An evaluation of submarine groundwater discharge along the continental shelf of Louisiana using a multiple tracer approach

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[1] Natural geochemical tracers (^{222}Rn, ^{3}H, ^{3}He, and ^{4}He) were used to assess submarine groundwater discharge (SGD) along the continental shelf west of the Mississippi River. In order to assess SGD, groundwater, surface water, and sediment samples were collected on land and during six 4-day cruises aboard the R/V *Pelican* between March 2003 and May 2004. A box model approach was used to quantify sources and sinks of ^{222}Rn in the study area and to calculate SGD rates. SGD estimates were we based on two end member values for the potential advecting fluids: (1) that supported by ^{226}Ra in the sediments; and (2) groundwater activities measured in monitoring wells. Calculated ^{222}Rn SGD rates based on sediment supported activities ranged from 0.04 to 0.14 cm d^{-1}, and estimates based on monitoring well activities ranged from 0.01 to 0.07 cm d^{-1} and corresponds to 1.41 km^3 yr^{-1} of discharged water over our study area, equivalent to <1% of the Mississippi River during the same time frame. ^{3}He and ^{4}He, longer-lived tracers, exhibited significantly greater anomalies in the eastern portion of the study area which corresponds with greater oil and gas extraction and the release of formation water into the water column in this region. While the total SGD was relatively minor, potential sources of SGD are many and we suggest formation water associated with oil and gas extraction, geothermal convection, and seawater recirculation are the primary sources with a minimal contribution from terrestrially derived topography driven flow.

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1. Introduction

[2] Major rivers play a significant role in the transport of terrestrially derived materials to the coastal ocean, with the world's ten largest rivers accounting for approximately 40% of the fresh water and particulate matter entering the ocean [*Milliman*, 1983]. Coastal seas represent only 10% of oceanic area and 0.5% of oceanic volume, but they account for 30–50% of new primary production of global oceans [*Paerl*, 1995], with deltaic and shelf sediments incorporating as much as 80% of the organic carbon sequestered in marine sediments [*Berner*, 1982]. While rivers play a significant role in contributing to the nutrient budgets of nearshore marine environments, recent research indicates that submarine groundwater discharge (SGD) into coastal oceans also plays a significant role in the transport of nutrients and geochemical constituents in large deltaic regions [*Moore et al.*, 1996; *Moore*, 1997; *Krest et al.*, 1999; *Moore and Krest*, 2004]. SGD has previously been defined as, "Any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force" [*Burnett et al.*, 2003]. Terrestrially derived, topography driven groundwater discharge to the coastal ocean can occur through three major pathways: seepage through sediments in the surficial aquifer, seepage across confining units for confined aquifers, and point sources such as ruptured confining layers of confined aquifers [*Burnett et al.*, 2001]. These three pathways along with advection, flow due to compaction of pore waters, geothermal convection, and tidal pumping are all included under the definition of SGD.

[3] The Mississippi Delta region has been intensely studied by scientists interested in the connection between major rivers and coastal oceans because of the discharge magnitude of the Mississippi River and its economic importance to the region (e.g., commerce, fisheries, gas, oil). Hypoxic conditions have been documented on the continental shelf adjacent to the Mississippi River since the early 1980s. Recent research indicates nitrogen loading, along with landscape changes in the drainage basin, including organic loading of the Mississippi River, channelization of the delta, and loss of wetlands, are the major contributors of hypoxic conditions [*Rabalais et al.*, 1999]. Although these natural and anthropogenic processes are surely contributing to eutrophic conditions, *Krest et al.* [1999] and *Moore and*

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Krest [2004] suggest that SGD may contribute significant amounts of groundwater-derived nutrients to the continental shelf of Louisiana near the mouth of the Mississippi River.

[4] *Krest et al.* [1999] used ^{226}Ra and ^{228}Ra as indicators of SGD and by process of elimination suggested that elevated activities were most likely due to advection of radium-rich SGD. *Moore and Krest* [2004] reported enriched ^{223}Ra and ^{224}Ra activities around the Atchafalaya and Mississippi Rivers and estimated a SGD rate of 2.5 cm d^{-1}, equivalent to 7% of average Mississippi River discharge, would be required to support the observed activities.

[5] With the potential for such a large influence from groundwater and its dissolved constituents, the Mississippi River Delta region provides an ideal location for study of groundwater contributions to river dominated ocean margins. The primary goal of this research was to quantify SGD onto the continental shelf of Louisiana adjacent to the Mississippi River using a multiple tracer approach. In addition to quantification, the study also assesses seasonal fluctuations in SGD input associated with low and high river flow conditions.

[6] The hydrogeology of deltaic regions can be fairly complex. However, the use of multiple tracers should alleviate many of the complexities associated with assessing groundwater in the system. Many studies have utilized natural geochemical tracers to quantify groundwater in coastal systems [*Cable et al.*, 1996a; *Moore*, 1998; *Corbett et al.*, 2000; *Top et al.*, 2001; *Charette and Buesseler*, 2004], which are found in elevated concentrations relative to surface waters [*Davis et al.*, 1980]. This study incorporates ^{222}Rn and ^{4}He/^{3}He/^{3}H as natural tracers of groundwater.

[7] ^{222}Rn ($t_{1/2}$ = 3.83 days) has been used in many studies of groundwater quantification into marine systems including: northeastern Gulf of Mexico [*Cable et al.*, 1996a, 1996b], Chesapeake Bay [*Hussain et al.*, 1999], and Florida Bay [*Corbett et al.*, 2000]. *Burnett et al.* [1996] list its usefulness as being: (1) 2–4 orders of magnitude more concentrated in groundwater than surface water, (2) conservative, (3) estimated relatively accurately from known source/decay terms, and (4) easily measured even at low concentrations. Elevated groundwater concentrations are due to production and recoil processes occurring from radium in the aquifer, allowing radon to accumulate as a dissolved gas in groundwater.

[8] Helium isotopes and tritium have recently been applied to SGD studies in coastal systems [*Top et al.*, 2001]. The main source of helium in the earth's crust is derived from the radioactive decay of the uranium and thorium-series nuclides. The relationship between large underground uranium concentrations and large positive helium anomalies in groundwater has been illustrated by several studies [*Clarke and Kugler*, 1969; *Clark et al.*, 1977; *Top and Clarke*, 1981]. These studies found a tight correlation between helium anomalies and known regional uranium mineralization in local lakes fed by groundwater. Helium is moved from its site of production by dissolution of the host mineral and by diffusion. Estimated helium accumulation rates in groundwater are based largely on diffusive processes that allow for the determination of groundwater age in shallow, confined aquifers [*Top et al.*, 2001]. In environments that have been isolated from the atmosphere on geologic timescales, ^{4}He is predominantly produced from the α-decay of natural U-Th series nuclides. In contrast, helium in shallow shelf environments is typically in equilibrium with the atmosphere, which acts as a source for most dissolved helium. The slight solubility of helium and the ability to precisely measure concentrations (±0.5%) allow for anomalies of water out of solubility equilibrium with the atmosphere as small as 1% to be detected, which corresponds roughly with the groundwater-seawater mixing ratio of 1:100 with groundwater at 50–100% enriched in helium.

[9] The less abundant isotope, ^{3}He (^{3}He/^{4}He = 1.384 $\times$ 10^{-6}), is produced from the β-decay of tritium, referred to as tritiogenic ^{3}H, and from the ^{6}Li(n, α)^{3}H reaction, which yields nucleogenic ^{3}He [*Castro*, 2004]. An excess air component, a product of small air bubble dissolution as a result of water table fluctuations, and contribution from the mantle also contribute ^{3}He and ^{4}He to the earth's helium budget. Tritium was emitted to the atmosphere primarily by nuclear tests in the late 1950s and early 1960s and nucleogenic ^{3}He accumulates in groundwater from in situ crustal decay and external crust and mantle sources. Refinements of helium and tritium measurements have justified the use of these tracers in several groundwater studies [*Poreda et al.*, 1988; *Solomon et al.*, 1996; *Schlosser et al.*, 1998].

2. Setting and Methods

2.1. Coastal Lowland Aquifer System

[10] The hydrogeology of the area has been highly influenced by the Mississippi River over geologic time. Progradation followed by transgression and reworking of sediments has led to a complex and highly variable subsurface matrix and aquifer framework. The aquifer system of study is the Coastal Lowland Aquifer system (CLAS) (Figure 1). The CLAS is composed of 5 permeable zones (A–E) that merge with the Mississippi River Valley alluvial aquifer to the north and thickens southward to a maximum thickness of 3650 m at the edge of the continental shelf. In the study region, the CLAS extends from land surface to a depth of 3050–3650 m. Permeable zone A, the upper most portion of the aquifer and the zone of interest for this study, extends from the surface to 305–365 m below sea level. Permeable zone A spans an area of 193,110 km^2 and is composed of 65% sand on average with a maximum of 80% sand [*Grubb*, 1998].

[11] Groundwater in Permeable zone A is often found under confined conditions even though there is no regional confining unit due to numerous discontinuous beds of sand, silt, and clay [*Pettijohn et al.*, 1992]. Since the early 1900s, large amounts of water have been withdrawn from the aquifer, altering groundwater flow by producing large water-level declines and cones of depression. Large groundwater withdrawals from the New Orleans/Baton Rouge area and southwest Louisiana have influenced the direction of groundwater flow in the region [*Renken*, 1998]. Under predevelopment conditions in the study region, models indicate groundwater flows to toward the coast, while models based on postdevelopment conditions indicate groundwater flows to the north, away from the coast [*Martin and Whiteman*, 1999].

2.2. Surface Water Hydrology

[12] The Mississippi River, with a drainage basin of 3.2 million km^2, drains approximately 40% of the contig-

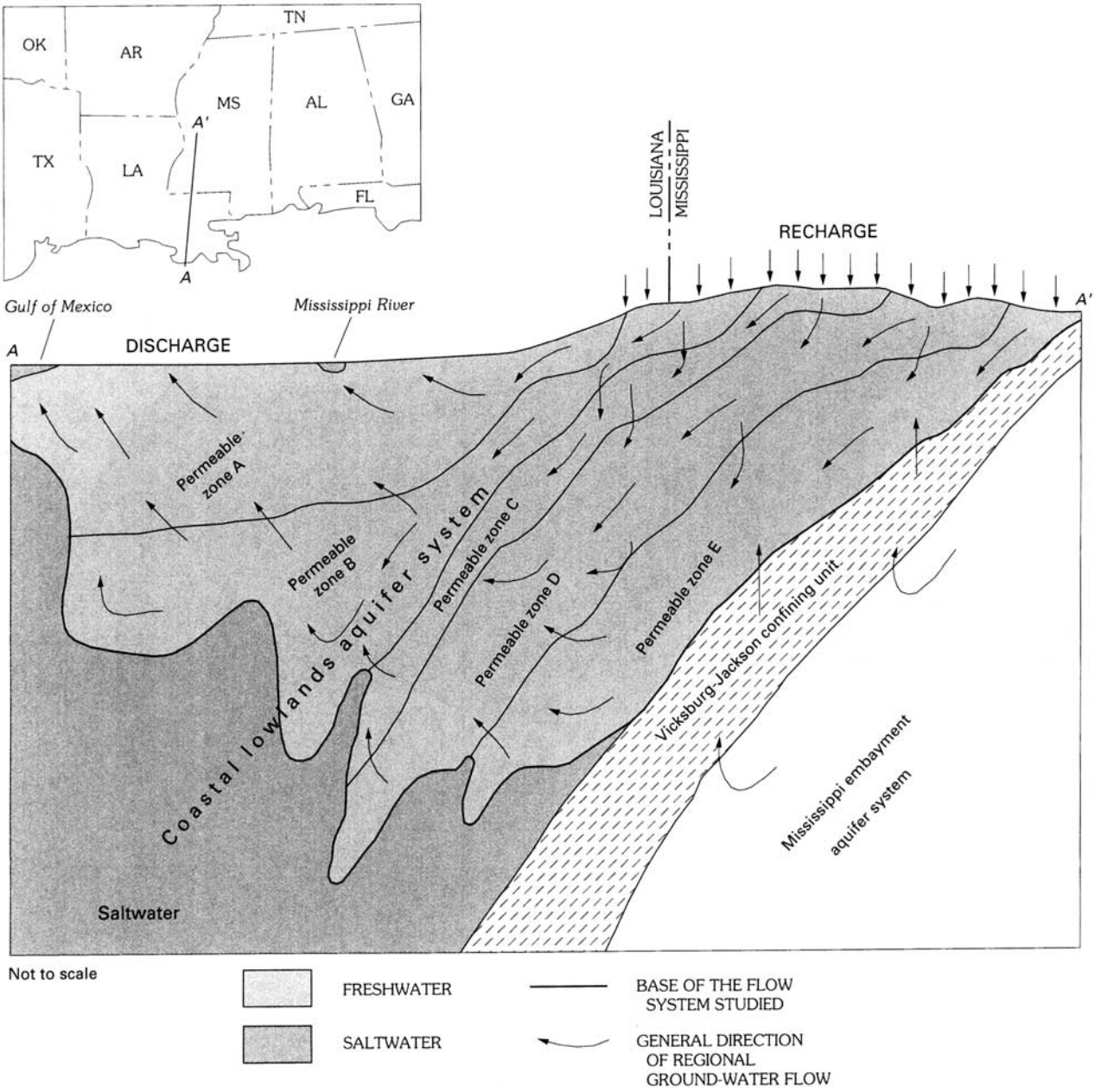

Figure 1. Cross-section map of the Coastal Lowlands Aquifer System indicating hydrostratigraphic units and the direction of groundwater flow under prepumping conditions [*Martin and Whiteman*, 1999].

uous United States and discharges fresh water and associated sediment loads into the Gulf of Mexico. The U.S. Army Corps of Engineers diverts an average of 30% of the combined flow of the Mississippi and Atchafalaya Rivers down the Atchafalaya River while the remaining water is discharged into the Gulf of Mexico at the bird's foot delta with approximately 50% being discharged to the west [*United States Army Corps of Engineers* (*USACE*), 1974]. Southwest Pass (SWP) discharges water, suspended sediment, and bed load from the Mississippi River onto the continental shelf into water roughly 50 m in depth (Figure 2). Seawater on the continental shelf west of the river is influenced by discharge from the Mississippi River, prevailing currents, and exchange with Barataria Bay.

2.3. Water Column Samples

[13] Water column samples were collected aboard the R/V *Pelican* during six cruises on the continental shelf adjacent to the Mississippi River. The dates of the cruises were October 19–22, November 20–23, December 12–15, 2003, March 6–9, April 20–23, and May 20–23, 2004. Water column and sediment samples were collected at approximately 15 stations per cruise (Figure 2), using the ship's CTD rosette and ponar, respectively. Water column samples were collected at each station for ^{222}Rn and ^{226}Ra analysis and at selected stations for helium and tritium analysis using a CTD equipped with 12–20 l Niskin-bottles. ^{222}Rn and ^{226}Ra samples were collected in 6 l bottles and immediately sealed to prevent gas loss. Samples for helium

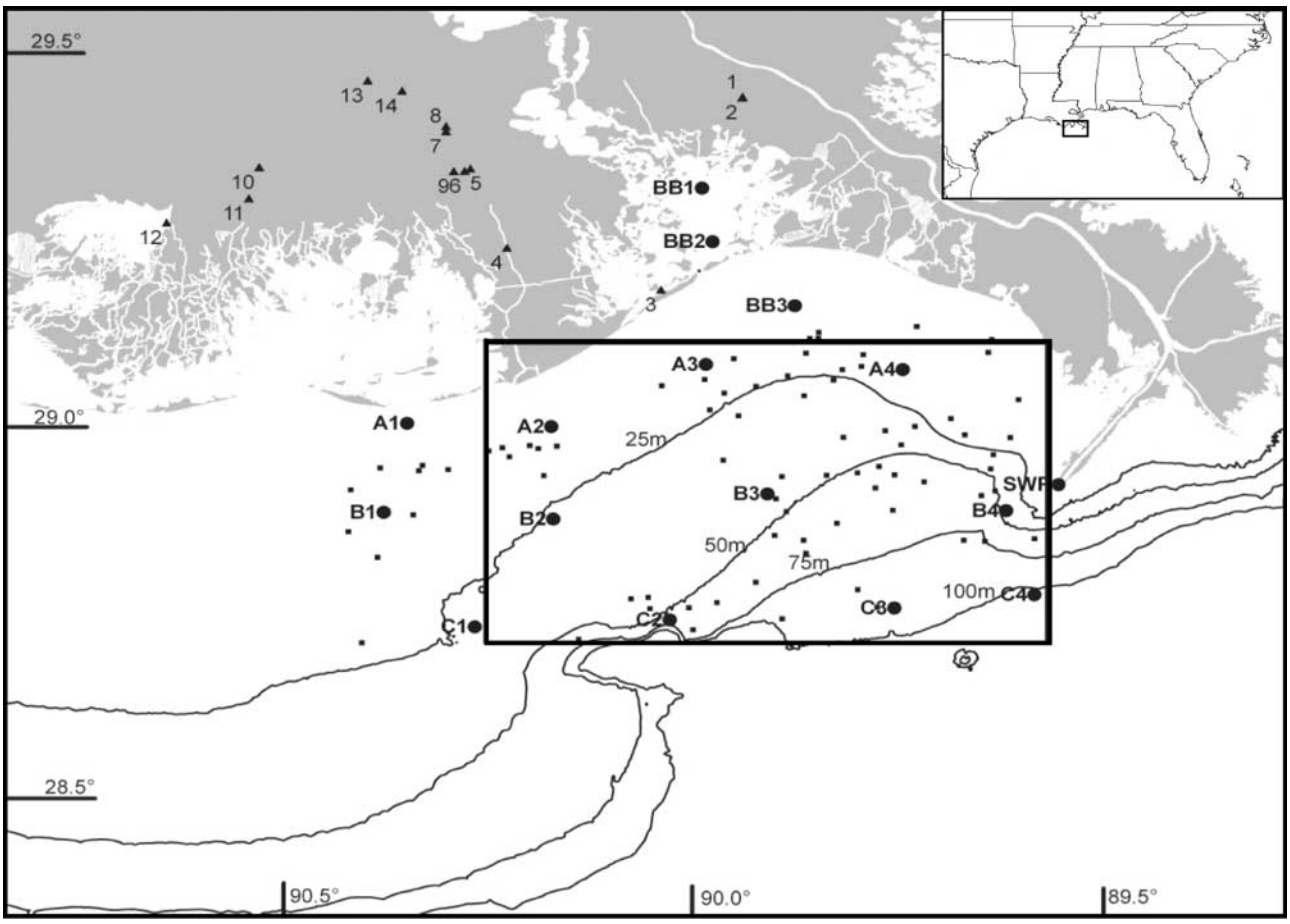

Figure 2. Site map of study area. Monitoring well locations and water column stations are indicated. The shelf area used in the radon box model is enclosed in a box. Squares indicate locations of active oil and gas leases. SWP, Southwest Pass; BB (1,2), Barataria Bay. Contour intervals in meters.

analysis were collected in 35 cm length refrigeration grade copper tubes that were sealed with clamps on both ends to prevent atmospheric exchange and an additional sample was collected in 1 l Nalgene bottles for tritium analysis.

2.4. Monitoring Well Samples

[14] Water samples were collected from 14 wells sampled six times between March 2003 and May 2004 (Figure 2). Monitoring wells were either fit with submersible pumps with screened intervals between 91 and 131m below land surface (MW-01, 02, 03, 04, 10, 11, 12) or were artesian wells screened between 55 and 73 m below land surface (MW-05, 06, 07, 08, 09, 13, 14). Each water sample was measured for conductivity and temperature (YSI 30), dissolved oxygen (YSI 55), and pH (Orion 290A). All measurements were recorded in an overflow container after values had stabilized. Water samples were collected from the overflow container using a peristaltic pump. Samples for radon analysis were collected in triplicate with a 10 ml glass syringe and transferred into a 20 ml scintillation vial that was prefilled with 10 ml of high efficiency mineral oil scintillator. The water sample was slowly injected below the mineral oil and immediately sealed to prevent gas loss. Helium, tritium, and ^{226}Ra samples were collected at selected sites throughout the sampling periods. Helium, tritium, and ^{226}Ra samples were collected as described in the above section.

2.5. Analytical Methods

[15] Water column radon samples were analyzed for total radon using an onboard radon laboratory. Radon samples were sparged with helium, transferred to an alpha scintillation cell, and counted by an emanation technique similar to *Mathieu et al.* [1988]. After allowing for ^{222}Rn ingrowth from ^{226}Ra (>5 days), samples were analyzed a second time for supported ^{222}Rn, and excess ^{222}Rn (excess ^{222}Rn = total ^{222}Rn – supported ^{222}Rn) was decay corrected to the time of sampling to obtain an in situ activity. Radon samples collected from monitoring wells were analyzed by liquid scintillation (Packard 1900 TR Liquid Scintillation Analyzer).

[16] Helium and tritium samples were shipped to the University of Miami Noble Gas Laboratory for analysis. Briefly, dissolved gases were extracted from the water samples and collected on charcoal with glass ampoules and ^{3}He was separated on two cryogenic charcoal traps. Before ^{3}He was measured, roughly 20% of the gas was analyzed for neon to correct for any atmospheric influences (in situ bubble dissolution or introduction during sampling) that could alter observed helium concentrations

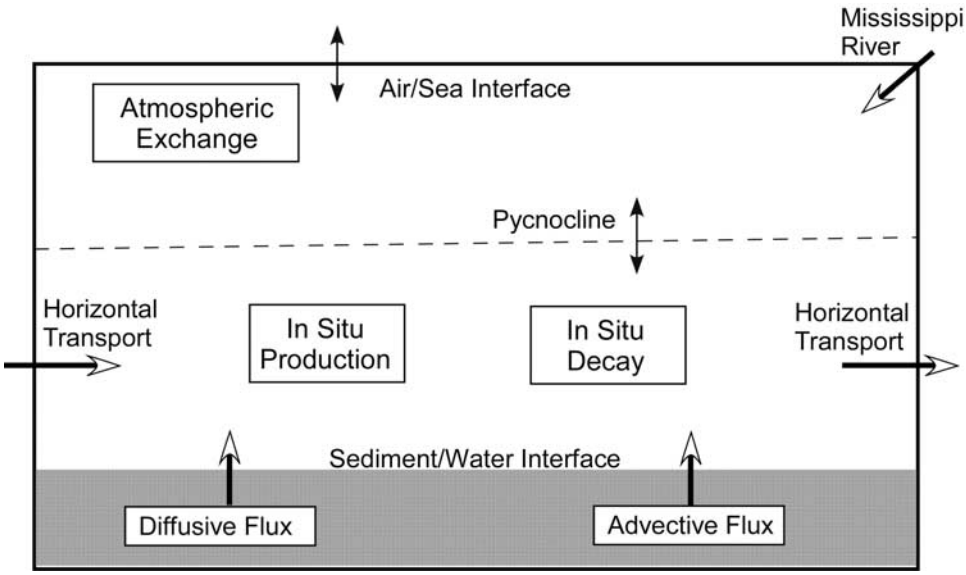

Figure 3. A box model representing the sources and sinks of radon on the continental shelf adjacent to the Mississippi River.

[*Clarke and Kugler*, 1969]. Tritium samples were transferred to 1 l Corning 1724 alumina-silicate glass flasks that were degassed, sealed, and stored at −20°C for 4–6 months. Tritium was then back calculated from accumulated ^{3}He. Determination of ^{4}He concentrations was accomplished by comparing measured sample peak heights against a standard. For a more detailed description of these methods, see *Top et al.* [2001].

[17] In order to evaluate the flux of radon via diffusion, a sediment equilibration technique developed by *Martens et al.* [1980] was utilized. Sediment equilibrated ^{222}Rn activities were calculated by analysis of sediment grab samples collected at each station. Approximately 200 g of wet sample was transferred into 4 l bottles prefilled with 2.5 l of radium-free water and sealed. Samples were allowed to sit for 30 days so ^{222}Rn in pore waters would reach equilibrium with the ^{226}Ra in sediments. Samples were then analyzed by emanation, which is described above. The sediment equilibrated ^{222}Rn values (C_{eq}), after accounting for porosity and bulk density, were then used to determine the flux of radon via diffusion. Sediment grab samples were weighed, dried and reweighed for porosity calculation.

2.6. Mass Balance

[18] A mass balance approach was used to quantify sources and sinks of radon in the study area (Figure 3). In general, the water column ^{222}Rn inventory is a balance between: (1) benthic advective-diffusive exchange (molecular diffusion, sediment irrigation and resuspension, and fluid flow through the sediment); (2) in situ production and loss; (3) horizontal water column advection; and (4) vertical exchange. A mass balance equation for ^{222}Rn modified from *Cable et al.* [1996a] in the water column, assuming steady state, is:

$$J_{ben} - J_{vert} + V_s C_i A_o - V_s C_f A_n + (\lambda_{Rn} C_{Ra}) V_n - (\lambda_{Rn} C_{Rn}) V_n = 0 \quad (1)$$

where J_{ben} is the total benthic flux (including advection and diffusion); J_{vert} is the flux of radon across a pycnocline or the air-sea interface; V_s is the low frequency (nontidal) current flow moving through the study area; C_i represents the initial radon activity entering the box; A_o is the area of the initial side of the box; C_f is the final radon activity horizontally exiting the box; A_n is the area of the exit side of the box, λ_{Rn} is the decay constant of ^{222}Rn; $\lambda_{Rn}C_{Ra}$ and $\lambda_{Rn}C_{Rn}$ account for production and decay of radon in the water column, respectively; and V_n is the volume of water in the box.

[19] The study area includes the entire ocean area between 28.65° N to 29.15° N and −89.45° W to −90.25° W and covers roughly 4940 km^2 (Figure 2). Twelve stations were located on the continental shelf in depths ranging from 10 m to 106 m with most stations located in <50 m of water and a final station was sampled at Head of Passes (HOP) or Southwest Pass in the Mississippi River during each cruise. Stations A2–A4, B2–B4, and C2–C4 are located inside the box and were used to calculate water column inventories, benthic flux and atmospheric exchange. Stations A1, B1, C1, C3, and C4 were used to calculate radon fluxes entering and exiting the box model depending on prevailing currents.

2.6.1. Horizontal Exchange

[20] The ^{222}Rn flux entering and exiting the box was calculated based on ^{222}Rn activities of entering and exiting seawater, the current direction and velocity, and the subpycnocline water column area at the entrance and exit zones on the perimeter of the box. ADCP data was collected from buoy CSI-6, located just west of site B1 (−90.48°, 28.87°) in 20 m of water, to determine average current direction and velocity (http://www.wavcis.lsu.edu). As a simplification and to conserve mass, the volume of water exiting the study area was assumed equal to the volume of water entering the study area and on the opposite side.

2.6.2. Vertical Exchange

[21] Vertical exchange of ^{222}Rn can occur across a pycnocline or across the air-sea boundary when a pycno-

cline is not present. Eddy diffusive flux of radon across the pycnocline (J_{pyc}) can be calculated using:

$$J_{pyc} = K_v\left({}^{dC}/_{dz}\right) \quad (2)$$

where K_v is the vertical eddy diffusivity, and $({}^{dC}/_{dz})$ is the ^{222}Rn gradient vertically across the pycnocline. *Sarmiento et al.* [1976] determined the K_v as a function of the oceanic buoyancy flux divided by the local buoyancy gradient $[(g/\rho)(\partial\rho_{pot}/\partial z)]$. Using the oceanic buoyancy flux calculated by *Sarmiento et al.* [1976] of -4×10^{-6} cm^2 s^{-3} from 14 deep sea ^{222}Rn and ^{228}Ra profiles, we calculated an average K_v over all cruises of 4.02×10^{-3} cm^2 s^{-1}.

[22] Exchange of radon at the air-sea interface is calculated using the following equation [*MacIntyre et al.*, 1995]:

$$J_{atm} = k(C_w - \alpha C_{air}) \quad (3)$$

where J_{atm} is the flux of radon with the atmosphere (dpm m^{-2} min^{-1}); C_{air} and C_w are the ^{222}Rn activities in air and surface waters (dpm m^{-3}), respectively; α is the Ostwald's solubility coefficient describing the distribution of radon between the air and water phases; and k is the piston velocity or gas transfer velocity (m s^{-1}) which is a function of kinematic viscosity, molecular diffusion, and turbulence [*Wanninkhoff*, 1992; *Jahne et al.*, 1987; *MacIntyre et al.*, 1995; *Bugna et al.*, 1996; *Corbett et al.*, 1997]. The gas transfer coefficient is the velocity of gas transfer at the air-sea boundary, a function of physical processes, kinematic viscosity of the water (v), and the molecular diffusion coefficient of the gas ($D_m = 1.16 \times 10^{-5}$ cm^2 s^{-1} at 20°C for ^{222}Rn). An equation representing the piston velocity (k) at a given wind speed normalized to the Schmidt number (Sc) was presented by *MacIntyre et al.* [1995]:

$$k(600) = 0.45{u_{10}}^{1.6}(Sc/600)^{-0.5} \quad (4)$$

where u_{10} is the wind speed at 10 m above the water surface and Sc for the dissolved gas is divided by 600 to normalize k to CO_2 at 20°C in freshwater. The Schmidt number, Sc, is the ratio of the kinematic viscosity to the molecular diffusion coefficient (v/D_m). *Turner et al.* [1996] determined the (Sc/600) term should be raised to the power of -0.667 for $u_{10} \leq 3.6$ m s^{-1} and -0.5 for $u_{10} \geq 3.6$ m s^{-1}.

[23] *Gesell* [1983] states that atmospheric radon concentrations typically range from 220 to 890 dpm m^{-3} and an average concentration of 560 dpm m^{-3} was used for calculations. Wind data was collected from Station BURL 1 - Southwest Pass, LA (National Oceanic and Atmospheric Administration National Data Buoy Center) and surface water temperature data was collected at each site via CTD.

2.6.3. Benthic Flux

[24] Advection and diffusion are the two components of the benthic flux evaluated in this study. Diffusion across the sediment-water interface is a function of the associated concentration gradients and mechanisms of exchange and can be enhanced by advection. The diffusive flux of ^{222}Rn can be estimated using a sediment equilibration technique described by *Martens et al.* [1980]:

$$J_{diff} = (\lambda D_s)^{1/2}(C_{eq} - C_o) \quad (5)$$

where J_{diff} is the flux of radon from sediments (dpm m^{-2} d^{-1}); λ is the decay constant for radon (0.181 d^{-1}); D_s is the effective wet bulk sediment diffusion coefficient; C_{eq} is the radon released by sediment bound radium determined from sediment equilibration experiments (dpm m^{-3}), and C_o is the radon activity at the sediment-water interface multiplied by sediment porosity to obtain the radon activity in wet sediments (dpm m^{-3}).

[25] After solving for the total benthic flux (J_{ben}) in equation (1), the advective component can be calculated using a one-dimensional advection-diffusion model adapted from *Craig* [1969]:

$$dC/dt = K_z(\partial^2 C/\partial z^2) + \omega(\partial C/\partial z) + P + \lambda C \quad (6)$$

where C is the radon activity in the sediments; z is positive depth downward; K_z 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; P is a zero order production term, which is the ^{222}Rn present in porefluids as a result of recoil from decaying ^{226}Ra in sediments ($P = \lambda C_{eq}$); and λC is radioactive decay. K_z is replaced by D_s, the effective wet sediment diffusion coefficient, after accounting for temperature ($-\log D_o = (980/T) + 1.59$) [*Peng et al.*, 1974] and sediment tortuosity ($Ds \approx \phi D_o$) [*Ullman and Aller*, 1981]. Advection and radioactive decay, ω and λ, respectively, are loss terms in the model and are defined as negative. The ^{222}Rn activities in the groundwaters and/or pore waters in combination with bottom water ^{222}Rn activities and an estimate of J_{ben} allows for the calculation of the advective fluid flux across the sediment-water interface.

3. Results and Discussion

3.1. ^{222}Rn-Monitoring Wells

[26] A summary of the activities of ^{222}Rn in monitoring wells is presented in Table 1. The average ^{222}Rn activity of all wells was 618 ± 32 dpm l^{-1} with no significant seasonal variability between ^{222}Rn sampling events. Activities varied as a function of well depth and geographic distribution. Average activities of shallow monitoring wells (55–73 m) was 627 ± 39 dpm l^{-1} and average activities of deeper monitoring wells (91–131 m) was 445 ± 32 dpm l^{-1}. Some degassing was observed during sampling at all deeper pumping wells and also at all artesian wells to a lesser extent, which indicates observed activities are minimum values.

[27] Spatially, ^{222}Rn activities can be characterized by three regions. Wells located in the central sampling area (MW5-MW9) had the greatest ^{222}Rn activities, with an over all average of 703 ± 29 dpm l^{-1}, wells to the west and north (MW10-MW14) had an average activity of 450 ± 20 dpm l^{-1}, and wells located near the Mississippi River (MW1-MW2) had the lowest average activity at 390 ± 31 dpm l^{-1}. Geographic variability is expected considering the extreme heterogeneity of the subsurface. Layers of sand, silt, clay, and gravel are rarely traceable for more than a few kilometers and changes occur laterally and vertically over very short distances [*Martin and Whiteman*, 1999].

3.2. ^{222}Rn-Box Model Parameters

[28] Radon samples were collected to determine a water column radon profile at each station. Bottom water and

Table 1. Summary of ^{222}Rn Activities at Monitoring Well Sites From March 2003 to May 2004[a]

Monitoring Well Sites	March 2003	July 2003	October 2003	December 2003	March 2004	May 2004
MW01	339 ± 18	317 ± 19	512 ± 18	574 ± 40	273 ± 17	349 ± 30
MW02	303 ± 9	364 ± 37	400 ± 48	586 ± 46	335 ± 12	333 ± 18
MW03	493 ± 12					
MW04	608 ± 53		578 ± 27			
MW05	790 ± 16	692 ± 15	813 ± 101	926 ± 39	664 ± 7	344 ± 24
MW06	559 ± 35	573 ± 39	614 ± 40	793 ± 108	539 ± 9	805 ± 49
MW07	585 ± 16	588 ± 27	660 ± 25	826 ± 62	563 ± 9	873 ± 57
MW08	586 ± 41	587 ± 25	743 ± 29	917 ± 47	554 ± 19	938 ± 70
MW09	658 ± 51	570 ± 30	857 ± 16	908 ± 86	540 ± 12	1011 ± 89
MW10	389 ± 26	375 ± 16	401 ± 22	432 ± 29	432 ± 17	610 ± 44
MW11	386 ± 21	354 ± 18	348 ± 26	423 ± 20	381 ± 18	461 ± 21
MW12	394 ± 34	461 ± 16	435 ± 28	862 ± 94	403 ± 13	
MW13	428 ± 21	453 ± 28	510 ± 31	522 ± 43	343 ± 31	699 ± 116
MW14	379 ± 11	377 ± 31	545 ± 32	403 ± 59	418 ± 9	455 ± 54
Average	492 ± 38	475 ± 35	570 ± 45	681 ± 61	453 ± 34	625 ± 73

[a]Units are in dpm l^{-1}. Values are average plus or minus standard error.

surface water samples were collected at each station and samples collected throughout the remainder of the water column were determined after analysis of CTD profiles. A summary of the total water column excess ^{222}Rn inventories and diffusion at each station is provided in Table 2.

[29] Sediment grab samples were collected at each station during each cruise to determine the potential diffusive flux of ^{222}Rn from sediments via sediment equilibration experiments. The diffusive flux of radon from sediments is summarized in Table 2. Average activities over all stations between fall and spring cruises were not significantly different with average fall and spring values of 347.6 ± 18.3 and 359.0 ± 20.2 dpm l^{-1}, respectively. Sediment equilibration analysis indicate stations A2, B1, B2, C1, and

Table 2. Summary of Total Excess ^{222}Rn Water Column Inventories and Diffusion From Sediments at Stations[a]

Station	Cruises	Inventory, dpm m^{-2}	Diffusion, dpm m^{-2} min^{-1}
A1	all	4020 ± 1340	0.72 ± 0.29
	fall	3330 ± 730	0.76 ± 0.04
	spring	4720 ± 2830	0.68 ± 0.07
A2	all	5720 ± 950	1.17 ± 0.48
	fall	4210 ± 1680	1.21 ± 0.06
	spring	5990 ± 1280	1.13 ± 0.18
A3	all	5100 ± 1020	0.67 ± 0.27
	fall	4210 ± 1680	0.68 ± 0.06
	spring	5990 ± 1280	0.65 ± 0.02
A4	all	6040 ± 1940	0.53 ± 0.22
	fall	5640 ± 4250	0.49 ± 0.06
	spring	6450 ± 770	0.58 ± 0.07
B1	all	9550 ± 3440	0.96 ± 0.39
	fall	3270 ± 420	0.84 ± 0.04
	spring	15820 ± 4430	1.07 ± 0.11
B2	all	11520 ± 2070	0.99 ± 0.40
	fall	8280 ± 3300	1.06 ± 0.05
	spring	14760 ± 2220	0.93 ± 0.20
B3	all	8170 ± 1050	0.55 ± 0.01
	fall	6770 ± 1040	0.55 ± 0.01
	spring	9560 ± 1590	0.55 ± 0.01
B4	all	7630 ± 3500	0.72 ± 0.29
	fall	19920 ± 4880	0.72 ± 0.04
	spring	28160 ± 4370	0.72 ± 0.08
C1	all	24040 ± 3460	1.19 ± 0.49
	fall	19920 ± 4880	1.01 ± 0.17
	spring	28160 ± 4370	1.38 ± 0.12
C2	all	12780 ± 4170	1.14 ± 0.47
	fall	10110 ± 3880	1.26 ± 0.15
	spring	15450 ± 8050	1.03 ± 0.12
C3	all	8730 ± 2460	0.72 ± 0.29
	fall	10840 ± 2510	0.68 ± 0.04
	spring	6630 ± 4420	0.76 ± 0.06
C4	all	12510 ± 3910	0.79 ± 0.32
	fall	12100 ± 5100	0.76 ± 0.03
	spring	12930 ± 7098	0.83 ± 0.05
All stations (average)	all	9650 ± 1550	0.85 ± 0.07
	fall	7770 ± 1430	0.83 ± 0.07
	spring	11530 ± 1930	0.86 ± 0.07

[a]Values for all cruises include averages over all six cruises, and fall and spring cruises include values averaged over the appropriate three cruises.

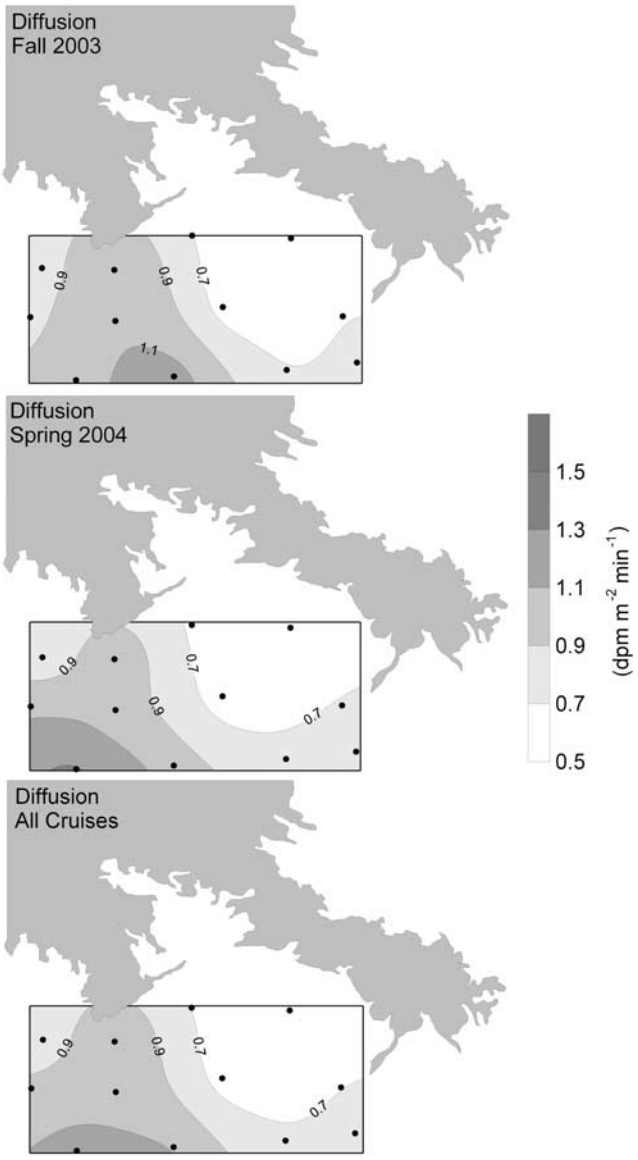

Figure 4. Regional diffusive flux of ^{222}Rn (dpm m^{-2} min^{-1}) from the seabed. Circles indicate locations of sampling stations.

C2 released $\geq$0.9 dpm m^{-2} min^{-1} of radon by diffusion while all other stations released $\leq$0.8 dpm m^{-2} min^{-1} (Figure 4). Diffusion is primarily driven by higher ^{222}Rn activities in the pore waters of surficial sediments and stations A2, B1, B2, C1, and C2 consistently yielded activities greater than 400 dpm l^{-1} while the remaining sites yielded activities around 300 dpm l^{-1} or less, after accounting for porosity, and there was no temporal variability.

[30] Total water column inventories of excess ^{222}Rn exhibit pronounced spatial variability with the greatest inventories located in the western portion of the study area and decreasing from west to east across all transects (Figure 5). Greater inventories in the western portion are potentially supported by greater diffusion rates across the sediment-water interface over the same area. Temporal variability was evident at stations B1, B2, B4, and C1 while all other stations yielded fall and spring values within error of each other (Figure 6). Station B4 was located near SWP and variability at the station was influenced by discharge from the Mississippi River via downward vertical exchange. Average activities of samples collected in the Mississippi River were 1.39 ± 0.34 and 2.30 ± 0.34 dpm l^{-1} for fall and spring cruises, respectively, and elevated activities of river water (spring vs. fall) combined with increased discharge account for elevated water column inventories during spring cruises at B4. Samples collected from the Atchafalaya River during December and May also exhibit greater activities in the spring (4.33 ± 0.17 dpm l^{-1}) versus fall (3.18 ± 0.29 dpm l^{-1}). Increased activities in the Atchafalaya River are likely a function of a shallower river channel and discharge onto a shallow, broad shelf while the Mississippi River is more channelized and discharges into water roughly 50 m in depth.

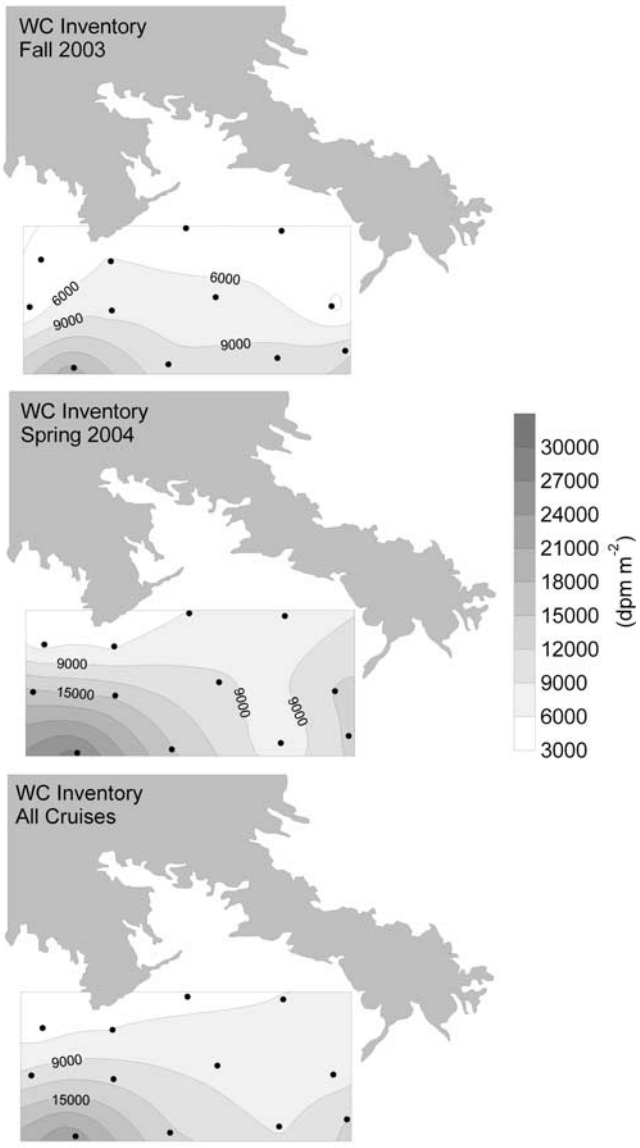

Figure 5. Water column inventories of excess ^{222}Rn (dpm m^{-2}). Circles indicate locations of sampling stations.

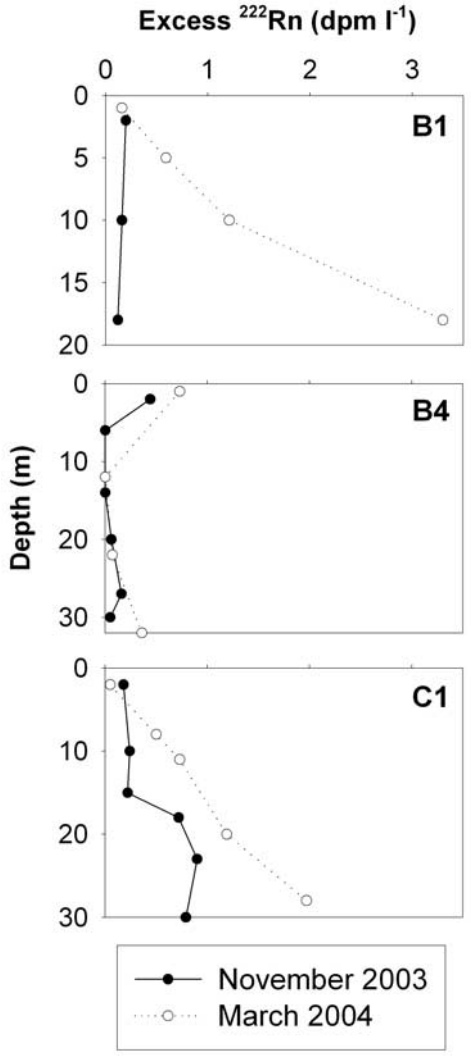

Figure 6. Excess ^{222}Rn water column profiles at stations B1, B4, and C1 during the November 2003 and April 2004 cruises. A pycnocline was present at the time of sampling for all stations except at B1 during the November 2003 cruise.

[31] Greater total water column inventories at stations B1 and C1 are primarily a function of elevated bottom water activities in the spring relative to fall (Figure 6). Average bottom water activities at B1 were 0.28 ± 0.11 dpm l^{-1} and 2.77 ± 0.56 dpm l^{-1} for fall and spring cruises, respectively, and 1.34 ± 0.49 dpm l^{-1} and 3.12 ± 0.95 dpm l^{-1}, respectively, at C1. The higher activities in the spring may be related to an increased tendency of sediment resuspension due to the highest average wave orbital velocities during two of the sampling periods (March, May) relative to the remainder of the time [*Corbett et al.*, 2007].

[32] A pycnocline was present throughout the April and May cruises at all stations. However, a pycnocline was not present at 10 stations over the October–March cruises, typically corresponding with the shallowest stations. Average exchange of ^{222}Rn across the pycnocline was 0.02 ± 0.01 dpm m^{-2} min^{-1} over all cruises and 0.03 ± 0.02 dpm m^{-2} min^{-1} and 0.01 ± 0.01 dpm m^{-2} min^{-1} for fall and spring cruises, respectively. The negative $J_{pyc/atm}$ values associated with the December and March cruises are driven by higher ^{222}Rn activities above the pycnocline associated with fresh water discharge from the Mississippi River. Representative profiles illustrating the influence of the Mississippi River on water column profiles near SWP is shown in Figure 6 (B4).

[33] Horizontal sources of radon into the study area are limited to water advected into the area due to prevailing currents. Discharge from Southwest Pass, which delivers approximately half of all water discharged from the Mississippi River to the west was not a horizontal source of ^{222}Rn because the presence of a pycnocline eliminated exchange with the subpycnocline water column. Currents were generally from the west during the October and November cruises with velocities of 0.08 and 0.06 m s^{-1}, respectively. Prevailing current was from the east during all other cruises with velocities ranging from 0.01 to 0.03 m s^{-1}.

[34] Prevailing currents introduced a larger flux of ^{222}Rn to the study area than it released during the October and November cruises, but served as a net loss of ^{222}Rn over all other cruises (Table 3). Higher input fluxes in October and November correspond with easterly currents introducing radon rich water from the western portion of the study area while generally lower input fluxes during other cruises corresponded with lower fluxes of ^{222}Rn being introduced to the study area by westerly currents.

[35] Table 3 summarizes the box model input parameters and the required total benthic flux (diffusion + advection) to support the excess ^{222}Rn in the study area (refer to equation 1). The average benthic flux over all cruises was 1.08 ± 0.25 dpm m^{-2} min^{-1} while fall and spring cruise averages were 0.74 ± 0.38 and 1.42 ± 0.22 dpm m^{-2} min^{-1}, respectively. Benthic flux estimates were used to calculate an average SGD rate for the study region.

3.3. Estimates of SGD

[36] In order to provide a more realistic range of SGD, two end member values of the potential advecting fluids were used: (1) the sediment equilibration activities (C_{eq}) which corresponds to the activities that would be supported by ^{226}Ra in the sediments; and (2) groundwater activities measured in monitoring wells within the study area, representing the upper limit of activity present in advecting fluids (see Table 4). Calculated SGD rates are dependent on the activity of advecting water, the activity of the overlying water, and the diffusion rate. SGD estimates using sediment equilibration activities indicate discharge during the

Table 3. Radon 222 Activities of Input Parameters for Box Model[a]

	WC_{inv}[b]	J_{vert}	J_{ho}[c]	J_{hi}[c]	J_{ben}[d]
Oct 2003	0.95	0.10	0.20	0.67	0.58
Nov 2003	0.56	0.12	0.25	0.58	0.35
Dec 2003	1.13	−0.05	0.46	0.16	1.38
Mar 2004	0.94	−0.03	0.08	0.00	0.99
Apr 2004	1.20	0.11	0.25	0.04	1.51
May 2004	1.66	0.06	0.27	0.14	1.87

[a] Values are dpm m^{-2} min^{-1}.
[b] WC_{inv} includes in situ ingrowth and decay.
[c] J_{ho} represents horizontal outputs, and J_{hi} represents horizontal inputs.
[d] J_{ben} was calculated using equation (1).

Table 4. SGD Rates Required to Support Calculated Benthic Fluxes (J_{ben})[a]

	C_{eq} End-Member Activity, dpm l^{-1}	Groundwater End-Member Activity, dpm l^{-1}	Sediment Equilibration (C_{eq}), cm d^{-1}	Monitoring Wells, cm d^{-1}
Oct 2003	358	678	0.00	0.00
Nov 2003	356	678	0.00	0.00
Dec 2003	329	678	0.07	0.05
Mar 2004	395	707	0.00	0.00
Apr 2004	352	707	0.23	0.06
May 2004	330	707	0.34	0.21

[a]SGD rates were calculated using averaged C_{eq} ^{222}Rn activities for each sampling period and ^{222}Rn activities of groundwater wells averaged by season.

December, April, and May cruises with rates of 0.07, 0.23, and 0.34 cm d^{-1}, respectively, into the study area and no SGD during any other cruise. An average SGD over all cruises (including those with a calculated 0.0 cm d^{-1} rate of discharge) of 0.11 ± 0.06 cm d^{-1} was calculated using sediment equilibration values, and fall and spring average rates were 0.02 ± 0.02 and 0.19 ± 0.10 cm d^{-1}, respectively. Calculations made using average ^{222}Rn activities in monitoring wells indicate a SGD of 0.05, 0.06, and 0.21 cm d^{-1} for the December, April, and May cruises, respectively, and no SGD during any other cruises. Average SGD based on average monitoring well activities over all cruises was 0.05 ± 0.03 cm d^{-1}, and 0.02 ± 0.02 cm d^{-1} and 0.09 ± 0.06 cm d^{-1} for fall and spring cruises, respectively.

[37] Our estimates of SGD rates are lower than previous research suggests. *Krest et al.* [1999] calculated a SGD on the order of 1.0 cm d^{-1} based on ^{226}Ra and ^{228}Ra data and *Moore and Krest* [2004] calculated a SGD rate of 2.5 cm d^{-1} based on ^{223}Ra and ^{224}Ra data. SGD rates from these data sets are approximately 12 to 30 times greater than our average SGD rates. Using radium measurements from *Kraemer and Reid* [1984], *Krest et al.* [1999] calculated a discharge of only 0.03 cm d^{-1} of formation water could support observed elevated bottom water radium activities without a groundwater component, but were reluctant to draw this ultimate conclusion. Formation water is a component of produced water, which is defined as, ''the water (brine) brought up from the hydrocarbon-bearing strata during the extraction of oil and gas, and can include formation water, injection water, and any chemicals added downhole or during the oil/water separation process'' [*U. S. Environmental Protection Agency* (*EPA*), 2000]. This minor contribution from formation water would have significantly decreased their calculated SGD rates to values similar to those presented here.

[38] To address the potential influence of formation water to the water column, we collected data from the Minerals Management Service database and determined there are approximately 80 active oil and gas leases in the study area that produced an average of 3.26 x 10^7 l d^{-1} of formation water from 2003–2004 (Figure 2). The average activity of ^{226}Ra in formation water of wells in Louisiana and Texas is 703 dpm l^{-1} [*Kraemer and Reid*, 1984]. Using an estimated ratio of the activities of ^{222}Rn:^{226}Ra (25:1) from monitoring well samples, we calculated the average activity of ^{222}Rn of formation water to be 17575 dpm l^{-1}. Using this estimated activity, an additional source term of 0.08 dpm m^{-2} min^{-1} of ^{222}Rn is provided to the study area. The addition of formation water to equation 1 reduces calculated SGD results based on sediment equilibrium values to 0.03, 0.19, and 0.30 cm d^{-1} for December, April, and May cruises, respectively, with an overall average of 0.09 ± 0.05 cm d^{-1}. Calculated SGD estimates based on monitoring well activities were 0.01, 0.02, and 0.18 cm d^{-1} for December, April, and May cruises, respectively, with an overall average of 0.04 ± 0.03 cm d^{-1}. Formation water, typically discharged below the water surface, is a significant component of the radon budget and is comparable to the pycnocline/atmospheric flux component and should be included in any elemental budget where oil and gas extraction is prevalent. Therefore, SGD (with its broad definition) introduces up to 1.41 km^3 yr^{-1} of subsurface fluids to continental shelf and accounts for <1% of the discharge of the Mississippi River to the study area, significantly less than that suggested by *Krest et al.* [1999] and the 7% suggested by *Moore and Krest* [2004].

[39] Our ^{222}Rn data further suggests that seasonal fluctuations in groundwater flow onto the continental shelf adjacent to the Mississippi River are minor. River discharge and riverine ^{222}Rn activities displayed pronounced seasonal variability. Average river discharge during fall and spring cruises was 4930 ± 1170 and 7690 ± 430 m^3 s^{-1}, respectively, and associated ^{222}Rn activities were 1.39 ± 0.34 and 2.30 ± 0.32 dpm l^{-1}, respectively. While discharge and ^{222}Rn activities from the Mississippi River were greater in the spring versus the fall, the presence of a pycnocline during all cruises allowed us to eliminate the riverine source of radon from the box model.

3.4. Helium/Tritium

[40] Observations from Δ^3He (%), Δ^4He (%), and ^{3}H-^{3}He are presented in Table 5. Bottom water observations of Δ^3He (%), Δ^4He (%), and ^{3}H-^{3}He were greater in the fall versus the spring while Mississippi River observations were within error over all cruises. Δ^3He of bottom water samples during fall cruises ranged from 2.1 ± 0.4% to 374.5 ± 296.9%, and from 5.4 ± 5.4% to 148.4 ± 128.1% during spring cruises. Δ^4He ranged from 28.0 ± 13.3% to 546.6 ± 446.4% during spring cruises and from 1.7 ± 0.0% to 128.8 ± 0.00% during spring cruises. ^{3}He-^{3}H indicates an average age 39.2 ± 5.7 years and 29.4 ± 3.1 years for fall and spring cruises, respectively, and roughly 10 years for Mississippi River water for both fall and spring cruises. Stations with elevated Δ^3He values were also elevated with respect to Δ^4He, and values associated with eastern stations were typically greater than western stations, in contrast to the ^{222}Rn data.

[41] Bottom water values of Δ^3He and Δ^4He compared with water column and Mississippi River values indicate an

Table 5. Δ ^{3}He, Δ ^{4}He, and ^{3}H-^{3}He Age Observations[a]

Location	Cruise	Δ ^{3}He, %	Δ ^{4}He, %	^{3}H-^{3}He Age
Bottom water	fall	85.3 ± 31.4	155.4 ± 54.9	39.2 ± 5.7
	spring	39.1 ± 12.1	40.6 ± 11.8	29.4 ± 3.1
Water column	fall	43.2 ± 12.0	91.7 ± 28.3	31.4 ± 5.7
Mississippi River	fall	21.9 ± 6.2	24.4 ± 11.0	10.2 ± 2.6
	spring	19.4 ± 8.1	16.9 ± 11.5	9.4 ± 3.6
Monitoring wells	all	3227.5 ± 1635.5	5385.0 ± 2035.6	older than detectible

[a]Values are average plus or minus standard error. Bottom water and water column values were calculated using samples collected from all stations on the A, B, and C transects. Water column observations are based on all water column samples – bottom water samples. Mississippi River samples were collected in the freshwater portion of the river at SWP or HOP.

additional source of Δ^3He and Δ^4He from the benthic environment that is quickly mixed with more diluted river and ocean water. Δ^4He anomalies rarely exceed 5% in the upper mixed layer of the world's coastal oceans and an anomaly greater than 10% is considered significant [*Top et al.*, 2001]. Our results are 1 to 2 orders of magnitude greater than that which is considered significant in coastal oceans and only station C4, during the spring, yielded a value less than 5%.

[42] Potential benthic sources of ^{3}He and ^{4}He include contributions from oil and gas production, geothermal convection, and seawater recirculation. The geographic distribution of oil and gas leases (Figure 2) shows most formation water is discharged in the eastern portion of the study area and potentially accounts for observed spatial variability. *Kraemer and Reid* [1984] suggest observed radium activities in formation water are supported by U and Th parents in the water and a continual supply from rocks to the fluid phase. Alpha decay is the major decay process of U and Th chain elements and provides a source of ^{4}He in the deep subsurface. Active faulting from oil and gas extraction also provides conduits for deeper, more confined groundwater to reach the shallow earth horizon [*Kuecher et al.*, 2001]. Although our data indicates groundwater is not discharged onto the shelf, groundwater flow along fault lines could add excess ^{4}He to Permeable Zone A throughout the entire region, including the southern coastal plain, continental shelf, and Mississippi River. The discharge of subsurface fluids via faulting is typically episodic [*Cartwright et al.*, 1998; *Wang and Xie*, 1998; *Lin and Nunn*, 1997], and could contribute to observed seasonal variability. In addition to extraction of formation water and faulting, mud diapirs, mud volcanoes, and gas hydrate mounds have been documented along the Texas-Louisiana continental shelf and potentially provide a conduit for deep subsurface fluids to enter the water column [*Roberts and Carney*, 1997; *Sassen et al.*, 2003].

[43] Observed Δ^3He anomalies were also high over all cruises with significant variability over fall and spring cruises. ^{3}He sources include: solubility equilibrium with water, in situ crustal origin, crustal production external to the aquifer with a mantle component, and tritium decay [*Castro*, 2004]. In addition, three nuclear power plants are located along the Mississippi River within roughly 250 miles of the coast, and could provide a near surface source of tritium. Based on data from the Carrizo aquifer in Texas, *Castro* [2004] determined the atmospheric source of ^{3}He in the groundwater is replaced by the external component with about 90% of ^{3}He being supplied by the external component at a distance of 87 km from the recharge area. *Castro* [2004] also determined ^{4}He to be of in situ and external origin rather than atmospheric at the same distance from the recharge area. Since groundwater samples collected from monitoring wells were approximately 100–150 km from the recharge area, we suggest the majority of observed ^{3}He and ^{4}He anomalies are of external crustal and mantle origin and are delivered to the seafloor via oil and gas extraction, geothermal convection, and seawater recirculation cells.

[44] Recent research by groundwater modelers on a regional scale suggest geothermal convection and seawater recirculation may be a large source of SGD along gently sloping continental shelf environments [*Thompson et al.*, 2007; *Wilson*, 2005]. These circulation cells and flow paths reach depths several kilometers below the seafloor and travel laterally upwards of 100 km and provide a path for enriched subsurface fluids to enter the water column.

[45] Seasonal variability associated with Δ^3He and Δ^4He could be a product of increased SGD during the spring, and/or episodic discharge as a function of faulting. An increase in SGD during fall cruises is not a likely source since SGD estimates based on ^{222}Rn are not significantly different from spring to fall and estimates are already minimal. Episodic discharge could enhance seasonal Δ^3He and Δ^4He, but we have no method to evaluate this phenomenon. In addition, comparisons between fall and spring helium/tritium results are limited due to a decreased number of samples collected during spring cruises and the loss of all May samples during shipping.

3.5. SGD Sources and Implications

[46] The current definition of SGD does not make any distinction between sources of groundwater to coastal environments. While quantification of SGD is an important step in understanding the geochemistry of coastal oceans, a true understanding of coastal ocean geochemistry will not be achieved until sources are quantified and characterized. The continental shelf of Louisiana is a complex system with possible SGD contributions from geothermal convection, pore water compaction, seawater recirculation, tidal pumping, and topography driven flow. Additionally, SGD rates based on geochemical tracers may be enhanced by radium, radon, and helium enriched fluids associated with oil and gas extraction, faulting, mud diapers, mud volcanoes, and gas hydrate mounds. We have illustrated the potential influence formation water can have on the water column inventory, but information concerning the quantity and geochemical contributions of mud diapers, mud volcanoes, and gas hydrate mounds in the region is not available. Inventories were measured and source terms defined, so any additional source

would only reduce the SGD estimates. Considering such low estimates of SGD, minor contributions from unquantified sources could be proportionately significant sources of the calculated benthic flux to the study area.

[47] Based on our data and research by *Thompson et al.* [2007] and *Wilson* [2005], we suggest that topography driven groundwater flow is not a significant contributor to SGD in the study region. This suggestion is also supported by *Martin and Whiteman* [1999], who define the entire land area from the coast northward to New Orleans as a recharge area for New Orleans. Elimination of a topography driven SGD component minimizes any potential contribution of groundwater derived from local or regional flow. The minimization of this component of SGD is important because local and regional groundwater is typically elevated in nutrients relative to surface waters. While terrestrially derived SGD is most likely not discharged onto the continental shelf, it is still potentially discharged locally into inland bays and bayous along the coast that flow into the coastal ocean.

4. Summary

[48] The use of multiple geochemical tracers to assess regional SGD in a river dominated continental shelf environment was an effective method. The ^{222}Rn model employed in this study was efficient at quantifying: atmospheric exchange, exchange across the pycnocline, horizontal exchange, riverine flux, diffusional flux, total benthic flux, water column inventories, and ultimately, SGD. Helium isotopes were effective in showing the potential influences of deep, long-lived flow paths of SGD and oil and gas extraction.

[49] SGD rates on the order of 0.00–0.14 cm d^{-1} indicate SGD is not a significant contributor of subsurface fluids to the continental shelf of Louisiana and is likely not contributing to observed nutrient enrichment in the region relative to the Mississippi River although the potential of SGD to inland areas and ultimately to the coastal ocean cannot be eliminated. In order to further constrain sources of SGD in the region, we would suggest research to be directed at quantification of subsurface fluids associated with inland bayous and bays as well as a more detailed study of the influences from oil and gas extraction.

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References

Berner, R. A. (1982), Burial of organic carbon and pyrite sulfur in the modern ocean: Its geochemical and environmental significance, *Am. J. Sci.*, *282*, 451–471.

Bugna, G. C., J. P. Chanton, J. E. Cable, W. C. Burnett, and P. H. Cable (1996), The importance of groundwater discharge to the methane budgets of nearshore and continental shelf waters of the northern Gulf of Mexico, *Geochim. Cosmochim. Acta*, *60*, 4735–4746.

Burnett, W. C., J. E. Cable, D. R. Corbett, and J. P. Chanton (1996), Tracing groundwater flow into surface waters using natural ^{222}Rn, paper presented at Symposium on Groundwater, Land-Ocean Interactions in the Coastal Zone, Moscow, 6–10 July.

Burnett, W. C., M. Taniguchi, and J. Oberdorfer (2001), Measurement and significance of the direct discharge of groundwater into the coastal zone, *J. Sea Res.*, *46*, 109–116.

Burnett, W. C., H. Bokuniewicz, M. Huettel, W. S. Moore, and M. Taniguchi (2003), Groundwater and pore water inputs to the coastal zone, *Biogeochemistry*, *66*, 3–33.

Cable, J. E., W. C. Burnett, J. Chanton, and G. L. Weatherly (1996a), Estimating groundwater discharge into the northeastern Gulf of Mexico using radon-222, *Earth Planet. Sci. Lett.*, *144*, 591–604.

Cable, J. E., G. Bugna, W. C. Burnett, and J. Chanton (1996b), Application of ^{222}Rn and CH_4 for assessment of groundwater discharge to the coastal ocean, *Limnol. Oceanogr.*, *41*(6), 1437–1444.

Cartwright, J., R. Bouroullec, D. James, and H. Johnson (1998), Polycyclic motion history of some Gulf Coast growth faults from high-resolution displacement analysis, *J. Geol.*, *26*, 819–822.

Castro, M. C. (2004), Helium sources in passive margin aquifers—New evidence for a significant mantle ^{3}He source in aquifers with unexpectedly low in situ ^{3}He/^{4}He production, *Earth Planet. Sci. Lett.*, *222*, 897–913.

Charette, M. A., and K. O. Buesseler (2004), Submarine groundwater discharge of nutrients and copper to an urban subestuary of Chesapeake Bay (Elizabeth River), *Limnol. Oceanogr.*, *49*(2), 376–385.

Clarke, W. B., and G. Kugler (1969), Dissolved helium in ground-water: A possible method for uranium and thorium prospecting, *Econ. Geol.*, *68*, 243–251.

Clark, W. B., Z. Top, A. P. Beavan, and S. S. Gandhi (1977), Dissolved helium in lakes: Uranium prospecting in the Precambrian terrain of Central Labrador, *Econ. Geol.*, *72*, 233–242.

Corbett, D. R., W. C. Burnett, P. H. Cable, and S. B. Clark (1997), Radon tracing of groundwater input into Par Pond, Savannah River Site, *J. Hydrol.*, *203*, 209–227.

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

Corbett, D. R., M. D. Dail, and B. A. Mckee (2007), High frequency time-series of the dynamic sedimentation processes on the western shelf of the Mississippi River delta, *Cont. Shelf Res.*, doi:10.1016/j.csr.2007.01.025, in press.

Craig, H. (1969), Abyssal carbon and radiocarbon in the Pacific, *J. Geophys. Res*, *74*(23), 5491–5506.

Davis, S. N., G. M. Thompson, H. W. Bentley, and G. Stiles (1980), Ground-water tracers—A short review, *Ground Water*, *18*, 14–23.

Gesell, T. F. (1983), Background atmospheric Rn-222 concentrations outdoors and indoors: A review, *Health Phys.*, *45*, 289–302.

Grubb, H. F. (1998), Summary of hydrology of the regional aquifer systems, Gulf Coastal Plain, South-Central United States, Regional Aquifer-System Analysis-Gulf Coastal Plain, *U.S. Geol. Surv. Prof. Pap. 1416-A*, 61 pp., Washington, D. C.

Hussain, N., T. M. Church, and G. Kim (1999), Use of ^{222}Rn and ^{226}Ra to trace groundwater discharge into the Chesapeake Bay, *Mar. Chem.*, *65*, 127–134.

Jahne, B., K. O. Munnich, R. Bosinger, A. Dutzi, W. Huber, and P. Libner (1987), On the parameters influencing air-water gas exchange, *J. Geophys. Res.*, *92*, 1937–1950.

Kraemer, T. F., and D. F. Reid (1984), The occurrence and behavior of radium in saline formation water of the U.S. Gulf Coast region, *Isot. Geosci.*, *2*, 153–174.

Krest, J. M., W. S. Moore, and Rama (1999), ^{226}Ra and ^{228}Ra in the mixing zone of the Mississippi and Atchafalaya Rivers: Indicators of groundwater input, *Mar. Chem.*, *64*, 129–152.

Kuecher, G. J., H. H. Roberts, M. D. Thompson, and I. Matthews (2001), Evidence for active growth faulting in the Terrebonne Delta Plain, South Louisiana: Implications for wetland loss and the vertical migration of petroleum, *Environ. Geosci.*, *8*(2), 77–94.

Lin, G., and J. A. Nunn (1997), Evidence for recent migration of geopressured fluids along faults in Eugene Island, Block 330, offshore Louisiana, from estimates of pore water salinity, *Trans. Gulf Coast Assoc. Geol. Soc.*, *47*, 419–423.

MacIntyre, S., R. Wanninkhof, and J. P. Chanton (1995), Trace gas exchange across the air-sea interface in freshwater and coastal marine environments, in *Biogenic Trace Gases: Measuring Emissions From Soil and Water*, edited by P. A. Matson and R. C. Harriss, Blackwell Sci., Malden, Mass.

Martens, C. S., G. W. Kipphut, and J. V. Klump (1980), Sediment-water chemical exchange in the coastal zone traced by in situ Radon-222 flux measurements, *Science*, *208*, 285–288.

Martin, A., Jr., and C. D. Whiteman Jr. (1999), Hydrology of the Coastal Lowlands Aquifer System in parts of Alabama, Florida, Louisiana, and

Mississippi, Regional Aquifer-System Analysis-Gulf Coastal Plain, *U.S. Geol. Surv. Prof. Pap. 1416-H*, 51 pp., Reston, Va.

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

Milliman, J. D. (1983), World-wide delivery of river sediment to the oceans, *J. Geol.*, *91*, 1–21.

Moore, W. S. (1997), High fluxes of radium and barium from the mouth of the Ganges-Brahmaputra River during low discharge suggest a large groundwater source, *Earth Planet. Sci. Lett.*, *150*, 141–150.

Moore, W. S. (1998), Application of ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra in coastal waters to assessing coastal mixing rates and groundwater discharge to oceans, *Earth Planet. Sci.*, *107*(4), 343–349.

Moore, W. S., and J. Krest (2004), Distribution of ^{223}Ra and ^{224}Ra in the plumes of the Mississippi and Atchafalaya Rivers and the Gulf of Mexico, *Mar. Chem.*, *86*, 105–119.

Moore, W. S., D. J. DeMaster, J. M. Smoak, B. A. McKee, and P. W. Swarzeski (1996), Radionuclide tracers of sediment-water interactions on the Amazon shelf, *Cont. Shelf Res.*, *16*, 645–665.

Paerl, H. (1995), Coastal eutrophication in relation to atmospheric nitrogen deposition: Current perspectives, *Ophelia*, *41*, 237–259.

Peng, T.-H., T. Takahashi, and W. S. Broecker (1974), Surface radon measurements in the north Pacific station Papa, *J. Geophys. Res.*, *79*, 1772–1780.

Pettijohn, R. A., J. F. Busby, and J. D. Beckman (1992), Properties and chemical constituents in ground water from the Mississippi River Valley alluvial aquifer and permeable zone A (Holocene-upper Pleistocene deposits) south-central United States, *U.S. Geol. Surv. Water Resour. Invest. Rep. 91-4149*, scale 1:3,500,000, 5 pp., U.S. Geol. Surv., Reston, Va.

Poreda, R. J., T. E. Cerling, and D. K. Solomon (1988), Tritium and helium isotopes as hydrologic tracers in a shallow unconfined aquifer, *J. Hydrol.*, *103*, 1–9.

Rabalais, N. N., R. E. Turner, D. Justic, Q. Dortch, and W. J. Wiseman Jr. (1999), Characterization of hypoxia: Topic 1 report for the integrated assessment of hypoxia in the Gulf of Mexico, *NOAA Coastal Ocean Program Decision Anal. Ser. 15*, 167 pp., Natl. Oceanic and Atmos. Admin., Silver Spring, Md.

Renken, R. A. (1998), Ground water atlas of the United States, Segment 5: Arkansas, Louisiana, Mississippi, *Hydrol. Invest. Atlas 730-F*, 28 pp., U.S. Geol. Surv., Reston, Va.

Roberts, H. H., and R. S. Carney (1997), Evidence of episodic fluid, gas, and sediment venting on the northern Gulf of Mexico continental slope, *Econ. Geol.*, *92*, 863–879.

Sarmiento, J. L., H. W. Feely, W. S. Moore, A. E. Bainbridge, and W. S. Broecker (1976), The relationship between vertical eddy diffusion and buoyancy gradient in the deep sea, *Earth Planet. Sci. Lett.*, *32*, 357–370.

Sassen, R., A. V. Milkov, H. H. Roberts, S. T. Sweet, and D. A. DeFreitas (2003), Geochemical evidence of rapid hydrocarbon venting from a seafloor-piercing mud diaper, Gulf of Mexico continental shelf, *Mar. Geol.*, *198*, 319–329.

Schlosser, P., S. D. Shapiro, M. Stute, W. Aeschbach-Hertig, N. Plummer, and E. Busenberg (1998), Tritium/He-3 Measurements in young groundwater, paper presented at Symposium on Isotope Techniques in the Study of Environmental Change, Int. At. Energy Assoc., Vienna, 14–18 April.

Solomon, D. K., A. Hunt, and R. J. Poreda (1996), Source of radiogenic helium 4 in shallow aquifers: Implications for dating young groundwater, *Water Resour. Res.*, *32*(6), 805–813.

Thompson, C., L. Smith, and R. Maji (2007), Hydrogeological modeling of submarine groundwater discharge on the continental shelf of Louisiana, *J. Geophys. Res.*, *112*, C03014, doi:10.1029/2006JC003557.

Top, Z., and W. B. Clarke (1981), Dissolved helium isotopes and tritium in lakes: Further results for uranium prospecting in Central Labrador, *Econ. Geol.*, *76*, 2018–2031.

Top, Z., L. Brand, D. R. Corbett, W. C. Burnett, and J. Chanton (2001), Helium as a tracer of groundwater input into Florida Bay, *J. Coastal Res.*, *17*(4), 859–868.

Turner, S. M., G. Malin, P. D. Nightingale, and P. S. Liss (1996), Seasonal variation of dimethyl sulphide in the North Sea and an assessment of fluxes to the atmosphere, *Mar. Chem.*, *54*, 552–556.

Ullman, W. J., and R. C. Aller (1981), Diffusion coefficients in nearshore marine sediments, *Limnol. Oceanogr.*, *27*(3), 552–556.

United States Army Corps of Engineers (USACE) (1974), Deep draft access to the ports of New Orleans and Baton Rouge, draft environmental statement, New Orleans Dist., New Orleans, La.

U.S. Environmental Protection Agency (EPA) (2000), Fact Sheet: Proposed National Pollutant Discharge Elimination System (“NPDES”) General Permit No. CAG280000 for Offshore Oil and Gas Exploration, Development and Production Operations off Southern California, EPA Region 9, CWA Stand. and Permits Off., San Francisco, Calif.

Wang, C., and X. Xie (1998), Hydrofracturing and episodic fluid flow in shale-rich basins-a numerical study, *Am. Assoc. Pet. Geol. Bull.*, *82*, 1857–1869.

Wanninkhoff, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, *97*, 7373–7382.

Wilson, A. M. (2005), Fresh and saline groundwater discharge to the ocean: A regional perspective, *Water Resour. Res.*, *41*, W02016, doi:10.1029/2004WR003399.

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