

The subterranean estuary: a reaction zone of ground water and sea water

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Abstract

Mixing between meteoric water and sea water produces brackish to saline water in many coastal aquifers. In this mixing zone, chemical reactions of the salty water with aquifer solids modify the composition of the water; much as riverine particles and suspended sediments modify the composition of surface estuarine waters. To emphasize the importance of mixing and chemical reaction in these coastal aquifers, I call them subterranean estuaries. Geochemical studies within subterranean estuaries have preceded studies that attempt to integrate the effect of these systems on the coastal ocean. The mixing zone between fresh ground water and sea water has long been recognized as an important site of carbonate diagenesis and possibly dolomite formation. Biologists have likewise recognized that terrestrial inputs of nutrients to the coastal ocean may occur through subterranean processes. Further evidence of the existence and importance of subterranean estuaries comes from the distribution of chemical tracers in the coastal ocean. These tracers originate within coastal aquifers through chemical reactions of the saline water with aquifer solids. They reach the coastal ocean as the surface and subterranean systems exchange fluids. Exchange between the subterranean estuary and the coastal ocean may be quantified by the tracer distribution in the coastal ocean. Examples from the east and Gulf coasts of the U.S., as well as the Bay of Bengal, will be used to evaluate the importance of these unseen estuaries in supplying not only chemical tracers, but also nutrients, to coastal waters. Anthropogenic effects on subterranean estuaries are causing significant change to these systems. Ground water mining, sea level rise, and channel dredging impact these systems directly. The effects of these changes are only beginning to be realized in this vital component of the coastal ecosystem. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

To an oceanographer, water seeping from the land into the coastal ocean is considered ground water, regardless of its salinity or history. The same process

may be considered by a hydrologist as sea water recycling, if the water has a salinity similar to ocean water. In this paper, I attempt to reconcile these viewpoints by introducing a new term: the subterranean estuary. This is defined as a coastal aquifer where ground water derived from land drainage measurably dilutes sea water that has invaded the aquifer through a free connection to the sea.

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The widely accepted definition of an estuary, as proposed by Pritchard (1967), is:

A semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage.

In this paper, I shall argue that some coastal aquifers can be considered subterranean estuaries because they display the most important features of surface estuaries. I shall further argue, as others have before, that fluxes of fluids from subterranean estuaries are important to the chemistry and biology of the coastal ocean (Marsh, 1977; Johannes, 1980; D'Elia et al., 1981; Simmons, 1992; Moore, 1996, 1997; Snyder, 1996).

In subterranean estuaries, chemical reactions between the mixed waters and aquifer solids modify the fluid composition; much as riverine particles and suspended sediments modify the composition of surface estuarine waters. Geochemists studying coastal aquifers have long recognized the importance of chemical reactions between aquifer solids and a mixture of sea water and fresh ground water (Runnels, 1969; Back et al., 1979). For example, mixing of sea water supersaturated with respect to calcite with fresh ground water 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 non-linear dependence of activity coefficients on ionic strength and on changes in the distribution of inorganic carbon species as a result of mixing. This mechanism was proposed by Back et al. (1979) to explain the massive dissolution of limestone along the northern Yucatan Peninsula. Dissolution of submarine limestone by ground water flow creates distinctive canyons and escarpments on continental margins (Paull et al., 1990).

Calcite dissolution may also be driven by the addition of CO_2 to fluids in the subterranean estuary. Burt (1993) has shown that salt water penetrating the Floridan aquifer near Savannah, GA, is enriched in inorganic carbon and calcium, as well as ammonia and phosphate, relative to sea water and fresh ground water endmembers. He attributed these enrichments to oxidation of organic carbon within the aquifer or CO_2 infiltration from shallower aquifers.

Sea water–ground water mixing has 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 ground water could be undersaturated with respect to calcite, yet remain supersaturated with respect to dolomite. They suggested that this solution could lead to the replacement of calcite by dolomite. Other studies reveal that dolomite formation is inhibited by the presence of sulfate ion (Folk and Land, 1975; Baker and Kastner, 1981). The formation of dolomite may be favored in sea water–ground water mixtures where sulfate has been reduced. Evidence of this process comes from the formation of dolomite in recent sediments in a mixing zone between relatively fresh ground water and low sulfate brines from the Dead Sea (Shatkay and Magaritz, 1987).

Biologists have also recognized the importance of sea water recycling through coastal sediments. Riedl et al. (1972) pointed out that advection of oxygenated water across the sediment surface must occur to prevent sediments from becoming reducing. These authors proposed that the circulation of sea water through sediments was driven by 'surge pumping'. They estimated that the residence time of the ocean relative to circulation through continental margin sediments was 14,000 years. Other studies have revealed that ground water discharge or sea water cycling may be an important source of nutrients for coral reefs (Marsh, 1977; Johannes, 1980; D'Elia et al., 1981) or other communities on the continental shelf (Simmons, 1992; Snyder, 1996). Simmons (1992) estimated that the fluxes of nitrogen and phosphorus to the Georgia shelf from submarine ground water discharge exceeded fluxes from local rivers.

Ground water-borne nutrients may have significant effects on water quality in surface estuaries (Reay et al., 1992). Because nutrient concentrations in coastal ground water may be several orders of magnitude greater than surface waters, ground water input may be a significant factor in the eutrophication of coastal waters (Valiela et al., 1990). Input of high nitrate ground water may be linked to the initiation of intense algal blooms called brown tides

in coastal waters near Long Island, NY (LaRoche et al., 1997).

2. Mechanisms of flow in subterranean estuaries

Several mechanisms have been proposed to explain the cycling of ground water–sea water mixtures through coastal sediments. The classic Ghyben–Herzberg relation predicts that the discharge of such mixtures will be restricted to a few hundred meters from shore in unconfined aquifers. However, coastal sediments often comprise a complex assemblage of confined, semi-confined and unconfined aquifers. Simple models do not consider the anisotropic nature of the coastal sediments; dynamic processes of dispersion, tidal pumping and sea level change; or the non-steady state nature of coastal aquifers due to ground water mining (Moore and Church, 1996).

Kohout (1965) recognized that cyclic flow of sea water through coastal aquifers could be driven by geothermal heating. He postulated that the Floridan aquifer in western Florida is in hydraulic contact with sea water at depths of 500–1000 m in the Gulf of Mexico. Cool sea water (5–10°C) entering the deep aquifer would be heated as it penetrates the interior of the platform. The warm water would rise through fractures or solution channels, mix with fresh ground water and emerge as warm springs along the Florida coast. Kohout (1967) presented temperature profiles in deep wells that revealed a negative horizontal temperature gradient from the interior of the Florida platform to the margin, where cool sea water penetration was hypothesized. Wells near the margin displayed negative vertical temperature gradients at depths of 500–1000 m. These observations were consistent with the proposed large-scale cycling of sea water–ground water mixtures through the aquifer.

Another mechanism that may be important for localized cycling is evaporation of sea water in restricted coastal systems. This reflux mechanism (Adams and Rhodes, 1960; Simms, 1984) is driven by the increased density of isolated sea water after evaporation. Reflux cycling can occur in response to daily, monthly, or longer sea level changes.

Cycling of sea water through coastal aquifers may also be driven by an inland hydraulic head. As fresh water flows through an aquifer to the sea above a layer of salt water, it encounters an irregular interface where mixing of the fluids is driven by diffusion and dispersion (Cooper et al., 1964). This pattern of two-layer circulation and mixing is similar to that observed in many surface estuaries (Pritchard, 1967). Dispersion along the interface may be enhanced by tidal forces operating in an anisotropic medium. Tidal forces are clearly reflected in semi-confined coastal aquifers (Burt et al., 1987). During rising tide, sea water enters the aquifer through breaches in confining units; during falling tide, it flows back to the sea. Through each tidal cycle, the net movement of the fresh water–salt water interface may be small; but during rising tide, preferential flow of salt water along channels of high hydraulic conductivity may be caused by anisotropic permeability. This produces irregular penetration of salt water into fresh water zones. Diffusion mixes the salt into the adjacent fresh water and chemical reactions may ensue. During falling tide, the reverse occurs as fresher water penetrates along these same paths and gains salt by diffusion. 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. The fluid expelled to the sea may be quite different chemically from the sea water that entered.

An additional mechanism that may affect subterranean estuaries is the upward flow of fluids from deep, pressurized aquifers. The continental shelf off the southeastern U.S. coast consists of a thick sequence of Tertiary limestone overlain by relic sand. Drilling has revealed that substantial fresh water lies trapped in the deep sediments. The AMCOR project (Hathaway et al., 1979) drilled 19 cores on the continental shelf and noted that fresh or slightly brackish waters underlie much of the Atlantic continental shelf. JOIDES test hole J-1B drilled 40 km offshore from Jacksonville, FL, was set in the Eocene Limestone (equivalent to the Floridan aquifer onshore) 250 m below sea level. This well tapped an aquifer that produced a flow of fresh water to a height of 10 m above sea level (Kohout et al., 1988). Manheim (1967) has reviewed substantial evidence

for submarine discharge of water on the Atlantic continental slope of the southern United States.

Bisson (1994) introduced the term ‘mega-watersheds’ to describe the broadest possible catchment areas that may contribute water to deep reservoirs. He explains the existence of large deep reservoirs of fresh and brackish water in arid as well as other regions as due to tectonically induced regional fracture permeability, largely controlled by basement tectonism. Upward leakage along fractures from these deep systems may provide an additional source of fluids to the shallow subterranean estuary.

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. During low glacial sea stands, modern surface and subterranean estuaries did not exist in their present locations. Twenty thousand years ago, subterranean estuaries were probably restricted to the edge of the continental shelf. At this time, river channel cutting

may have caused breaches in overlying confining units. If these channels were filled with coarse clastics during sea level rise, the channel fill may currently serve as an effective conduit for shallow ground water flow across the shelf and the breaches may provide communication between the superficial and deeper confined aquifers. As the rising sea approached its current level, both surface and subterranean estuaries developed as sea water infiltrated into river basins and coastal aquifers.

In a provocative book titled *The Hidden Sea*, Chapelle (1997) pointed out that in *Life on the Mississippi*, Mark Twain noted a number of remarkable aspects of the Mississippi River. One of the most puzzling was the change in river level from droughts to floods:

The rise is tolerably uniform down to Natchez—about 50 ft. But at Bayou La Fourche, the river rises only 24 ft; at New Orleans only 15, and just above the mouth only two and one half.

Table 1

Comparison of the composition of fluids extracted from the subterranean estuary with river and ocean water

| Location | Salinity | Ba (nM) | ²²⁶ Ra (dpm l ⁻¹) | PO ₄ (μM) | NH ₃ + NO ₃ (μM) |
|------------------------|----------|---------|--|----------------------|--|
| <i>North Inlet, SC</i> | | | | | |
| 1–3 m wells | 0.36 | 50 | 0.4 | 0.1 | 33 |
| | 0.90 | 564 | 1.2 | 0.1 | 67 |
| | 3.49 | 1470 | 4.3 | 1.8 | 74 |
| | 10.28 | 500 | 3.2 | 1.1 | 138 |
| | 34.47 | 1000 | 10.5 | 8.5 | 93 |
| <i>Cape Fear, NC</i> | | | | | |
| Artesian well | 17.0 | 3300 | 9.00 | | |
| <i>Charleston, SC</i> | | | | | |
| Shallow well | 7.0 | | 1.30 | | |
| Deep well | 24.0 | | 5.30 | | |
| <i>Hilton Head, SC</i> | | | | | |
| AW 64 m | 20.3 | 1304 | 2.09 | 2.72 | 145 |
| AW 70 m | 16.8 | 1345 | 2.14 | 2.66 | 155 |
| TS 55 m | 0.4 | 49 | 0.13 | 4.64 | 36 |
| TS 64 m | 11.3 | 775 | 1.09 | 3.27 | 115 |
| TS 70 m | 5.3 | 1393 | 1.29 | 2.90 | 182 |
| Pee Dee River | 0.0 | 170 | 0.03 | 0.1 | 0.8 |
| Savannah River | 0.0 | 130 | 0.04 | 0.1 | 0.5 |
| Atlantic Ocean | 36.0 | 40 | 0.08 | 0.1 | 0.1 |

Data from Moore (1996); Moore and Shaw (1998); Krest, personal communication; Crotwell, personal communication; Shaw, personal communication.

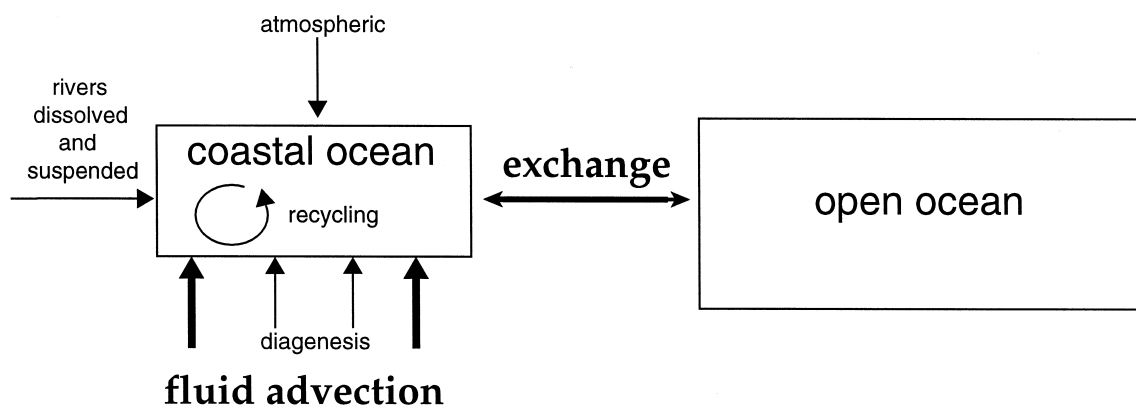
Chapelle (1997) pointed out that because the river channel becomes narrower toward the mouth, just the opposite behavior would be expected unless the river was storing large quantities of water in the underlying aquifer. The step from this observation to the concept of a subterranean estuary at the river mouth is not a long one. Changes in river level must cause changes in the amount of fluid discharged to the sea through the subterranean estuary.

Demand for fresh water by coastal communities has intensified infiltration of sea water into subterranean estuaries by decreasing the hydraulic pressure in coastal aquifers (Smith, 1988). In many cases, seasonal ground water usage causes considerable fluctuation in hydraulic pressure and salt infiltration

in these systems. Changes in ground water usage are also reflected in the position of the fresh water–salt water interface in semi-confined coastal aquifers (Smith, 1994). Over-pumping of coastal aquifers has caused some water to become non-potable due to salt encroachment. When such aquifers are abandoned, they may recharge with fresh water. In this case, salty fluids in the aquifer may be discharged to the sea. Examples from the South Carolina coast will be presented later in the paper.

3. Use of tracers to study subterranean aquifers

Unlike their surface counterparts, subterranean estuaries cannot be seen. Evidence of their function



Strategy to determine the importance of fluid advection

1. Identify tracers derived from fluid advection that are not recycled in the coastal ocean.
2. Map the distribution of the tracer in the coastal ocean and evaluate other sources.
3. Determine the exchange rate with the open ocean.
4. Calculate the tracer flux to the ocean, hence the tracer flux from fluid advection.
5. Measure the average tracer concentration in subsurface fluids to calculate fluid flux.
6. Measure other components of interest in the fluids to calculate fluxes of reactive species to the coastal ocean due to submarine fluid input.

Fig. 1. Strategy to use tracers in the coastal ocean to assess fluid inputs from subterranean estuaries.

and importance relies on signals they exchange with coastal waters. An estimate of recent salt water encroachment into these systems comes from the penetration of ^{14}C into coastal aquifers from the adjacent ocean (Back et al., 1970; Burt, 1993). Additional evidence of exchange with coastal waters is provided by chemical tracers that are highly enriched in fluids contained in the subterranean estuary and relatively non-reactive in coastal waters. Elevated concentrations of such tracers in the coastal ocean provide the evidence that subterranean estuaries are freely connected to the sea and that fluid exchange in these systems is substantial. Several tracers have been used in this regard including ^{222}Rn , Ra isotopes, Ba, and methane. These tracers are highly enriched in the salty pore waters of coastal aquifers. Some examples of the contrasting composition of subsurface fluids with surface waters are given in Table 1.

The release of subsurface fluids to the coastal ocean may create chemical anomalies that can be recognized over large areas. These chemical signals integrate the effects of fluid input over the study area. By combining the distribution of long-lived tracers (e.g., ^{226}Ra , ^{228}Ra , Ba) with estimates of coastal ocean exchange rates, the offshore flux of the tracer may be estimated. For short-lived tracers (e.g., ^{222}Rn , ^{224}Ra , ^{223}Ra), decay may be more important to the balance than exchange. The net offshore flux or decay of the tracer must be balanced by new input of the tracer. The input of the tracer from subterranean estuaries may be established after other sources (e.g., rivers, suspended sediments, diffusion) are quantified. Ratios of other elements to the tracer in the advecting fluids may be used to estimate the fluxes of other elements due to this process. This strategy is illustrated in Fig. 1. Currently, estimates of fluid composition are not well constrained; this will change as more data become available.

4. Case studies of tracer applications

To illustrate the use of tracers to qualitatively or quantitatively estimate the input of subsurface fluids, I will review a number of case studies. These studies provide evidence that water exchange between subterranean estuaries and ocean waters may occur

throughout the coastal ocean. There are studies that reveal the input of subsurface fluids to coastal salt marshes, the inner continental shelf, the middle/outer continental shelf and even to deep troughs. The following case studies are examples of the interaction of the subterranean estuary with the ocean.

Fanning et al. (1981) documented thermal and chemical anomalies in water from submarine springs near Ft. Myers, FL. The warm spring water had the same chlorinity as deep Gulf of Mexico water, but was highly enriched in ^{222}Rn , ^{226}Ra , ^{228}Ra , and SiO_2 , slightly depleted in Mg, and contained negligible O_2 . These authors concluded that the circulation was driven by the geothermal process envisioned by Kohout (1965). Because the water exiting these springs was not measurably diluted by fresh ground water, these springs do not qualify as true examples of subterranean estuaries. However, the geothermal circulation process may be active in systems where dilution of sea water is evident. Kohout (1965) clearly intended to include the mixing of fresh ground water and sea water for his model.

In Spencer Gulf, Australia, a system that receives only intermittent surface freshwater discharge Veeh et al. (1995) reported high ^{226}Ra activities (15–25 dpm/100 l) in surface waters. These ^{226}Ra activities could not be explained by river/sediment input or by evaporation. They suggested that the excess ^{226}Ra in the gulf may be derived from the discharge of ground water enriched in Ra. In this arid region, intense evaporation may initiate the reflux mechanism discussed earlier.

The North Inlet, SC, salt marsh is a coastal system with negligible surface freshwater input. Here, ^{226}Ra and ^{228}Ra activities in the tidal creeks exceed offshore values by factors of 2 to 4. Because the surface water in North Inlet has only a 12-h residence time, a considerable internal source of ^{226}Ra and ^{228}Ra is required to maintain the large difference with the coastal ocean. Rama and Moore (1996) computed the input of ^{226}Ra and ^{228}Ra to this system by regeneration from Th parents in surface sediments and diffusion from deeper sediments. These sources were at least two orders of magnitude too low to explain the fluxes exiting the system. They concluded that the subsurface advection of fluids enriched in Ra isotopes was required to balance the fluxes from North Inlet to the coastal ocean.

Cable et al. (1996) reported high ^{222}Rn and ^{226}Ra activities in subsurface coastal waters near the Florida State University Marine Laboratory (FSUML). They modeled the measured ^{222}Rn and ^{226}Ra distributions and water residence times based on current velocities to derive fluxes of ^{222}Rn and ^{226}Ra to the study area. The potential supply of Ra to the region by local rivers could support less than 10% of the ^{226}Ra enrichment and less than 3% could be supported by diffusion from surface sediments. Cable et al. concluded that the flow of submarine ground water highly enriched in ^{222}Rn and ^{226}Ra into the study

area was the major source of these radionuclides. They estimated that the fluid flux to this 620 km² 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.

Along the coast of South Carolina, ^{226}Ra concentrations exceed the amount that can be supported by local rivers (Moore, 1996). Fig. 2 is a map of the distribution of ^{226}Ra in surface waters along this coast. Moore (1996) demonstrated that less than 10%

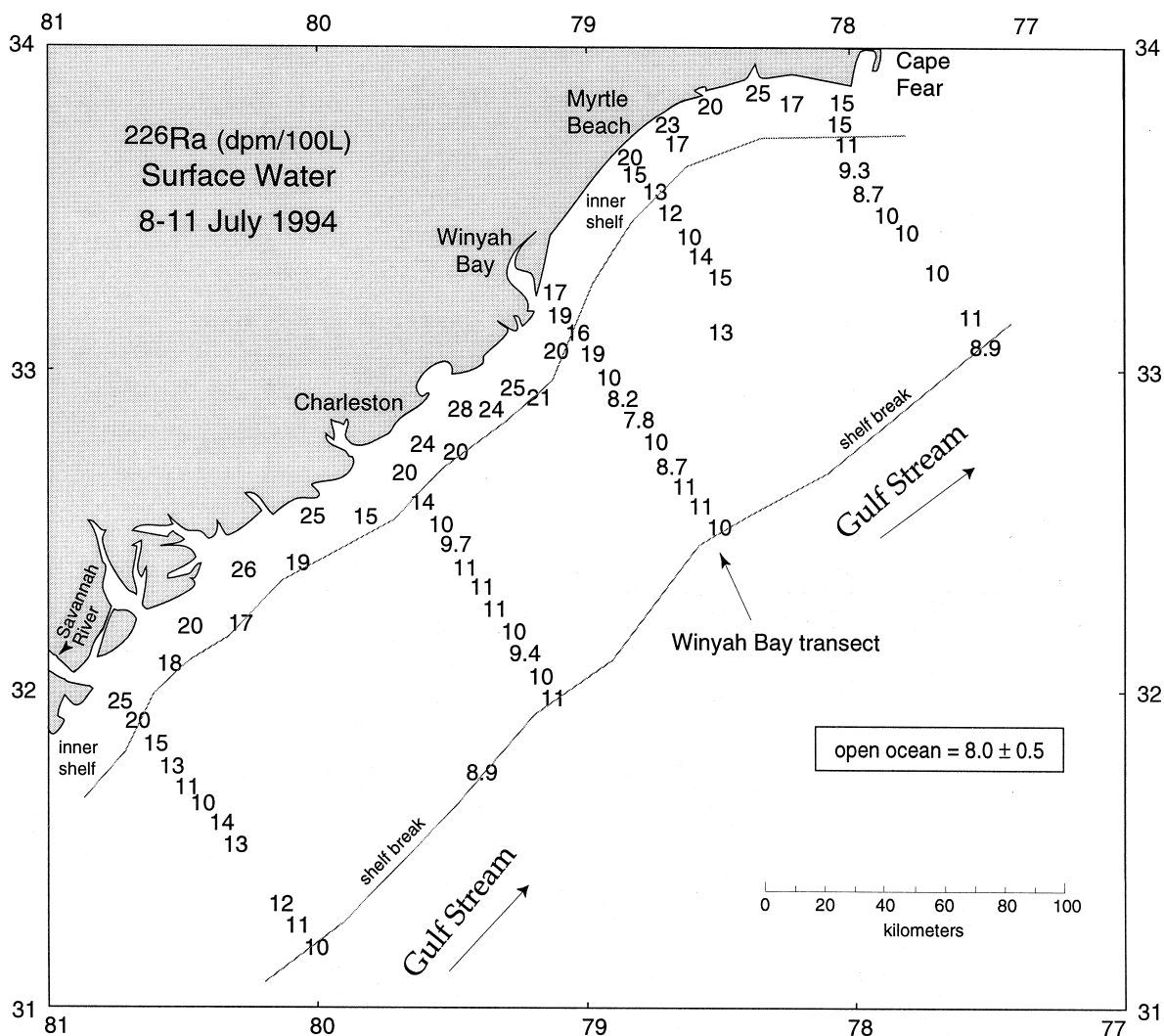


Fig. 2. The distribution of ^{226}Ra in surface waters of the South Atlantic Bight, July 1994. Modified from Moore (1996).

of the excess ^{226}Ra in these coastal waters can be explained by river discharge and desorption from river-borne particles or other sediments. He used the distribution of ^{226}Ra in the coastal ocean (Fig. 2) and an estimate of the exchange time of the inner shelf water with offshore waters to calculate the ^{226}Ra flux from the coast. Combining this flux estimate with measurements of ^{226}Ra in subsurface fluids (e.g., Table 1) led to the startling conclusion that the flux of subsurface fluid (that is water containing ~ 100 times more ^{226}Ra than ocean surface water) must have been about 40% of the total river flow during the period of investigation. Moore (1996) cautioned that these estimates could not be extrapolated to other seasons because concentrations of ^{226}Ra on the inner shelf are lower in winter and spring. Whether these changes are due to lower fluid inputs, a change in the composition of the fluid, or faster exchange of coastal waters is unknown.

Shaw et al. (1998) reached essentially the same conclusion as Moore (1996), based on measured concentrations of Ba in subsurface fluids and the distribution of Ba in these surface waters. The offshore transport of Ba was calculated from the average inner shelf concentration and the residence time of inner shelf waters. This was compared to the Ba flux calculated from measured subsurface fluid end-members and the measured fluid flux (Simmons, 1992). The agreement between these two independent estimates of Ba input confirmed the subsurface fluid flow estimate from Moore (1996). The Ba flux from advecting fluids was found to be on the order of four times the river flux (Shaw et al., 1998). The Ba concentration in subsurface fluids in the region can exceed saturation with respect to barite by up to a factor of 6. Coastal waters approach, but do not exceed, saturation. This work confirms that, for Ba, subsurface fluids are chemically distinct from river waters and very important for supplying Ba to the ocean.

Exchange of subsurface fluids from subterranean estuaries below the continental shelf may also impact deeper regions of the shelf. Here, the input will be into bottom waters and the signal may not reach the surface if the water is stratified vertically. In another study of South Carolina coastal waters, Moore and Shaw (1998) measured Ra isotopes and Ba along the Winyah Bay transect (refer to Fig. 2 for location).

Concentrations of ^{226}Ra and Ba showed two elevated regions: on the inner shelf in < 15 m depth and 40–70 km offshore at 25–45 m depth (Fig. 3). Based on high activities of ^{228}Ra as well as ^{226}Ra in the deep Ra-enriched zone, they concluded that the high concentrations of Ra and Ba were due to submarine fluid input rather than upwelling of deeper water or the dissolution of ^{226}Ra from phosphorite.

Moore and Shaw (1998) mapped the ^{226}Ra and Ba distribution over a 2600 km² area to estimate a total deep ^{226}Ra inventory. They used physical observations and the distribution of the short lived ^{224}Ra (half life = 3.6 days) in the enriched zone to estimate a residence time of 10–20 days. In this way, they converted the excess ^{226}Ra inventory to a flux. The flux calculated for this 80 km segment of the outer shelf was similar to the flux from the entire 320-km long inner shelf. Moore and Shaw also demonstrated that the region impacted by fluid flow exhibited high chlorophyll concentrations. They suggested that the leaking fluids supply nutrients to support primary productivity in this region. This study suggested that fluid flow onto the middle and outer shelf may be an important chemical and biological process.

Studies from the north coast of the Bay of Bengal in Bangladesh reveal that subterranean estuaries are not restricted to the southeast United States. The coast of Bangladesh is dominated by drainage of the Ganges and Brahmaputra Rivers. The annual flux of sediment to the ocean from these rivers is among the highest in the world. Desorption of ^{226}Ra and Ba from this riverine sediment produces a major point source of ^{226}Ra and Ba input to the ocean. Highest ^{226}Ra and Ba fluxes are expected to occur during high river flow (June–September) when almost all of the sediments are discharged. Moore (1997) reported that during low discharge of the Ganges–Brahmaputra Rivers in March 1991, fluxes of ^{226}Ra and Ba to the northern Bay of Bengal were comparable to expected river-derived fluxes during peak river discharge. A large non-riverine source of Ra and Ba was required to explain the high fluxes during low river discharge. He suggested that this source was the discharge of submarine fluids containing high concentrations of ^{226}Ra and Ba.

Tsunogai et al. (1996) reported fluid seepage at a depth of 900–1100 m in Sagami Bay, Japan. Al-

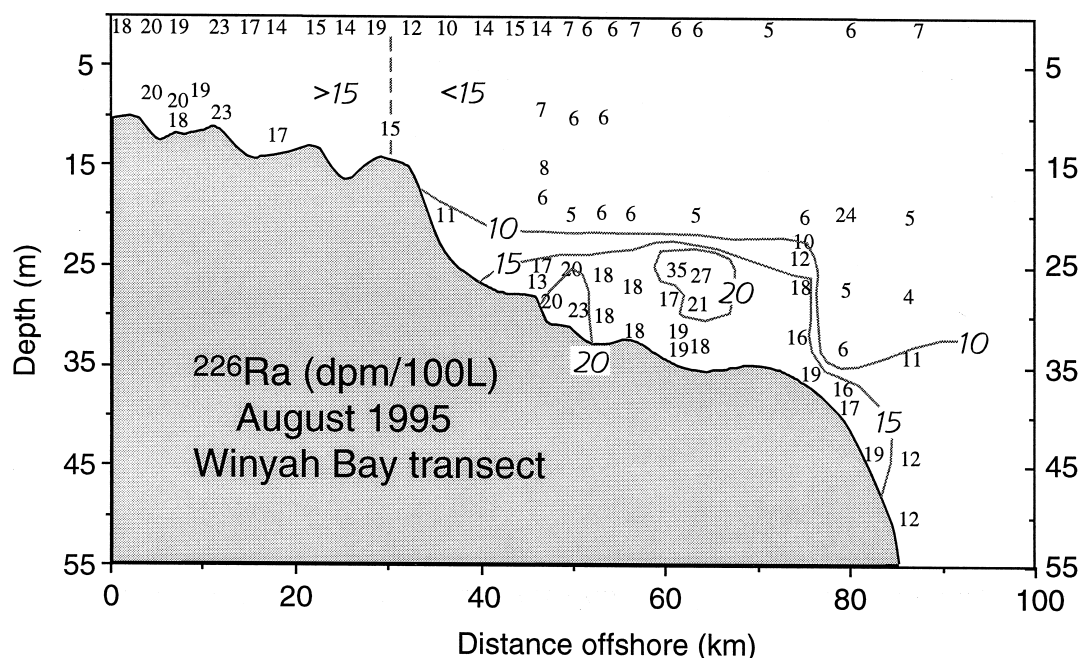


Fig. 3. Cross-section of the distribution of ^{226}Ra along the Winyah Bay transect of the South Atlantic Bight, August 1995. Modified from Moore and Shaw (1998).

though they did not have Ra data, the fluid was enriched in Ba (300 nM), NH_3 (1500 μM) and total CO_2 (6 mM) and depleted in chloride relative to sea water. The water they sampled on the sea bed at 1100 m depth was similar in composition to the brackish waters reported in Table 1. They concluded that this fluid was a mixture of fresh ground water

and sea water that had reacted with sediment pore water and solid phases. They further concluded that the discharge of such fluids into the ocean is an important factor controlling ocean chemistry.

The studies listed above which attempt to quantitatively estimate tracer fluxes are summarized in Table 2. This summary demonstrates that submarine

Table 2

Comparison of estimated ^{226}Ra fluxes based on different case studies

| Region | Setting | Size (km^2) | ^{226}Ra flux (dpm day^{-1}) | ^{226}Ra flux ($\text{dpm m}^{-2} \text{ day}^{-1}$) | Reference |
|----------------------|-------------------------------------|---------------------------|---|--|--------------------------|
| North Inlet | salt marsh | 32 | 3×10^9 | 100 | Rama and Moore (1996) |
| FSUML | near shore | 620 | 8×10^{10} | 130 | Cable et al. (1996) |
| South Atlantic Bight | inner shelf | 6400 | 2×10^{11} | 30 | Moore (1996) |
| South Atlantic Bight | section of outer shelf | 2600 | 3×10^{11} | 100 | Moore and Shaw (1998) |
| Bay of Bengal | inner shelf, low river discharge | 18,000 | 1×10^{13} | 500 | Moore (1997) |
| Amazon River | total shelf annual average | 130,000 | 3×10^{12} | 20 | Moore et al. (1995) |

These studies illustrate that ^{226}Ra fluxes due to subsurface fluid input are comparable to fluxes from the Amazon River.

fluid flow occurs over different spatial scales. When normalized to area, most ^{226}Ra fluxes are on the order of $100 \text{ dpm m}^{-2} \text{ day}^{-1}$, the exception being the Bay of Bengal where the normalized flux is about five times greater. By contrast, the Amazon shelf only contributes about $20 \text{ dpm m}^{-2} \text{ day}^{-1}$, in spite of the enormous water and sediment discharge.

Translating the ^{226}Ra (or other tracer) flux to a flux of submarine fluid requires an estimate of the ^{226}Ra (or other tracer) concentration in the leaking fluids. Salty (2–34 ppt) fluids extracted from subterranean estuaries along the coast of South Carolina have ^{226}Ra concentrations ranging from 1 to 10 dpm l^{-1} (Table 1). Estimates of fluid fluxes, assuming concentrations in the upper part of this range ($7\text{--}10 \text{ dpm l}^{-1}$), indicate that such fluxes to the South Carolina coast during the summer are similar to total river fluxes (Moore, 1996; Moore and Shaw, 1998). Additional studies of the factors that regulate the composition of subterranean fluids are required before firm estimates of fluid fluxes are possible.

More specific information concerning the composition of the water producing the ^{226}Ra anomaly and its likely site of entry to overlying waters can be obtained using the other Ra isotopes. This approach was used by Rama and Moore (1996) in the North Inlet salt marsh to demonstrate that most of the exchanges occurred through sandy sediments or shell hash beneath tidal creeks or through deep worm tubes rather than through organic-rich sediments that cap much of the marsh.

5. Effects of sea level change on the subterranean estuary

During low sea level stands, many subterranean estuaries that are now in contact with the ocean would have been above sea level. These systems, like their surface counterparts, would not be considered estuaries during low sea stand. Ground water passing through these systems should have been fresh and may have contained higher oxygen concentrations. This different chemical environment would have produced different interactions between the ground water and aquifer solids. For example, during low sea stand, cations adsorbed on mineral surfaces

could be exchanged with dissolved species. This exchange could be driven by differences in abundance ratios between the new low ionic strength ground water and old salty water present at high sea stand. Additionally, changes in surface sites may be caused by dissolution or precipitation of mineral phases. Precipitation of Fe–Mn oxyhydroxides from oxygenated ground water could produce high surface area minerals with high exchange capacity. The combination of low ionic strength ground water and the presence of Fe–Mn oxyhydroxides as well as other mineral surfaces could produce an effective mechanism for adsorption of dissolved metals and nutrients from fresh ground water passing through the aquifer. A rise of sea level would expose portions of this aquifer to saline waters and initiate desorption of adsorbed ions; much as a water softener is recharged by flushing with a strong saline solution. This scenario could produce a flux of desorbed metals and nutrients to the ocean during sea level rise. This flux should continue as long as sea water was encroaching into the subterranean estuary and a portion of the fluid was exchanging into the ocean. During periods of stable sea level, these effects should be diminished unless sea water encroachment was being driven by changes in ground water flow.

6. Anthropogenic effects on the subterranean estuary

During the last century, subterranean estuaries, like their surface counterparts, have experienced considerable change due to anthropogenic pressure. Dredging of channels through surface estuaries and coastal regions has breached underlying confining layers and increased contact between sea water and subterranean estuaries (Duncan, 1972). Increased ground water usage has lowered potentiometric surfaces in coastal aquifers and caused infiltration of sea water into these formations (Smith, 1994). The result has been an increased rate of salinization of subterranean estuaries (Burt, 1993). Sea level rise, whether natural or induced, has also caused increased salinization of the subterranean estuary. Some of the anthropogenic changes effected over the last 100 years are equivalent to one third of a glacial–in-

terglacial sea level cycle in terms of changes in the fresh–salt interface in subterranean estuaries. These changes are taking place worldwide due to increased

demands of a rising coastal population for fresh water (Chapelle, 1997). In this section, I shall illustrate some of these changes through a discussion of

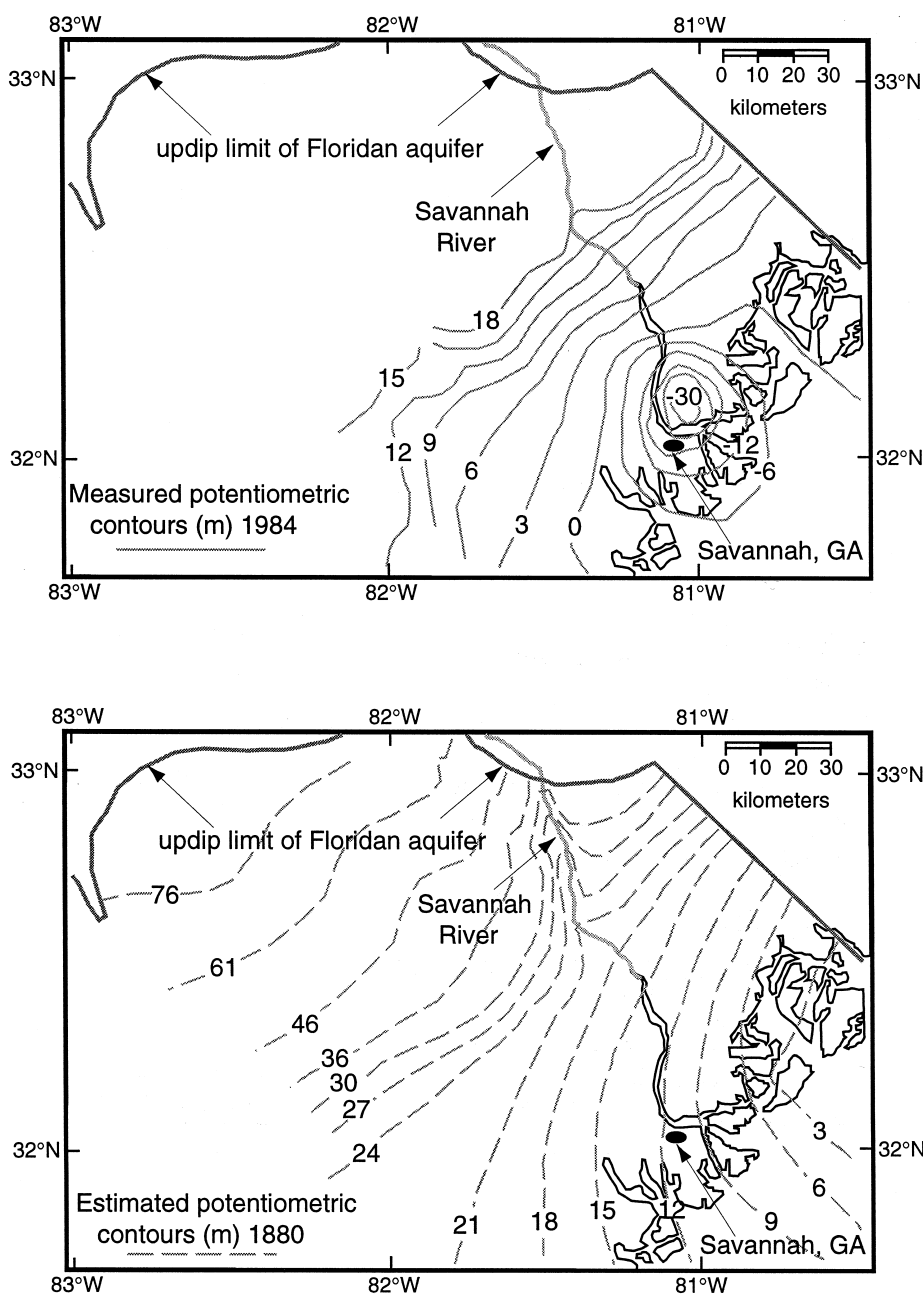


Fig. 4. Changes in the potentiometric head of the Upper Floridan aquifer near the GA–SC boundary. The bottom figure shows the estimated 1880 surfaces (modified from Bush and Johnston, 1988); the top figure shows the piezometric surfaces measured in 1984 (modified from Smith, 1988).

effects that have been documented along the coasts of South Carolina and northern Georgia.

As people migrate to the coast, either to live or for holiday, they require adequate fresh water for domestic use, industry, agriculture, and to keep the landscape attractive, especially on golf courses. Along the southeastern U.S. coast, this water has largely been derived from ground water wells. As the demand for ground water has increased, the potentiometric head (the level relative to sea level to which a column of water will rise in a tightly cased well drilled into the aquifer) has declined sharply. Early in this century, artesian (free-flowing) wells were common along the southeast coast (Warren, 1944); now, they are rare. In 1880, potentiometric surfaces in the Floridan aquifer at Savannah, GA, were +10 m (Bush and Johnston, 1988); now, they are –30 m (Smith, 1988), a drop of 40 m (Fig. 4). In 1880, fresh water discharged into Port Royal Sound east of Savannah, GA (Smith, 1988, 1994). Now, the Floridan aquifer is being recharged with sea water from the Sound (Burt, 1993). Analyses of ^{14}C in these salty ground waters reveal that they contain up to 74% modern carbon, in contrast to eastern and northern regions of the aquifer where the fraction is <2% (Burt, 1993; Landmeyer and Stone, 1995). The salinization of the aquifer has been facilitated by dredging. Duncan (1972) documented breaches in the confining unit above the Floridan aquifer that correlate well with channels and turning basins dredged through Port Royal Sound. Where the aquifer is in direct contact with the ocean, water exchange will occur. In addition to rendering the ground water non-potable, salt water intrusion into these aquifers causes ion exchange and other reactions to occur which chemically alter the intruding sea water and enrich the fluids in Ra, Ba and nutrients.

In other regions of the South Carolina coast, depression of potentiometric surfaces has caused communities to shift to deeper aquifers or surface water. An example of the effect of changing ground water usage on coastal aquifers is provided by an observation well (HO-269) at North Myrtle Beach, SC (Fig. 5). The water level in this well decreased from –13 m in 1977 to –35 m in 1985 (data from U.S.G.S. Water Resources Data, SC, 1977–1995). Superimposed on this trend are large annual fluctuations due to increased fresh water demand in the

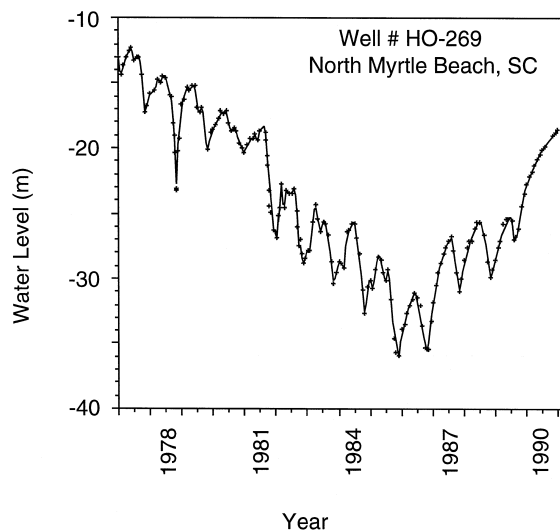


Fig. 5. Changes in the water level for well HO-269 in North Myrtle Beach, SC, 1976–1992. Data from U.S.G.S. Water Resources Data, SC, 1976–1993.

summer. For example, in 1978, the water level in this well fluctuated by 8 m. Severe drought conditions in 1984–1985, coupled with salinization of other wells in this aquifer, led the city to shift to surface water and deeper aquifers. From 1985 to 1991, the water level in this well increased from –35 m to –18 m. Unfortunately, HO-269 was lost in 1992, so additional data of the aquifer recovery are not available.

Most models of fluid flow in coastal aquifers are designed to evaluate residual flow. The boundary between salt and fresh water is considered a plane that may move inland as potentiometric surfaces are reduced, or to the sea if they are increased. Superimposed on the residual flow are fluctuations due to differences in recharge and demand. An analysis of residual flow would smoothen the annual variations in well HO-269. However, these variations amplify dispersion in the aquifer and may cause considerable exchange between water in the aquifer and the coastal ocean.

The changes documented in these examples provide an insight into how vulnerable coastal aquifers are to over pumping. The North Myrtle Beach example also reveals how quickly an aquifer may recover if pumping is diminished. Unfortunately, recovery of

Table 3
Comparison of surface and subterranean estuaries

| Surface estuaries | Subterranean estuaries |
|---|---|
| Mixing zone of river and sea water | mixing zone of meteoric and sea water |
| Tidal and river forces, estuarine circulation, residual flow to sea, short residence time | hydraulic and tidal forces, circulation? residual flow may be either way, long residence time |
| High particle concentrations lead to strong particle–water interactions | direct water contact with solids leads to strong particle–water interactions |
| Sea level exerts a major control | sea level exerts a major control |
| Human impact is often significant | human impact is often significant |
| In contact with atmosphere, high oxygen, oxidized Fe and Mn (sediments may be different) | no contact with atmosphere low to high oxygen, high $p\text{CO}_2$, Fe and Mn may be reduced |
| Abundant, diverse life | bacteria are primary life |
| Major ions dominated by sea salts | major ions may reflect diagenesis |

water level and recovery of water quality may proceed differently.

7. Summary

The subterranean estuary is an important component of many coastal regions. Ground water passing through these systems is modified by mixing with sea water and reacting with aquifer sediments. The reactions release chemical tracers into fluids contained in subterranean aquifers. Injection of these fluids into the ocean may be recognized by the presence of specific tracers in coastal waters. For some regions, the injection of subsurface fluids may be an important source of nutrients to coastal waters.

There are a number of similarities as well as differences between surface and subterranean estuaries. Some of the characteristics of these systems are outlined in Table 3.

As we become more aware that the subterranean estuary is a vital component of the coastal ecosystem, ideas concerning its function and importance will change. The purpose of this paper is not to establish dogma concerning this system, but to open

discussion as to its role in the coastal ecosystem. The expertise and viewpoints of a wide variety of scientists are required to understand the subterranean estuary.

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