Estimating the groundwater contribution into Florida Bay via natural tracers, \(^{222}\text{Rn}\) and \(\text{CH}_4\)

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Abstract

Groundwater may represent a significant pathway for nutrients and other dissolved solutes into Florida Bay, especially near the Keys where wastewater disposal practices add large amounts of nitrogen and phosphorus to the subsurface each year. Previously, we suggested that high water column inventories of the tracers \(^{222}\text{Rn}\) and \(\text{CH}_4\) may be indicative of groundwater discharge. In this study, we employed mass balance calculations to determine that the total benthic fluxes required to maintain the measured water column tracer inventories were significantly larger than diffusive fluxes and varied between 4.2–5.6 dpm m\(^{-2}\) min\(^{-1}\) and 5.8–15.4 nmoles m\(^{-2}\) min\(^{-1}\) for \(^{222}\text{Rn}\) and \(\text{CH}_4\), respectively. Independent estimates of the diffusive flux and porewater activities/concentrations allowed us to calculate an advective groundwater velocity, assuming that the difference between the total benthic flux (given above) and the diffusive flux is driven by seepage-driven porewater advection. These calculated velocities ranged from 0.2 to 4.3 cm d\(^{-1}\) for all sites, tracers, and sampling periods, with a best estimate of approximately 1.7 cm d\(^{-1}\). These estimates of groundwater velocities compare very well with previous measurements of groundwater flux (1–3 cm d\(^{-1}\)) at the same sites via seepage meters.

Florida Bay, a mosaic of shallow water banks and deeper water basins, was once characterized by clear waters and healthy seagrass meadows. Massive seagrass die-offs, planktonic algae blooms, and salinity excursions have occurred in the last decade (Boesch et al. 1993; Philips et al. 1995; Philips and Badylak 1996; Philips et al. 1999; Fourqurean and Robblee 1999). There is no simple answer available for what has caused these dramatic events, but it is certain that they are related to a combination of natural phenomena and anthropogenic activities. A better understanding of the complete hydrologic and nutrient budget of Florida Bay is essential for interpreting past and current change, as well as for development of good management strategies for this and other coastal systems.

Some patterns of ecological change and environmental degradation in Florida Bay point to increased nutrient loading as one likely cause (Lapointe et al. 1990). However, the sources and pathways of these hypothesized nutrient additions are not clear. Nutrient inputs to the bay include freshwater flowing from the Everglades, Gulf of Mexico waters flowing into the bay, atmospheric deposition, and local sources (Rudnick et al. 1999). Localized inputs include diffusion from sediments, nutrient release during sediment re-suspension, surface runoff from the Keys, wastewater associated with boating activities, and direct discharge of groundwater into the bay. Although little is known about groundwater input into Florida Bay, it has been shown that tidal forcing is responsible for subsurface flow and significant localized groundwater input along the Keys (Shinn et al. 1994; Corbett et al. 1999; Dillon et al. 1999, 2000).

Submarine groundwater discharge may be ecologically important because it may transport nutrients and/or organic matter that could contribute to the eutrophication and degradation of surface waters. Groundwater input into surface waters has also been shown to be a contributor of nutrients in several estuaries (D’Elia et al. 1981; Capone and Bautista 1985; Capone and Slater 1990; Oberdorfer et al. 1990; Valiela et al. 1990). Corbett et al. (1999) suggested that groundwater in the eastern part of Florida Bay may provide as much nitrogen and phosphate as surface freshwater sources from the Everglades. However, this estimate was based solely on direct measurements via seepage meters and estimates of groundwater nutrient concentrations.

As Corbett et al. (1999) noted, the hydrogeology of Florida Bay is unlike most hydraulically driven freshwater coastal aquifers. We use the term “groundwater” for the Florida Keys in a very general manner, i.e., it includes recirculated seawater from the Atlantic Ocean and/or Florida Bay, meteoric water, and wastewater components. Nearly all groundwaters sampled by shallow wells in Florida Bay are saline to hypersaline (Corbett et al. 1999). There are several driving forces influencing the movement of subsurface waters within Florida Bay. Near the Florida Keys, the groundwater flow direction and rate is thought to be driven by tides rather than topography. Groundwater entering the bay along the north coast may be characterized by more typical topographic gradient flow. In addition, the Floridan Aquifer lies approximately 350 m below Florida Bay. Piezometric surface maps indicate that the hydraulic head of the aquifer below Florida Bay is approximately 6 m above mean sea level (Miller 1982; Bush and Johnston 1988). The artesian nature of this...
Corbett et al. (1999) reported high $^{222}$Rn and CH$_4$ water column activities/concentrations in certain parts of Florida Bay. These elevated activities/concentrations could be associated with turbulent mixing by bioturbation or current/wave mixing, gas bubble ebullition, plant gas transport, groundwater discharge, or a combination of these factors. Our objective in this study was to evaluate whether the elevated tracer activities/concentrations in the water column were consistent with our previous observations of groundwater advection rates made by direct measurements (seepage meters).

Experimental methods

General approach—In order to evaluate the connection between surface water tracer inventories and groundwater inputs, we constructed a balance of all possible inputs and outputs of these natural tracers. Although both $^{222}$Rn and CH$_4$ are enriched in groundwater relative to surface waters, they are present throughout the environment, and therefore other sources must be considered. Simple box models for both radon (Fig. 2A) and methane (Fig. 2B) may be used to de-
Radon was extracted, transferred, and counted with a modified emanation technique similar to that described by Mathieu et al. (1988). Samples were run a second time for assay of $^{222}$Ra by measuring $^{222}$Rn ingrowth, and the “excess” $^{222}$Rn ($\text{Excess}^{222}\text{Rn} = \text{Total}^{222}\text{Rn} - ^{226}\text{Ra}$) was decay-corrected to the time of sampling in order to determine the in situ radon activities (Corbett et al. 1999). Radon results are presented as excess radon values unless otherwise noted. Bottom grab sediment samples were also obtained at each site in order to assess potential diffusive fluxes of $^{222}$Rn from sediments (see next section).

Water samples for CH$_4$ analysis were collected in Wheaton BOD bottles and stored (<12 h) on ice until analysis. Upon return to the laboratory, water samples were transferred to 60-ml disposable syringes, which were preflushed with nitrogen. An extraction volume of 15 ml of N$_2$ was added to each syringe, and the methane was extracted from 45 ml of water via headspace equilibration (McAuliffe 1971). Samples were run on a Shimadzu flame ionization gas chromatograph equipped with a 2-m stainless steel column packed with Poropack Q.

**Diffusive benthic fluxes**—Two types of approaches are generally applied to measure fluxes of any component across the sediment–water interface: (1) measurements of gradients in the sediment and/or water column (e.g., Broecker 1965; Hesslein 1976; Key et al. 1979; Gruebel and Martens 1984; Berelson et al. 1990); and (2) in situ benthic chambers (e.g., Martens et al. 1980; Gruebel and Martens 1984; Berelson et al. 1990). In addition, Martens et al. (1980) described a depth-independent mathematical approach specifically for the determination of diffusive fluxes of $^{222}$Rn. This approach allows radon flux to be calculated by equilibrating sediment grab samples (~80 g wet sediment) collected from the field with surface waters (~100 ml) over at least a 30-d period in sealed containers. After this time period, the equilibration activity of radon supported by radium in the sediments should be established and the $^{222}$Rn activity in the water phase is measured. Assuming steady state conditions with negligible advective transport, the radon flux across the sediment–water interface can then be calculated from the following:

$$ J = \left(\lambda D_S D_e\right)^{1/2} \left(A_{eq} - A_s\right), $$

where $J$ is the flux of radon from the sediments (dpm m$^{-2}$ min$^{-1}$), $\lambda$ is the decay constant for $^{222}$Rn (min$^{-1}$), $D_S$ is the effective wet bulk sediment diffusion coefficient in the sediments (m$^2$ min$^{-1}$) corrected for temperature and tortuosity (Peng et al. 1974; Ullman and Aller 1982), $A_{eq}$ is the equilibrium activity of radon measured in the laboratory (dpm m$^{-3}$ wet sediment), and $A_s$ is the radon activity in the overlying water multiplied by the sediment porosity to obtain a value corresponding to the activity in wet sediment (dpm m$^{-3}$). The $D_S$ value was calculated for each site from the free solution diffusion coefficient, $D_{so}$, of radon (1.14 $\times$ 10$^{-5}$ cm$^2$ s$^{-1}$ at 18°C; Rona 1917) by correcting for temperature and sediment tortuosity (Ullman and Aller 1982).

In order to be certain that the sediment equilibration approach would provide accurate estimates of the diffusive flux of radon, we elected to perform an independent assessment. Fig. 2. Box models depicting sources and sinks supporting water column inventories of (A) $^{222}$Rn and (B) CH$_4$ in waters of Florida Bay.
of this flux in a manner similar to that of Corbett et al. (1998). A 14-cm diameter sediment core was collected off Rock Harbor with a custom-made device and transported back to the laboratory. Florida Bay water (collected at the same site) was then added to this core, and the radon activity in the overlying water was monitored over time to produce a direct measurement of diffusive transport. The radon activity was monitored for over a 2-week period, and a direct estimate of the diffusive flux of $^{222}\text{Rn}$ was made by evaluating the increase in activity while accounting for decay in the overlying water during the experiment. After these initial time-series experiments were complete, a subcore was collected and partitioned into several depth intervals. These sediment samples were sealed in glass bottles with approximately 80 ml of Florida Bay water. The wet sediments were analyzed immediately (by radon emanation) for $^{222}\text{Rn}$ to determine radon porewater activities before any significant ingrowth of $^{222}\text{Rn}$ could occur due to $^{226}\text{Ra}$ in the sediment. The samples were then reanalyzed after a 30-d holding period in order to obtain the "sediment equilibrated" $^{222}\text{Rn}$ for each sample. Porosities and wet bulk densities of these sediments were calculated at the same depth intervals from measured water contents and grain densities determined on companion sediment samples collected in a second subcore.

Estimates of the diffusive flux of methane were conducted at the Rock Harbor and Flamingo field sites by measuring the porewater concentration gradient in the sediments with a peeper, a close interval porewater sampling device described by Hesslein (1976). A 0.2-$\mu$m polycarbonate membrane covered the open 10-ml compartments of the peeper (initially filled with deionized water), and the entire assembly was inserted into the sediments and allowed to equilibrate with in situ porewaters for approximately 6 d. After this equilibration period, samples were collected with a syringe and needle and placed on ice until analysis. Once the analyses were complete and the concentration gradient had been estimated graphically, Fick’s law was used to estimate the diffusive flux, using a diffusion coefficient ($1.72 \times 10^{-5}$ cm$^2$ s$^{-1}$) estimated by Chanton et al. (1989) for similar types of sediments and conditions.

**Benthic flux experiments**—Clear acrylic chambers, enclosing 59 liters of ambient water and covering 0.21 m$^2$ of bottom sediment, were used to assess benthic fluxes during August 1998 and January 1999. After inserting them into the sediment, the chambers were sterilized, either manually with a small fan or with a small submersible pump, and initial samples were collected for $^{222}\text{Rn}$ and CH$_4$. The two stirring methods provided insight into any potential artifacts due to any disturbances during mixing. Intermediate samples were collected when possible at about 6 h, and final samples were collected after approximately 12 h after the initial collection. At that point, the chambers were either reset by opening ports to the ambient surface water and mixing for approximately 30 min, or they were removed and reinserted at a different location. The flux of $^{222}\text{Rn}$ and CH$_4$ across the sediment–water interface could then be calculated by relating the change in activity/concentration inside the chamber to the enclosed water volume, deployment time, and the enclosed sediment area.

**Computational methods**

**Tracer mass balance**—In order to assess the groundwater flux entering Florida Bay via radon and methane measurements, all sources and sinks of the two gases must be considered. Simple box models for $^{222}\text{Rn}$ (Fig. 2A) and CH$_4$ (Fig. 2B) were used to describe the measurements necessary to complete a mass balance at each experimental site. Mathematically, the $^{222}\text{Rn}$ balance can be expressed as

$$J_{\text{benthic}} + \lambda A_{\text{Ra}} z - J_{\text{am}} - A_{\text{Ra}} = 0,$$

and for CH$_4$,

$$J_{\text{benthic}} + J_{\text{production}} - J_{\text{am}} - J_{\text{oxidation}} = 0,$$

where $J_{\text{benthic}}$ represents the combined advective ($J_{\text{flush}}$) and diffusive ($J_{\text{diff}}$) flux of either $^{222}\text{Rn}$ or CH$_4$ to the overlying water column (dpm m$^{-2}$ min$^{-1}$ or nmol m$^{-2}$ min$^{-1}$); $\lambda$ is the decay constant of $^{222}\text{Rn}$ (min$^{-1}$); $A_{\text{Ra}}$ and $A_{\text{Ra}}$ accounts for production and decay of radon in the water column (dpm m$^{-2}$ min$^{-1}$ or nmol m$^{-2}$ min$^{-1}$); and $J_{\text{production}}$ and $J_{\text{oxidation}}$ refer to the amount of methane produced and consumed within the water column, respectively (nmol m$^{-2}$ min$^{-1}$).

Horizontal transport of the trace gases was not considered in the mass balance equations since the horizontal activity/concentration gradient at each study site was observed to be small (Corbett et al. 1999). The most likely source for $^{222}\text{Rn}$ in the surface waters of Florida Bay is via benthic flux (Eq. 2), since production of $^{222}\text{Rn}$ in the water column is fairly small due to the low $^{226}\text{Ra}$ activities (~1,500 dpm m$^{-3}$) relative to typically observed $^{222}\text{Rn}$ activities (>5,000 dpm m$^{-3}$). Sources of radon across the sediment/water interface include both diffusive and advective fluxes. All sediments contain trace amounts of uranium and daughter products including $^{226}\text{Ra}$, the progenitor of $^{222}\text{Rn}$. Thus, diffusion of $^{222}\text{Rn}$ would add some amount of unsupported radon to the overlying waters due to its relatively high mobility in the environment as a noble gas.

The production and oxidation of CH$_4$ in coastal and offshore waters of the northeastern Gulf of Mexico has been studied extensively by Bugna et al. (1996). They showed that incubations of unfiltered seawater produced a mean net oxidation rate of $0.8 \pm 0.7$ nmol m$^{-2}$ min$^{-1}$ and a mean methane production rate of $0.4 \pm 0.5$ nmol m$^{-2}$ min$^{-1}$ in nearshore waters. We have used the mean values of the oxidation and production rates of methane from Bugna et al. (1996) in all calculations.

**Benthic fluxes**—The benthic fluxes were assessed experimentally in the field with benthic flux chambers and from water column tracer activities/concentrations by solving the mass balance equation (Eq. 2 or Eq. 3) after estimating all other sources and sinks. The total benthic flux ($J_{\text{total}}$) will exceed the estimated diffusive flux ($J_{\text{diff}}$) if there is also an advective flux ($J_{\text{flush}}$) present, such as from groundwater flow or a turbulent transfer mechanism like bioirrigation or bio-
estimate the advective flux of groundwater into surface waters with methane as a tracer:

$$\text{Seepage Rate} = \frac{(J_{\text{bethic}} - J_{\text{diff}})}{[\text{CH}_4]_{\text{pw}}}$$  \hspace{1cm} \text{(4)}$$

where

$$J_{\text{seep}} = J_{\text{bethic}} - J_{\text{diff}}$$  \hspace{1cm} \text{(5)}$$

The seepage rate is the velocity of groundwater across the sediment–water interface, and $[\text{CH}_4]_{\text{pw}}$ is the maximum porewater methane concentration measured at each site. This approach has been used for the methane results collected in Florida Bay.

We used a one-dimensional, vertical advection-diffusion model to estimate radon exchange from sediments. This model was initially developed by Craig (1969) to describe radiocarbon profiles in the deep sea and later applied by Cable et al. (1996) to model $^{222}$Rn fluxes from marine sediment. The flux of radon supplied to the overlying water can be estimated with

$$\frac{\partial C}{\partial t} = K_e \frac{\partial^2 C}{\partial z^2} + \omega \frac{\partial C}{\partial z} + P + \lambda C$$  \hspace{1cm} \text{(6)}$$

where $C$ is the radon activity in the sediments; $z$ is depth positive downwards; $K_e$ is the vertical diffusivity; $\partial^2 C/\partial z^2$ and $\partial C/\partial z$ are the $^{222}$Rn activity gradients across the sediment–water interface for diffusion and advection, respectively; $\omega$ is the vertical advective velocity; $P$ is a zero-order production term; and $\lambda C$ is radioactive decay. To model radon activity in sediments, $K_e$ is set equivalent to $D_s$, the effective wet sediment radon diffusion coefficient. For $^{222}$Rn in sediments, $P$ is the result of radon present in pore fluids due to recoil after production by decaying $^{226}$Ra in mineral grains ($P = \lambda A_{\text{eq}}$, where $A_{\text{eq}}$ is defined for Eq. 1). Advection ($\omega$) and radioactive decay ($\lambda C$), represent losses from the sediments and are defined as negative terms in the model. We used this approach to estimate the advective flux necessary to balance the total radon inventories (including loss via gas exchange to the atmosphere) for the three study sites in Florida Bay.

**Fluxes to the atmosphere**—Gas exchange across the air–water interface is a significant sink for dissolved gases in coastal waters. The total flux to the atmosphere depends on the molecular diffusion produced by the concentration gradient across this interface and on turbulent transfer, which is dependent on physical processes. The flux ($J_{\text{atm}}$) of a soluble gas across the air–water interface can be calculated from the equation from MacIntyre et al. (1995):

$$J_{\text{atm}} = k(C_w - aC_{\text{atm}})$$  \hspace{1cm} \text{(7)}$$

where $C_w$ and $C_{\text{atm}}$ are the concentration of the gas of interest in surface water and air, respectively (dpm m$^{-3}$); $a$ is Ostwald’s solubility coefficient (dimensionless); and $k$ is the gas transfer coefficient (m min$^{-1}$). The gas transfer coefficient is a function of the kinematic viscosity, molecular diffusion of the gas, and turbulence at the interface, which is dependent on wind speed (Jahne et al. 1987; Wunminkhof 1992; MacIntyre et al. 1995; Bugna et al. 1996; Corbett et al. 1997). Gesell (1983) showed that the atmospheric $^{222}$Rn activities are on the order of 220 to 890 dpm m$^{-3}$. An average value of 560 dpm m$^{-3}$ was used for the flux calculations presented here.

**Results and discussion**

**Diffusive flux experiments**—Results obtained from the laboratory core experiment provided three independent approaches to estimate the diffusive flux of radon: (1) direct observation of radon buildup in the overlying water, (2) porewater profiles, and (3) the sediment equilibration technique. Sediment characteristics of the laboratory core were similar to samples collected from other sites, although the $^{226}$Ra activities in the sediment were slightly higher (Table 1). Initially, $^{222}$Rn was monitored in the overlying water after the apparatus was sealed. The flux was then estimated by relating the inventory ($I$) of $^{222}$Rn in overlying waters as a direct function of the flux ($J$) with consideration for decay over time ($t$):

$$I = J \left( \frac{1 - e^{-\lambda t}}{\lambda} \right)$$  \hspace{1cm} \text{(8)}$$

Fitting Eq. 8 to the observed data over the entire sampling period (Fig. 3, solid line) resulted in an estimated diffusive flux of $1.8 \pm 0.4$ dpm m$^{-2}$ min$^{-1}$ (Table 2). The dashed lines represent 95% confidence limits of the fitted data.

The $^{222}$Rn porewater profile, obtained from the subcore that was extracted from the incubated sediment after completion of the experiment (approximately 30 d), showed a middepth maximum at approximately 5 cm, suggesting diffusion both upward and downward (Fig. 4A). The change in $^{222}$Rn activity at depth was due to lower $^{226}$Ra content of the sediments deeper in the core (Fig. 4B, closed squares), possibly associated with the high organic matter content of the sediments deeper in the core (Fig. 4B, open circles). Carbonate muds dominated the top 6–8 cm of the core, with an average $^{226}$Ra activity of $2.3 \pm 0.5$ dpm g$^{-1}$, whereas the bottom section was a fibrous organic rich peat-like deposit with an average $^{226}$Ra activity of $1.3 \pm 0.3$ dpm g$^{-1}$. A

<table>
<thead>
<tr>
<th>Sediment parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity ($\Phi$, ml cm$^{-1}$)*</td>
<td>0.82 ± 0.06</td>
</tr>
<tr>
<td>Wet bulk density (g cm$^{-3}$)†</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>$^{226}$Ra (dpm g$^{-1}$)‡</td>
<td>1.9 ± 0.7</td>
</tr>
<tr>
<td>Effective diffusion coefficient (cm$^2$ s$^{-1}$) $^{222}$Rn equilibration activity (dpm L$^{-1}$ porewater)§</td>
<td>$(7.6 \pm 0.6) \times 10^6$</td>
</tr>
<tr>
<td>530 ± 90</td>
<td></td>
</tr>
</tbody>
</table>

* $\Phi = (W_r/\rho_r)\{[(W_r/\rho_r) + (1 - W_r/\rho_w)]\}$, where $W_r$ is the fraction of water present in the sediments, $\rho_r$ is the density of sea water, and $\rho_w$ is the measured dry grain density.
† $B_{c, \text{ave}} = [(\Phi\rho_r)] + [(1 - \Phi)\rho_w]$.‡ Value is the mean and standard deviation of subsamples collected from core.
§ Reported value is the mean and standard deviation of top three subsections of core, representing the top 8 cm of the sediment bed.
Groundwater discharge into Florida Bay

Fig. 3. Rn-222 inventory in overlying water of experimental core. Solid line represents best fit to Eq. 8. Dashed lines represent 95% confidence limits of equilibrium activity.

Table 2. Rn-222 flux estimates from experiments performed in the laboratory from sediments taken from Rock Harbor, Florida Bay.

<table>
<thead>
<tr>
<th>Measurement method</th>
<th>Radon flux (dpm m(^{-2}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accumulation in overlying water</td>
<td>1.8 ± 0.4</td>
</tr>
<tr>
<td>Porewater profile</td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td>Sediment equilibration</td>
<td>1.1 ± 0.3</td>
</tr>
</tbody>
</table>

Theoretical profile of Rn-222 in the pore solutions may be constructed, and an estimate of the diffusive flux of Rn-222 into the overlying water can be obtained using Eq. 6 (Fig. 4A, solid line), assuming advection is negligible and using the best fit of the top 8 cm of the core. The estimated diffusive flux obtained from the sediment profile was 0.9 ± 0.2 dpm m\(^{-2}\) min\(^{-1}\) (Table 2).

Finally, surface sediment from the experimental core was analyzed by the same sediment equilibration technique used for all the other samples in this study. Rn-222 equilibration values (A\(_{eq}\)) for samples collected in the top 8 cm averaged 530 ± 90 dpm L\(^{-1}\) porewater. The diffusive flux estimated from Eq. 1 was 1.1 ± 0.3 dpm m\(^{-2}\) min\(^{-1}\) (Table 2). Thus, the diffusive flux calculated with the sediment equilibration technique was not statistically different (t-test, α = 0.05) from the other two methods used in the core experiment. In summary, we feel that these experiments validated the sediment equilibration approach and we used the results from the sediment equilibration experiments for our balance calculations.

Sediment samples collected from each study site were used to estimate the porosity, wet bulk density, effective diffusion coefficient, and 222Rn equilibration activity (Table 3). Diffusion coefficients calculated for each site were in good agreement with other theoretical and experimental values obtained in comparable studies (Broecker and Peng 1974; Berner 1980; Martens et al. 1980; Hartman and Hammond 1984). Estimated diffusive fluxes measured from the sites ranged from 0.5 to 0.7 dpm m\(^{-2}\) min\(^{-1}\) (Table 4), with no statistical difference between the field sites (t-test, α = 0.05). Samples collected during the two time periods and duplicates run on splits from the same site were generally within 10 to 20%. The average diffusive flux from each site will be used in all subsequent calculations.

The methane diffusive flux was estimated at Rock Harbor and Flamingo from the upper portion of the porewater concentration gradients obtained with peepers in January 1999. Measured porewater methane concentrations from the two sites showed similar concentration gradients in the upper 15
cm of the sediment column (Fig. 5). It is not known why the Flamingo site had much higher concentrations in the bottom portions than that of Rock Harbor. It should be noted that these measurements were only made once during this study and cannot address seasonal variation. The estimated methane diffusion from Rock Harbor and Flamingo were 0.3 ± 0.1 and 0.4 ± 0.1 nmoles m⁻² min⁻¹, respectively (Table 4). Since the diffusive fluxes at these two sites were so similar and all the field sites are not very different geologically, the average diffusive flux has been applied for subsequent calculations at all three sites.

Water column tracer inventory and mass balance—Initially, a mass balance of the tracers was completed using Eqs. 2 and 3 and the simple box models (Fig. 2). Assuming that all other sources and sinks could be estimated, the mass balance equation was solved for the benthic flux necessary to balance the tracer inventory. Rn-222 samples were corrected for ²²⁶Ra in the water column. By initially subtracting the ²²⁶Ra activity in the water column from the total ²²²Rn,

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**Table 3.** Calculated and measured parameters for samples recovered from three sites in Florida Bay.

<table>
<thead>
<tr>
<th>Site parameters</th>
<th>Rock Harbor</th>
<th>Flamingo</th>
<th>Rabbit Key Basin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean water column excess radon activity (dpm L⁻¹)*</td>
<td>7.5 ± 4.5</td>
<td>8.6 ± 2.0</td>
<td>5.2 ± 1.5</td>
</tr>
<tr>
<td>Mean water column methane concentration (nM)*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>August 1998</td>
<td>42.6 ± 4.5</td>
<td>44.8 ± 7.5</td>
<td>9.9 ± 1.6</td>
</tr>
<tr>
<td>January 1999</td>
<td>10.2 ± 5.4</td>
<td>12.2 ± 3.8</td>
<td></td>
</tr>
<tr>
<td>Porosity (Φ, ml cm⁻³)†</td>
<td>0.57 ± 0.04</td>
<td>0.79 ± 0.05</td>
<td>0.77 ± 0.04</td>
</tr>
<tr>
<td>Wet bulk density (g cm⁻³)†</td>
<td>1.5 ± 0.1</td>
<td>1.3 ± 0.1</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>²²⁶Ra activity (dpm g⁻¹)</td>
<td>0.8 ± 0.2</td>
<td>1.4 ± 0.4</td>
<td>2.1 ± 0.4</td>
</tr>
<tr>
<td>Effective radon diffusion coefficient (cm² s⁻¹)</td>
<td>(6.3 ± 1.0) × 10⁻¹</td>
<td>(6.9 ± 1.0) × 10⁻⁶</td>
<td>(6.9 ± 1.0) × 10⁻⁶</td>
</tr>
<tr>
<td>²²²Rn equilibration activity (dpm L⁻¹ porewater)</td>
<td>400 ± 120</td>
<td>350 ± 160</td>
<td>390 ± 50</td>
</tr>
<tr>
<td>Methane porewater concentration (nmoles L⁻¹ porewater)</td>
<td>460‡</td>
<td>1,400‡</td>
<td>710 ± 350**</td>
</tr>
</tbody>
</table>

* Values represent the mean and standard deviation of several water column samples collected during flux experiments.
† See footnote in Table 1.
‡ Values are based on the highest concentration measured in the sediment column.
** Average and standard deviation of samples collected from shallow groundwater wells in Florida Bay (n = 6).

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**Table 4.** Field and laboratory measurements of ²²²Rn and methane flux from the sediments at three sites in Florida Bay.

<table>
<thead>
<tr>
<th>Method</th>
<th>Radon flux (dpm m⁻² min⁻¹)</th>
<th>Methane flux (nmoles m⁻² min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux chambers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rock Harbor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>August 1998 (n = 9)</td>
<td>4.4 ± 1.7</td>
<td>5.6 ± 2.1</td>
</tr>
<tr>
<td>January 1999 (n = 7)</td>
<td>3.8 ± 0.6</td>
<td>7.3 ± 0.7</td>
</tr>
<tr>
<td>Flamingo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>August 1998 (n = 3)</td>
<td>2.3 ± 0.4</td>
<td>22.0 ± 7.5</td>
</tr>
<tr>
<td>January 1999 (n = 3)</td>
<td>3.6 ± 0.9</td>
<td>7.2 ± 2.0</td>
</tr>
<tr>
<td>Rabbit Key Basin (n = 3)</td>
<td>1.5 ± 0.5</td>
<td>2.7 ± 0.8</td>
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<tr>
<td>Diffusive flux estimates</td>
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<td></td>
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<tr>
<td>Sediment equilibration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rock Harbor</td>
<td>0.5 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Flamingo</td>
<td>0.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Rabbit Key Basin</td>
<td>0.7 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Peeper</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rock Harbor</td>
<td>0.3 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Flamingo</td>
<td>0.4 ± 0.1</td>
<td></td>
</tr>
</tbody>
</table>

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Fig. 5. Porewater methane concentrations measured at Rock Harbor and Flamingo. Rock Harbor reaches an equilibrium concentration below 14 cm.
giving excess $^{222}\text{Rn}$, in situ production of $^{222}\text{Rn}$ could be neglected in further calculations (i.e., the production term was already incorporated into the $^{222}\text{Rn}$ results). The average excess $^{222}\text{Rn}$ activity in the water column was used to estimate the loss due to decay. Estimates of the production and oxidation of methane in the water column were taken from Bugna et al. (1996). Although Florida Bay is a quite different environment than the area studied by Bugna et al. (northeastern Gulf of Mexico), a large change ($\pm 100\%$) in either component does not significantly alter the final result. Wind speed data used to calculate the atmospheric evasion rate of the gases were obtained from NOAA weather stations located at Key West and Miami, Florida. An average wind speed from these two locations over 30 yr was $3.8 \pm 0.8 \text{ m s}^{-1}$. This long-term average agrees with the wind speeds observed at these same NOAA weather stations during our field experiments in August 1998 and January 1999 of $2.5 \pm 0.9$ and $4.3 \pm 1.6 \text{ m s}^{-1}$, respectively. The wind speeds during the sampling events generated August and January exchange coefficients ($k$) for $^{222}\text{Rn}$ of $(1.2 \pm 0.5) \times 10^{-3}$ and $(5.2 \pm 2.3) \times 10^{-4} \text{ cm s}^{-1}$, respectively. These wind speeds gave a calculated value of $k$ for CH$_4$ in August and January of $(1.4 \pm 0.7) \times 10^{-3}$ and $(6.0 \pm 3.1) \times 10^{-4} \text{ cm s}^{-1}$, respectively. The average calculated benthic fluxes and the average values used to obtain them are presented in Tables 5 and 6. Rn-222 estimated fluxes were averaged between the two sampling periods, since the difference in water column activities was not significant and the atmospheric evasion rates were well within the uncertainty. The $^{222}\text{Rn}$ total benthic flux at all sites ranged from 2.8 to $8.0 \text{ dpm m}^{-2} \text{ min}^{-1}$, with the highest average flux at Rock Harbor (Table 5). The CH$_4$ flux was separated into the two sampling periods, August 1998 and January 1999 (Table 6), since water column concentrations were significantly higher in August and large differences in the atmospheric evasion rates were observed. Methane concentrations in January 1999 were approximately four times lower than in August. This difference in concentration is more than likely due to the dependence of methane production on microbial activity. Cooler water column temperatures in January may have inhibited the microbial activity, thus reducing the production of methane. Benthic methane fluxes at all the sites ranged from 9.6 to $24.0 \text{ nmoles m}^{-2} \text{ min}^{-1}$ and 2.9 to $13.2 \text{ nmoles m}^{-2} \text{ min}^{-1}$ in August 1998 and January 1999, respectively. The highest estimated methane flux was calculated for the Flamingo site during both sampling periods.

The calculated benthic fluxes were as much as 50 times greater than the estimated diffusive fluxes (Table 4). The

<table>
<thead>
<tr>
<th>Site parameters</th>
<th>Rock Harbor</th>
<th>Flamingo</th>
<th>Rabbit Key Basin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inventory (dpm m$^{-2}$)</td>
<td>$10,500 \pm 6,300$</td>
<td>$6,900 \pm 1,600$</td>
<td>$9,400 \pm 2,700$</td>
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<tr>
<td>Sources (dpm m$^{-2}$ min$^{-1}$)</td>
<td></td>
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</tr>
<tr>
<td>Total benthic flux*</td>
<td>$5.6 \pm 1.6$</td>
<td>$5.5 \pm 1.5$</td>
<td>$4.2 \pm 1.0$</td>
</tr>
<tr>
<td>Sinks (dpm m$^{-2}$ min$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In situ decay</td>
<td>$1.3 \pm 0.8$</td>
<td>$0.9 \pm 0.3$</td>
<td>$1.2 \pm 0.3$</td>
</tr>
<tr>
<td>Atmospheric evasion</td>
<td>$4.3 \pm 1.4$</td>
<td>$4.6 \pm 1.5$</td>
<td>$3.0 \pm 1.0$</td>
</tr>
</tbody>
</table>

* Estimated using Eq. 2, other values in the table, and solving for the total benthic flux.

* Estimated using Eq. 3, other values in the table, and solving for the total benthic flux.
magnitude of the calculated benthic fluxes was primarily determined by the atmospheric evasion rates in this shallow water environment. However, even if losses to the atmosphere were assumed to be negligible, there would still be an excess of tracer by as much as tenfold above that which diffusion alone could supply. Thus, there must have been an additional source of these tracers to the water column. As previously noted, turbulent mixing, gas bubble ebullition, plant gas transport, and groundwater discharge may all enhance benthic flux. Gas bubble ebullition may enhance diffusive benthic fluxes by as much as 2.5 times due to an increase in the surface area of the sediment–water contact associated with invagination of the sediment by bubble tubes (Martens et al. 1980). At up to 50 times the diffusive flux, the benthic fluxes estimated for Florida Bay appear to be greater than what would be expected from the effects of bubble ebullition alone. Turbulent mixing by bioturbation and current/wave mixing have often been invoked to explain near-bottom tracer inventories greater than those that could be supplied by diffusion alone (Hammond et al. 1977; Emerson et al. 1984; Hartman and Hammond 1984; Rutgers van der Loeff et al. 1984). For example, Hartman and Hammond (1984) attributed total $^{222}$Rn benthic fluxes that exceeded those expected from molecular diffusion by as much as a factor of 4 to macrofaunal irrigation. However, many previous studies in coastal systems have not considered advection of groundwater as a potential source of the parameter of interest. Although turbulent mixing in Florida Bay waters cannot be ruled out as a potential source of the excess $^{222}$Rn and CH$_4$ in this mass balance approach, our previous direct measurements of advective benthic fluxes (Corbett et al. 1999) were consistent with the fluxes calculated here. In addition, benthic chamber experiments (see below) suggested an additional source of the tracers to the water column besides turbulent mixing.

**Benthic chamber experiments**—An independent estimate of benthic flux was obtained experimentally using benthic flux chambers at all three field sites. Three benthic chambers were deployed at each site over at least a 2-d period. The fluxes measured via the benthic chamber approach were consistently higher than could be accounted for by diffusion alone (Table 4). One explanation may be the seepage of porewater into the chambers. Although we attempted to keep the chambers sealed, it is difficult to halt slow seepage of water. An experiment performed at the Rock Harbor site showed no significant difference in the tracer flux between a chamber that was apparently closed and another chamber allowed to seep through a small hole in the top.

Gas transport through seagrasses may also contribute to an enhanced benthic flux. In order to account for this potential artifact, we placed chambers in both vegetated and unvegetated areas. If the seagrasses provided a conduit for the gases, we would have expected benthic fluxes of both gases to be higher in vegetated areas. In fact, there was no statistical difference in the $^{222}$Rn fluxes between the vegetated and unvegetated sites. Methane fluxes were slightly higher in vegetated (6.6 ± 1.2) compared to unvegetated (4.2 ± 1.1) areas. However, this difference was probably associated with higher organic matter content in vegetated sediments rather than gas transport through seagrasses, since it was observed in the methane flux but not the radon flux.

Artifacts caused by sediment resuspension and/or stirring may have contributed to the higher than expected values. However, several chambers at the same site gave the same flux estimate regardless of stirring method. In addition, every attempt was made to limit the effects of resuspension within the chamber while inserting them into the sediment. In most cases there was no visual resuspension of sediment. In any case, this method has provided conservative estimates of the total benthic flux, which may include advection as well as diffusion.

There was little difference in the $^{222}$Rn flux at all sites and the CH$_4$ flux at Rock Harbor measured from the benthic flux chambers between August and January, although there was a significant change in the methane flux at the Flamingo field site between August and January (Table 4). A similar pattern can be seen in the surface water activities/concentrations of the two trace gases. There was no significant difference in the radon activities, thus all of the data were pooled for this analysis. However, the methane surface water concentrations changed dramatically at both field sites between the two sampling events, indicating a potential link between the surface water concentration and benthic flux (Table 3).

** Estimates of groundwater input**— Estimates of the advective velocity of groundwater necessary to support the benthic fluxes determined from both in situ experiments and the water column mass balance calculations can be obtained by establishing the tracer activity/concentration in the advecting fluids (Eqs. 4 and 5). Since the fluids are seeping through the sediments, one would ideally use an in situ porewater concentration. However, methane porewater concentrations did not show a constant concentration with depth (Fig. 5). In order to be more conservative, we elected to use the highest concentration of methane measured in the porewaters at each site. These concentrations are also within the range of previously reported methane groundwater concentrations in wells located throughout Florida Bay (Corbett et al. 1999) and groundwater samples collected during this study. Since in situ methane concentrations were not measured at Rabbit Key Basin, the average groundwater concentration in wells sampled in Rabbit Key Basin during the same period was used as the advective fluid concentration for the site. Radon-222 activities in porewater were not obtained from the field sites during the sampling trips. However, equilibrium activities measured in the laboratory sediment equilibration experiments have been used in previous studies as an estimate of the in situ $^{222}$Rn porewater activity (Cable et al. 1996; Corbett et al. 1997). In addition, the estimates of the equilibrium $^{222}$Rn activity (Table 3) were within one standard deviation of groundwater values reported by Corbett et al. (1999). Furthermore, these equilibrium values are similar to the porewater activities measured in the test core (Fig. 4).

Using the estimated porewater activity, the seepage velocity was calculated using Eq. 4. Estimates of seepage velocity using the mass balance calculations for $^{222}$Rn and CH$_4$ range between 0.3–2.5 and 0.3–4.3 cm d$^{-1}$, respectively (Fig. 6). The average measured and calculated seepage velocities were all very close and typically within the estimated un-
Corbett et al. (1999) reported measurements of groundwater flow based on seepage meter measurements for areas in Florida Bay along the Keys bay side (within ~3 km of the Keys coastline), north coast (within ~3 km of the Everglades coastline), and in the midbay (west of Black Betsy Keys). 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. Converting these seepage rates to velocity units showed that all sites were in the range of 1–3 cm d⁻¹, in very good agreement with the average velocity estimated via tracers (1.7 cm d⁻¹). Although this agreement could be fortuitous, it is encouraging that these two completely independent techniques converge at a common value for the upwelling velocity.

We have examined all the parameters in our tracer calculations to evaluate the sensitivity of our results to the various assumptions and estimations. This sensitivity analysis was intended to verify the lower limit of the results, i.e., to evaluate whether we made any assumptions that have resulted in too high an advective velocity. The calculated advective velocities based on the tracer mass balance estimates were most sensitive to the atmospheric evasion rate and the porewater tracer activity. Loss to the atmosphere was most sensitive to wind speed and the water column tracer concentrations/activities. To constrain our results, we solved Eq. 7 for several reasonable values of these two parameters for ²²⁶Rn (Fig. 7A). The different curves represent the ²²⁶Rn water column activity. Values included in the plot effectively represent the entire range of activities measured at all three sites. Rock Harbor, Flamingo, and Rabbit Key Basin had ²²⁶Rn water column activities averaging 7.5 ± 4.5, 8.6 ± 2.5, and 5.2 ± 1.5 dpm L⁻¹, respectively. We assumed an upper limit for surface water ²²⁶Rn of 9.0 dpm L⁻¹. Note that any further increase in water column activity would have
further increased the required advective velocity by the mass balance approach. The boxed area in Fig. 7 encompasses the 30-yr average wind speed and standard error estimate from the NOAA weather stations at Key West and Miami, as well as the reasonable range in $^{222}$Rn water column activities. Based on these assumptions, we estimated a reasonable atmospheric evasion rate of $^{222}$Rn ranging from 1.0 to 5.0 dpm m$^{-2}$ min$^{-1}$. Using these estimates together with a reasonable range for in situ decay (which is well constrained), we estimated the total benthic flux from the sediments to be between 1.6 and 6.5 dpm m$^{-2}$ min$^{-1}$ (Eq. 2). This range in total benthic flux was between 2 and 13 times greater than the amount that diffusion alone could supply to the water column.

In order to calculate the advective velocity via $^{222}$Rn, Eq. 6 not only required an estimate of the total benthic flux (see above), but the porewater $^{222}$Rn activity as well (Fig. 7B). We were able to constrain this value fairly well in this system. Corbett et al. (1999) measured the $^{222}$Rn activities from wells in several locations of Florida Bay and observed a range of 325–650 dpm L$^{-1}$ (Fig. 7B). In addition, the $^{222}$Rn equilibrium activities ($A_e$) measured from the three sites all fall within this range (Table 3). Based on the estimated total benthic flux (1.6–6.5 dpm m$^{-2}$ min$^{-1}$) and the observed groundwater activities, the calculated advective velocities must lie between 0.4 and 3.0 cm d$^{-1}$. Advection velocities calculated specifically for the three field sites were well within these reasonable limits (shown as open symbols in Fig. 7B). This same “sensitivity” analysis was performed for the CH$_4$ model and gave similar results (data not shown).

We were able to evaluate the advective flux of groundwater using a mass balance approach based on the two natural tracers, $^{222}$Rn and CH$_4$. Corbett et al. (1999) had previously presented potential groundwater-derived nutrient fluxes to eastern Florida Bay that showed that groundwater could supply up to 2–3 times as much N and P as that derived from surface waters of Taylor Slough and C-111. Although the previous estimates were based solely on seepage meter measurements and nutrients were not measured in the present study, the estimated groundwater flux via the tracer approach agrees with that based on the seepage meters. Therefore, we feel that the argument for the potential importance of groundwater to the overall nutrient budget of Florida Bay has been strengthened.

Groundwater may have several potential sources into Florida Bay. These sources include tidally driven recirculated seawater, upward transport from the underlying Floridan Aquifer, and long-distance transport through subsurface quartz sand channels of Miocene to Plio-Pleistocene age that have been discovered in south Florida (Warzeski et al. 1996; Cunningham et al. 1998; Guertin et al. 1999). Although the exact sources and pathways remain unclear, it is clear that groundwater may be an important input into Florida Bay and should be considered in future studies.

**Summary**

Measurements of trace gases, radon and methane, in the waters of Florida Bay indicate substantially higher benthic fluxes than can be accounted for by diffusion alone. These higher fluxes can be supported by groundwater velocities ranging from 0.2 to 4.3 cm d$^{-1}$. We suggest a best estimate of approximately 1.7 cm d$^{-1}$ for all three sites. Direct measurements using seepage meters are consistent with these results. Thus, groundwater may provide an additional and potentially important pathway for nutrients and other dissolved solutes to enter Florida Bay.

**References**


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Groundwater discharge into Florida Bay

1557