

Patterns of groundwater discharge into Florida Bay

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Abstract

Natural chemical tracers of groundwater discharge (^{222}Rn and CH_4) were surveyed to evaluate possible patterns of groundwater interactions with surface water in Florida Bay. Radon and methane concentrations in water samples collected from wells, solution holes, canals, and Florida Bay showed a significant correlation, despite the fact that these two trace gases have independent sources. Groundwater flux was also measured directly via seepage meters in several Florida Bay locations. Natural abundance of nitrogen isotopes measured on attached algae and seagrass showed the greatest ^{15}N enrichment near the Keys. Collectively, our results suggested greater groundwater flow along the bay side of the Florida Keys. Nutrient flux estimates, based on interstitial nutrient concentrations and groundwater flux measurements, suggested that groundwater in the eastern part of Florida Bay may provide as much nitrogen ($110 \pm 60 \text{ mmol N m}^{-2} \text{ yr}^{-1}$) and phosphate ($0.21 \pm 0.11 \text{ mmol PO}_4^{3-} \text{ m}^{-2} \text{ yr}^{-1}$) as surface freshwater sources from the Everglades (i.e., Taylor Slough and C-111). However, the inputs are clearly not uniform, and areas near solution holes or tidal springs may have a substantially greater nutrient flux into surface waters than these estimates.

Submarine groundwater discharge (SGD) is an often overlooked yet possibly significant process in the geochemical and nutrient budgets of marine near-shore waters. According to Johannes (1980), "SGD should occur anywhere that an aquifer is hydraulically connected with the sea through permeable rocks or bottom sediments and where the head is above sea level." Such conditions are met in most coastal areas. A simple model of SGD from a homogeneous unconfined aquifer indicates that freshwater flows out along the coast through a narrow gap between the freshwater-seawater interface where the water table outcrops at the shoreline. Harr (1962) predicted theoretically that the seepage discharge rate should decrease rapidly from shore in such a setting. This phenomenon has been confirmed in several lake

studies and at least a few marine areas. For example, Bokuniewicz (1980) showed that seepage rates decreased roughly exponentially with distance from the shore in Great South Bay, New York. Although the zone in which significant seepage occurs is usually thought to be narrow ($\leq 100 \text{ m}$ in Great South Bay), this may not always be the case. Kohout (1960) stated, for example, that in parts of Florida the saltwater front within the sediments (zone of mixing or diffusion) may be as much as 14 km seaward of the coast, thus allowing SGD to occur well offshore. Furthermore, seepage may also occur through breaks or permeable portions of an overlying bed of a confined aquifer.

Groundwater discharge has been documented to be highly significant for nutrient supply in some coastal areas (Valiela et al. 1978; Valiela and Teal 1979; Capone and Bautista 1985; Lapointe and O'Connell 1989; Capone and Slater 1990; Valiela et al. 1990). SGD may be particularly important in these cases because shallow groundwaters are often enriched in nitrogen, possibly by contamination from septic tanks.

However, most prior studies have addressed the case of a hydraulically-driven freshwater aquifer in contact with typical coastal marine or lake environments. The situation in the Florida Keys is much different than most coastal environments because (1) most subsurface fluids are saline to hypersaline, and (2) the driving force is thought to be tides rather than topography. Groundwater entering Florida Bay along the north coast, however, would be characterized by more typical topographic gradient flow. Subsurface samples collected in this region vary from relatively fresh (< 1 practical salinity units (psu)) to hypersaline (> 36 psu). Waters sampled from wells as deep as 10 m within Florida Bay tend to have elevated salinities (> 35 psu).

Moore (1999) referred to this subsurface region of mixing between meteoric water and sea water in coastal aquifers as

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“subterranean estuaries.” He makes the point that water entering surface waters from the subsurface may be considered groundwater, regardless of its salinity. Younger (1996) has referred to all water flowing to the sea, regardless of its source, as “total” groundwater discharge, in an attempt to distinguish fresh groundwater of a coastal aquifer from recycled seawater. However, the individual sources of groundwater discharge may not be as important as the dissolved constituents that the final fluid brings into surface waters after mixing within the “subterranean estuary.” The mixing of these water masses in the subsurface creates an active chemical environment. Chemical reactions between aquifer solids and a mixture of seawater and meteoric water modifies the fluid composition, and eventually this altered mixture returns to surface waters as a consequence of SGD (Runnels 1969; Back et al. 1979; Moore 1999). In addition to these natural processes, wastewater disposal in the Florida Keys adds yet another source of water to the subsurface environment.

It is evident from the salinity in groundwater below the Keys and Florida Bay that there has been much interaction of surface water with the subsurface fluids. Therefore, the definition of groundwater discharge adopted here includes recirculated seawater from the Atlantic Ocean and/or Florida Bay, meteoric water, and wastewater. The direction of groundwater flow beneath the Keys is thought to oscillate as the fluctuating Atlantic tides create a differential head with respect to sea level in Florida Bay, where tides are significantly damped. The Atlantic Ocean can have tides on the order of 1 m, while tides in Florida Bay range from approximately 0.1 m around Key Largo to 0.25 m near Long Key. Halley et al. (1994) showed that there are positive and negative head differentials of the surface of the Atlantic relative to that of the Bay, and the difference can be as great as 0.7 m. Another study concerning the dynamics of the subsurface seawater circulation around Key Largo has demonstrated that the Florida Keys are surprisingly open systems (Halley et al. 1995). The response of hydraulic heads and flows in a series of wells located in Florida Bay have suggested considerable water movement through the porous carbonate rock formations characteristic of these islands (Shinn et al. 1994). Previous groundwater studies in the Florida Keys have shown a range of transport rates between 1.4 and 420 m d⁻¹, dependent on both the geological terrain (Key Largo Limestone or Miami Limestone) and differential tidal influences (Lapointe et al. 1990; Paul et al. 1995; Paul et al. 1997; Dillon 1998).

Ecological problems in Florida Bay

Florida Bay is a large (2,200 km²), shallow (mean depth <2 m) coastal lagoon lying between the southern tip of the Florida mainland and the coralline Keys (Fig. 1). The bay has witnessed significant changes in the past decade (Boesch et al. 1993), including seagrass die-offs, more frequent planktonic algal blooms (Phlips et al. 1995; Philips and Badylak 1996), and water quality problems that could be related to excess nutrient input (Lapointe and Clark 1992). Algal blooms may also have played a role in the die-off of the

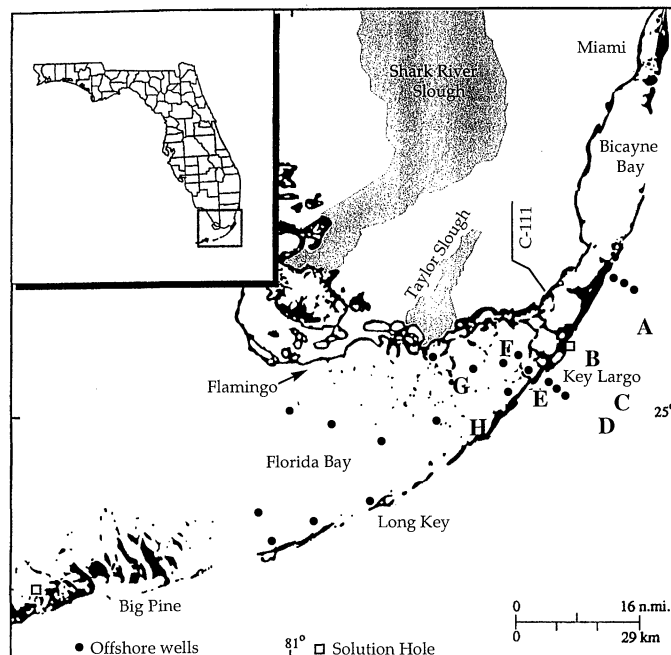


Fig. 1. Groundwater samples from offshore wells were collected where indicated by the circles. (A) Carysfort Reef; (B) Algae Reef; (C) French Reef; (D) Molasses Reef; (E) Rock Harbor; (F) Porjoe Key; (G) Black Betsy Keys; and (H) Tavernier Basin.

bay's sponge population (Hunt and Herrnkind 1993). A number of hypotheses to explain this environmental deterioration have been offered. Lapointe et al. (1990) suggested that sewage-derived inputs of nitrogen and dissolved organic phosphorus to canals and surface waters may be a key factor in starting the phytoplankton blooms in the area. Also, reductions in freshwater inflow from the Everglades have contributed to hypersaline conditions, which may be responsible for the seagrass declines (Boesch et al. 1993). Freshwater is delivered to Florida Bay mainly through the Taylor and Shark River Sloughs, although other sources (e.g., C-111) may be locally important. Much freshwater flow has been diverted to the Atlantic through canals, and it has been estimated that less than 25% of the “natural” surface water flow through Taylor Slough is presently occurring (Light and Dineen 1994).

Few data are available on groundwater flow into Florida Bay. This is unfortunate, as groundwater may be important because of the porous limestone underlying the region's soil and sediments (Boesch et al. 1993). Groundwater flow rates in the Miami Limestone, considered to be the least permeable of the two prominent geologic formations in the area, were reported to be as high as 7.2 m d⁻¹ (Lapointe et al. 1990; Dillon 1998). This formation is also reported to underlie Florida Bay (Perkins 1977).

Groundwater in the shallow subsurface has been shown to contain more dissolved nitrogen than surface water because of decaying organic materials disseminated within the matrix (Sansone et al. 1990). Another cause of elevated nutrients in our study area may be the waste-disposal practices in the Florida Keys (Shinn et al. 1994). Sewage in the Florida Keys is discharged into more than 600 disposal wells

that penetrate the permeable Key Largo Limestone (Pleistocene) at depths of 10 to 30 m. In addition to these wells, used by hotels and commercial establishments, there are an estimated 24,000 septic tanks and 5,000 cesspools. Subsurface waters in the Florida Keys receive an estimated 2.3×10^{10} mmol of nitrogen and 9.3×10^8 mmol of phosphate per year from wastewater. In an environment believed to be extremely permeable, groundwater-derived nutrients from the Key's subsurface, whether from sewage or natural sources, may be important to the overall nutrient budget of Florida Bay (U.S. EPA 1996).

Our purpose was to evaluate the significance of groundwater discharge into Florida Bay and evaluate the potential of groundwater as a contributor to the surface-water nutrient pool. We attempted to locate areas in the bay where groundwater seepage was most pronounced by reconnaissance surveys of radon and methane concentrations in the bay water. Because these trace gases have significantly higher concentrations in groundwater than in surface water, they function as natural indicators of submarine groundwater discharge (Cable et al. 1996a,b; Bugna et al. 1996). Radon is typically elevated in groundwater because of production and recoil processes originating from radium within the aquifer matrix, while methane is produced from the decay of organic matter disseminated in the rock. Both processes occur within aquifers and result in elevated tracer concentrations within groundwater, but the production of each gas is completely independent.

Groundwater discharge was measured directly with seepage meters at selected sites along the Keys and in the bay. Nutrient samples were collected and analyzed from surface and pore waters within the bay, along the reef tract, and in some solution holes, wells, and canals. In addition, the natural abundance of ^{15}N in attached macroalgae and seagrasses collected at various sites may also indicate groundwater nutrient input (Sweeny et al. 1980; Jordon et al. 1992; Fry 1994; McClelland et al. 1997). Algae with a groundwater N input may be considerably enriched in ^{15}N (>10–20‰) due to denitrification in suboxic environments.

Methods

Radon and methane sampling—Samples for tracer analysis were collected at over 170 stations in Florida Bay between December 1994 and July 1997. Radon samples were collected from about 0.3 m above the bottom at each station using a peristaltic pump and 4-liter evacuated bottles. Standing water was purged from the hose at each depth before the sampling bottles were filled, and the bottles were immediately sealed to prevent gas loss. Radon gas was extracted and transferred with a modified emanation technique similar to that described by Mathieu et al. (1988). After radon stripping and transfer into alpha scintillation cells, samples were counted with Ludlum flask counters. The samples were sealed after the initial radon analysis and stored for at least 5 d to allow ^{222}Rn ingrowth, then sparged again to determine the ^{226}Ra activity. "Excess" (unsupported) radon was determined as the difference between the "total" ^{222}Rn in samples and the supported ^{222}Rn , assumed to be equal to the ^{226}Ra

activity. The excess ^{222}Rn values were decay-corrected to the sampling time in order to assess the in situ concentrations. All radon results presented are excess radon values unless otherwise noted.

Methane samples were collected in Wheaton BOD bottles and stored on ice until analysis. At the laboratory, water samples were transferred to 50-ml disposable syringes pre-flushed with nitrogen. An extraction volume of 10 ml N_2 to 40 ml of water was added to each syringe and the methane was extracted via headspace equilibration. Samples were run on a Shimadzu flame ionization gas chromatograph equipped with a 2-m stainless steel column packed with Poropack Q (Alltech Associates) (McAuliffe 1971).

Samples for ^{222}Rn and CH_4 in groundwater were also obtained from monitor wells at depths ranging from 5 to 60 m. These sites were primarily located within Florida Bay, onshore and offshore of Key Largo, and at the Keys Marine Laboratory located on Long Key (Fig. 1).

Seepage measurements—Direct measurements of groundwater seepage were made with an instrument design modified from Lee (1977). The seepage meter is simply an open-bottomed chamber (0.25 m^2) implanted in bottom sediments. The chamber has an open port where a plastic bag can be attached to collect seepage over measured time intervals. The volume in the collection bags can then be converted to a seepage flux because the collection time and area are known. All seepage meters were placed in areas with enough sediment to provide a seal between the meter and surrounding sediment. Four-liter plastic bag collectors were used, pre-filled with 1,000 ml of bay water to prevent short-term artifacts (Shaw and Prepas 1989). An initial volume also allows for measurement of negative seepage, i.e., recharge into the underground aquifer. The lower reliable limit of measurement for seepage meters depends upon the length of deployment and the conditions under which the sampling occurs; based on our experience, we normally expect a lower useful limit of $3\text{--}5 \text{ ml m}^{-2} \text{ min}^{-1}$ (Cable et al. 1997).

Nitrogen isotope ^{15}N —Attached macroalgae and seagrass (primarily *Thalassia*) samples collected from sites in Florida Bay and along the reef tract were sealed in plastic bags and frozen. In the laboratory, samples were thawed, dried, and ground to a fine powder. Preweighed powdered samples were analyzed at either Florida International University (FIU) or Isotope Services, Inc., in Los Alamos, New Mexico. Samples were encapsulated in tin foil, in duplicate, and placed in a Finnegan EA-IRMS in flow mode (FIU) or a Carlo-Erba NA 1500 elemental analyzer (Isotope Services). The elemental analyzer combusts the sample and a gas chromatograph column yields a pure nitrogen pulse, which is sampled by a VG-Isomass mass spectrometer for ^{15}N isotope analysis. The analysis system relies on a reference gas, which is injected into the helium carrier stream and measured along with every sample.

Nutrients—Nutrient concentrations (ammonia, nitrate, and phosphate) were determined at sampling sites by standard methods. Water samples taken in the field were kept in the dark on ice until analysis. A procedure involving vanadium

Table 1. Concentrations of ^{222}Rn and CH_4 in groundwater wells. Uncertainties represent the standard error of the mean for multiple measurements at several sites (n represents the number of different sites).

Date	Site	Rn-222 (dpm/liter)	Methane (nM)
Feb 95	NURC, Key Largo	537 ± 4 ($n = 2$)	96 ± 78 ($n = 2$)
Apr 95	Offshore Wells, Atlantic side	455 ± 35 ($n = 12$)	465 ± 150 ($n = 11$)
	Offshore wells, bay side	641 ± 169 ($n = 3$)	655 ± 122 ($n = 3$)
	Ranger Station, Key Largo	338 ± 47 ($n = 2$)	322 ± 172 ($n = 2$)
May 96	Keys Marine Lab, Long Key	245 ± 13 ($n = 28$)	998 ± 503 ($n = 2$)
	Ranger Station, Key Largo	442 ± 100 ($n = 2$)	
Dec 96	Offshore Wells, bay side	615 ± 59 ($n = 16$)	$2,520 \pm 1,189$ ($n = 16$)
Jun 97	Offshore Wells, bay side	294 ± 21 ($n = 8$)	545 ± 176 ($n = 8$)
Total average		398 ± 24 ($n = 73$)	$1,241 \pm 452$ ($n = 44$)

reduction followed by chemiluminescence detection of NO_x was used for nitrate-plus-nitrite analysis and, after a persulfate digestion, total dissolved nitrogen analysis (Braman and Hendrix 1989). Ammonia and orthophosphate concentrations were determined with the phenate and the ascorbic acid methods, respectively (Strickland and Parsons 1972).

Results and discussion

Tracer concentrations—Groundwater samples collected onshore and offshore exhibited higher tracer concentrations than surface waters did (Table 1). Both radon and methane displayed considerable spatial variation in groundwaters ($82\text{--}1,124$ disintegrations per minute (dpm) liter^{-1} and $10\text{--}16,604$ nM, respectively). Although we do not have extensive results for either parameter at one location, we did note that radon did not vary significantly in the same well between measurements collected more than a year apart (April 1995 = 291 ± 58 dpm liter^{-1} and June 1996 = 342 ± 118 dpm liter^{-1}). Although radon and methane are produced by different processes, there is a statistically significant correlation between them in these groundwater samples ($r = 0.46$, $n = 47$, $P < 0.01$). Radon and methane concentrations in groundwater averaged 80 and 50 times greater, respectively, than those in Florida Bay surface waters. This large difference in concentrations should allow use of these gases as indicators of groundwater discharge into surface waters in the area.

Surface-water radon and methane concentrations in Florida Bay (Table 2) varied from <1 dpm liter^{-1} to >20 dpm liter^{-1} and from 5 to 100 nM, with an overall average and standard deviation of 4.8 ± 2.7 and 27 ± 26 , respectively. (Note that the averages exclude samples collected from ca-

nals and solution holes). Radon and methane samples collected from the reef side of the Keys varied from <1 dpm liter^{-1} to approximately 20 dpm liter^{-1} and 4 to 40 nM, with overall averages of 1.5 ± 1.4 and 11 ± 6 , respectively (Table 2). Highest concentrations were observed near shore, not along the reef tract. As with groundwater, radon and methane were statistically correlated on both the bay side ($r = 0.51$, $n = 191$, $P < 0.01$) and the reef side ($r = 0.81$, $n = 84$, $P < 0.01$) of the Keys. Radon and methane were statistically

Table 2. Average ^{222}Rn and CH_4 concentrations from samples collected in various surface waters. Uncertainties represent the standard error of the mean for multiple measurements at several sites (n represents the number of different sites).

Site	Rn-222 (dpm/liter)	Methane (nM)
Canals	19 ± 11 ($n = 10$)	$830 \pm 1,140$ ($n = 10$)
Garden Cove Spring, Key Largo	66 ± 19 ($n = 4$)	141 ± 176 ($n = 4$)
Garden Cove Surface water, Key Largo	4.3 ± 1.2 ($n = 4$)	41 ± 11 ($n = 2$)
Lois Key Spring, Sugarloaf Key	122 ± 2 ($n = 2$)	493 ± 41 ($n = 3$)
Porjoe Key interstitial fluid (seepage meter)	67 ± 1 ($n = 1$)	176 ± 11 ($n = 3$)
Porjoe Key surface water	0.2 ± 0.1 ($n = 1$)	7.0 ± 0.2 ($n = 3$)
Bay surface water average	4.8 ± 2.7 ($n = 178$)	27 ± 26 ($n = 173$)
Reef surface water average	1.5 ± 1.4 ($n = 57$)	11 ± 6 ($n = 57$)

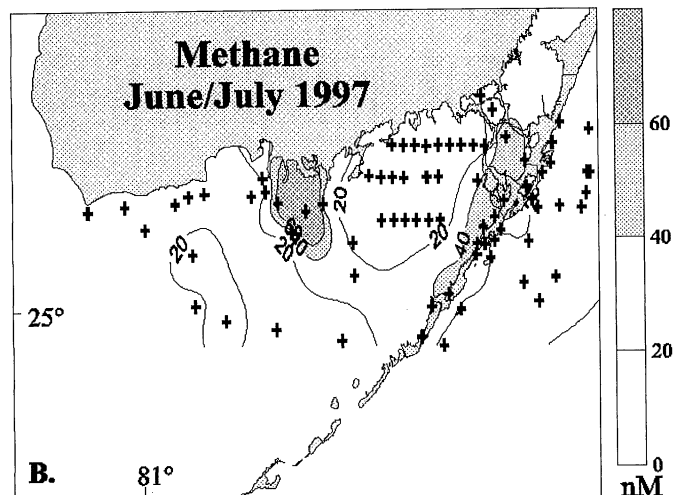
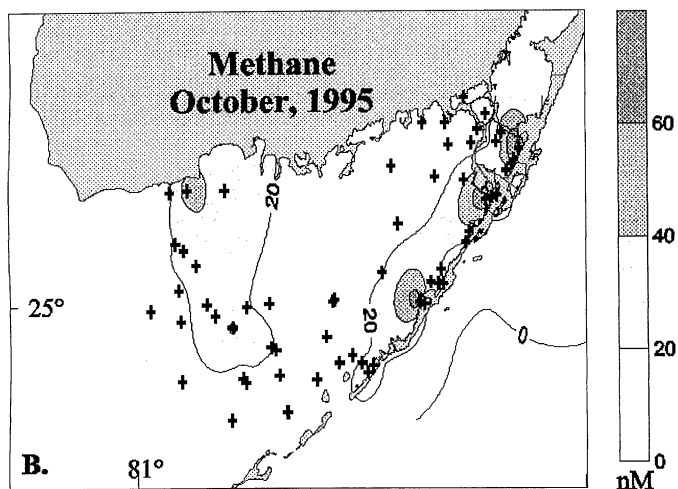
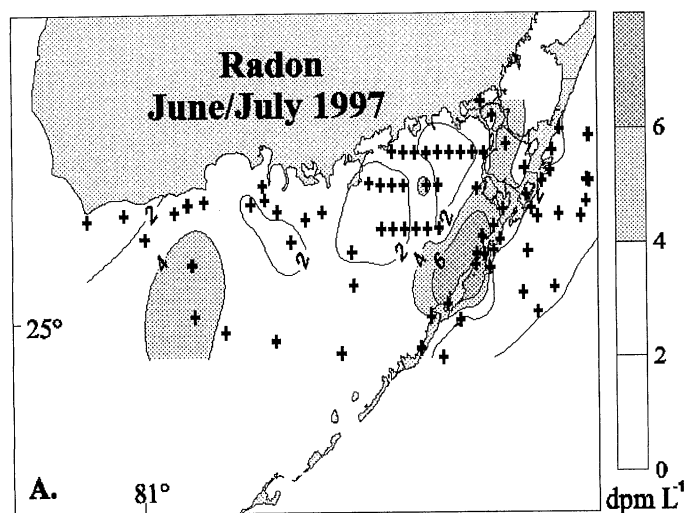
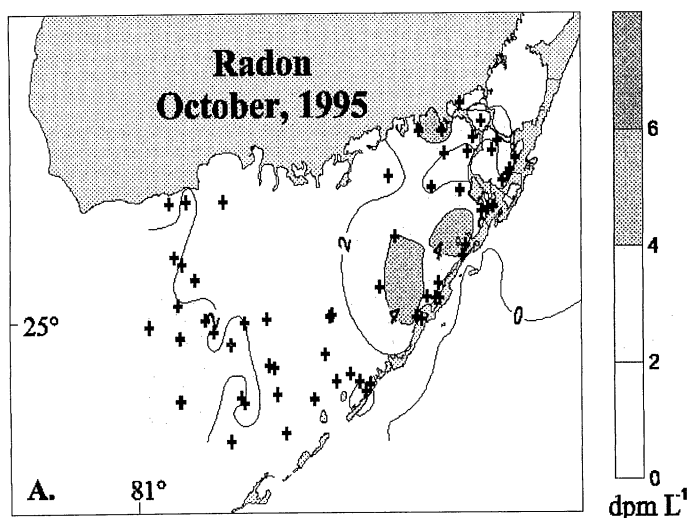


Fig. 2. Contours of radon (A) in dpm liter^{-1} and methane (B) in nM for samples collected in October 1995. Solid crosses indicate sampling locations. Note the darker contours, indicating higher concentrations of both parameters, near the upper Keys.

Fig. 3. Contours of radon (A) in dpm liter^{-1} and methane (B) in nM for samples collected in June/July 1997. Solid crosses indicate sampling locations. Note the darker contours, indicating higher concentrations of both parameters, near the upper Keys.

correlated in all surface waters sampled throughout the Keys, consistent with a common source such as groundwater discharge.

Tracer distributions in Florida Bay—General trends in surface water concentration were established by contouring data from each tracer survey with a kriging method (an interpolation technique) by use of the software package Surfer (Golden Software). Although kriging interpolates between data points, creating some artifacts, the general trends described are independent of the contouring method or a reasonable change in contouring concentration. These contour plots showed very little apparent seasonal variation during the study period. The lack of a seasonal trend may have resulted from our sampling periods, which favored the summer months, or it may have resulted from the primary fluid-driving force near the Keys, tides, which do not have a seasonal trend. More recent results do suggest seasonal

variations throughout the Florida Bay (Burnett et al. 1998; Brand and Top 1998).

During each period we sampled, high concentrations of both tracers were observed near the Keys. Plots for fall 1995 and summer 1997 show the typical trends observed (Figs. 2–3). As an alternative way of presenting the natural tracer data and evaluate spatial differences, samples were grouped into four different categories according to region. Regions included the north coast (within ~ 3 km of the Everglades coastline), Keys bay side (within ~ 3 km of the Keys coast), mid-northeast bay (east of Black Betsy Keys, Fig. 1G), and mid-bay (west of Black Betsy Keys). Samples collected from the Keys bay side had consistently higher radon and methane concentrations than those from other bay regions throughout the study period (Table 3). In particular, one of the narrowest areas of Key Largo (near Rock Harbor, Fig. 1E) continually showed some of the highest tracer concentrations in surface waters on both the bay and reef sides of the Keys, excluding

Table 3. Average tracer concentrations by region, and significant difference relative to Keys bay side. Keys bay side was defined as sites located on the Florida Bay side of the upper Keys (Key Largo, Plantation Key, and the Matecumbe Keys). Mid-bay sites were typically basins within the mud-banked areas of the middle bay. North coast sites were along the Everglades Coast in muddy-bottomed areas. Mid-northeast sites were in the northeastern areas of the bay and typically had very little sediment overlying a rock bay floor.

Florida Bay region	Natural tracers			
	^{222}Rn (dpm liter $^{-1}$)	^{226}Ra (dpm liter $^{-1}$)	CH_4 (nM)	^{15}N (‰)
Keys bay side	4.38	1.44	38.2	7.89
(σ , n)	(3.24, 73)	(0.59, 73)	(23.3, 73)	(2.54, 23)
Mid-bay	2.23	1.42	16.4	3.92
(σ , n, p)	(1.43, 40, <0.01)	(0.41, 40, 0.86)	(8.8, 40, <0.01)	(1.98, 26, <0.01)
North Coast	2.89	1.49	22.0	5.83
(σ , n, p)	(2.15, 33, 0.02)	(0.48, 33, 0.63)	(19.3, 30, <0.01)	(2.26, 13, 0.02)
Mid-northeast	2.40	1.95	13.2	5.57
(σ , n, p)	(1.96, 32, <0.01)	(0.61, 32, <0.01)	(10.8, 30, <0.01)	(2.46, 7, 0.04)

canals and solution holes. Taken at face value, the tracer results suggest that the greatest degree of groundwater/surface water interaction in Florida Bay occurs along the bay side of the Keys and that groundwater input into the mid-bay, mid-northeast bay, and north bay regions is less important.

Samples collected along the reef side of the Keys showed very little variation throughout the study period. Surface water concentrations were relatively low on the reef side (Table 2), except near Rock Harbor (Atlantic side). Tracer concentrations near Rock Harbor were typically 2–4 times higher than other sampling stations on the reef side for both radon and methane. Samples were also collected along the reef tract and from cracks within some of the healthy reefs (e.g., Molasses, French; Fig. 1C,D) and degraded reefs (e.g. Algae, Carysfort; Fig. 1A,B). There was not any statistically significant difference between tracer concentrations in samples from cracks and surface waters or in those from degraded and healthy reefs. Concentrations along the reef tract were generally lower than those in samples collected near shore. These differences in concentration between the reef and near-shore surface waters, as well as the lack of differences between surface water along the reef and water within the reef, probably result from the highly energetic environment along the reef tract and may indicate seepage in some near-shore areas. Dilution in the high-energy environment along the reef tract is expected because water within the reef is quickly exchanged with ambient surface water. At any rate, our data do not provide any evidence for groundwater directly discharging along the reef tract, except for some Atlantic-side areas near the Keys, especially near Rock Harbor. This does not necessarily mean that the phenomenon does not occur. Early studies by Simmons and Love (1987) indicated that a mixture of freshwater and recirculated seawater may be discharging out on the reef. Subsequent reports have shown that the subsurface waters within the reefs were saline to hypersaline, demonstrating that there must be some exchange of surface and subsurface waters (Simmons 1992; Shinn et al. 1994).

Within the Keys, samples collected from artificial canals,

trenches, or solution holes (locally referred to as “submarine springs”), had much higher tracer concentrations and salinity than samples from surficial waters at the time of sampling (Table 2). Three solution holes were identified and investigated during this study (Fig. 1): (1) Garden Cove spring, located on the Atlantic side of N. Key Largo (25°10.22'N, 80°22.02'W, 1.5-m ambient depth); (2) Lois Key spring on the Atlantic side of Sargarloaf Key (24°36.11'N, 81°27.48'W, 3-m ambient depth); and (3) a solution hole located on the bay side of Big Pine Key, locally called “Four Corners” spring (24°45.00'N, 81°24.28'W, 4.5-m ambient depth). Elevated tracer concentrations were measured in Lois and Garden Cove springs and in several canals, suggesting that subsurface fluids were actively seeping into and out of these features, where they may spill into Florida Bay/Atlantic Ocean. The solution holes (Lois and Garden Cove) appeared to be heavily influenced by the Atlantic tide. During high tide in the Atlantic, surface waters were pulled into the holes. During periods of low Atlantic tides, waters moved out of the holes at relatively high flow rates (Table 4). This is consistent with other observations of tide-driven groundwater flow beneath the Keys. Water samples were collected during both high and low tides whenever possible. Not surprisingly, tracer concentrations in solution holes appeared to fall on a mixing line between surface water and groundwater (Fig. 4). The natural tracer concentrations in groundwater and samples collected from solution holes (Lois and Garden Cove) had a significant correlation (Fig. 4, $r = 0.98$, $n = 9$, $P < 0.01$). Radon and methane ratios for the two water masses were almost identical (groundwater $\text{Rn}:\text{CH}_4 = 0.32 \pm 0.12$ dpm liter $^{-1}/\mu\text{M}$, spring water $\text{Rn}:\text{CH}_4 = 0.30 \pm 0.19$ dpm liter $^{-1}/\mu\text{M}$; ratios are based on averages for each water mass). The similarities in the water masses suggest that groundwater, rather than rapidly recirculated surface water, is a major source for the solution holes (reef-side surface water $\text{Rn}:\text{CH}_4 = 0.13 \pm 0.14$ dpm liter $^{-1}/\mu\text{M}$, bay-side surface water $\text{Rn}:\text{CH}_4 = 0.12 \pm 0.15$ dpm liter $^{-1}/\mu\text{M}$). Flow rates from Garden Cove spring at low tide were strong enough to produce a boil on the surface of the water on an outgoing tide.

Table 4. Nutrient concentrations of spring, groundwater, and surface waters.

Site	Flow rate (ml m ⁻² min ⁻¹)	NH ₄ ⁺ (μM)	NO ₃ ⁻ (μM)	PO ₄ ³⁻ (μM)	Salinity (psu)
KML well (15 and 60 ft.) (n = 2)*		13.3 ± 0.04	0.62 ± 0.48	0.98 ± 0.18	
Canals/trenches (n = 3)		6.2 ± 4.7	0.90 ± 0.33	0.07 ± 0.03	
Garden Cove Spring, Key Largo (n = 3)†	(2.5 ± 0.3) × 10 ⁷	0.53 ± 0.15	0.40 ± 0.16	0.08 ± 0.04	31
Garden Cove Surface, Key Largo (n = 3)		BD‡	1.24 ± 0.09	BD	29
Lois Key Spring, Sugarloaf Key		12.03	0.1	0.94	38
Porjoe Key interstitial fluid (seepage meter)§	288 ± 48	15.17	0.68	0.03	25.7 ± 1.9 (n = 4)
Porjoe Key surface		BD	1.14	BD	28.5 ± 0.5 (n = 2)
Bay average (n = 27)		1.2 ± 1.5	1.1 ± 0.96	BD	
Reef average (n = 49)		BD	0.30 ± 0.38	BD	

* KML refers to Key Marine Laboratory located on Long Key; wells were within 10 m of class V sewage injection well.

† Flow rate measured by a General Oceanics flow meter with low flow propeller.

‡ BD, below detection (NH₄⁺ = 0.01 μM; NO₃⁻ = 0.01 μM; PO₄³⁻ = 0.01 μM).

§ Sample taken directly from seepage meter port. Seepage meter covers an area of 0.25 m².

Unlike the other solution holes, Four Corners spring did not appear to be moving water in or out of the solution hole, which measured about 2 ft. in diameter, during high or low tides. Samples for tracer analysis, collected in May 1997 during a relatively dry period, had concentrations similar to surface water. The low rainfall and possible low water table may explain the lack of flow from the spring. Thus, some solution holes may be more dependent on rainfall than tidal influences.

Canals had a low tracer ratio (0.02 ± 0.03 dpm liter⁻¹/μM) because higher methane concentrations were measured in these features, probably due to the higher organic content in the underlying sediments. A canal is typically a low-energy environment and therefore act as a sink for particulate matter. We therefore observed low Rn:CH₄ ratios, since decaying organic matter is a source for methane without corresponding radon production. The high organic content and low energy of the canals also tends to lead to eutrophic conditions (Lapointe and Clark 1992; Florida Department of Pollution Control 1973). In spite of these differences, the high radon concentrations in the solution holes and canals/trenches are consistent with a significant groundwater influx. It is likely that when these features were dredged, less permeable layers in the rock were removed, which resulted in greater conductivity between subsurface and surface waters.

¹⁵N enrichment in macrophytes—We observed a strong spatial gradient in δ¹⁵N of macrophytes (seagrasses and macroalgae) in Florida Bay, with relatively light (−1–4‰) macrophytes in western Florida Bay and relatively heavy (6–13‰) macrophytes in northeastern Florida Bay (Fig. 5). This gradient is likely a function of two processes: (1) progressive denitrification of DIN brought into Florida Bay via tidal exchange with the Gulf of Mexico; and (2) entry of ¹⁵N-enriched water from the subsurface adjacent to the Keys in northeastern Florida Bay. Rudnick et al. (1999) hypothesized that exchange with the Gulf of Mexico is the most important source of nitrogen to the western region of Florida Bay (west of 80°40'W, the meridian just west of Black Betsy Keys;

Fig. 1G). The DIN pool in an ecosystem can become enriched in ¹⁵N due to denitrification (Cline and Kaplan 1975; Horrigan et al. 1990; Fourqurean et al. 1997). Because denitrification is an important respiratory process in suboxic sediments like the benthos of Florida Bay, progressive denitrification of DIN brought into Florida Bay from the Gulf of Mexico should lead to a heavier DIN pool as distance from the Gulf of Mexico increases.

Overlaid on this regional gradient in δ¹⁵N is the significantly heavier δ¹⁵N of macrophytes collected along the bay side of the Florida Keys (Fig. 5, Table 3). We hypothesize that denitrification takes place in the suboxic sediments of Florida Bay as a whole, but the region of Florida Bay immediately adjacent to the Florida Keys is relatively sediment-poor. Thus it is likely that the measured enrichment in δ¹⁵N in this area is caused by ¹⁵N enrichment in the subsurface, within the carbonate framework of the Keys. Tribble et al. (1990) and Sansone et al. (1993) have shown that the interiors of coral reef frameworks are themselves sites of anoxic and suboxic organic matter diagenesis. The Florida Keys, simply an ancient coral reef, is known to typically have groundwater enriched in ¹⁵N (J.K. Bohlke pers. comm. 1996). Groundwater seepage can thus act as a pathway for suboxic ¹⁵N-enriched fluids to come in contact with overlying surface water and therefore with primary producers (McClelland et al. 1997). Although this cannot be seen clearly in Fig. 5 because of its resolution, the most pronounced enrichment with ¹⁵N and other tracers occurs near Rock Harbor (Fig. 1E) on both sides of the island (Bay, 11–13‰; Atlantic, 5–7‰). As mentioned before, the radon and methane patterns suggest that this area has the most significant groundwater/surface water interaction of the entire region. Interestingly, this area is also one of the thinnest points of the island, is remote from any passes that connect Florida Bay to the Atlantic, and is near a large commercial sewage injection well. The enrichment of the heavier nitrogen isotope in the seagrasses and algae collected in the area suggest a source of water that has undergone significant denitrifica-

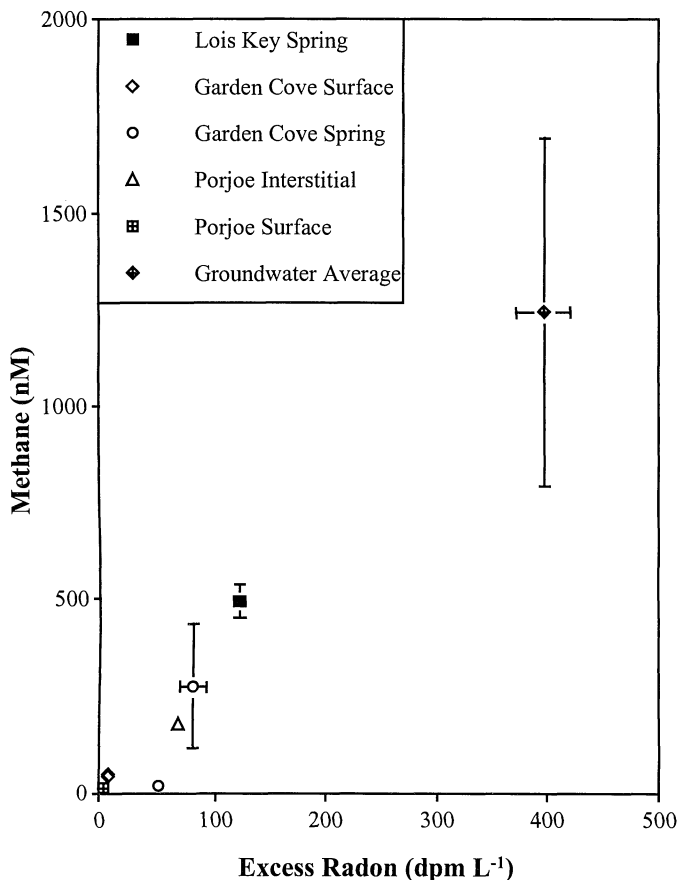


Fig. 4. Radon and methane concentrations in waters sampled throughout the Keys. The groundwater tracer concentrations are based on the overall average of all samples collected.

tion, either in a suboxic zone or due to waste disposal practices.

Estimated nutrient fluxes—Samples for nutrient analyses were collected and analyzed from select surface waters, groundwaters, solution holes, and canals (Table 4). It is interesting to note that many phosphate concentrations are below the detection limit, except for samples from areas also characterized by high concentrations of groundwater tracers. Surface waters were typically low in nutrient concentrations, relative to groundwater, canals, etc. Nitrate was the only parameter present in all waters sampled. The presence of nitrogen and the continued absence of phosphate in the Florida Bay waters reconfirms that most of the bay appears to be a phosphate-limited environment (Powell et al. 1989; Fourqurean et al. 1992a,b; Fourqurean et al. 1993). On average, nitrate and ammonia concentrations were equivalent within Florida Bay.

Although the nutrient content of these various water masses appears low, the groundwater flux may still be important. For instance, Garden Cove spring waters have relatively low nitrogen and phosphate concentrations, yet they contribute approximately 1.2×10^7 mmol N m⁻² yr⁻¹ and approximately 1.0×10^6 mmol PO₄³⁻ m⁻² yr⁻¹, based on the area of the solution hole, the nutrient concentration in the water exiting the solution hole, and the flow out of the orifice measured by

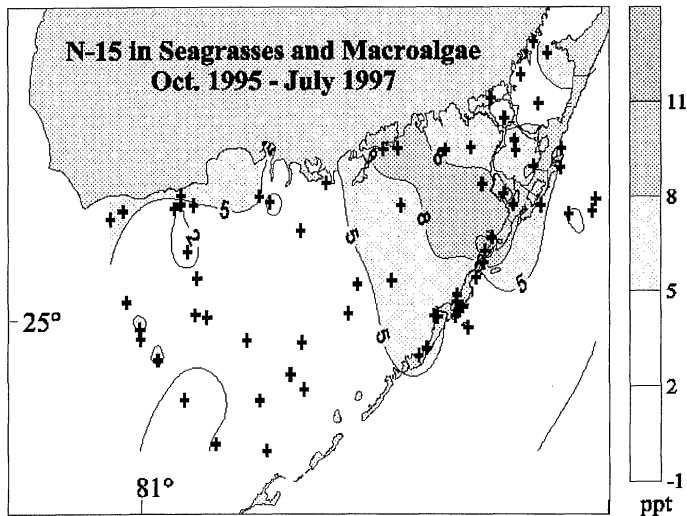


Fig. 5. Contours of ¹⁵N in microalgae collected throughout the study period. Solid crosses indicate sampling locations. Note the darker contours, indicating higher enrichment, near the upper Keys.

a hand-held mechanical flow meter (General Oceanics). Seepage-meter measurements made throughout Florida Bay may help us estimate the approximate nutrient flux via groundwater. We recognize that estimating such fluxes in this manner is somewhat tenuous because of possible artifacts due to the spatial variability of groundwater flow in sediments and possible anomalies associated with the water flux measurements due to wave action and currents (Libelo and MacIntyre 1994). However, reliable results have been produced under similar conditions in other environments (Bugna et al. 1996; Cable et al. 1996; Cable et al. 1997). We therefore present these nutrient flux estimates as a first approximation of how the magnitude of groundwater-associated influx compares to freshwater surface discharge estimates.

As with tracer data, seepage results collected throughout each region were pooled into groups according to location: (1) Keys bay side; (2) north coast; and (3) mid-bay. Average seepage rates for these regions were 21.2 ± 5.2 ($n = 17$), 7.2 ± 2.5 ($n = 6$), and 13.4 ± 2.3 ($n = 10$) ml m⁻² min⁻¹, respectively. (Error presented as standard error, n represents the number of sites sampled within the area, and each site had at least three measurements employing multiple meters). The standard errors of these averaged estimates are primarily due to the large areas over which the measurements were obtained and the inherent spatial variability associated with groundwater flow. However, the same general trend was observed with these direct groundwater flux measurements as those inferred from the natural tracer measurements; i.e., the area of most apparent groundwater/surface water interactions was on the inside of the Keys within Florida Bay.

One seepage meter located near Porjoe Key (Fig. 1F) in a circular seagrass bed had an extremely high flow rate (288 ± 48 ml m⁻² min⁻¹; Fig. 6A, meter 32) relative to the average rate for the area (13.4 ± 2.3 ml m⁻² min⁻¹; Fig. 6A). These circular seagrass beds grow in depressions in the hard limestone bay floor. They are sediment-filled and may have formed as dissolution pits during low stands of sea level

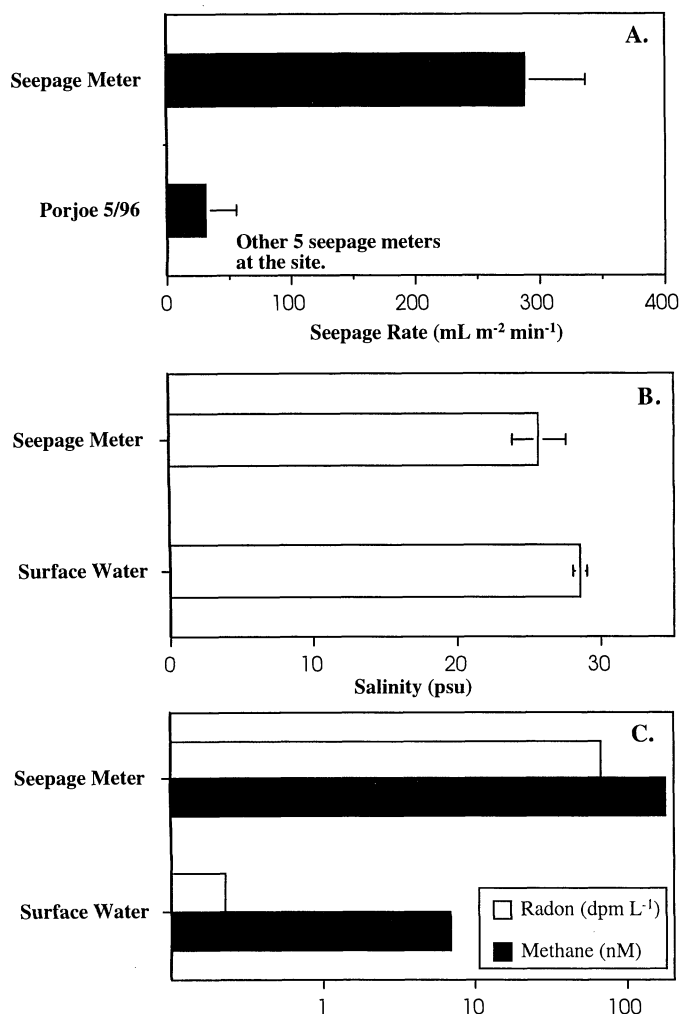


Fig. 6. Seepage rates (A), salinity (B), and tracer concentrations (C) measured at Porjoe Key, north of Key Largo (Fig. 1F) on 9 May 1996. Salinity of seepage meters is the average of four samples taken from two different meters. There is a significant difference ($P < 0.05$) in the salinity between the meter and the overlying water. Note that tracer concentrations are plotted on a log scale.

(Zieman 1972). Similar features have been observed in the Everglades, and there is radioisotopic evidence consistent with groundwater flow through these features (C. Holmes, U.S. Geologic Survey, pers. comm.). At Porjoe Key, we observed a large flow of brackish water from the site, indicating conduit flow from a deeper, less saline aquifer. The salinity of the interstitial water from the fast-flowing seepage meter and another meter nearby were significantly different (25.7 ± 1.9 psu, $n = 4$, $P < 0.05$) than the ambient seawater (28.5 ± 0.5 psu, $n = 2$) when measured by silver nitrate titration (Fig. 6B). In addition, tracer samples collected directly from the seepage meter showed significantly higher concentrations than those in surface waters (Fig. 6C). The radon and methane ratio of the seeping water was almost identical to that of groundwater (seeping water $\text{Rn}:\text{CH}_4 = 0.38 \pm 0.07$ dpm liter $^{-1}/\mu\text{M}$, groundwater $\text{Rn}:\text{CH}_4 = 0.32 \pm 0.79$ dpm liter $^{-1}/\mu\text{M}$). Collectively, these data may indicate a fresher groundwater source.

From the interstitial nitrogen and reactive phosphate concentrations measured at the Porjoe seepage site (Table 4) and the average seepage rate for the entire mid-bay area (13.4 ± 2.3 ml $\text{m}^{-2} \text{min}^{-1}$), we estimated nutrient input associated with groundwater flow. Based on this calculation, the nitrogen and reactive phosphate contribution from advective flow could be as great as approximately 110 ± 19 mmol N $\text{m}^{-2} \text{yr}^{-1}$ and 0.21 ± 0.04 mmol $\text{PO}_4^{3-} \text{m}^{-2} \text{yr}^{-1}$. This may be a conservative estimate, since pore-water samples collected by Fourqurean et al. (1992a) at 18 sites across the Bay had considerably higher nitrogen (NH_4) and reactive phosphate concentrations, $78.6 \mu\text{M}$ and $0.34 \mu\text{M}$, respectively. Although this is described as a groundwater flux, we are not ruling out the possibility that a major source of these nutrients is organic matter degradation and recycled nutrients in the surficial sediment. Thus, all of the nutrients may not represent a true groundwater source or "new" nutrient input. However, the advective motion of the groundwater may promote the delivery of recycled nutrients to surface waters.

Surface-water inputs from the Everglades are currently considered one of the more important nutrient sources to the eastern portion of Florida Bay (the area east of $80^\circ 40' \text{W}$, just west of Black Betsy Keys, Fig. 1G). This area of Florida Bay is relatively isolated from the Gulf of Mexico, which is the largest contributor of total nitrogen to the Bay's nutrient budget. Measurements made by Rudnick et al. (1999) from major surface-water contributors to eastern Florida Bay (Taylor Slough and C-111) were used to estimate the mean annual input of total nitrogen and total phosphate at approximately 1.8×10^{10} mmol yr^{-1} and 8.4×10^7 mmol yr^{-1} , respectively. In order to compare these surface-water contributions from the Everglades to the estimated groundwater input calculated above, we normalized both the surface input and the groundwater flux to the estimated area of the eastern Florida Bay (600 km^2). The normalized flux of surface-water inputs (total N = $30 \text{ mmol m}^{-2} \text{yr}^{-1}$ and $\text{PO}_4^{3-} = 0.1 \text{ mmol m}^{-2} \text{yr}^{-1}$) are similar, although lower, to the groundwater estimates for the Porjoe Key area (total N = $110 \text{ mmol m}^{-2} \text{yr}^{-1}$; $\text{PO}_4^{3-} = 0.2 \text{ mmol m}^{-2} \text{yr}^{-1}$). We assumed the groundwater seepage rate and nutrient concentrations to be equal over the entire area. Although this assumption is highly unlikely because of spatial variability in groundwater flow and in nutrient concentrations of interstitial sediments, the contribution of nutrients from groundwater appears to be at least on the same magnitude as the estimated freshwater sources from the Everglades to the eastern part of the bay. Also, although tidal springs or solution holes may be relatively rare, their potential contribution to the nutrient flux per unit area appears to be large.

Also, consider the possible nitrogen contribution for an area on the bay side of the Keys, Tavernier Basin (approximately $1.9 \times 10^6 \text{ m}^2$, 2-m depth), which is also located in the eastern area of Florida Bay. Seepage measurements collected along the bay side of the Keys, including this basin, averaged 21.2 ± 5.2 ml $\text{m}^{-2} \text{min}^{-1}$ ($n = 17$). Dissolved N-species and phosphate in groundwaters along the Keys ranged from $15\text{--}50 \mu\text{M}$ and $0.03\text{--}1.3 \mu\text{M}$, respectively (Shinn et al. 1994). However, Kump (1998) showed nitrogen and phosphate concentrations in groundwaters surrounding a sewage injection facility to be as high as $200 \mu\text{M}$ and 50

μM , respectively. Areas affected by these sewage injection wells could provide a much greater nitrogen and phosphorous flux to surface waters. From the more conservative data presented by Shinn et al. (1994), we estimated the nitrogen and phosphate flux to Tavernier Basin to be $160\text{--}560\text{ mmol N m}^{-2}\text{ yr}^{-1}$ and $0.3\text{--}10\text{ mmol PO}_4^{3-}\text{ m}^{-2}\text{ yr}^{-1}$, respectively. This range of nitrogen flux is similar to estimates of inorganic N input of three large river-dominated Atlantic estuaries: Long Island Sound, Chesapeake Bay, and Pamlico River estuaries have an estimated nitrogen input from rivers of 400, 510, and $860\text{ mmol N m}^{-2}\text{ yr}^{-1}$, respectively (Nixon and Pilson 1983). Based on these calculations, groundwater could be a significant nutrient source to surface waters within the eastern area of Florida Bay, especially in certain areas along the inside of the Keys.

Summary

We were able to establish patterns of potential groundwater input into Florida Bay by using radon and methane as natural tracers of SGD. The results suggest that interactions between groundwater and surface water are greatest near shore along the Florida Bay side of the Florida Keys. In addition, we observed that seagrasses and other macroalgae showed significant ^{15}N enrichment in the same areas. This enrichment may also indicate a ^{15}N -enriched nitrogen groundwater source. The nitrogen in groundwater may be produced by denitrification fueled by organic matter in the subsurface, or it may result from wastewater sources. Groundwater seepage, measured with the Lee-type meters, appears to be significant in certain areas and may be important for the nutrient budgets of Florida Bay. Our results have shown that groundwater circulation may provide nutrients to the eastern portion of Florida Bay similar in magnitude to surface inputs from the Everglades.

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