

## Chapter 4

# Coastal Nutrient Inputs from Groundwater: Case Studies from the East Coast of the United States



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### 4.1 Introduction

Non-point source nutrient fluxes are a growing issue in the assessment of coastal ocean and estuarine biogeochemistry. Surface water discharge has long been recognized as an important source of dissolved compounds, including nutrients, to the coastal zone and the transport of river-borne dissolved constituents continues to be a well-studied realm of environmental science (Maybeck, 1982; Berner & Berner, 1987). River discharge has been

gauged for centuries and long-term studies have been performed to assess the chemistry of fluvial discharge and its biogeochemical impact on estuarine and coastal ocean waters (e.g., Maybeck, 1982; Sharp *et al.*, 1986; Pennock, 1987; Cifuentes *et al.*, 1990; Lebo *et al.*, 1994). More recently, environmental regulators and researchers have come to recognize the importance of non-point source discharges, including land surface runoff and atmospheric deposition of dissolved and aerosol compounds Paerl (1997). As has been discussed elsewhere in this text, both fluvial discharge and non-point source discharges play an important role in nutrient fluxes to the coastal zone.

In recent decades, researchers have begun to turn attention to an underground path to the coastal oceans: submarine groundwater discharge. Submarine freshwater springs in the coastal ocean were used as sources of potable water for sailors and coastal residents alike for at least 2,000 years Kohout (1966). Originally considered a novel process, limited to the existence of occasional springs, it has taken some time for the true extent of coastal groundwater discharge to be recognized. In research initiated over the past 25 years, we are becoming aware of the fact that groundwater inputs account for a significant portion of the water and chemical flux to the coastal zone.

The role of groundwater transport has gained

increasing attention in both marine (Dahm *et al.*, 1998) and freshwater (Church, 1996) aquatic research, particularly in light of research showing considerable groundwater fluxes directly to estuaries and the coastal ocean (e.g., Cable *et al.*, 1996; Moore, 1996). The use of new groundwater tracers and the expansion of the scope of submarine groundwater discharge research has led to the still-growing realization that the direct discharge of groundwater to coastal zones is not a novel process, but, does indeed occur “anywhere that an aquifer . . . is connected hydraulically with the sea through permeable bottom sediments and the [potentiometric] head is above sea level” (Johannes, 1980).

## 4.2 Submarine Groundwater Discharge: Processes

### 4.2.1 Water transport via SGD

The term ‘submarine groundwater discharge’ (SGD) commonly refers to the exchange of terrestrially-derived groundwater with fresh, estuarine, and coastal waters (though Burnett *et al.*, 2003 correctly point out that SGD can also include wave pumping and other processes that involve the flushing of sediments that are saturated with surface water). Groundwater will flow within an aquifer if there is a potentiometric head between the aquifer recharge zone and the discharge zone; that is, water will flow ‘downhill’ even when present in the pores of sedimentary material.

When an aquifer’s discharge zone intersects with porous bottom sediments in the coastal zone, groundwater will flow into the coastal ocean (or estuary) as SGD (Figure 4.1). Unconfined aquifers will interact with the seawater-saturated sediments and create a restricted, and often diffuse, zone of SGD that is typically within 100–200 m from the coast (Taniguchi *et al.*, 2002). As illustrated in Figure 4.1, groundwater discharge from confined aquifers can occur as springs or diffuse discharge at distances of several to hundreds of kilometers from shore.

### 4.2.2 Nutrient transport via SGD

The environmental quality of groundwater is a near-universal concern. Groundwater quality is affected by anthropogenic activities ranging from the application of agricultural pesticides and fertilizers to leaking petroleum underground storage tanks. While the immediate effect of groundwater contamination is the pollution of potable drinking water sources in the vicinity of the contamination source, groundwater flow transports dissolved constituents away from the source area. Where groundwater flow is toward the coastline, SGD can discharge these nutrients and contaminants to the coastal zone and, along with surface runoff and atmospheric deposition, provides an important non-point source discharge to estuarine and coastal ocean receiving waters.

In the eastern United States, the land bordering estuaries and the coastal zone is the site of both agricultural and industrial activities, as well as the site of large urban population centers, including Washington, D.C.; Philadelphia, PA; New York, NY; and Boston, MA (Figure 4.2). Industrial activities and ubiquitous petroleum underground storage tanks are a continuing threat to groundwater quality. Compounds such as polycyclic aromatic hydrocarbons (PAHs), chlorinated aliphatics (e.g., trichloroethylene), and petroleum constituents (benzene, toluene, ethylbenzene, and xylenes) and additives (e.g., MTBE) have affected both surface and confined aquifers in urban and suburban regions throughout the world.

Even rural areas experience risks to groundwater quality. Nitrate contamination of aquifers is common in agricultural areas that border estuaries (Hamilton *et al.*, 1993). Reclaimed marshland and undeveloped coastal plain areas are also widely utilized as cropland and for animal husbandry. Groundwater chemistry in aquifers underlying agricultural regions is affected by the infiltration of pesticides, fertilizers, and animal waste products from industrial farming centers.

In addition to the transport of allochthonous chemical compounds to the coastal zone, SGD also has local effects due to groundwater-surface water

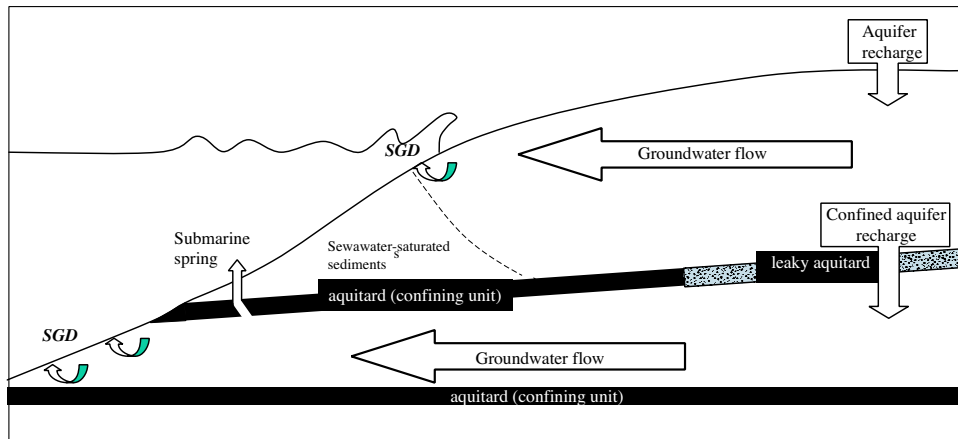


Figure 4.1: Submarine groundwater discharge schematic. Submarine groundwater discharge can occur from confined and unconfined aquifers. Discharge from confined aquifers can take the form of submarine springs and can occur at some distance from the shoreline, even at the shelf break. Potentiometric head can be visualized as the difference in elevation between the recharge and discharge zones of the source aquifer.



Figure 4.2: Eastern United States, showing selected urban areas.

interactions. This ‘subterranean estuary’ (Moore, 1999) is a particularly dynamic area where the interaction of water masses with different alkalinity and chemical composition precipitate and liberate both dissolved and solid phases. Strong redox gradients in this zone will enhance chemical reactions and can liberate both organic and inorganic compounds and stimulate biogeochemical processes that further affect groundwater chemistry (Dahm *et al.*, 1998). Organic matter degradation can take place through a variety of pathways in the groundwater, including aerobic oxidation, sulphate reduction, and methanogenesis, further altering groundwater chemistry prior to discharge.

The interaction between seawater-saturated sediments and freshwater aquifers is not a one-way exchange. Groundwater withdrawal in the coastal zone has increased to satisfy the growing demand for drinking water and agriculture as the coastal population increases (Paerl, 1997); this has led to saltwater intrusion into coastal aquifers. In addition to rendering the groundwater non-potable, salt water intrusion into these aquifers causes ion exchange and other reactions to occur, which chemically alter the intruding seawater and enrich the fluids in metals and nutrients (Burnett *et al.*, 2003). Subterranean interactions between

seawater and fresh water can induce the liberation of ions adsorbed to sediment particles, including radium (Ku *et al.*, 1992; Moore, 1999). Researchers can make use of these geochemical processes to identify SGD tracers and quantify groundwater fluxes.

### 4.3 Locating and Measuring Submarine Groundwater Discharge

Identifying where SGD occurs and the rates of groundwater flux is no trivial matter. The most obvious SGD tracer in the coastal zone is *salinity*. Terrestrial aquifers contain freshwater while the salinity of coastal zone receiving waters will be higher, up to full oceanic salinity of 35 (or even higher in tropical lagoons). Through careful assessment of salinity signals, Johannes (1980) identified groundwater discharge as an important source of water and dissolved compounds to a western Australian coastal lagoons, while, in the process, proposing the theoretical ubiquity of SGD.

Although the first ancient evidence of SGD was via the observation of active submarine springs in the coastal ocean, most groundwater discharge to the coastal zone (especially that from unconfined aquifers; Figure 4.2) is not accompanied by a marked freshening of surface receiving waters. Often SGD occurs with no discernible salinity signal at all. Other tracers may be helpful in cases where SGD is suspected due to coastal aquifer geometry (i.e., strike and dip) or biogeochemical observations in the absence of salinity anomalies.

Seasonally, *temperature* anomalies may be useful SGD tracers. Because groundwater temperatures remain relatively constant throughout the year, the temperature difference between surface water and groundwater will increase when surface water is warmed or cooled. Miller and Ullman (2004) identified localized groundwater discharge to the Delaware coastal zone using remote thermal imaging to locate warm water plumes in cold winter surface waters. Sim-

ilar techniques were used by Banks and colleagues (1996) and Portnoy and colleagues (1998) in separate studies of groundwater-surface water interactions. Moore and colleagues (2002) inferred groundwater-surface water interactions from annual temperature excursions in a submarine confined aquifer located on the South Carolina continental shelf. Finally, Taniguchi and colleagues (2003) calculated groundwater flux rates using subsurface temperature trends in Cockburn Sound, Western Australia.

An increasingly common, and powerful, tool for identifying SGD in the coastal zone is via chemical tracers, both natural and introduced. *Natural radioactive elements*, including radon-222 and a suite of radium isotopes ( $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$ ,  $^{226}\text{Ra}$ , and  $^{228}\text{Ra}$ ) have been used as valuable tracers of SGD to estuarine and coastal zones (e.g., Moore, 1996; Cable *et al.*, 1996; Krest *et al.*, 2000; Schwartz, 2003; Charette *et al.*, 2003). *Artificial chemical tracers* can be introduced into aquifer recharge zones to assess groundwater flow where flow lines are short (i.e., rapid discharge). In coastal zone receiving areas with restricted surface water exchange, *dissolved nutrients* may serve as an indicator of SGD, though it has proved difficult to use nutrients as a primary groundwater tracer. *Stable isotope signatures* of dissolved nutrients (e.g.,  $^{15}\text{NO}_3$ ) hold some promise for utility as SGD tracers (Schwartz, 2001)

Groundwater radium concentrations are altered by seawater-fresh water interactions in coastal aquifers. As noted above, surface water-groundwater interactions in submarine aquifers can release ions adsorbed to charged particles, such as clay minerals and glauconite sands. This is particularly common in aquifers that are subjected to saltwater intrusion or regular saltwater flushing. Radium is one such ion that can be liberated by gradients in groundwater conductivity. Dissolved radium concentrations can, therefore, be much higher in the discharged groundwater than in the receiving surface waters (oceanic or salt marsh). Rama and Moore (1996), Krest and colleagues (2000), and Charette and colleagues (2000) utilized the differences in half-life of the

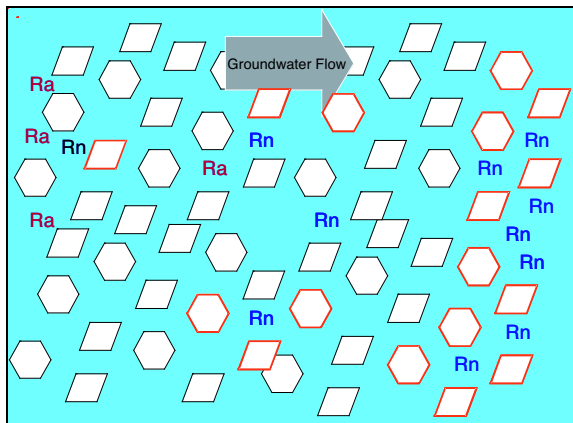


Figure 4.3: Illustration of radon enrichment in aquifers. As groundwater flows through the aquifer,  $^{226}\text{Ra}$  decays to form  $^{222}\text{Rn}$ , a noble gas that does not react with dissolved or particulate material in the aquifer. Radium is very particle reactive and will bind to charged mineral surfaces (depicted by red coatings of some mineral grains).

radium isotope quartet (ranging from 3.7 days to 1600 years) to simultaneously quantify SGD fluxes (and differentiate groundwater input) from surficial and confined aquifers.

Radon-222 is enriched in groundwater because its geochemical properties differ significantly from  $^{226}\text{Ra}$ , its parent nuclide. Radon is a noble gas and does not react with other ions, while radium is highly particle reactive and will adsorb onto particles in the water column or in aquifers. Even in saline water, much radium will be adsorbed to particle surfaces. As groundwater flows through an aquifer, radium will be adsorbed onto charged surfaces of mineral grains. The radon formed by the decay of dissolved and particle-bound radium is transported as a dissolved gas within the groundwater (Figure 4.3). This process leads to a progressive enrichment in groundwater radon prior to discharge.

By measuring excess  $^{222}\text{Rn}$  (i.e., the amount of dissolved radon that is not supported by water column and benthic  $^{226}\text{Ra}$ ), Cable and colleagues (1996) and Hussain and colleagues (1999) identified significant groundwater flow to the northeastern Gulf of Mexico and Chesapeake Bay, respectively.

In areas where groundwater flow is rapid and

discharge occurs quickly, artificial tracers can also be used to identify the location and rate of groundwater discharge. Working in the Florida Keys, Dillon et al. (1999) injected sulfur hexafluoride ( $\text{SF}_6$ ) into the surficial aquifer to trace the flow of wastewater effluent through the carbonate platform.

While dissolved nutrients, including nitrate and silicate, are difficult to use as primary tracers of SGD, they may have a value as a secondary tracer in studies that pair thorough investigations of nutrient dynamics with the use of a primary tracer such as those mentioned above. Methane ( $\text{CH}_4$ ) has been combined with  $^{222}\text{Rn}$  to assess SGD in the Gulf of Mexico and Florida Bay (Cable et al., 1996; Corbett et al., 1999).

#### 4.4 Nutrient Fluxes from Submarine Groundwater Discharge

The nature of chemical tracers of groundwater discharge underscores the fundamental issue of SGD vis--vis nutrient fluxes: groundwater chemistry differs from surface water chemistry. Therefore, groundwater discharge to surface waters can alter the chemistry (and, by extension, the biogeochemistry) of the receiving waters in the coastal zone.

Surface water discharge to the coastal zone undergoes physical and biogeochemical processing via the estuarine filter (Kennedy, 1984), within which particle precipitation, geochemical transformation, and biological uptake alter the water chemistry such that the water that leaves the estuary is different from that which enters the estuary as fluvial discharge. Submarine groundwater discharge bypasses the estuarine filter, though there is evidence that the groundwater discharge is geochemically altered via passage through a 'subterranean estuary' (Paerl, 1997; Charette & Sholkovitz, 2002). Where aquifer chemistry has been affected by anthropogenic activities (e.g., infiltration of fertilizers and agricultural runoff), inorganic nutrients may be transported with groundwater, bypassing the estuarine

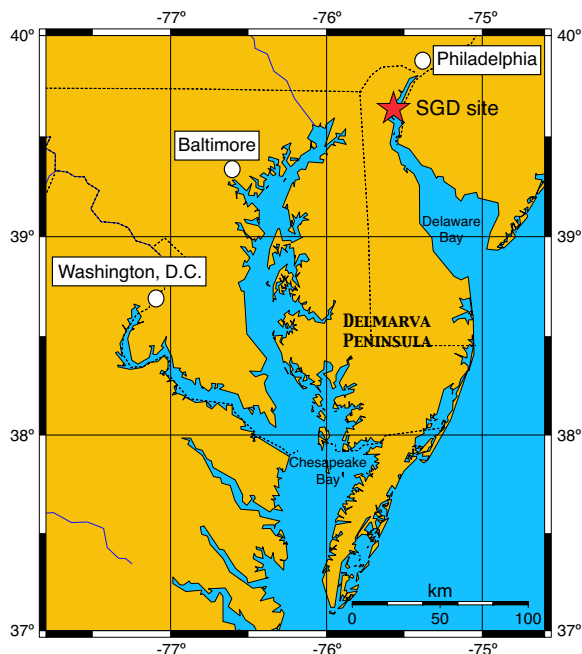


Figure 4.4: Delmarva Peninsula. The peninsula is located on the mid-Atlantic bight of the eastern United States and contains portions of the states of Delaware, Maryland, and Virginia. Star indicates location of SGD study site in Schwartz (2003).

filter to be transported (more or less) directly into receiving waters.

#### 4.4.1 Case study: Nitrate and SGD in the Delaware River and Bay Estuary

Using excess  $^{222}\text{Rn}$  as a groundwater tracer in the Delaware Estuary, Schwartz (2003) calculated a groundwater flux of  $14.5\text{--}29.3\text{ m}^3\text{ s}^{-1}$ , equivalent to the discharge of the Schuylkill and Brandywine Rivers, the second and third largest tributaries to the Delaware River and Bay. This discharge occurred along 12 km of the estuary and is equal to an upward flow velocity of  $5\text{--}10\text{ cm d}^{-1}$ .

Agriculture, including crop and chicken farming, is a major industry on the Delmarva Peninsula, a broad coastal plain peninsula located near several major urban centers and separating the Chesapeake Bay and the Delaware Bay (Figure 4.4).

Two aquifers are hydraulically connected to the surficial aquifer in the vicinity of the Delaware SGD site. These units were identified by reviewing stratigraphic maps of the underlying geology of the Delmarva Peninsula and appear to be the source of the groundwater discharge (Schwartz, 2003). The geochemistry of these source aquifers has been affected by agricultural activities and groundwater nitrate concentrations are as high as  $1,000\text{ }\mu\text{M}$  (Bachman & Ferrari, 1995). Nitrate is a potential nutrient for both heterotrophic and autotrophic organisms in the estuary.

The groundwater-mediated nitrate flux to the Delaware SGD zone was calculated by multiplying the groundwater flux rate by the average nitrate concentrations in the two source aquifers ( $175\text{ }\mu\text{M}$ ); this resulted in a groundwater nitrate flux of  $2.5\text{--}5.1\text{ moles s}^{-1}$ . The groundwater nitrate flux compares favorably to non-point source and fluvial nitrate sources to the Delaware Estuary (Table 4.1).

It must be noted that this groundwater nitrate flux refers only to the 12-km long site studied by Schwartz (2003); additional SGD sites in the Delaware estuary have been indicated by excess radon data (Schwartz, 2001) and subcropping stratigraphy (Krantz, personal communication). Therefore, the groundwater nitrate flux calculated above should be considered to be the minimum groundwater contribution to the estuarine receiving waters.

#### 4.4.2 Other SGD nutrient flux investigations

While assessing global new-nitrogen fluxes to the coastal ocean, Paerl (1997) observed that “parallel estimates for groundwater-nitrogen inputs into these [coastal] waters . . . indicate a growing budgetary role for this nitrogen source, ranging from  $<10$  to  $30\%$  of the new nitrogen inputs.” This same study estimated that SGD to the coastal ocean accounts for  $5\text{--}10\text{ Tg N y}^{-1}$ ; this value is up to one-third that of the coastal ocean new-nitrogen loading by both atmospheric deposition (ca.  $35\text{ Tg N y}^{-1}$ ) and the combined effect of flu-

Table 4.1: Delaware River and Bay nitrate fluxes.

Delaware Estuary Nitrate Source	Nitrate flux [moles s <sup>-1</sup> ]	SGD Nitrate Flux as Percentage of Cited Flux	Citation
SGD	2.5–5.1	N/A	Schwartz, 2001
Wet atmospheric deposition	7	36–73%	Scudlark & Church, 1993
Municipal industrial effluent	16	16–32%	Scudlark & Church, 1993
14 Major municipal and sewage effluents, combined	7.1	35–72%	Frake <i>et al.</i> , 1983
Delaware R. at Trenton	18	14–28%	Scudlark & Church, 1993
Delaware R. at Trenton	20.7	12–25%	Frake <i>et al.</i> , 1983
Delaware River at S=0	55	5–9%	Scudlark & Church, 1993
Schuylkill River	14.7	17–35%	Frake <i>et al.</i> , 1983
Lower Delaware Bay tributaries, combined	8	31–64%	Scudlark & Church, 1993

vial discharge and surface runoff (30 Tg N y<sup>-1</sup>). Both the aforementioned case study and the results summarized above certainly suggest that the ‘growing budgetary role’ ascribed to groundwater nutrient fluxes by Paerl (1997) may yet increase as additional studies are undertaken.

Several SGD assessments were performed throughout the eastern USA over the past 25 years. Though this SGD research constitutes only a fraction of the studies on surface water impacts on estuarine and coastal biogeochemistry, many studies have revealed that the biogeochemical impact of SGD can be important both locally and regionally. These studies have determined the flux of dissolved nutrients, including nitrate, phosphate, the dissolved inorganic nitrogen (DIN), and dissolved inorganic phosphate (DIP). Some notable research into SGD nutrient fluxes to the coastal zone include:

- Great South Bay, New York: Capone and Bautista (1985)
  - SGD flux of 3.6–18.3 m<sup>3</sup> m<sup>-2</sup> y<sup>-1</sup>
  - SGD nitrate concentration at discharge: 10 μM (average)
- Coastal Ocean of the South Atlantic Bight, South Carolina: Krest *et al.* (2000)
  - SGD-derived marsh input to coastal ocean:
    - \* 6.6 × 10<sup>8</sup> mol N y<sup>-1</sup>

- SGD nitrate loading accounts for ≥ 20% of the new nitrogen inputs via surface runoff

- Waquoit Bay, Massachusetts: Valiela *et al.* (1992)

- SGD nitrate loading in three subtributaries: 61 mmol m<sup>-2</sup> y<sup>-1</sup>

- Eastern Florida Bay, Florida: Corbett *et al.* (1999)

- SGD DIN: 110 ± 60 mmol m<sup>-2</sup> y<sup>-1</sup>

- SGD PO<sub>4</sub>: 0.21 ± 0.11 mmol m<sup>-2</sup> y<sup>-1</sup>

- SGD DIN flux is 3.7 times higher than area-normalized Everglades surface water flux, while SGD DIP flux is 2.1 times higher than area-normalized Everglades surface water flux

- \*  $3.2 \times 10^7$  mol P  $y^{-1}$
- Fluvial input to coastal ocean:
  - \*  $6.0 \times 10^8$  mol N  $y^{-1}$
  - \*  $2.6 \times 10^7$  mol P  $y^{-1}$
- Estimated that half of the terrestrially-derived nutrient flux to the coastal ocean originates from salt marshes, with groundwater being the primary source of marsh nutrients
- Pettaquamscutt River, Rhode Island: Kelly and Moran (2002)
  - SGD DIN: 61–180 mmol  $m^{-2} y^{-1}$
  - SGD DIP: 4.4–13 mmol  $m^{-2} y^{-1}$
- Elizabeth River, Virginia: Charette and Buessler (2004)
  - SGD DIN:  $1644 \pm 1680$  mmol  $m^{-2} y^{-1}$
  - SGD DIP:  $58 \pm 62$  mmol  $m^{-2} y^{-1}$
  - SGD DIN flux is 1.7 times the Chesapeake Bay areal average for DIN loading, while the SGD DIP flux is 2.7 times greater than areal-averaged Chesapeake Bay DIP loading

As a comparison, the Delaware SGD nitrate flux, above, is equivalent to 3300–6700 mmol N  $m^{-2} y^{-1}$  throughout the groundwater discharge zone.

## 4.5 The Future

According to a recent summary, estimates of the global magnitude of SGD based on hydrological and water balance calculations range from 0.3–16% of river discharge, with most estimates in the range of 6–10% (Burnett *et al.*, 2003). These values refer only to the discharge of fresh, terrestrially-derived water via SGD and, therefore, ignore the contribution of seawater discharged to the coastal zone following mixing with fresh groundwater. As this mixing of fresh water and

seawater within the aquifer has important ramifications for the chemistry of the discharged groundwater, these freshwater-only estimates must be considered the lower boundary.

The increased use of radioisotope tracers over the past ten years has allowed researchers to more accurately constrain groundwater discharge fluxes. By pairing multiple tracers and improved seepage meter technologies, groundwater flux estimates can be made more accurate yet (Burnett *et al.*, 2003). Improved accuracy in groundwater flux calculations will yield better nutrient flux data. Furthermore, as multiple tracers, including dissolved nutrients and stable isotope signatures, are added to the existing radioisotope tracers, we can increase our understanding of how SGD transports dissolved nutrients to the coastal zone.

The number of investigations into the transport of nutrients to the coastal zone via SGD is growing, but this remains a relatively new field of research. Most of the existing research has been performed in the eastern United States and in limited regions of Europe, Japan, and Oceania (Taniguchi *et al.*, 2002). There is a conspicuous lack of SGD studies in Asia, India, Africa, South America, and the western United States. An expansion of SGD studies, including assessments of SGD-nutrient fluxes to estuaries and the coastal ocean, will provide insight into anthropogenic impacts on, and non-point source nutrient fluxes to, the coastal zone.

## References

- BACHMAN, L.J., & FERRARI, M.J. 1995. *Quality and geochemistry of groundwater in southern New Castle County, Delaware*. Tech. rept. 52. USGS Report of Investigations.
- BANKS, W.S., PAYLOR, R.L., & HOUGHES, W.B. 1996. Using thermal infrared imagery to delineate ground-water discharge. *Ground Water*, **34**, 434–443.
- BERNER, E.K., & BERNER, R. A. 1987. *The Global Water Cycle: Geochemistry and Environment*. Englewood Cliffs, NJ: Prentice-Hall.

- BURNETT, W.C., BOKUNIEWICZ, H., HUETTEL, M., MOORE, W.S., & TANIGUCHI, M. 2003. Groundwater and pore water inputs to the coastal zone. *Biogeochemistry*, **66**, 3–33.
- CABLE, J.E., BURNETT, W.C., CHANTON, J.P., & WEATHERLY, G.L. 1996. Estimating groundwater discharge into the northeastern Gulf of Mexico using radon-222. *Earth and Planetary Science Letters*, **144**, 591–604.
- CAPONE, D.G., & BAUTISTA, M.F. 1985. A groundwater source of nitrate in nearshore marine sediments. *Nature*, **313**, 214–216.
- CHARETTE, M.A., & BUSSLER, K.O. 2004. Submarine groundwater discharge of nutrients and copper to an urban subestuary of Chesapeake Bay (Elizabeth River). *Limnology and Oceanography*, **49**, 376–385.
- CHARETTE, M.A., & SHOLKOVITZ, E.R. 2002. Oxidative precipitation of groundwater-derived ferrous iron in the subterranean estuary of a coastal bay. *Geophysical Research Letters*, **29**, doi:10.1029/2001GL014512.
- CHARETTE, M.A., SPLIVALLO, R., HERBOLD, C., BOLLINGER, M.S., & MOORE, W.S. 2003. Salt marsh submarine groundwater discharge as traced by radium isotopes. *Marine Chemistry*, **84**, 113–121.
- CHURCH, T.M. 1996. An underground route for the water cycle. *Nature*, **380**, 579–580.
- CIFUENTES, L.A., SCHEMEL, L. E., & SHARP, J.H. 1990. Quantitative and numerical analyses of the effects of river inflow variations on mixing diagrams in estuaries. *Estuarine, Coastal and Shelf Science*, **30**, 411–427.
- CORBETT, D.R., CHANTON, J.P., BURNETT, W.C., DILLON, K.S., RUTKOWSKI, C., & FOURQUREAN, J. 1999. Patterns of groundwater discharge into Florida Bay. *Limnology and Oceanography*, **44**, 1045–1055.
- DAHM, C.N., BRIMM, N.B., MARMONIER, P., VALETT, H.M., & VERVIER, P. 1998. Nutrient dynamics at the interface between surface waters and groundwaters. *Freshwater Biology*, **40**, 427–451.
- DILLON, K.S., CORBETT, D.R., CHANTON, J.P., BURNETT, W.C., & FURBISH, D.J. 1999. The use of sulfur hexafluoride (SF<sub>6</sub>) as a tracer of septic tank effluent in the Florida Keys. *Journal of Hydrology*, **220**, 129–140.
- FRAKE, A.C., SHARP, J.H., PIKE, S.E., PENNOCK, J.R., CULBERSON, C.H., & CANZONIER, W.J. 1983. Nutrients (nitrogen, phosphorus, and silica). In: SHARP, J.H. (ed), *The Delaware Estuary: Research as background for estuarine management and development. Report to Delaware River and Bay Authority*. Newark, Delaware: University of Delaware (College of Marine Studies) and New Jersey marine Science Consortium.
- HAMILTON, P.A., DENVER, J.M., PHILLIPS, P.J., & SHEDLOCK, R.J. 1993. *Water-quality assessment of the Delmarva Peninsula, Delaware, Maryland, and Virginia — effects of agricultural activities on, and distribution of, nitrate and other inorganic constituents in the surficial aquifer*. Tech. rept. Open-File Report 93–40. U.S. Geological Survey.
- HUSSAIN, N., CHURCH, T.M., & KIM, G. 1999. Use of Rn-222 and Ra-226 to trace groundwater discharge into the Chesapeake Bay. *Marine Chemistry*, **65**, 127–134.
- JOHANNES, R.E. 1980. The ecological significance of the submarine discharge of groundwater. *Marine Ecology Progress Series*, **3**, 365–373.
- KELLY, R.P., & MORAN, S.B. 2002. Seasonal changes in groundwater input to a well-mixed estuary estimated using radium isotopes and implications for coastal nutrient budgets. *Limnology and Oceanography*, **47**, 1796–1807.

- KOHOUT, F.A. 1966. Submarine springs: A neglected phenomenon of coastal hydrology. *Hydrology*, **26**, 391–413.
- KREST, J.M., MOORE, W.S., GARDNER, L.R., & MORRIS, J.T. 2000. Marsh nutrient export supplied by groundwater discharge: evidence from Ra measurements. *Global Biogeochemical Cycles*, **14**, 167–176.
- KU, T.-L., LUO, S., LESLIE, B., & HAMMOND, D. E. 1992. Decay-series disequilibria applied to the study of rock-water interactions and geothermal systems. *Pages 631–668 of: IVANOVICH, M., & HARMON, R.S. (eds), Uranium-series disequilibrium: applications to earth, marine, and environmental sciences*, 2nd edition edn. Oxford: Clarendon Press.
- LEBO, M.E., SHARP, J.H., & CIFUENTES, L.A. 1994. Contribution of river phosphate variations to apparent reactivity estimated from phosphate-salinity diagrams. *Estuarine, Coastal and Shelf Science*, **39**, 583–594.
- MAYBECK, M. 1982. Carbon, nitrogen, and phosphorus transport by world rivers. *American Journal of Science*, **282**, 401–450.
- MILLER, D.C., & ULLMAN, W.J. 2004. Ecological consequences of estuarine groundwater discharge at Cape Henlopen, Delaware Bay, USA. *Ground Water*, in press.
- MOORE, W.S. 1996. Local groundwater inputs to coastal waters revealed by <sup>226</sup>Ra enrichments. *Nature*, **380**, 612–614.
- MOORE, W.S. 1999. The subterranean estuary: a reaction zone of ground water and sea water. *Marine Chemistry*, **65**, 111–125.
- MOORE, W.S., KREST, J.M., TAYLOR, G., ROGGENSTEIN, E., JOYE, S.R., & LEE, R. 2002. Thermal evidence of water exchange through a coastal aquifer: implications for nutrient fluxes. *Geophysical Research Letters*, **29**, doi:10.1029/2002GLO14923.
- PAERL, H. W. 1997. Coastal eutrophication and harmful algal blooms: Importance of atmospheric deposition and groundwater as "new" nitrogen and other nutrient sources. *Limnology and Oceanography*, **42**, 1154–1167.
- PENNOCK, J.R. 1987. Temporal and spatial variability in phytoplankton ammonium and nitrate uptake in the Delaware Estuary. *Estuarine, Coastal and Shelf Science*, **24**, 841–857.
- PORTNOY, J.W., NOWICKI, B.L., ROMAN, C.T., & URISH, D.W. 1998. The discharge of nitrate-contaminated groundwater from developed shoreline to marsh-fringed estuary. *Water Resources Research*, **34**, 3095–3104.
- SCHWARTZ, M.C. 2001. *Using excess radon-222 to trace submarine groundwater discharge into the Delaware estuary*. PhD thesis, University of Delaware, College of Marine Studies.
- SCHWARTZ, M.C. 2003. Significant groundwater input to a coastal plain estuary: assessment from excess radon. *Estuarine, Coastal and Shelf Science*, **56**, 31–42.
- SCUDLARK, J.R., & CHURCH, T.M. 1993. Atmospheric input of inorganic nitrogen to Delaware Bay. *Estuaries*, **16**, 747–759.
- SHARP, J.H., CIFUENTES, L.A., COFFIN, R.B., PENNOCK, J.R., & WONG, K.-C. 1986. The influence of river variability on the circulation, chemistry, and microbiology of the Delaware Estuary. *Estuaries*, **9**, 261–269.
- TANIGUCHI, M., BURNETT, W.C., CABLE, J.E., & TURNER, J. V. 2002. Investigations of submarine groundwater discharge. *Hydrological Processes*, **16**, 2115–2129.
- TANIGUCHI, M., TURNER, J. V., & SMITH, A.J. 2003. Evaluation of groundwater discharge rates from subsurface temperature in Cockburn Sound, Western Australia. *Biogeochemistry*, **66**, 167–176.