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Submarine groundwater discharge estimates at a Florida coastal site based on continuous radon measurements

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Abstract. The direct discharge of groundwater into the coastal zone has received increased attention in the last few years as it is now recognized that this process represents an important pathway for material transport. Assessing these material fluxes is difficult, as there is no simple means to gauge the water flux. We estimated the changing flux of groundwater discharge into a coastal area in the northeast Gulf of Mexico (Florida) based on continuous measurements of radon concentrations over a several day period. Changing radon inventories were converted to fluxes after accounting for losses due to atmospheric evasion and mixing. Radon fluxes are then converted to groundwater inflow rates by estimating the radon concentration of the fluids discharging into the study domain.

Groundwater flow was also assessed via seepage meters, radium isotopes, and modeling during this period as part of an "intercomparison" study. The radon results suggest that the flow is: (1) highly variable with flows ranging from ~5 to 50 cm/day; and (2) strongly influenced by the tides, with spikes in the flow every 12 hours. The discharge estimates and pattern of flow derived from the radon model matches the automated seepage meter records very closely.

Introduction

Recent studies have shown that SGD may account for a significant fraction of the fresh water inflow in areas where river input is not significant (Valiela & D'Elia 1990; Buddemeier 1996; Moore 1996). Since many of the land-sea interfaces of the world are characterized by "leaky" coastal aquifer systems, it should be clarified how important the flow of groundwater through the "leaks" is to the overall marine geochemical cycle. In addition to fresh groundwater from land, recirculated seawater is also driven through bottom sediments by a number of processes (Burnett et al. 2003).

The influence of submarine groundwater discharge (SGD) on the geochemistry of the coastal ocean has been a difficult scientific question to address because of the difficulty in measuring SGD fluxes with any degree of certainty. To meet this challenge, a working group established by the Scientific Committee on Oceanic Research (SCOR) and the Land-Ocean Interactions in the Coastal Zone (LOICZ) project of the International Geosphere-Biosphere Program (IGBP) is conducting a series of groundwater discharge assessment intercomparison experiments (Burnett & Turner 2001; Burnett et al. 2002). Three such experiments have been held to date, one along the Gulf of Mexico coast in Florida (August, 2000), a second in a coastal plain environment south of Perth, Australia (November/December, 2000), and a third on Shelter Island, New York (May, 2002). In each case, a multi-disciplinary group of investigators made estimates of submarine groundwater discharge based on manual and automated seepage meter measurements, natural isotopic tracers, and hydrogeological modeling approaches. This paper presents estimates of SGD based on continuous radon measurements from the Florida intercomparison experiment.

Specific groundwater discharge (volume per unit area per unit time) has been measured in the past using automated (Taniguchi & Fukuo 1993; Paulson et al. 2001) or manual Lee-type seepage meters (Lee 1977) and then total discharge (volume per time into a designated area or volume per unit width of shoreline per unit time) can be calculated by integrating the measured seepage over space and time. While this procedure can produce useful results it is very time consuming, is subject to artifacts (e.g. Shinn et al. 2002), and is usually relegated to the near coastal zone where water depths are shallow enough to emplace the seepage meters and collect samples. For areas further from shore researchers have used geophysical techniques to identify depressions or vents that allow for seepage of groundwater; applied hydrogeologic modeling methods to attempt to describe the system; or they use tracing methods to locate and quantify areas of seepage. Use of remote sensing and geophysical techniques has shown some success for determining the location of direct discharge from confined aquifers but these techniques have not advanced to the point where they can determine the location of disseminated seepage nor quantify groundwater discharge. Modeling methods are a popular approach for estimating SGD but they have certain limitations. For example, most analytical solutions assume a homogeneous aquifer system, which is rarely true. Similarly, modeling analysis frequently assumes steady state in the system, which is often an oversimplification. Hydrograph separation techniques used in modeling are only suitable for near coastal zones where well-developed drainage systems exist. Alternately, tracing techniques can be used in all areas of the coastal zone as long as the tracer "signal" is strong enough to be measured. Radon-222 is a useful geochemical tracer for analyzing groundwater discharge because:

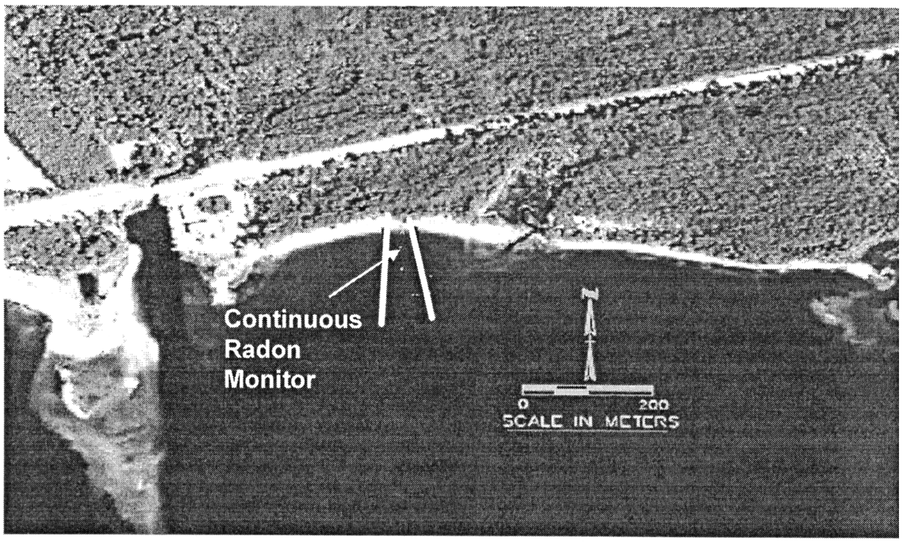

Figure 1. An aerial view of the intercomparison study area near the FSUML. The lines on the map represent manual "Lee" type seepage meter transects and are to scale. The continuous radon monitoring station was set up approximately 50 meters from shore and in the center of the two transects.

(1) it is greatly enriched in groundwater relative to seawater; (2) is chemically conservative in the water column; and (3) can be measured at very low concentrations.

An intercomparison study of SGD assessment approaches was conducted at the Florida State University Marine Laboratory (FSUML) on the coastal Gulf of Mexico from August 14–18, 2000 in order to evaluate these various techniques at the same time and place. A 100 m $\times$ 200 m area approximately 300 m east of FSUML was designated as the study domain (Figure 1). This paper will present results based on ^{222}Rn measurements and other papers in this issue will present results based on radium isotopes (Moore 2003), seepage meters (Taniguchi et al. 2003), and hydrogeological modeling (Smith & Zawazski 2003).

Study site

The FSUML is located approximately 55 km southwest of Tallahassee, Florida on the eastern edge of St. George Sound. In general the area off of the FSUML is characterized by gently sloping topography away from the coast resulting in a water depth of only $\sim$2 m as far as 1000 m off shore. This area of the Florida panhandle sits atop a layered dolomite and limestone platform called the Florida Plateau. The carbonate strata in this region contains "one of the worlds most prolific (confined) aquifers" (Clemens et al. 1998), the Floridan Aquifer. This large confined aquifer system is overlain by a clay, silt, and sand surficial aquifer. Groundwater reaches the coast through movement through the Floridan Aquifer System where it discharges off the coast via offshore seepage and spring flow into the Gulf of Mexico. Nearshore discharge around the FSUML is thought to consist primarily of seepage from the surficial unconfined surface aquifer although there are several small springs in the area that may be delivering deeper Floridan water to both nearshore and offshore waters.

Hydraulic conductivities of the surficial sand and silt aquifer have been reported as ranging from 2.6×10^{-5} cm sec^{-1} at 0.3 m below the surface to 1.7×10^{-6} cm sec^{-1} at 3 m below the surface. In contrast conductivities in the confined aquifer have been reported to range from 9.7×10^{-3} cm sec^{-1} in recrystalized limestone to 8×10^{-7} cm sec^{-1} in the denser dolomite (Rasmussen et al. 2003). Limestone bedrock is reported below a depth of 3 m in this area of coastline based on core data (Young 1996). The potentiometric surface of the aquifer in the region indicates that groundwater is flowing towards the coastline over much of the area (Wagner 1989).

For the intercomparison experiment, the research area was set up by establishing two transects normal to the shoreline – each containing six Lee-type (manual) seepage meters, together with various types of automated seepage meters. The seepage meter transects were roughly parallel to each other about 70 m apart and extending to approximately 200 m from the shoreline. In between the seepage meter transects were six sets of piezometer nests in a single transect set roughly perpendicular to the shoreline (Figure 2). For the sake of method comparisons, we defined a study domain of 20,000 m^2 (100 m $\times$ 200 m) centered on these transects.

Radon measurements

Systems that combine radon sparging techniques and continuous measurements have been used in Japan to study the use of radon as a predictor of earthquake activity (Igarashi et al. 1995). The device used in that study continuously degasses radon from the water into a chamber where daughter products are electrostatically collected and counted via a silicon semiconductor detector. We used a similar approach that combines a continuous flow of seawater pumped to an air-water exchanger where the radon in the water can equilibrate with the radon in the air. The air is then pumped to a commercially available radon-in-air monitoring system (RAD-7, made by Durridge Co., Inc.) for measurement (Burnett et al. 2001). The radon in air

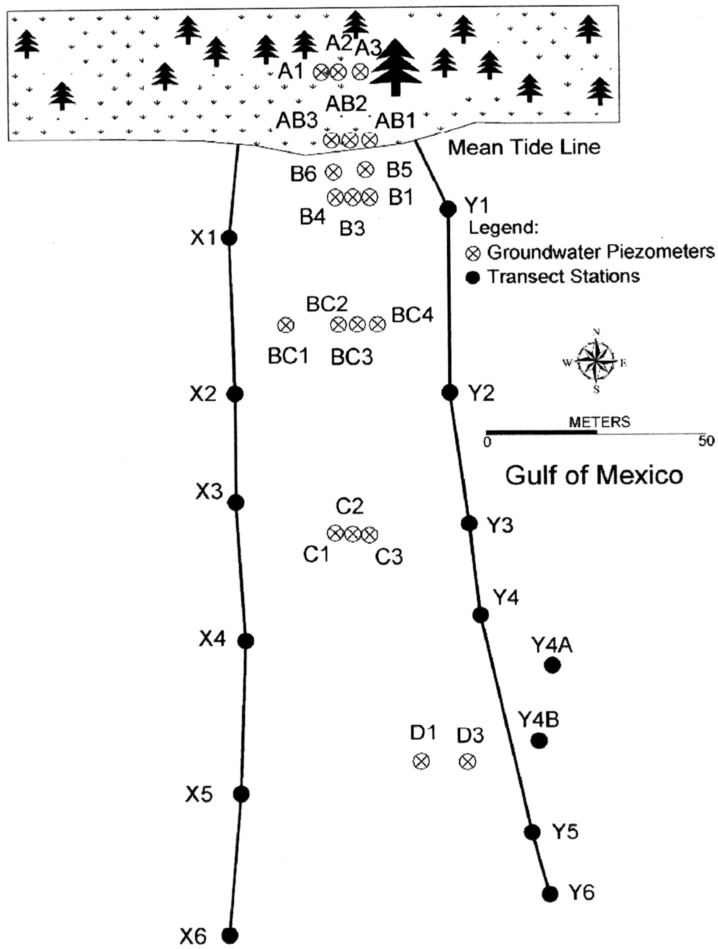

Figure 2. A graphical representation of the physical setup of the intercomparison study area. The continuous Rn monitor was anchored at piezometer BC2.

within the system is kept in equilibrium with the radon in water entering the exchanger by keeping the atmospheric portion of the system in a closed loop. Since the radon in the air is in equilibrium with the seawater flowing through the exchanger, one can calculate the radon in the water phase based on the temperature and solubility coefficient.

The continuous radon monitor was set up on a floating platform next to piezometer BC2 to take continuous radon measurements. This station was about 50 meters from shore in a central location in between the two seepage meter transects. The intake for the monitor was fixed at ~25 cm above the sea floor. A portable Honda EU-1000 generator provided power for the system.

Water was pumped into the exchanger at a rate of approximately 2.5 L/min using a 500 GPH Rule submersible bilge pump with an added flow controller. Air was pumped through the air loop of the detector-exchanger system at a rate of 1 L/min for one minute out of every five using the internal pump in the RAD-7. The radon detector was set to run 1 hour-long integrations which resulted in uncertainties in the radon measurements of $\sim$5%, 1σ.

In addition to the continuous radon measurements of the coastal ocean water, measurements were made of 1) the radon concentration in air using a scintillation type radon in air monitor (Pylon E.L. detector with model AB-5 controller) set for continuous two hour measurements; 2) temperature of the water entering the radon exchanger using a temperature data logger (Cole Palmer 23500 series) set for 30 min measurements; 3) wind speed, wind direction and air temperature at one hour averages of 30 second measurements using a Davis Weather Monitor II weather station with data logger; 4) water depth at piezometer BC2 every ten minutes throughout the experiment using an Infinities model # 220 water level data logger; 5) porosity and pore water concentration of radon in the sediment; and 6) ^{222}Rn and ^{226}Ra activities of the sea water in and around the study area by standard grab sampling and measurement techniques (Mathieu et al. 1988; Cable et al. 1996).

Results and discussion

Radon results

Duplicate samples of water were taken throughout the experiment from the area immediately adjacent to the continuous monitor for radon measurement via classical emanation methods to validate the continuous measurements. Comparison of the measurements shows excellent agreement between the grab samples and the continuous monitor with a few minor exceptions (Figure 3). It seems likely that inadvertent loss of radon during the sampling, handling, or analysis of the grab samples is responsible for the few samples that are not in agreement. We note that when the measurements are not within the estimated $\pm$ 1σ uncertainties (duplicates for samples 2, 4 and 5), the traditional analysis is lower than the RAD-7 analysis; an indication that loss is responsible. Furthermore, the other duplicate sample in each case was higher and agreed with the result from the continuous radon monitor.

When radon concentrations in the coastal waters are plotted over the elapsed time, systematic variations in the ^{222}Rn activities are observed. When radon concentration is compared with the water depth at the same station (Figure 4) a relationship linking decreasing tidal height and increasing radon

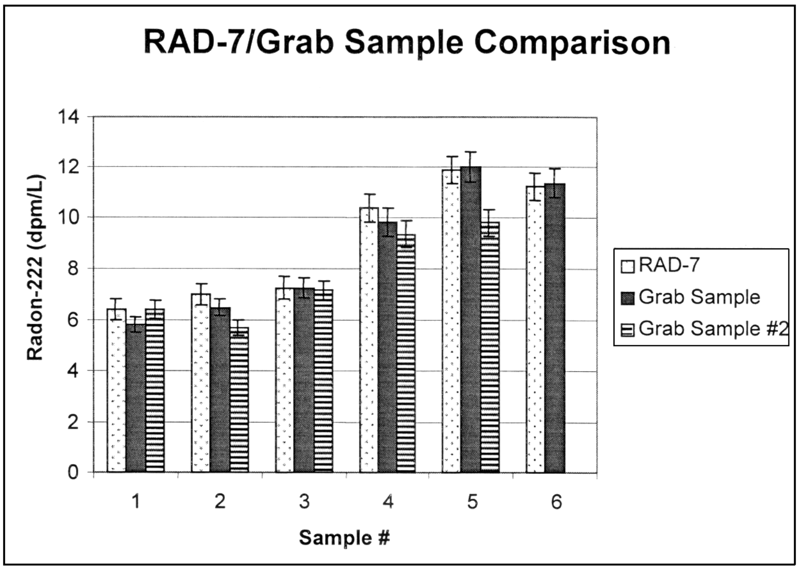

Figure 3. A comparison between radon measurements made with the continuous radon monitor (RAD-7) and grab samples of water measured for radon using classical radon emanation techniques. The uncertainties expressed are $\pm 1\sigma$ based on counting statistics.

concentration is evident. In general, radon concentrations tend to be highest at the lowest tide. A 12-hour periodicity in the ^{222}Rn activities at this site was noted earlier (Burnett et al. 2001).

Calculation of radon fluxes

To calculate SGD from radon concentrations, the measured radon activities must be converted to the flux of excess (unsupported by ^{226}Ra) ^{222}Rn into the system from the sediment and corrected for various losses (Cable et al. 1996; Burnett & Dulaiova 2003). To calculate flux of radon and estimate the SGD in the study domain a model must be used that addresses all known inputs and losses. Figure 5 depicts a basic "box" type model created for the FSUML system. The model is similar to those used in previous radon studies (e.g. Corbett et al. 2000; Burnett & Dulaiova 2003) in that it describes various source and sink terms for radon in the system but this model uses a geometry that reflects a more realistic wedge shape of the study domain and changes in size to allow for tidal influences. The concentration of radon that is measured in the coastal waters at any time is a function of 1) production from ^{226}Ra dissolved in the seawater; 2) input from the sediment (from both groundwater discharge and diffusion); 3) loss of radon via aerial evasion; 4) lowering of the radon concentration by mixing with lower concentration waters offshore; and

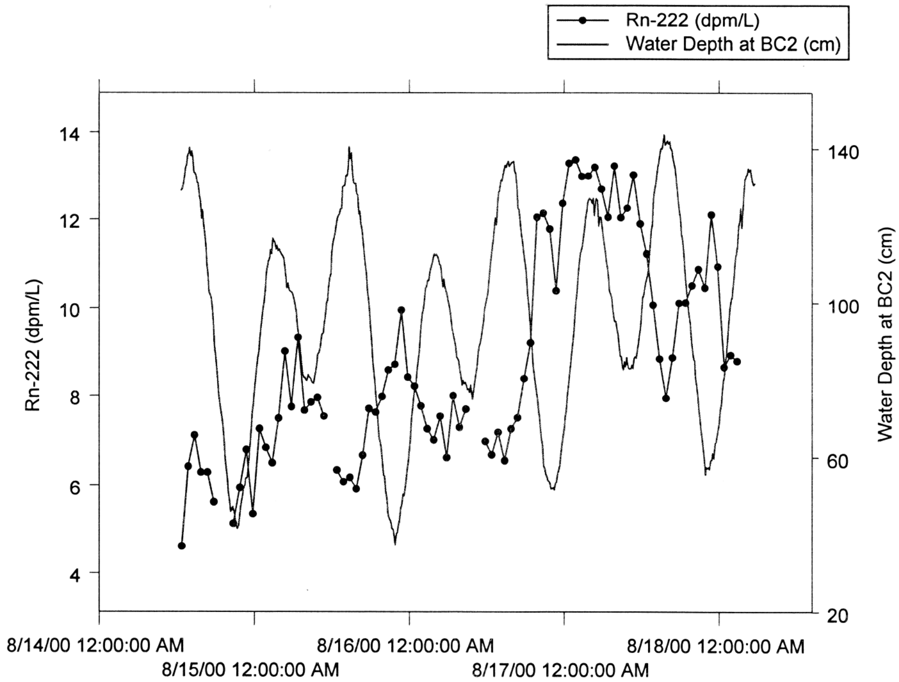

Figure 4. A plot of measured ^{222}Rn activity (dpm/L) in the water column and water depth (cm) at the same station over the study period. In general, radon concentrations tend to increase as the water depth decreases.

5) decay. Since we will examine ^{222}Rn in terms of inventories (concentration multiplied by water depth) and our study domain is in shallow water where tidal variations are significant, we also adjust the inventories to remove the effect of the tidal changes. This is done by subtracting the amount of radon that enters with the flood tide (Δ tidal volume above a reference height multiplied by the offshore radon activity) and a similar (but opposite) correction for the outgoing tide.

Atmospheric loss

The flux of radon out of the water column by aerial evasion is calculated using the relationship:

$$F = k(C_w - \alpha C_{air}) \tag{1}$$

where F is the flux of Rn to the atmosphere (dpm/m^2 hr); k is piston velocity (also referred to as the gas transfer velocity; m/s); C_w is the total activity of Rn in the water column (dpm/m^3); C_{air} is the activity of radon measured in air

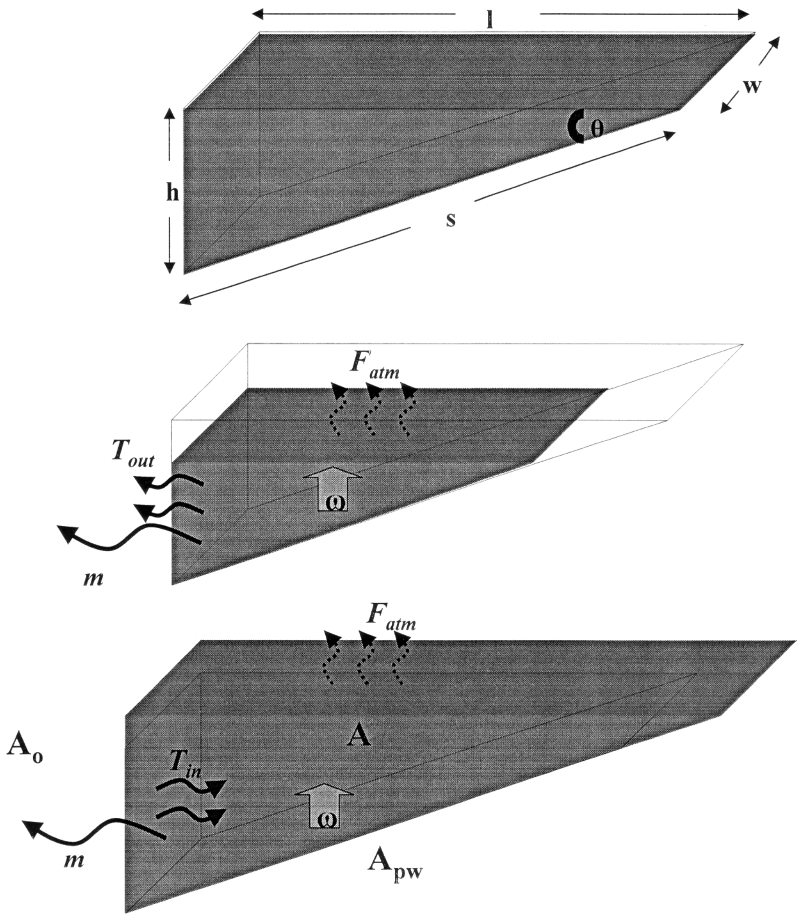

Figure 5. The box model for the FSUML study area showing input and output of Rn in the study domain. In this diagram, h is the tidal height (m); s is the sediment length; w is the study area width; θ is the angle of the seabed slope; ω is the radon flux from the sediment (dpm m^{-2} hr^{-1}); F_{atm} is atmospheric flux (dpm m^{-2} hr^{-1}); T_{in} is the flux of radon entering the system with the incoming tide (dpm m^{-2} hr^{-1}); T_{out} is the flux of radon departing the system with the outgoing tide (dpm m^{-2} hr^{-1}); A_o is the activity of radon offshore of the study area; A is the measured activity of radon inside the study area; and A_{pw} is the measured porewater activity of radon in the sediment.

(dpm/m^3); and α (dimensionless) is the solubility coefficient that describes the distribution of radon at equilibrium as the fluid-to-gas ratio ($\sim$0.2 at 20 °C). The piston velocity, k, is the measure of the velocity of gas transfer at the air-sea boundary and is a function of the physical processes at the interface boundary including turbulence and molecular diffusion. The ratio of the kinematic viscosity (ν) to the molecular diffusion coefficient (ν/D) is referred to as the Schmidt number, Sc, (Macintyre et al. 1995). Turner et al. (1996) described an empirical formula that relates the wind speed and Schmidt number to k:

$$k_{600} = 0.45\mu^{1.6}(Sc/600)^{-a} \tag{2}$$

where μ is wind velocity (m/s); Sc is the Schmidt number for radon at the desired water temperature (Sc is divided by 600 to normalized to CO_2 at 20 °C); and "a" is a variable power function dependant on wind speed where a = 0.6667 for $\mu \leq 3.6$ m/s, and a = 0.5 when $\mu > 3.6$ m/s. This equation is based on observational data that relates wind speed (m/s) to gas transfer velocity (cm/h). At wind speeds of less than 1.5 m/s the value for k becomes constant (0.91 cm/hr). The constant piston velocity calculated here for very low wind speeds is based on the measured zero velocity wind speed value of k for CH_4 (0.75 ± 0.54 cm/hr, Happell et al. 1995) which was converted to a k value for radon using the relationship:

$$k_1/k_2 = (Sc_1/Sc_2)^{-0.6667} \tag{3}$$

The amount of radon lost to the atmosphere is calculated by multiplying the derived atmospheric flux by the unit area and the integration time of the measurement (1 hour). The constant low wind speed piston velocity could also be estimated by calculating the piston velocity for a wind speed of 1.5 m/s using equation (2) and assuming this value is true for all lower wind speeds. The atmospheric flux calculated in this manner is only ~4% higher resulting in a final calculated SGD rate that is higher by the same amount.

During the period of this experiment the percentage of the total radon inventory lost to the atmosphere per hour ranged from < 2% to 14% with a mean of 2.7%. The low average is due to generally calm winds at the study site during much of the experimental period (Figure 6).

Diffusion from sediments

Diffusion of radon from bottom sediment into the overlying water column may be an important source of radon in some cases (e.g. if the sediments contain high ^{226}Ra and/or other sources, as SGD, are very low). To estimate the diffusive flux for this case, six sediment grab samples from the study domain were equilibrated in sealed Erlenmeyer flasks with 150 mL of seawater from the site for 30 days following the procedure of Corbett et al. (1998). The samples were kept agitated on a shaker table during the entire equilibration period. The ^{222}Rn in the water was then measured and the diffusive flux was estimated using an equation from Martens et al. (1980):

$$J = (\lambda D_S)^{1/2}(C_{eq} - C_o) \tag{4}$$

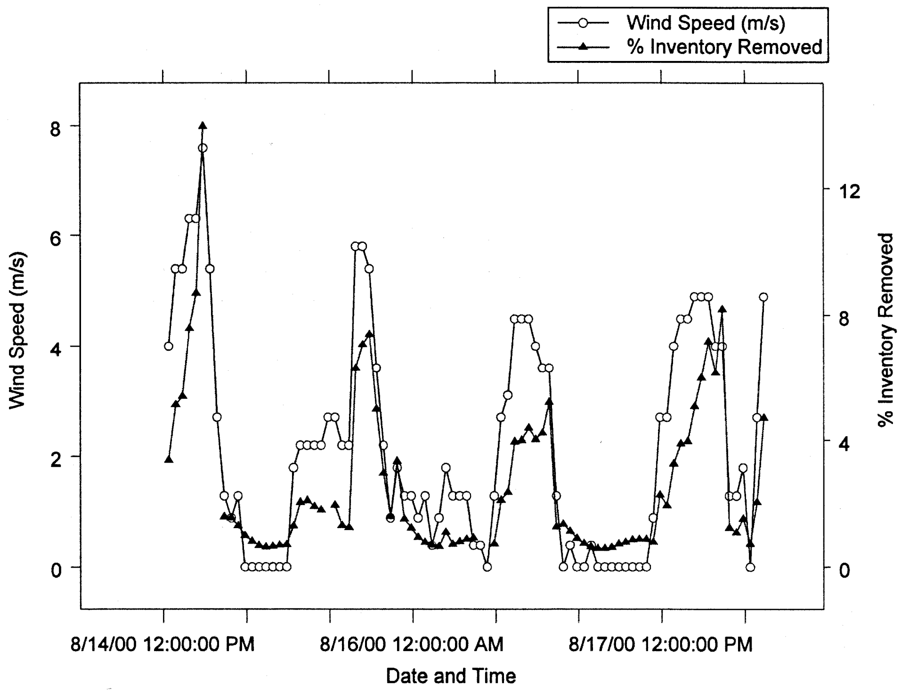

Figure 6. A plot of wind speed and the calculated percentage of the radon inventory lost per hour via atmospheric evasion.

where J is the flux of radon from the sediment (dpm/m^2 day); λ is the decay constant for radon (0.181 d^{-1}); C_{eq} is the equilibrium activity released by radium into the sediment (dpm/m^3); C_o is the radon activity in the overlying sea water at the sediment water interface multiplied by the porosity of the sediment to convert to the corresponding value in wet sediment (dpm/m^3); and D_s is the effective wet bulk sediment diffusion coefficient (m^2/d) corrected for temperature and sediment tortuosity. The expression for the temperature dependency of D_s as outlined in Peng et al. (1974) is:

$$-\log D_o = (980/T) + 1.59 \tag{5}$$

D_o (the ^{222}Rn molecular diffusivity coefficient; 1.42×10^{-5} cm^2/sec at 28.5 °C) is then corrected for sediment tortuosity by multiplying by the sediment porosity ($D_S \sim \Phi D_O$) (Ullman & Aller 1981).

The porosity (Φ) and wet bulk density (B_{D-wet}) of each sediment sample were calculated using the formulas:

$$\Phi = \frac{(W_D/\rho_w)}{(1 - W_D/\rho_{dry}) + (W_D/\rho_W)} \tag{6}$$

Table 1. Individual sample measurements for estimation of the diffusive flux at the FSUML experimental site. Terms in the table are parameters in the equations described in the text. D_S used for these calculations is 6.9×10^{-5} m^2/d. The uncertainties expressed for C_o and C_{eq} are $\pm 1\sigma$ based on counting statistics from the ^{222}Rn measurements. The error in the diffusive flux, J, was propagated from these uncertainities and is also $\pm 1\sigma$

Station	Wet Sample Weight (g)	f_{H_2O}	ρ_{dry}	Φ^a pore/sed	$B_{D-Wet}{}^b$ (g/cm^3)	C_o dpm/m^3	C_{eq} dpm/m^3	J^c dpm/m^2 d
B	138.3	0.18	2.5	0.35	1.98	2430 ± 144	49700 ± 5300	164 ± 18
AB	119.2	0.19	2.6	0.38	1.99	2620 ± 156	39000 ± 5090	126 ± 18
mid AB-C	103.9	0.18	2.7	0.38	2.08	2600 ± 155	34600 ± 5230	111 ± 18
C	106.4	0.19	2.8	0.40	2.10	2760 ± 164	46100 ± 5990	150 ± 21
D	115.6	0.28	2.7	0.51	1.84	3510 ± 209	52600 ± 5740	170 ± 20
mid C-D	99.1	0.20	2.6	0.40	1.98	2760 ± 164	88900 ± 8330	298 ± 29

$^a\Phi = \frac{(W_D/\rho_w)}{(1-W_D/\rho_{dry})+(W_D/\rho_w)}$.
$^bB_{D-wet} = [\Phi(\rho_w)] + [(1-\Phi)(\rho_{dry})]$.
$^cJ = (\lambda D_S)^{1/2}(C_{eq} - C_o)$.

and

$$B_{D-wet} = [\Phi(\rho_w)] + [(1-\Phi)(\rho_{dry})] \tag{7}$$

where W_D is the fraction of water present in the sediment; ρ_w is the density of seawater; and ρ_{dry} is the dry sediment density measured by volume displacement (Corbett et al. 1998). The wet bulk densities in the samples collected here ranged from 1.84 to 2.10 g/cm^3 with a mean of 2.00 ± 0.10 g cm^{-3} (n = 6) and estimated sediment porosities from these samples ranged from 0.35 to 0.51 with a mean of 0.42 ± 0.06. Based on these results, the total diffusive flux from the bottom sediments was estimated at 169 ± 69 dpm/m^2 day (Table 1). The ^{226}Ra content of the sediment samples was determined by gamma spectrometry to be 0.31 ± 0.07 dpm/g (n = 6).

Calculation of SGD rates

The geometry of study domain was described as a simple wedge assuming that the downward slope of the area is constant from the shoreline out to the point where the seepage rate has decreased to zero (~200 m based on seepage meter measurements; Taniguchi et al. 2003). The angle of downward slope can be easily calculated if the depth of the system and distance from the water line are measured concurrently. Once the angle of downward slope is calculated (2° in this case) we only need to know the water depth at any given time to calculate the distance both along the water and the sediment surfaces.

The radon flux (net change of total radon activity, A, over time) can be described by the following expression:

$$\frac{dA}{dt} = \frac{dA_{sed}}{dt} + \frac{dA_o}{dt} - \frac{dA_{atm}}{dt} - \frac{dA_i}{dt} - \frac{dA_m}{dt} - \lambda A \tag{8}$$

where A_{sed} is the activity of radon entering from the sediment; $A_o$is the activity of radon in offshore waters entering with the incoming tide; A_{atm} is the activity of radon leaving the system via air-sea exchange; A_i is the activity of radon in inshore waters leaving with the outgoing tide; A_m represents the activity of radon lost by mixing processes; and loss of radon by decay is represented by the decay constant (λ) multiplied by the activity (A) at time t. All ^{222}Rn activities have been corrected for the supported levels by subtracting an average ^{226}Ra activity based on several grab sample measurements. We may describe these fluxes in and out of the study domain by:

$$F_t = F_{sed} + F_o - F_{atm} - F_i - F_m - \lambda A \tag{9}$$

If this equation is simplified to describe the change in activity from one time period to another and redefined using terms that were measured or may be easily derived from measurements made during this experiment, we can calculate the flux of radon from the sediment (F_{sed}) at any time period by the following:

$$A_{pore}\nu = \frac{V\frac{\Delta A}{\Delta t} - A_o\frac{\Delta V}{\Delta t} + A\frac{\Delta V}{\Delta t}}{(lxw)} + F_{atm} + F_m \tag{10}$$

where A_{pore} is the radon concentration in the sediment pore water; v is the advection rate of the pore water into the domain; V is the total volume of water in the system; A is the excess concentration of radon that was measured at each time (t); $(lxw)_{sed}$ is the area of sediment in the system; A_o is the concentration of radon seaward of the site; F_{atm} is the flux of radon into the atmosphere; and F_m is the flux of radon out of the system by mixing. The mixing loss was not measured directly but an estimate can be made based on inspection of the change in the measured inventories (corrected for atmospheric loss and tidal fluctuations) over time or the "net fluxes" (see below). We have ignored decay because it is considered negligible because of the short duration between the time steps in our measurements, i.e. 1 hour.

The initial calculation of "net fluxes" of radon in the study domain without consideration for the mixing component shows major spikes in the data about

Table 2. Mean values and standard deviations of radon fluxes into and out of the study site in the coastal Gulf of Mexico from Aug 14–18, 2000

Radon Flux Terms	Fluxes dpm.m^2.hr
Atmospheric loss (F_{atm})	210 ± 190
Ebb tide (T_{out}, +)	490 ± 680
Flood tide (T_{in}, –)	–160 ± 200
Mixing Loss (m)	340 ± 120
Total Flux (ω)	880 ± 740

24 hours apart with secondary spikes about 12 hours later (Figure 7a). We assume that the negative flux values observed on the plot must represent losses of radon due to mixing processes that were not initially taken into account in the calculation. We estimated approximate mixing losses for the different periods indicated in the plot based on the maximum absolute values of these negative fluxes. These estimates should represent conservative (lower) estimates of the mixing losses as they are based on measurements of radon inventories present at any one time. Higher mixing losses could have occurred and were compensated for by higher input fluxes at the same time (Burnett & Dulaiova 2003). These estimated mixing losses can then be added to the measured net fluxes to derive total input fluxes to the study domain (Figure 7b). These estimates are more than an order of magnitude larger than the fluxes calculated for diffusion of radon into the system. We can thus assume that the flux of radon into this system is almost exclusively from advection and the diffusive component can be ignored. A summary of our estimated ^{222}Rn flux balance, averaged over the entire experimental period, is presented in Table 2. The large standard deviations in these estimates reflect the dynamic nature of radon exchange in this tidally dominated environment.

When the total radon flux estimates are smoothed via a best-fit polynomial and plotted together with the water level (tidal) variations, a clear pattern of increasing radon flux with falling tide emerges (Figure 7c). The largest peaks occur during each transition from the highest high tide to the lowest low tide each 24 hours. Secondary maxima occur during the transition from the lower high tide to the higher low tide. The radon flux (and thus SGD) thus seems to have a close relationship to the semidiurnal mixed tides in this area. These observations of the pattern of radon flux (that should relate directly to SGD) suggest that a tidal pumping mechanism may be an important process driving SGD in this area.

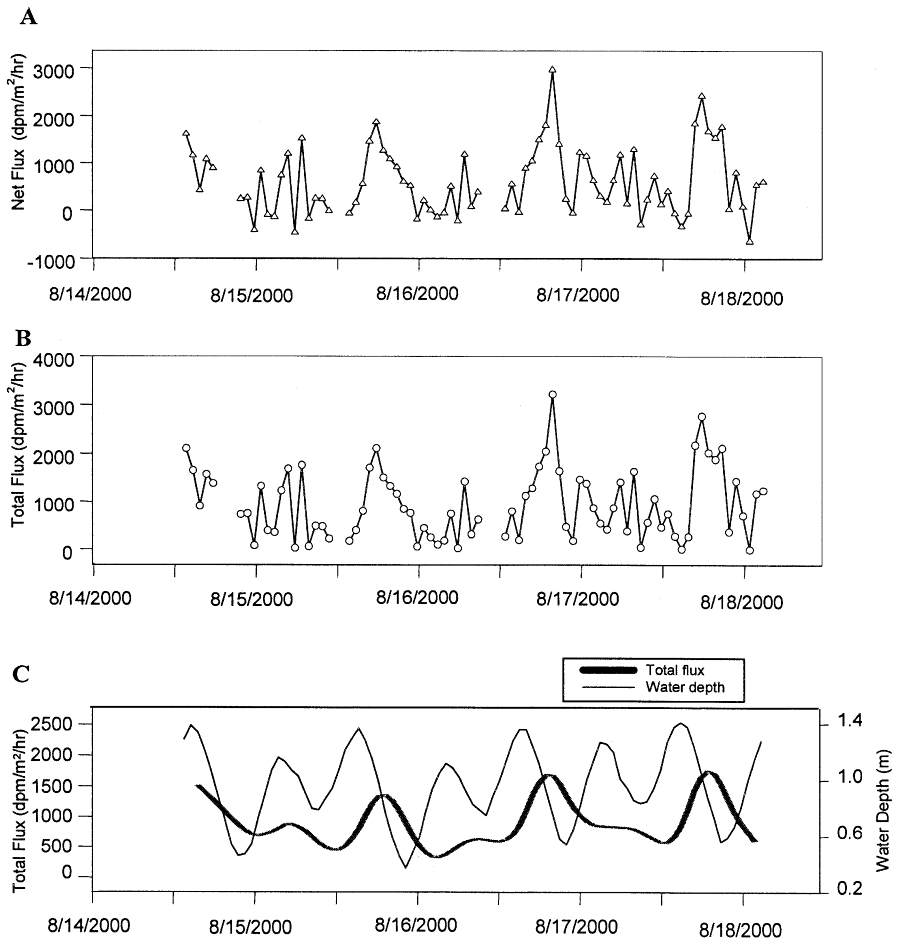

Figure 7. (A) A plot of net flux of radon from the sediment showing constant periods of negative flux assumed to be mixing of radon out of the study domain. (B) A plot of total flux derived from plot A by adding the estimated negative flux values back into the calculated flux for each constant period. (C) A smoothed line of the total flux of radon from the sediment plotted together with the water depth variations at the same station.

Advection rates (SGD) may be estimated from the radon flux data by dividing these fluxes by the radon activity in the sediment pore waters (estimated from the sediment equilibration experiments at 130 ± 50 dpm/L). The pattern of SGD rates (Figure 8) will thus be essentially the same as the radon flux pattern and shows the same relationship to the tides and agrees quite well with the pattern of SGD measured by both automatic and manual seepage meters (Taniguchi et al. 2003).

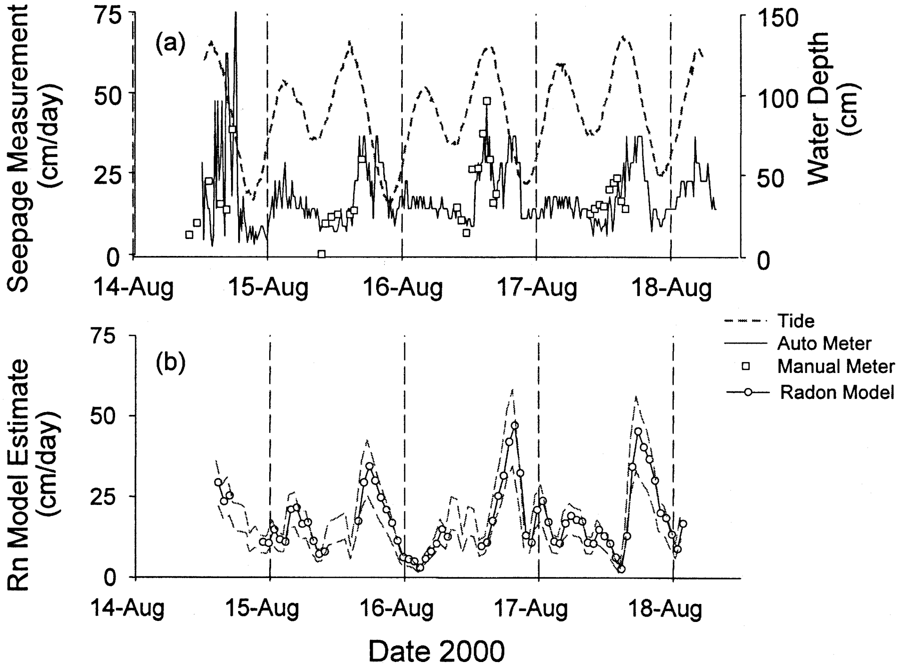

Figure 8. (A) Automated and manual seepage measurements at station Y4 (~140 m offshore; left-hand scale) and water depth (right-hand scale). (B) Seepage flux estimates based on modeling the continuous radon measurements. The gray dashed lines display 25% uncertainties of the SGD estimates.

Discharge estimates

Discharge rates into the study domain were calculated using these advection rates averaged over 24 hours. The results (Table 3) ranged from 1.7 m^3/min to 2.5 m^3/min, which compare well with discharge rates calculated from seepage meters (Taniguchi et al. 2003) and radium isotopes (Moore 2003).

The uncertainties in the estimates made by the radon model are difficult to quantify, but the calculation for mixing can be a significant source of uncertainty because it can be a significant fraction of the total flux into the system and was not measured directly. Additional uncertainty comes from the determination of tidal input of radon into the system. The tidal input calculations were based on an average of only three grab sample measurements of radon in the offshore waters. An estimate of the uncertainty in the calculated SGD rate can be made by a sensitivity test to determine the response of the model to large changes in these two parameters, i.e. mixing and tide normalization. If we systematically change the mixing and tidal input values by increasing the values by 100% (2x) or reducing the values by 50%

Table 3. A comparison of SGD discharge rates obtained using different measurement methods

	Lee-Type Meters (m^3/min)	Continuous Taniguchi Meters (m^3/min)	Short Lived Radium Isotopes (m^3/min)	Continuous Radon Model (m^3/min)
14 Aug	1.9	1.8*	1.1#	1.7
15 Aug	1.6			2.0
16 Aug	2.3			2.1
17 Aug	2.5			2.5
18 Aug				

*Based on data in Taniguchi et al. (2003).
#Moore (2003).

while keeping all other parameters constant we find that the resulting SGD rate changes by about $\pm$ 25%. In order to constrain the radon model better, future experiments should incorporate measurements to determine mixing rates as well as additional radon measurements offshore. A more recent study in the same area by Burnett & Dulaiova (2003) showed that mixing rates determined by measurements of short-lived radium isotopes (Moore 2000) combined with the offshore gradient in ^{222}Rn produced an apparent mixing loss of 390 dpm/m^2.hr while inspection of the "net" benthic ^{222}Rn fluxes as done here showed a range of 180–500 dpm/m^2.hr. The two approaches thus agree reasonably well.

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References

Buddemeier RW (Ed) (1996) Groundwater discharge in the coastal zone: Proceedings of an international symposium. LOICZ/R&S/96-8, iv+179 pp. LOICZ, Texel, The Netherlands

Burnett WC, Kim G & Lane-Smith D (2001) A continuous radon monitor for use in coastal ocean waters. Jour. Radioanal. Nucl. Chem. 249: 167–172

Burnett WC & Turner J (2001) LOICZ group investigates groundwater discharge in Australia. LOICZ Newsletter 18: 1–4

Burnett WC & Dulaiova H (2003) Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. Jour. Environ. Radioactivity: submitted

Burnett WC, Bokuniewicz H, Huettel M, Moore WS & Taniguchi M (2003) Groundwater and porewater inputs to the coastal zone. Biogeochemistry: this issue

Burnett WC, Chanton J, Christoff J, Kontar E, Krupa S, Lambert M, Moore W, O'Rourke D, Paulsen R, Smith C, Smith L & Taniguchi M (2002) Assessing methodologies for measuring groundwater discharge to the ocean. EOS 83: 117–123

Cable JE, Burnett WC, Chanton JP & Weatherly GL (1996) Estimating groundwater discharge into the northeastern Gulf of Mexico using radon-222. Earth and Planet. Sci. Lett. 144: 591–604

Clemens LA, Hatchett L & Hartnett FM (1998) Hydrogeology of the St. Marks River Basin. Wakulla Springs/Woodville Karst Plain Symposium, Florida Geological Survey Special Publication # 46: 11–20

Corbett DR, Burnett WC, Cable PH & Clark SB (1998) A multiple approach to the determination of radon fluxes from sediments. Jour. Radioanaly. Nucl. Chem. 236: 247–252

Corbett DR, Dillon K, Burnett W & Chanton J (2000) Estimating the groundwater contribution into Florida Bay via natural tracers ^{222}Rn and CH_4. Limnol. Oceanogr. 45: 1546–1557

Happell JD, Chanton JP & Showers WJ (1995) Methane transfer across the air-water interface in stagnant wooded swamps of Florida: Evaluation of mass-transfer coefficients and isotopic fractionation. Limnol. Oceanogr. 40(2): 290–298

Igarashi G, Saeki N, Takahata N, Sumikawa K, Tasaka S, Sasaki Y, Takahashi M & Sano Y (1995) Ground-water radon anomaly before the Kobe earthquake in Japan. Science 269: 60–61

Lee DR (1977) A device for measuring seepage flux in lakes and estuaries. Limnol. Oceanogr. 22: 140–147

Macintyre S, Wanninkhof R & Chanton JP (1995) Trace gas exchange across the air-water interface in freshwater and coastal marine environments. In: Matson PA & Harris RC (Eds) Biogenic Trace Gasses: Measuring Emissions from Soil and Water (pp 52–97). Blackwell Science Ltd

Martens CS, Kipphut GW & Klump JV (1980) Sediment-water chemical exchange in the coastal zone traced by in situ radon-222 flux measurements. Science 208: 285–288

Mathieu G, Biscayne P, Lupton R & Hammond D (1988) System for measurements of ^{222}Rn at low levels in natural waters. Health Physics 55: 989–992

Moore W (1996) Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. Nature 380: 612–614

Moore WS (2000) Determining coastal mixing rates using radium isotopes. Continental Shelf Res. 20: 1995–2007

Moore WS (2003) Sources and fluxes of submarine groundwater discharge delineated by radium isotopes. Biogeochemistry: this issue

Paulsen RJ, Smith CF, O'Rourke D & Wong TF (2001) Development and evaluation of an ultrasonic groundwater seepage meter. Ground Water 39(6): 904–911

Peng TH, Takahashi T & Broecker WS (1974) Surface radon measurements in the North Pacific station Papa. J. Geophy. Res. 79: 1772–1780

Rasmussen LL, Chanton JP, Furbish DJ, Meacham SP & Burnett WC (2003) Groundwater flow, tidal mixing and haline convection in coastal sediments: Field and modeling studies. Cont. Shelf Research: in press

Shinn EA, Reich CD & Hickey TD (2002) Seepage meters and Bernoulli's revenge. Estuaries 25: 126–132

Smith L & Zawazski W (2003) A Hydrogeologic model of submarine groundwater discharge: Florida intercomparison experiment. Biogeochemistry: this issue

Taniguchi M & Fukuo Y (1993) Continuous measurements of ground-water seepage using an automatic seepage meter. Ground Water 31: 675–679

Taniguchi M, Burnett WC, Christoff J, Smith CF, Paulsen RJ, O'Rourke D & Krupa S (2003) Spatial and temporal distributions of submarine groundwater discharge rates obtained from various types of seepage meters at a site in the northeastern Gulf of Mexico. Biogeochemistry: this issue

Turner SM, Malin G, Nightingale PD & Liss PS (1996) Seasonal variation of dimethyl sulphide in the North Sea and an assessment of fluxes to the atmosphere. Marine Chemistry 54: 245–262

Ullman W & Aller R (1981) Diffusion coefficients in nearshore marine sediments. Limnol. Oceanogr. 27: 552–556

Valiela I & D'Elia C (1990) Groundwater inputs to coastal waters. Special Issue Biogeochemistry 10: 328 p

Wagner JR (1989) Potentiometric surface of the Floridan aquifer system in the Northwest Florida Water Management District. Northwest Florida Water Management District Water Resources Map, Series 89-001

Young JE (1996) Tracing groundwater flow into the northeastern Gulf of Mexico using naturally-occurring radon-222. Ph.D. Dissertation, Florida State University: 286 p