coastal aquifers.

Faure et al. (2002) suggested that springs of fresh SGD were present at the margin of the emerged continental shelf during low sea stands. These coastal oases might have provided essential drinking water for people migrating along coastal routes.

During the last century, subterranean estuaries, like their surface counterparts, have experienced considerable change due to anthropogenic pressure. Dredging of channels through surface estuaries has breached underlying confining layers and increased contact between surface water and subterranean estuaries (Duncan 1972). Increased groundwater usage has lowered potentiometric heads in coastal aquifers and caused infiltration of sea water into these formations (e.g., Bush & Johnston 1988, Burt 1993, Landmeyer & Stone 1995). The result has been an increased rate of salinization of coastal potable water and subterranean estuaries. Sea level rise, whether natural or induced, has also caused increased salinization. Additionally, expansion of hard surfaces (roads, parking lots, buildings, drainage canals) reduces infiltration and channels precipitation into surface runoff, often as flash flooding events in coastal streams. These changes are taking place worldwide due to increased demands of a rising coastal population. It is likely that the flux of fresh SGD to the ocean has decreased, but changes of total SGD are less certain. Inland expansion of the subterranean estuary may lead to greater total SGD fluxes of nutrients, carbon, and metals because the biogeochemical reactions that affect their concentrations may operate over larger spatial scales and affect aquifers that have not been in contact with sea water for thousands of years.

SUMMARY POINTS

Over 100 studies have demonstrated that submarine groundwater discharge (SGD) constitutes a significant source of nutrients to specific coastal areas. Additional studies emphasize the importance of SGD in supplying metals, carbon, and bacteria to coastal waters. An integrated tracer study concluded that the total flux of SGD to the Atlantic Ocean was similar to the river flux. The results of the local and integrated studies provide compelling evidence that SGD is a significant source of nutrients, carbon, and metals to coastal waters that probably exceeds the input of these materials by rivers. Thus, SGD must be a primary component in global ocean budgets and models of these constituents.

FUTURE ISSUES

1. The volume flux of SGD is easier to establish than the constituent fluxes because coastal aquifers contain wide concentration ranges of nutrients, carbon, and metals. More information is required regarding the controls of these constituents within coastal aquifers and how these concentrations change along the flow path of SGD to the ocean.
2. Coastal aquifers are responding to sea level rise, groundwater mining, harbor dredging, and changes in coastlines due to the construction of dikes, canals, roads, and structures. The overall effect of these changes on the aquifers and on SGD is unknown. Most changes will expand the volume of the subterranean estuary, but the effect on the concentrations of nutrients, carbon, and metals is uncertain.
3. The oceanographic and hydrogeological communities should recognize the local and global importance of SGD and work together to achieve a better understanding of processes that control SGD and its constituents.

DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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Contents

Errata

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