ground water

Ground Water Discharge and Nitrate Flux to the Gulf of Mexico

by Carolyn B. Dowling[1], Robert J. Poreda[2], Andrew G. Hunt[3], and Anne E. Carey[4]

Abstract

Ground water samples (37 to 186 m depth) from Baldwin County, Alabama, are used to define the hydrogeology of Gulf coastal aquifers and calculate the subsurface discharge of nutrients to the Gulf of Mexico. The ground water flow and nitrate flux have been determined by linking ground water concentrations to $^3H/^3He$ and ^4He age dates. The middle aquifer (A2) is an active flow system characterized by postnuclear tritium levels, moderate vertical velocities, and high nitrate concentrations. Ground water discharge could be an unaccounted source for nutrients in the coastal oceans. The aquifers annually discharge $1.1 \pm 0.01 \times 10^8$ moles of nitrate to the Gulf of Mexico, or 50% and 0.8% of the annual contributions from the Mobile-Alabama River System and the Mississippi River System, respectively.

In southern Baldwin County, south of Loxley, increasing reliance on ground water in the deeper A3 aquifer requires accurate estimates of safe ground water withdrawal. This aquifer, partially confined by Pliocene clay above and Pensacola Clay below, is tritium dead and contains elevated ^4He concentrations with no nitrate and estimated ground water ages from 100 to 7000 years. The isotopic composition and concentration of natural gas diffusing from the Pensacola Clay into the A3 aquifer aids in defining the deep ground water discharge. The highest ^4He and CH_4 concentrations are found only in the deepest sample (Gulf State Park), indicating that ground water flow into the Gulf of Mexico suppresses the natural gas plume. Using the shape of the CH_4-He plume and the accumulation of ^4He rate (2.2 $\pm$ 0.8 μcc/kg/1000 years), we estimate the natural submarine discharge and the replenishment rate for the A3 aquifer.

Introduction

Protection of ground water resources from sea water intrusion is a concern for coastal communities as sea level rises and land development increases. Typically, studies on coastal aquifers are concerned with water supply issues, but the potential of nonpoint source discharge of nutrients to the coastal oceans has become an increasingly important

[1]Now at Byrd Polar Research Center, Ohio State University, Columbus, OH 43210; formerly with the Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627

[2]Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627

[3]Now at U.S. Geological Survey, Denver, CO 80225; formerly with the Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627

[4]Department of Geological Sciences, Ohio State University, Columbus, OH 43210

issue. Sea water intrusion studies have been conducted on coastal aquifers throughout the world including those in California (Bond and Bredehoeft 1987; Izbicki 1996), Florida (Mercer et al. 1986; Anderson et al. 1988; Hickey 1989; Meyer 1989), India (Sukhija et al. 1996), Israel (Schmorak 1976), Egypt (Kashef 1983), Japan (Kakinuma et al. 1988), the Bahamas (Cant and Weech 1986; Whitaker and Smart 1990), and small oceanic islands (Wheatcraft and Buddemeier 1981; Anthony et al. 1989; Contractor and Srivastava 1990). Other investigations have used computer simulations and laboratory experiments to study the dynamics of salt water intrusion as well as density coupled flow (Lee and Cheng 1974; Peterson et al. 1978; Carey et al. 1993; Carey and Wheatcraft 1995; Carey et al. 1995; Wheatcraft and Burns 1997; Benson et al. 1998; Simmons et al. 2001; Zhang et al. 2001).

One important component of the field studies, laboratory experiments, and computer simulations is the ground water flow at the sea water/fresh water boundary. Because ground water and sea water are miscible, the transition zone, created as the fresh ground water flows past the

underlying sea water, is controlled by mechanical dispersion, molecular diffusion, and sediment permeability (Lee and Cheng 1974; Carey et al. 1993; Carey and Wheatcraft 1995; Carey et al. 1995; Benson et al. 1998). To understand more about the nonpoint discharge of trace metals and nutrients to the coastal oceans, the fresh water/salt water transition zone and the effects of ground water pumping on the ground water supply, it is important to appreciate the mechanics and magnitude of the submarine ground water discharge.

Most often, the ground water discharge to the oceans has been disregarded because it occurs as a nonpoint source distributed over a broad submarine area. However, many recent studies have shown that ground water discharge can be substantial and affect the coastal oceanic chemistry because of higher-than-river concentrations of trace metals and nutrients from the infiltration of fertilizers, the weathering of the aquifer protolith, and by adsorption and desorption reactions (Loeb and Goldman 1979; Johannes 1980; Bokuniewicz and Pavlik 1990; Burnett et al. 1990; Giblin and Gaines 1990, LaPointe et al. 1990; Oberdorfer et al. 1990; Valiela et al. 1990; Valiela et al. 1992; Harris 1995; Moore 1996; Speiran 1996; Moore 1997; Portnoy et al. 1998; Shaw et al. 1998; Corbett et al. 1999; Dowling et al. 1999; Katz et al. 2001; Panno et al. 2001; Swarzenski et al. 2001; Dowling et al. 2003). The nutrient loading by ground water discharge has been shown to have an impact on lakes, streams, and the coastal oceans (Capone and Slater 1990; Giblin and Gaines 1990; LaPointe et al. 1990; Oberdorfer et al. 1990; Valiela et al. 1990; Valiela et al. 1992; Harris 1995; Portnoy et al. 1998; Corbett et al. 1999; Katz et al. 2001; Panno et al. 2001).

Submarine discharge, in addition to the Mississippi and Atchafalaya rivers, could be an important source of nitrate for the Gulf of Mexico. High nitrate levels, along with phosphate and silica, in the gulf may contribute to the eutrophication, algal blooms, and hypoxia in the commercial and recreational fishing grounds (Rabalais et al. 1999). Rabalais et al. (1999) suggest that ground water may be a source of nitrate, but there are no studies investigating ground water discharge for the Gulf coastal states. We examined the aquifer system in Baldwin County, Alabama, in an effort to understand the magnitude of the ground water discharge and the nitrate flux to the Gulf of Mexico. We chose Baldwin County because of its relatively simple hydrology; deep, active flow system; and long history of agriculture. This Gulf Coast aquifer is an uncomplicated system with little river surface discharge. The purpose of this study is to characterize the ground water flow of a regional Gulf Coast aquifer system, determine the submarine flux of nutrients into the coastal ocean, and establish a safe ground water withdrawal rate for a population that is increasing their dependency on the deeper parts of the aquifer. To quantify ground water travel times and ground water flow in Baldwin County, we use ^{3}H/^{3}He ground water ages and ^{4}He concentrations. We estimate the ground water fluxes by calculating the ground water ages and combining the results with our dissolved nutrient concentrations. The nutrient data may be integrated over the coastline, yielding long-term averages for the ground water flux to the Gulf of Mexico.

Baldwin County, Alabama, has several advantages as a regional study area. There are many agricultural and municipal wells that are available for sampling. High average precipitation ensures adequate recharge in the region. The aquifers are relatively pristine with little development and have not been drawn down on a regional scale by ground water pumping (that is, on a regional scale, the ground water pumping rate is much lower than the aquifer recharge rate). The aquifers are mostly low uranium quartz sand that maximizes the utility of ^{3}H/^{3}He ages for postnuclear age water and ^{4}He ages for Holocene ground water.

Hydrogeology of Baldwin County, Alabama

Baldwin County, Alabama, is located on the Gulf of Mexico, east of Mobile Bay (Figure 1). The area is undergoing increasing development. From 1966 to 1995, the ground water pumping increased from 2.7×10^7 L/day to 1.6×10^8 L/day (Reed and McCain 1971; Robinson et al. 1996a). The sixfold increase in ground water use was mainly caused by an expansion in agricultural water use (25% of total use in 1966 to 68% of total use in 1995), with the remainder serving the growing population. The annual precipitation in the region is 167 cm/yr (Robinson et al. 1996a). Only a small percentage of the recharged water is discharged to the surface river system, and there are no major rivers flowing across the county. Most of the water that enters the aquifers becomes part of the deeper aquifer system and ultimately discharges into the Gulf of Mexico.

The relatively uncomplicated geology of Baldwin County consists of Oligocene-Miocene Carbonates, Miocene Pensacola Clay, Miocene series undifferentiated, Pliocene-Pleistocene Citronelle Formation, and the Pleistocene-Holocene alluvial deposits (Figure 2) (Chandler et al. 1985; Mooty 1988; Smith 1991). Pleistocene-Holocene alluvium that forms the A1 aquifer, a very small aquifer located on the Gulf Coast, is ~30 m thick and consists of fine to coarse quartz sand with varying degrees of heavy minerals, shell fragments, and silt (Chandler et al. 1985). ~10 m of fine-grained silt extending ~9 km landward separates the A1 aquifer from the more extensive A2. The A2 aquifer is 60 to 75 m thick and is composed of the Pliocene-Pleistocene Citronelle Formation and the upper part of the undifferentiated Miocene series (Chandler et al. 1985). The Citronelle Formation is thinly layered nonfossiliferous fine to medium reddish-brown sands with thin, discontinuous lenticular beds of clay (Isphording 1977; Chandler et al. 1985). Isphording (1977) proposed the name of Ecor Rouge Sand for the Miocene undifferentiated series, which can be found at several outcrops throughout Alabama (e.g., most noticeably on the cliffs along east Mobile Bay in Fairhope). The Miocene undifferentiated series are massive thickly bedded units consisting of micaceous, fine to coarse quartz sands with some ironstone and minor laminated clay layers (Isphording 1977; Raymond 1983; Smith 1991). Because there is no continuous confining unit between the Citronelle Formation and the Miocene undifferentiated series, they act as a single hydrologic unit (the A2 aquifer) and serve as the major source of ground water for Baldwin County. However, as fertilizers and other pollutants are infiltrating into the A2 aquifer, more municipal supply wells are being
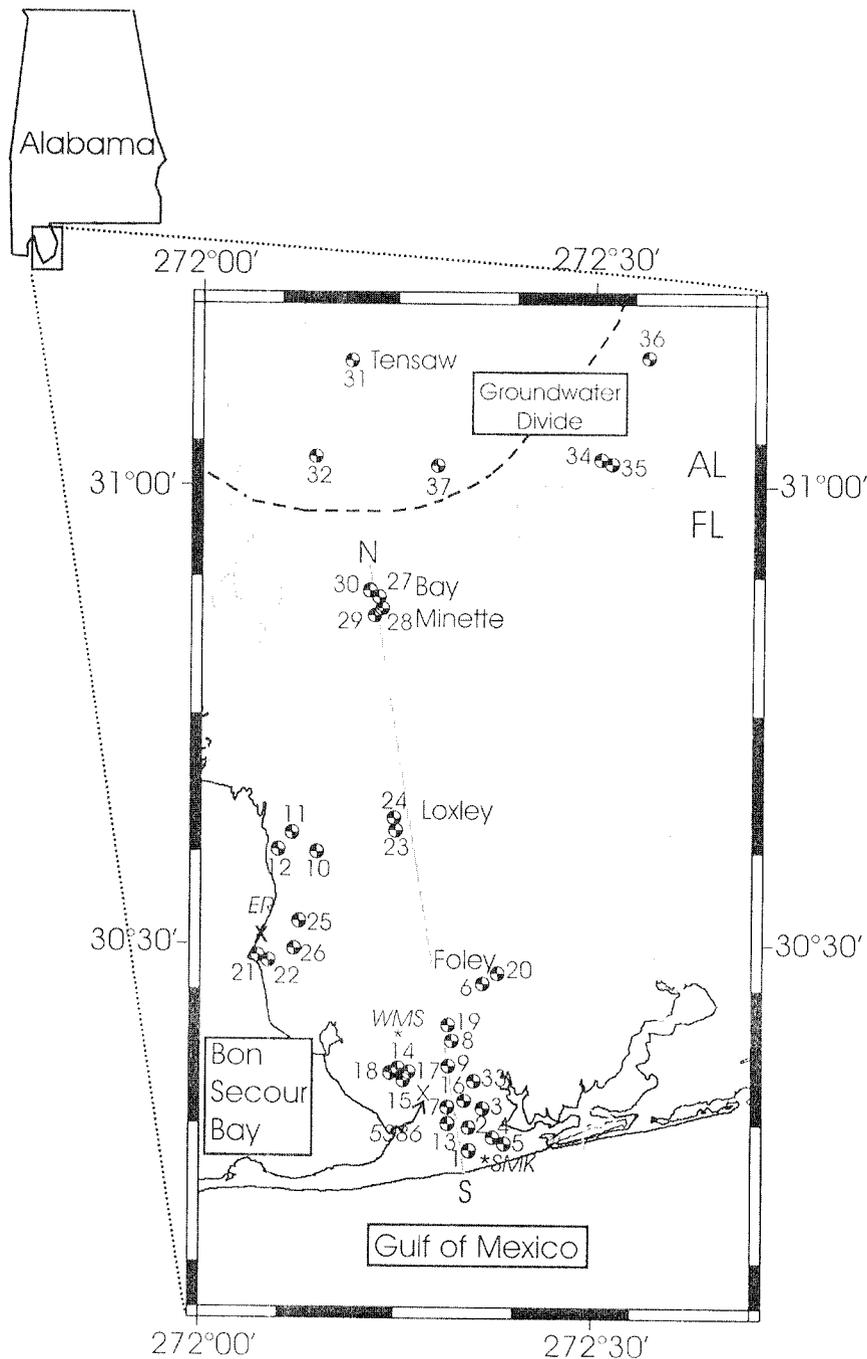
Figure 1. The sample locations in Baldwin County. This map of Baldwin County, Alabama, shows the locations of the ground water, sediment, and natural gas samples. A black-and-white patterned circle indicates the ground water wells, an X represents the sediment samples, and an * specifies the natural gas wells. Each well has been given a number that is referenced to Table 1. The proposed ground water divide is based on the changes in structural geology (e.g., faults), ground water geochemistry, and potentiometric contours.

drilled into the A3 aquifer to provide the principal drinking water source in the future. The A3 aquifer is ~100 to 150 m thick and partially separated from the A2 aquifer by a transgressive clay unit that extends landwards ~40 km (Chandler et al. 1985).

The basal boundary of the A3 aquifer system is the Pensacola Clay and the Tampa Formation-Chickasawhay Limestone undifferentiated. The Miocene Pensacola Clay consists of gray to brown, slightly calcareous, slightly micaceous, silty to sandy clay (Raymond 1983). The Escambia Sand, a fine to very coarse sand, divides the Pensacola Clay into lower and upper unnamed members

(Smith 1991). Within the Pensacola are several economically important natural gas bearing sands named the Meyer (upper Pensacola Clay member), Luce (lower Pensacola Clay member), and Amos sands (lower Pensacola Clay member) (Raymond 1983; Smith 1991). The Meyer Gas Sand, a fine-grained quartz sand that occurs only in southern Baldwin County in the Pensacola Clay (Smith 1991), has a relatively unusual helium isotopic signature (Table 2b). Underlying the Pensacola Clay in southern Baldwin County is the Oligocene-Miocene Tampa Formation-Chickasawhay Limestone undifferentiated (Chandler et al. 1985; Smith 1991). The relatively thick limestone beds dip
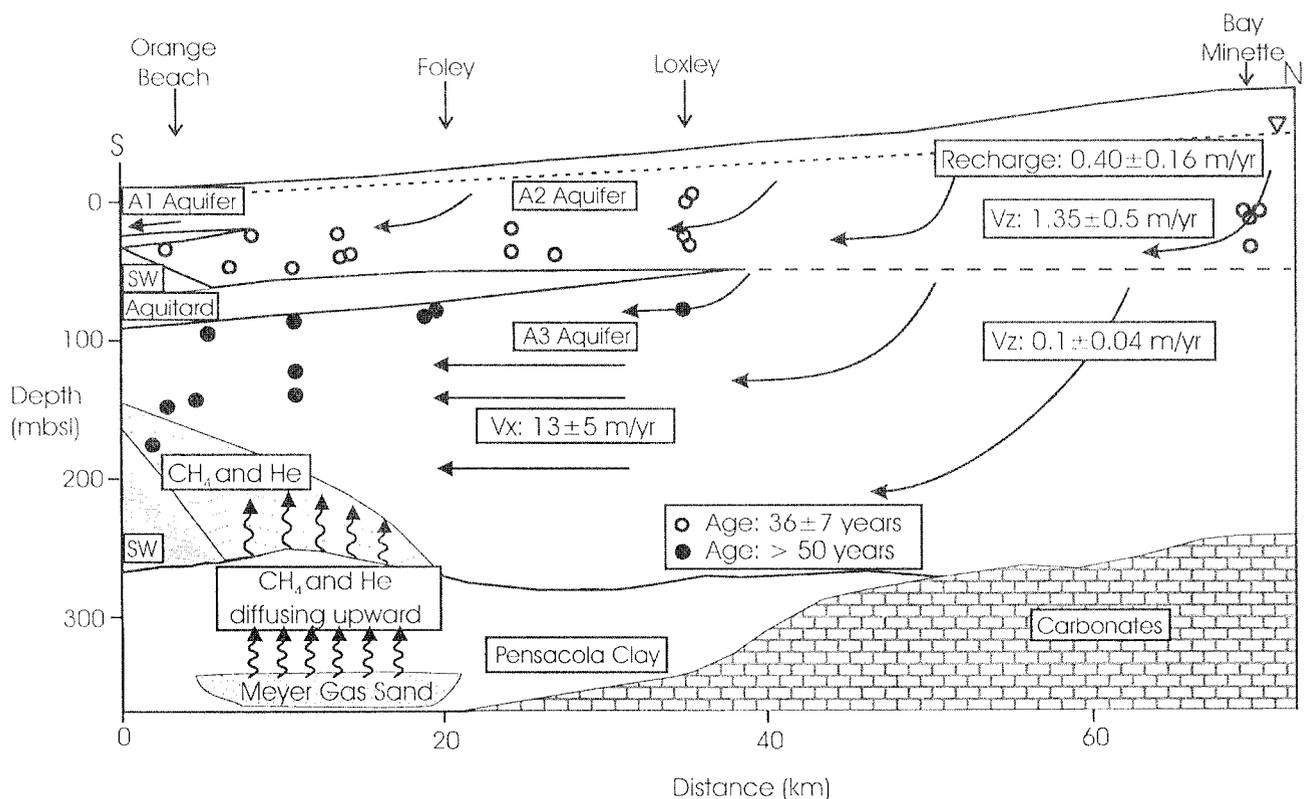
Figure 2. Schematic cross section of ground water flow in Baldwin County. All wells in the southern two-thirds of the county (Bay Minette to the Gulf of Mexico) are projected to the north-south line in Figure 1. The wells in the A2 aquifer contain tritium and have an average ground water residence time of 36 ± 7 years. The wells in the A3 aquifer have no tritium, moderate amounts of radiogenic ^{4}He, and are more than 50 years old. The water recharging into the aquifers must be balanced by discharge into the Gulf of Mexico. The recharge in the highly permeable sediments of the A2 aquifer drives the ground water flow in the lower part of the aquifer. Gulf 9 and 58 do not appear in the cross section because their depths are not known. SW stands for sea water wedge.

gently to the southwest (Smith 1991). They become the lower boundary of the aquifer system in northern Baldwin County (north of Bay Minette and west of Atmore) when the Pensacola Clay thins out (Smith 1991).

Sampling and Methodology

Water samples from agricultural and municipal ground water wells throughout Baldwin County, Alabama, were collected from 1997 to 2001 (Figure 1). The ground water samples were analyzed for nutrients, dissolved gas, and tritium. Field parameters (i.e., pH, temperature, conductivity) and the latitude and longitude (using Global Positioning System |GPS| technology) were recorded at each site. All the samples were collected from taps at the wellhead (after purging). The nutrient samples were refrigerated in the dark until they were filtered and then frozen until analyzed. The results of the nutrient data are reported in Carey et al. (in review).

The dissolved gas samples were collected at the surface in ¼-inch copper tubes and sealed with refrigeration clamps. Amber glass bottles with polyethylene caps to minimize headspace were used to store the tritium samples. Gas concentrations and isotopic ratio measurements of the ground water samples were carried out at the Rare Gas Facility at the University of Rochester. The dissolved gas was extracted and processed on a high vacuum line (Poreda et al. 1988). The helium isotope ratio measurements were

made with a VG 5400 noble gas mass spectrometer by peak height comparison to a calibrated air standard with errors of ~2% (Poreda and Farley 1992). Helium isotope ratios are expressed as R/R_{air}, where R is the ^{3}He/^{4}He ratio in the sample and R_{air} is the ^{3}He/^{4}He ratio in the measured air standard. Errors in the reported values of R/R_{air} are ~0.5%. The tritium values were determined using the ^{3}He ingrowth technique (Clarke et al. 1976). The errors depend on the amount of ^{3}H and are ± 0.5% at 30 TU (tritium units), 2% at 5 TU, and 4.5% at 0.5 TU (Gröning et al. 2001). The detection limit of ^{3}H is 0.05 TU.

The sediment samples obtained from the GSA 5386 drill cutting and the Ecor Rouge outcrop (Figure 1), as well as the gas samples from the West Magnolia Springs and Smacko wells (Figure 1), were measured for helium concentrations and isotopic ratios. Total concentration and isotopic composition of helium and neon for the drill core quartz separates of the core samples were determined by fusing ~100 to 200 mg of sample at 1800°C in a modified Turner double-walled furnace and measured on a VG 5400 noble gas mass spectrometer (Poreda and Farley 1992). An air standard of known volume was used to calibrate helium and neon. Fractions of the sediment core sample were prepared for ICP-MS analysis by digestion in a Milestone MLS 1200 microwave digestion system, evaporated to dryness, and re-acidified using ultrapure nitric acid.

To prepare the sediment digestions for trace metal analysis on the ICP-MS, the samples were further diluted

Table 1
Dissolved Gas Data and Ages of the Baldwin County Ground Waters and Natural Gas Data of the Meyer Gas Sand

Sample Name	Sample Date	Figure 1 Reference	Local Well Name	Aquifer	Depth m	^{4}He μcc/kg	Ne μcc/kg	Ar cc/kg	N_2 cc/kg	Excess N_2 cc/kg	CH_4 cc/kg	R/R_{air}	Temp. °C	^{3}He* T.U.	^{3}H T.U.	^{3}He/^{3}H Age Years	^{4}He$_{rad}$ μcc/kg
Ground Water																	
Gulf-01	Oct 96	1	Gulf State Park	A3	186	1332.87	330.59	0.424	18.32	0.00	10.73	0.525	*	347.46	<0.05	>100	1287.49
Gulf-02	Oct 96	2	RC Craft Farms	A3	152	59.07	245.36	0.370	15.28	0.00	<0.02	0.896	16	3.67	<0.05	>50	13.69
Gulf-03	Oct 96	3	RC Craft, Cotton Creek	A2	*	50.99	255.84	0.328	12.95	*	<0.02	2.117	24	34.52	7.160	31.7	5.60
Gulf-04	Oct 96	4	Orange Beach, deep	A3	151	116.80	271.95	0.357	14.40	0.00	<0.02	0.696	20	18.70	<0.05	>50	71.41
Gulf-05	Oct 96	5	Orange Beach, shallow	A2	37	49.15	237.16	0.338	14.04	0.00	<0.02	1.544	20	16.64	4.45	28.0	3.76
Gulf-07	Oct 96	6	Woerner T. Farm, Big Bertha	A3	105	50.79	259.19	0.346	14.21	0.00	<0.02	1.261	21	10.01	0.48	>50	5.40
Gulf-08	May 97	1	Gulf State Park	A3	186	*	*	*	*	*	*	*	*	*	0.21	>100	*
Gulf-09	May 97	7	Gulf State Utilities #2	A2	*	43.35	218.80	0.316	13.86	0.86	*	1.412	23	10.93	3.74	23.4	0.00
Gulf-13	May 97	8	Riveria #9	A2	42	56.34	249.55	0.367	18.15	2.83	*	1.169	16	6.29	6.67	15.2	11.26
Gulf-15	May 97	9	Riveria #10	A2	64	47.00	201.90	0.331	13.97	1.03	*	1.579	18	16.40	3.17	32.6	1.93
Gulf-22	Nov 98	10	Belforest #1	A2	56	57.06	217.47	0.322	13.14	0.01	<0.02	1.476	21	15.35	1.91	39.7	0.00
Gulf-23	Nov 98	11	Daphne Utilities #4	A2	60	56.44	206.03	0.302	12.82	0.59	0.47	1.569	24	19.23	2.91	36.8	1.86
Gulf-24	Nov 98	12	Daphne Utilities #2	A3	138	83.48	258.87	0.352	15.07	0.00	<0.02	0.774	20	0.00	<0.05	>100	14.18
Gulf-26	Nov 98	13	Gulf Shores Utilities #6	A2	59	66.02	247.40	0.355	15.98	1.07	0.33	1.207	18	8.28	1.06	37.9	0.64
Gulf-27	Nov 98	14	Woerner T. Farm, Faust	A3	146	54.27	214.71	0.325	12.87	0.00	<0.02	1.011	21	0.00	<0.05	>50	0.00
Gulf-28	Nov 98	15	Woerner T. Farm, Tindall	A3	91	75.79	244.38	0.351	15.00	0.30	<0.02	0.819	19	0.00	0.07	>100	11.16
Gulf-29	Nov 98	1	Gulf State Park	A3	186	1452.55	260.09	0.319	14.67	0.41	8.96	0.524	*	370.03	0.26	>100	1381.08
Gulf-30	Nov 98	16	Gulf Shores Utilities #9	A3	113	62.56	238.04	0.341	14.47	0.24	<0.02	0.967	20	0.00	<0.05	>50	0.00
Gulf-31	Nov 98	17	Woerner T. Farm, Magnolia	A3	158	77.42	227.56	0.361	15.72	1.21	0.03	0.838	16	3.56	0.12	>50	18.77
Gulf-32	Nov 98	18	Woerner T. Farm, new well	A2	79	54.21	221.93	0.313	13.52	0.52	<0.02	1.330	24	7.51	1.63	35.8	0.00
Gulf-33	Nov 98	4	Orange Beach, deep	A3	151	149.52	278.95	0.340	15.05	0.00	<0.02	0.678	24	13.34	<0.05	>100	72.99
Gulf-34	Nov 98	5	Orange Beach, shallow	A2	37	57.74	220.69	0.335	14.57	0.98	<0.02	1.509	19	16.74	1.61	43.7	0.08
Gulf-35	Nov 98	8	Riveria Utilities #9	A2	42	57.11	221.37	0.322	14.01	0.76	<0.02	1.586	22	18.20	2.22	40.6	0.00
Gulf-36	Nov 98	19	Riveria Utilities #12	A3	66	67.51	256.63	0.363	15.65	0.26	<0.02	0.945	18	0.00	<0.05	>50	0.00
Gulf-37	Nov 98	9	Riveria Utilities #10	A2	64	55.67	220.65	0.346	13.84	0.00	<0.02	1.608	17	18.40	1.15	51.7	0.00
Gulf-38	Nov 98	6	Woerner T. Farm, Big Bertha	A3	105	58.69	232.31	0.337	14.75	0.78	<0.02	1.359	20	10.59	<0.05	>50	0.00
Gulf-39	Nov 98	20	Woerner T. Farm, Lieterman	A3	101	62.33	236.77	0.361	14.92	0.15	<0.02	0.959	16	0.00	<0.05	>50	0.68

Table 1 (continued)
Dissolved Gas Data and Ages of the Baldwin County Ground Waters and Natural Gas Data of the Meyer Gas Sand

Sample Name	Sample Date	Figure 1 Reference	Local Well Name	Aquifer	Depth m	^{4}He μcc/kg	Ne μcc/kg	Ar cc/kg	N_2 cc/kg	Excess N_2 cc/kg	CH_4 cc/kg	R/R$_{air}$	Temp. °C	^{3}He* T.U.	^{3}H T.U.	^{3}He/^{3}H Age Years	^{4}He$_{rad}$ μcc/kg
Ground Water																	
Gulf-40	Nov 98	21	Grand Hotel. Hole #9	A2	49	56.05	219.62	0.315	13.62	0.62	<0.02	1.076	23	1.39	0.37	37.9	0.00
Gulf-41	Nov 98	22	Grand Hotel. Hole #14	A2	38	55.81	225.83	0.331	13.80	0.18	<0.02	1.525	20	14.62	2.60	36.0	0.00
Gulf-43	Nov 98	23	Flowerwood. Block 50	A2	45	53.22	205.86	0.351	13.97	0.35	<0.02	1.300	15	7.48	2.07	32.1	1.19
Gulf-44	Nov 98	24	Flowerwood. Block 58	A2	43	51.03	200.61	0.294	12.04	0.20	<0.02	1.577	26	16.15	1.69	42.1	0.00
Gulf-45	Nov 98	25	Fairhope #1	A2	68	52.01	202.92	0.309	12.71	0.36	<0.02	1.355	22	9.80	1.76	35.3	0.00
Gulf-46	Nov 98	26	Fairhope #6	A3	91	58.00	200.22	0.305	13.71	1.56	<0.02	0.992	23	10.32	<0.05	>50	5.47
Gulf-47	Oct 99	27	Bay Minnette #2	A2	62	54.32	206.11	0.349	13.24	0.00	<0.02	1.591	16	19.40	1.36	47.7	0.00
Gulf-48	Oct 99	28	Bay Minnette #4	A2	56	52.10	207.68	0.352	13.76	0.05	<0.02	1.454	15	14.73	1.82	38.0	0.00
Gulf-49	Oct 99	29	Bay Minnette #3	A2	56	51.52	209.45	0.359	13.59	0.00	<0.02	1.318	14	10.22	1.64	33.2	0.00
Gulf-50	Oct 99	30	Bay Minnette #5	A2	81	56.15	210.03	0.325	13.13	0.14	<0.02	1.417	20	15.66	2.05	37.2	1.46
Gulf-51	Oct 99	31	Tensaw	A3	91	1259.81	236.63	0.381	16.08	0.75	<0.02	0.128	13	44.90	<0.05	>200	1199.17
Gulf-52	Oct 99	32	Stockton #1	A3	63	148.80	224.32	0.333	14.11	0.49	<0.02	0.411	20	2.10	<0.05	>100	89.81
Gulf-58	Oct 99	33	Orange Beach. new well	*	*	65.99	249.48	0.337	14.96	0.50	<0.02	0.965	22	0.21	<0.05	>50	0.00
Gulf-59	Oct 99	34	Atmore Trammel, shallow	A2	40	57.74	231.01	0.321	14.34	0.80	<0.02	1.201	23	4.74	0.44	37.2	0.00
Gulf-60	Oct 99	35	Atmore Trammel, deep	A2	71	57.54	228.23	0.348	14.46	0.29	0.02	1.231	18	8.28	0.85	39.1	0.00
Gulf-61	Oct 99	36	Atmore Fountain #2	A2	107	52.59	205.98	0.300	12.86	0.64	<0.02	1.881	25	25.06	2.24	43.9	0.00
Gulf-62	Oct 99	37	Rabun	A3	130	*	*	*	*	*	*	*	*	*	<0.05	>100	*
Gulf-63	May 01	26	Fairhope #6	A3	91	54.69	219.11	0.314	12.80	0.00	<0.02	1.078	23	2.27	1.31	18.1	0.00
Gulf-64	May 01	19	Riveria #12	A3	66	59.06	216.34	0.343	14.45	0.76	<0.02	0.976	18	2.78	0.61	31.0	6.03
Gulf-65	May 01	20	Woerner T. Farm. Lieterman	A3	101	54.52	204.38	0.342	14.17	0.84	<0.02	0.994	17	2.94	<0.05	>50	5.21
Gulf-66	May 01	15	Woerner T. Farm. Tindall	A3	91	70.56	232.96	0.351	14.46	0.06	<0.02	0.834	18	0.72	0.26	24.0	12.74
Gulf-67	May 01	17	Woerner T. Farm. Magnolia	A3	158	70.40	219.58	0.347	14.42	0.52	<0.02	0.839	17	3.02	<0.05	>50	16.57
Gulf-68	May 01	16	Gulf Shores Utilities #9	A3	113	67.00	264.02	0.357	15.32	0.00	<0.02	0.973	19	0.00	*	*	0.00
			Equilibrium at 20°C	‡	‡	44.78	185.32	0.313	11.95	0.00	69.65	1	‡	0.00	‡	‡	‡
Natural Gas						(ppm)	(ppb)	(ppm)	(%)		(%)						
WMS	May 97	WMS	W. Magnolia Springs	‡	~400	155.26	<500	194.17	2.07	‡	95.53	0.548	‡	‡	‡	‡	‡
SMK	May 97	SMK	Smacko. Gulf State Park	‡	~400	191.64	<500	78.71	2.41	‡	95.85	0.841	‡	‡	‡	‡	‡

The sample locations are shown in Figure 1: *data not available; ‡not applicable

with 18 MΩ water and acidified with ultrapure nitric acid. The analyses were done on the VG ICP-MS Plasma Quad II+ at the University of Rochester according to U.S. Environmental Protection Agency Method 200.8 (Long and Martin 1991). To correct for drift, indium and bismuth were added as internal standards for the sediment digestions. A five-point calibration curve was created, and the standards, traceable to NIST, were analyzed before and after a set of samples. Two NIST water standards (NIST 1640 and NIST 1643d) were analyzed as unknowns. Based on these results, the errors in the trace metal concentration analyses were < 5% for the samples measured on the VG ICP-MS Plasma Quad II+.

Results

A2 Aquifer

Table 1 lists the dissolved gas concentrations (helium, neon, nitrogen, argon, and methane), ^{3}H, and ^{3}H/^{3}He ages for each ground water sample. Using these data, we developed a schematic cross section of the ground water flow (Figure 2) in Baldwin County from northwest to southeast where most of the wells are projected to the A–A′ line in Figure 1. The samples are divided between the A2 and A3 aquifers based on their ^{3}H content and ground water age (Figure 3).

Tritium (^{3}H) is a radioactive isotope of hydrogen ($t_{1/2}$ = 12.43 years), produced naturally in the upper atmosphere, and becomes part of the water molecule. Prior to aboveground nuclear testing, tritium levels in precipitation are estimated to be between 0.5 and 20 TU (Kaufman and Libby 1954; Robertson and Cherry 1989). Anthropogenic tritium, created in postnuclear age environments, reached peak concentrations in 1963 (the bomb-pulse) and identifies ground water recharged after 1950. By using the presence of anthropogenic tritium to indicate nuclear age water in our samples, we observe that 100% of the samples in the A2 that contain tritium (0.37 to 7.16 TU) have R/R$_{air}$ > 1 that allows for the calculation of ^{3}H/^{3}He ground water ages (Solomon et al. 1992; Solomon et al. 1995).

In the A3 aquifer, 88% of the samples contain < 0.2 TU and have R/R$_{air}$ < 1. Although three samples from the A3 aquifer (Gulf 63, 64, and 66) contained no tritium when sampled during 1996 through 1999, they had measurable tritium in 2001, suggesting that some areas are experiencing localized drawdown of the aquifer, causing young and old waters to mix. As shown by the Palmer Drought Severity Index (PDSI) from the NCDC web page, Baldwin and Mobile counties had normal rainfall and wetness conditions from 1996 through 1998 (October 1996 PDSI = –0.88, May 1997 PDSI = +0.99, and November 1998 PDSI = +2.27). Since 1999, Baldwin County experienced increasingly dry conditions (October 1999, PDSI = –1.79; May 2001, PDSI = –3.57). Drought conditions and subsequent greater pumping of the ground water produced larger cones of depression around the wells, causing the drawdown of tritiated water and the resultant mixing of older and younger water in the wells.

In these highly conductive sediments dominantly composed of fine quartz sand, rain (167 cm/yr) quickly recharges to depth. The ground water ages cluster near the
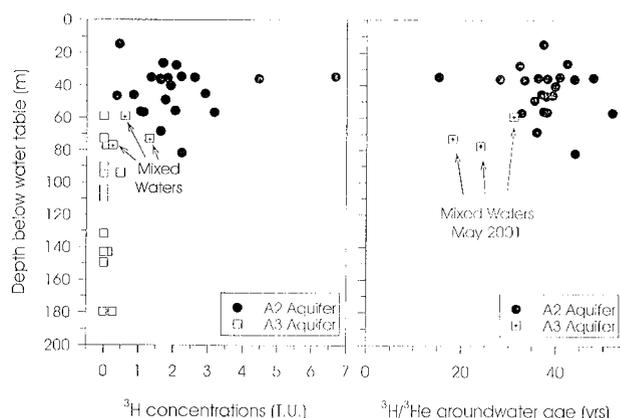
Figure 3. Tritium concentrations and ground water ages vs. depth in Baldwin County. The ground water age vs. depth plot shows the vertical velocities and associated recharge values in the A2 aquifer. The ground water of the A2 aquifer has detectable tritium and is at least 40 years old, but less than 80 years old. In 1998 and 1999, the A3 aquifer wells had either no measurable levels or very low concentrations of tritium. However, in the spring of 2001, tritium was detected in three A3 well samples. Greater than usual ground water withdrawals, due to a prolonged drought beginning in 1999, may have introduced tritiated water into the shallow part of the A3 aquifer. The elevations of A2 and A3 wells are different from their respective depths below the water table.

bomb-pulse in the A2 aquifer with an average ground water residence time of 36 ± 7 years. Figure 3 compares ^{3}H concentrations and ground water ages (^{3}H/^{3}He) to depth and establishes the age-depth relationship. The elevations of A2 and A3 wells are different from their respective depths below the land surface. We are plotting the depth below the water table in Figure 3 because the ^{3}H clock begins once the water parcel enters the aquifer system and is isolated from atmospheric exchange.

Long well-screen lengths that allow ground water of different ^{3}H/^{3}He ages to mix cause some of the scatter in the age-depth relationship observed in Figure 3. The bomb-pulse water with high ^{3}He and ^{3}He* (tritiogenic helium is determined by subtracting the estimated ^{3}He$_{excess\ air}$, ^{3}He$_{solubility}$, and ^{3}He$_{radiogenic}$ from the total measured ^{3}He [Schlosser et al. 1989]) has a disproportionate effect on ground water ages, leading to some scatter in the ^{3}H/^{3}He ground water age vs. depth relation. However, we are confident that the well samples with tritium, no excess radiogenic helium, and R/R$_{air}$ > 1 have reasonable ^{3}H/^{3}He ages, and that those ground water samples with R/R$_{air}$ < 1 are prenuclear. The age distribution demonstrates that bomb-pulse water has recharged to depths of 30 to 50 m below the water table with an average age of 36 years. From that measurement, we estimate an average vertical velocity of 1.35 ± 0.5 m/yr corresponding to a ground water recharge rate of 40 ± 16 cm/yr or ~24% of the precipitation, a reasonable estimate given the agriculture of the region and high evapotranspiration potential. A considerable amount of water that flows into the aquifers must ultimately be balanced by discharge to the Gulf of Mexico because there are no major regional rivers in Baldwin County. Shallow rivers (< 5 m) receive recharge very locally and that surface component does not affect the estimate of recharge rates that travel deeper in the aquifer.

C.B. Dowling et al. GROUND WATER 42, no. 3: 401–417   407

In the upper aquifer (A2), the ground water samples have ^{4}He, neon, and argon that lie on the air addition line trend away from the solubility concentrations at ~20° ± 3°C (Figure 4). The individual calculated recharge temperature (modified from Ballentine and Hall [1999] and Aeschbach-Hertig et al. [1999], and originally discussed in Solomon et al. [1992] and Solomon et al. [1995]) for each well ranges from 16° to 23°C with an average of 20° ± 3°C. Excess air typically results from water table fluctuations that trap air bubbles within the sediment and/or the introduction of air from the well pumps. We use only neon, N_2, and argon concentrations to correct for excess air rather than the more complete analysis that also measures krypton and xenon because the recharge temperatures are used for the resolution of the tritiogenic helium–3 (^{3}He*), not for paleotemperature profiles. These samples have little excess air, so the correction is small, and most of the error comes from the uncertainty in the argon concentration (± 2%). The errors associated with the recharge temperatures generate only a minor change to the solubility calculation of the ^{4}He due to the insensitivity of ^{4}He to recharge temperature.

Excess dissolved N_2 (above air addition levels) in the ground water results from denitrification, a process in which microbes reduce nitrate and nitrite to nitrogen gas. While nitrate levels in the A2 aquifer range from 3 to 269 µmol/L (mean 59 ± 76 µmol/L and median 26.8 µmol/L) (Carey et al., in review), there is no correlation between excess N_2 and NO_3 (Figure 5). However, excess N_2 in a number of samples suggests a small amount of denitrification (excess N_2 > 0.5 cc/kg) may occur. Nitrate, a modern pollutant in ground water, will be a long-term problem for Baldwin County.

A3 Aquifer

The ground water of the upper part of the A3 aquifer (Gulf 07, 30, 31, 36, 38, 39, 46, 65, and 67) has tritium typically < 0.5 TU, indicative of water recharged prior to 1960 (bomb peak water has 3 to 5 TU), and is estimated to be older than 40 years. The waters that contain detectable tritium (0.05 to 0.5 TU) are at least 40 years old, but < 80 years old (based on an estimate of transverse dispersion [D ≈ l²/t; 0.2–0.6 m²/yr] using the length [l] of screens [3–6 m] and the ground water residence time [t]). During the 1998 and 1999 sampling campaigns, several A3 aquifer wells had no measurable tritium; however, in the spring of 2001, tritium was detected in three A3 well samples. These wells were sampled after two years of dry conditions as expressed by the PDSI. Greater than usual ground water withdrawals during this time may have drawn tritiated water into the shallow part of the A3 aquifer (Figure 3). The ground water in the lower part of aquifer A3 is tritium dead (0.05 TU) and most likely older than 80 years. There are no substantial differences in dissolved gas concentrations between the A2 and A3 aquifers because the A3 aquifer has a calculated recharge temperature of 19° ± 3°C. The A3 aquifer does differ from the A2 in that it contains considerably less nitrate (0.7 ± 0.6 µmol/L), demonstrating that agricultural NO_3 is dominantly a mid- to late–20th century contaminant that has not infiltrated into the A3 aquifer (Carey et al., in review).

Discussion

^{4}He Age Dating

In the future, water utilities are planning to increase their withdrawals of A3 ground water. Ground water ages
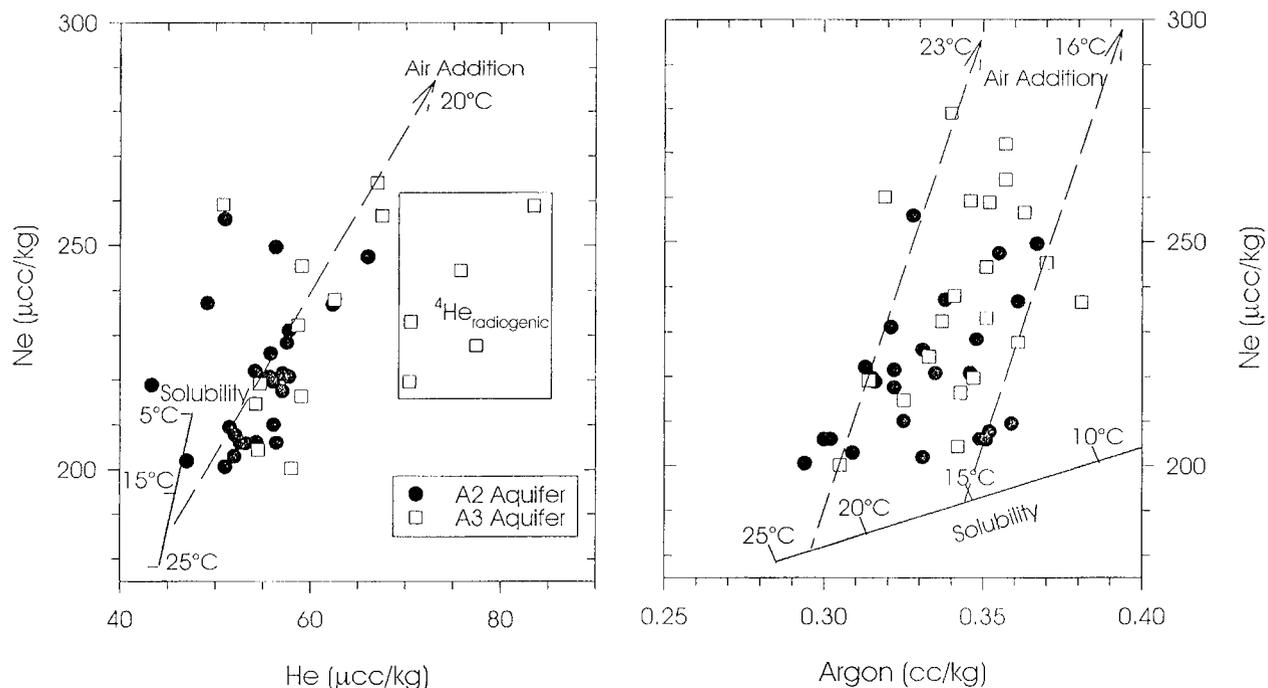
Figure 4. Dissolved neon vs. helium and argon. Typically, the A2 aquifer has ground water samples with ^{4}He, neon, and argon at or near the air addition line indicating excess air in the samples. The air addition typically ranges from 16° to 22°C. Based on the dissolved gas data, the recharge temperature for the A2 aquifer is 20° ± 3°C and the A3 aquifer is 19° ± 3°C. Some samples from the A3 aquifer also lie on the air addition line, but most show excess helium from in situ release from quartz.
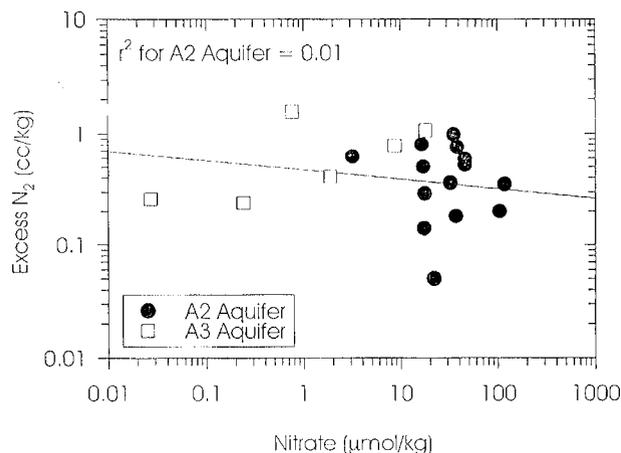
Figure 5. Excess N_2 vs. nitrate. Excess nitrogen and nitrate have an inverse correlation in the A2 aquifer, suggesting that denitrification is not an important process. Even though a small amount of denitrification (excess $N_2 > 0.5$ cc/kg) may occur, the nitrate will remain in the ground water for a long period of time.

and flow estimates can be used to determine safe ground water withdrawal amounts for domestic and agricultural use. To establish approximate ground water ages for those samples that did not contain tritium and have $R/R_{air} < 1$, we examined the release of ^4He from the Alabama aquifer sands dominated by quartz that contain a small amount of uranium and thorium (Table 2b). We excluded ground water samples from the northwest part of Baldwin County

(e.g., Tensaw, Stockton) because the changes in structural geology (e.g., faults), ground water geochemistry, and potentiometric contours show that the samples are not part of the same ground water flow system (Robinson et al. 1996a, 1996b). We focused on those ground water samples that contained a clear excess of ^4He above solubility (Figure 4).

We studied two kinds of sediment samples—quartz separates from the cliffs of Ecor Rouge (A2 aquifer—Fairhope) and drill core samples from the Pensacola Clay (GSA 5386). Only results from the helium release experiments from the Ecor Rouge quartz samples were used for the dissolved helium accumulation model in ground water. The drill core samples from the Pensacola Clay (GSA 5386) were used only for the diffusion model of the Meyer Gas into the lower part of the A3 aquifer from the underlying Pensacola Clay. The accumulation of radiogenic ^4He in water could be used as an indicator of ground water age if ^4He release rate from the aquifer protolith can be established (Solomon et al. 1996; Hunt 2000). The age dating method assumes the diffusional release of helium stored within the quartz grains to the aquifer is valid in areas of moderate recharge and where deep crustal sources of ^4He can be ruled out. As we have demonstrated earlier, the Baldwin County aquifers receive adequate recharge (40 ± 16 cm/yr). Further in our discussion, we will establish that the underlying sources of ^4He (e.g., Meyer Gas) are negligible.

We estimate the release of helium from quartz by modeling the diffusional release over time. Alpha particle generation (^4He) of the uranium–thorium series produces ^{21}Ne by ^{18}O (α, n) ^{21}Ne with a constant $^4He/^{21}Ne$ ratio of 2.2 ×

Table 2a
Noble Gas Data for the Ecor Rouge Outcrop

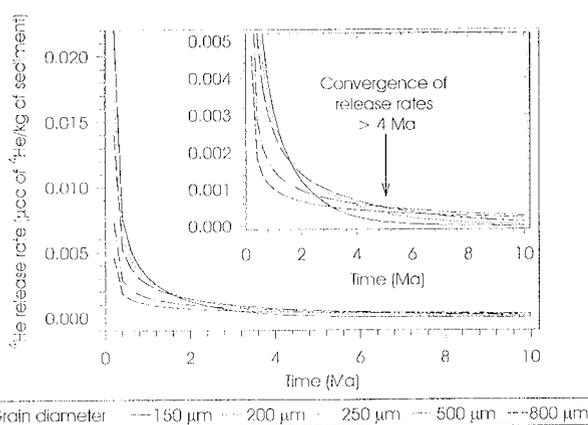| Sample Number	^4He µcc/g	^{21}Ne pcc/g	$^{21}Ne_{excess}$ pcc/g	$^4He/^{22}Ne$	$^4He/^{21}Ne_{excess}$ ($\times 10^{-6}$)	^4He Initial	% Loss of ^4He
Ecor Rouge-1	27.34	6.1	0.456	140316	59.91	10.04	None
Ecor Rouge-2	1.44	7.6	0.220	12394	6.56	4.83	70.2
Ecor Rouge-4	1.05	4.5	0.134	6979	7.85	2.95	64.3
Ecor Rouge-7	0.40	9.2	0.000	1248	—	—	—
Ecor Rouge-8A	0.93	3.6	0.301	3668	3.09	6.61	86.0

Table 2b
Noble Gas and Select Trace Metal Data for the GSA 5386 Drill Core

Sample Number	Depth m	R/R_{air}	^4He µcc/g	^3He pcc/g	^{21}Ne pcc/g	$^{21}Ne_{excess}$ pcc/g	$^4He/^{22}Ne$	$^4He/^{21}Ne_{ex.}$ ($\times 10^{-6}$)	^4He Initial	% Loss of ^4He	Th ppm	U ppm	Th/U
GSA 5386 (1240-1250) Blk	378–381	0.11	2.05	0.241	13.7	0.375	149	5.48	9.36	78.1	2.74	0.90	3.03
GSA 5386 (1280-1290) Blk	390–393	0.04	2.81	0.045	15.1	0.358	186	7.83	8.96	68.7	1.66	0.68	2.44
GSA 5386 (1430-1460) Qtz	436–445	0.13	1.64	0.227	11.6	0.418	142	3.93	10.45	84.3	*	*	*
GSA 5386 (1440-1450) Blk	439–442	0.07	2.61	0.135	14.2	0.705	183	3.70	17.62	85.2	2.67	0.77	3.48
GSA 5386 (Gas sand) Qtz	390–396	0.29	4.17	1.482	11.5	0.270	362	15.41	6.76	38.4	0.95	0.72	1.31

*Sample not analyzed

10^7 (Yatsevich and Honda 1997). Assuming a grain has an initially homogeneous distribution of ^{4}He and ^{21}Ne, then a simple spherical release model can be used for ^{4}He with ^{21}Ne being retained. The initial ^{4}He concentration can be estimated by multiplying the $(^4$He/^{21}Ne)$_{production\ ratio}$ by ^{21}Ne. Over time, the ^{4}He in the grain diffuses out and the helium concentration in the grain decreases, while ^{21}Ne levels rise slightly from uranium–thorium decay. The rate of ^{4}He loss is controlled by the initial ^{4}He concentration, the ^{4}He distribution in the grain, and the grain size. Thus, the initial diffusional release of ^{4}He follows an exponential decrease with time from an initial homogeneous distribution, as ^{4}He is quickly lost from the grain boundaries. In this environment, for grains of 150 to 800 μm diameter, the ^{4}He release rates becomes linear by 5 Ma and the model is equivalent to the simple mass transfer model of Solomon et al. (1996). For these low uranium sands, the release rate is not entirely sensitive to grain size after 5 Ma as shown in Figure 6, so it approaches steady-state release rate, which is equivalent to in situ production at 5 Ma (the age of the deposit). Conversely, for fine-grained clays, the release rate is very rapid for the first 100 ka (because of the clays' large surface area/volume ratio) and quickly approaches to steady-state with ^{4}He production (Hunt et al. 2000).

Using the measured helium and neon concentrations, calculated ^{21}Ne$_{excess}$ and theoretical ^{4}He/^{21}Ne production ratio (2.2×10^7) in the core samples, the initial concentration of helium is determined to be 5 ± 2 μcc/g (Table 2a) for the measured diameters of 150 to 800 μm for the Ecor Rouge quartz separates. We use our measured helium diffusion rate from quartz of 1.5×10^{-19} cm^2/sec at 20°C (recharge temperature for the A2 and A3 aquifers) and the total He$_{radiogenic}$ in the water to assess the age of the ground water (Solomon et al. 1996). Using the average initial ^{4}He concentration and the diffusion rate at 20°C, the model from Hunt et al. (2000) estimates a release rate from the quartz grains to be 0.0004 μcc (He)/kg (quartz)/yr (Figure 6), or a level about two to three times higher than the steady-state production from ura-

nium and thorium (1.5×10^{-4} μcc/kg/yr). The modeled accumulation rate of ^{4}He in the water is 0.0032 μcc/kg(water)/yr or 313 years for 1 μcc of radiogenic helium to accumulate in 1 kg of water. Using the same initial conditions as our helium accumulation model and the mass transfer model of Solomon et al. (1996), an accumulation rate of 2.2 ± 0.8 μcc/kg (water)/1000 years or 0.0022 μcc/kg (water)/yr is calculated. Based on these models, the ground water ages for the five samples that contain excess helium range from 2000 to 7500 years, becoming progressively older as they become deeper and closer to the sea.

The Gulf State Park well, which has methane, the highest ^{4}He (30 times solubility), and an R/R$_{air}$ value of 0.525, is excluded from the helium accumulation model. This well contains natural gas components (^{4}He, ^{3}He, and CH$_4$) in the ground water sample, attributed to a flux of He and CH$_4$ from the natural methane reservoir in the Meyer Gas Sand at 400 m depth in the Pensacola Clay. The gas well sample (West Magnolia Springs) and the Gulf State Park well have similar R/R$_{air}$ (0.548) and ^{4}He/CH$_4$ ratios (Table 1) that are quite anomalous for the Gulf Coast and passive tectonic settings in general. The helium and methane dissolve into the pore waters of the Pensacola Clay and then diffuse upward into the A3 aquifer; they are not from the diffusional release of ^{4}He from the quartz grains. In the A3 aquifer, the high CH$_4$, ^{4}He, and ^{3}He concentrations are observed only in the Gulf State Park well and not in any of the wells higher in the aquifer with the possible exception of the Orange Beach deep well. The excess ^{4}He in the deep Orange Beach well (Gulf 04, 33) is greater than can be explained by leakage from quartz and may result from the tail of the flux from the Pensacola Clay. The helium and CH$_4$ fluxes from the Pensacola Clay are confined close to the base of the A3 aquifer, indicating that substantial horizontal ground water flow (V$_x$) is occurring near the sea water/fresh water transition zone (Figure 7). If the ground water were stagnant and did not flow through the A3 aquifer, then all the samples would contain CH$_4$ and ^{4}He and have a similar R/R$_{air}$. Because only two samples in the A3 aquifer have elevated levels of ^{4}He and CH$_4$ and a comparable R/R$_{air}$, the dissolved ^{4}He in the ground water samples is not coming from an underlying source (e.g., Meyer Gas), but from in situ production. In the nitrate flux discussion, we expand this model and estimate the horizontal velocity based on the shape of the methane and helium plume, and flux from the Pensacola Clay.

Meyer Gas Sand

The Meyer Gas Sand occurs only in southern Baldwin County and has an unusual helium isotopic signature, which can be seen in the elevated ^{3}He and ^{4}He concentrations of the West Magnolia Springs and Smacko natural gas wells. The natural gas affects the helium concentrations and R/R$_{air}$ in the Meyer Gas Sand quartz and the other sediment samples from the Pensacola Clay (Table 2b, Figure 8). The Meyer Gas Sand quartz has an R/R$_{air}$ value of 0.29, ^{3}He concentration of 1.48 pcc/g, and ^{4}He content of 4.17 μcc/g that are considerably higher than the average sediments above or below (R/R$_{air}$ = 0.09 ± 0.04, ^{3}He = 0.16 ± 0.09 pcc/g, ^{4}He = 2.3 ± 0.5 μcc/g). The ^{4}He (from uranium–
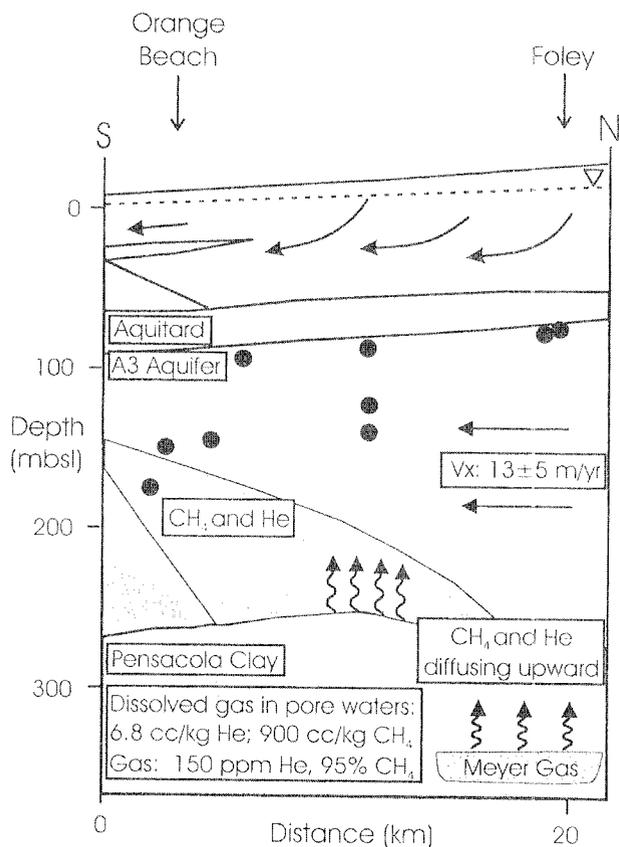

Figure 6. Modeled ^{4}He release rate from sediment vs. time. The modeled helium release rates for select grain diameters (150 to 800 μm), an initial helium concentration of 5 ± 2 μcc/g, and a diffusion coefficient of 1.5 × 10^{-19} cm^2/sec are shown. This model shows the helium release rate from the quartz grains to be 0.0004 μcc/kg(quartz)/yr which is comparable to, but slightly higher than, the steady-state diffusion from uranium and thorium.

Figure 7. Ground water samples in the deep A3 aquifer of southern Baldwin County. The natural gas components (^{4}He, ^{3}He, and CH_4) in the deepest ground water sample (Gulf State Park) are attributed to the flux of gas from the natural methane reservoir found in the Meyer Gas Sand. The helium and methane dissolve into the pore waters of the Pensacola Clay and then diffuse upward into the A3 aquifer. Substantial ground water flow (V_x) is occurring in the A3 aquifer since the helium and CH_4 fluxes from the Pensacola Clay are confined close to the lower limit of the A3 aquifer.

thorium decay series) diffusion from quartz occurs in the Pensacola Clay sediments above and below the Meyer Gas Sand quartz, and the estimated helium loss from diffusion is > 70%. Because the Meyer Gas Sand already has high concentrations of ^{3}He and ^{4}He from the natural gas reservoir, the estimated He loss through diffusion from the Meyer Gas Sand quartz is < 30%. The natural gas infuses the Meyer Gas Sand quartz with ^{3}He and ^{4}He, giving rise to elevated noble gas concentrations and distinctive ratios. One explanation for the ^{3}He and ^{4}He is that there exists a finite solubility of helium in quartz that leads to the unusual ratios and limits diffusional loss. An estimate of helium solubility in quartz at 400 m (40 atm) is 600 μcc/g/atm (Poreda 1982; Hunt et al. 2000). The finite solubility of helium in quartz may have important implications for the assumption of zero helium at the boundary and for uranium–helium systematics in apatites, which assumes a complete loss of ^{4}He and not a partial reset at depth. This same effect can be seen in Medina quartz gas sands (Hunt et al. 2000).

We do not know the source of the elevated ^{3}He natural gas, although other researchers have observed similar findings (Hiyagon and Kennedy 1992). Typical natural gas

reservoirs have ^{3}He/^{4}He < 0.05R$_{air}$ and are dominated by the loss of ^{4}He from uranium-rich sediment (Poreda et al. 1986). The presence of high ^{3}He/^{4}He gas causes the Meyer Gas Sand quartz to have elevated ^{3}He/^{4}He, which is distinctive from the sediment above and below that does not have high R/R$_{air}$ or ^{3}He levels (Table 2b, Figure 8). The gases also do not fit a simple mixing model between mantle and crustal gases in ^{3}He/^{4}He-CH_4/^{4}He space. In the absence of tectonic or magmatic activity (of which there is none along the southern coastline of the United States), the anomalous ^{3}He values may be from interplanetary dust particles (IDP) in the sediment or cosmic ray production of ^{3}He in the protolith of the Pensacola Clay. IDP typically retains ^{3}He at 20°C unless the mineral structure breaks down (Farley 1995). Cosmic ray production of ^{3}He in quartz would also leave a relict ^{21}Ne signature and require at least 1 Ma years of surface exposure at sea level, an unreasonable estimate for most fluvial settings. We cannot rule out cosmic ray production in the quartz as the origin of elevated ^{3}He in the Meyer Gas reservoir samples, but the release of ^{3}He from IDP appears more likely. The unique ^{3}He/^{4}He ratio in the Meyer Gas serves as the fingerprint for helium and CH_4 release from the Pensacola Clay.

Ground Water Withdrawal

As communities along the Gulf Coast look to exploit ground water resources that are not contaminated by agriculture or industry, they are withdrawing more ground water from the deep A3 aquifer. The question that needs to be
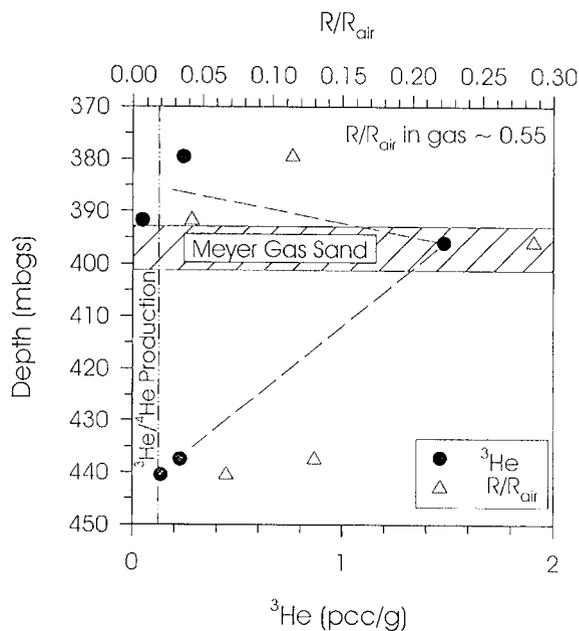
Figure 8. ^{3}He and R/R$_{air}$ vs. depth in the Pensacola Clay (GSA 5386). The Meyer Gas Sand quartz in the Pensacola Clay (drill core GSA 5386, Table 2b) has unusually high amounts of ^{4}He and ^{3}He compared to the sediment samples above and below it. Because the Meyer Gas Sand already has high concentrations of ^{3}He and ^{4}He from the natural gas reservoir, the estimated helium loss through diffusion from the Meyer Gas Sand quartz is < 30% (compared to the estimated 70% loss of the surrounding sediments). The natural gas infuses the Meyer Gas Sand quartz with ^{3}He and ^{4}He, giving rise to elevated noble gas concentrations and distinctive ratios.
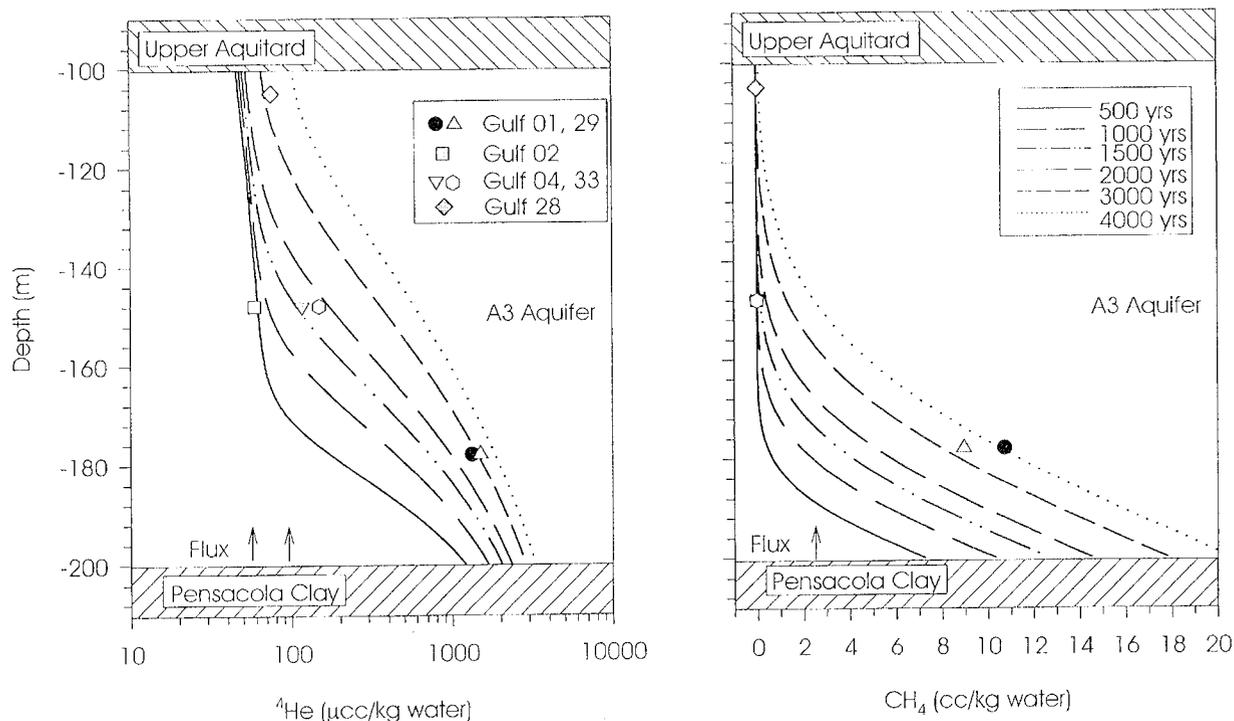
Figure 9. The basal flux model of ^{4}He and CH_4 from the Pensacola Clay into the A3 aquifer. The symbols indicate the measured concentrations of ^{4}He and CH_4 in the deep A3 ground water. The CH_4 and ^{4}He fluxes calculated from the one-dimensional model are 0.21 cc/m^2/yr and 6000 μcc/m^2/yr, respectively. Because the natural situation is more complex, the one-dimensional model can provide only limits to the horizontal velocity. The regional extent of the Meyer Gas Sand and the flux from the Pensacola Clay (controlled by permeability and effective diffusion coefficients) are some of the unknowns of this model. Because the highest ^{4}He and CH_4 concentrations are found only in the deepest sample (Gulf State Park) and not measured in the other samples, the ground water has to be flowing through the A3 aquifer and suppressing the ^{4}He and CH_4 plume from the Pensacola Clay.

addressed is if recharge can sustain the elevated withdrawal rate. The question centers on whether the ground water in the A3 aquifer is stagnant or discharging at a significant rate into the Gulf of Mexico. Our calculations of submarine discharge are based on three lines of evidence. The ^{3}H/^{3}He data from A3 wells in northern Baldwin County (the recharge zone for A3) suggest that < 10% of the total recharge flows into the A3 aquifer, which generates a ground water flux of 2.4 ± 0.9 × 10^8 m^3/yr to the sea. The ^{4}He age of the oldest ground water samples gives an approximate ground water travel time between the recharge area and the wells (a distance < 100 km), from which we can roughly estimate the horizontal velocity of the deeper aquifer at 13 ± 5 m/yr. This suggests that substantial ground water discharge into the coastal ocean is occurring from the A3 aquifer. The shape of the He-CH$_4$ plume emanating from the Pensacola Clay also constrains the fresh water flux estimate to the Gulf of Mexico. Simply put, if the ground water were stagnant in the A3 aquifer, then the natural gas and helium from the Pensacola Clay would migrate to the A3, resulting in high levels of dissolved CH$_4$ and helium from the ground water wells throughout the entire aquifer. Instead, only the lowermost and most seaward well contains elevated CH$_4$ and He concentrations.

The CH$_4$ and ^{4}He fluxes from the Pensacola Clay, which are calculated to be 0.018 cc/m^2/yr and 3000 μcc/m^2/yr, respectively, can further constrain the ground water velocity (Figure 7). We base these fluxes on the sol-

ubility of helium and methane gas in water at 40 atm (using the West Magnolia Gas) (Table 1), the effective aqueous diffusion coefficients (10% of the free solution value), and porosity of the clay (20 ± 5%). We apply the basal fluxes to a one-dimensional model of the A3 aquifer to determine the height of the plume within the A3 (Figure 9). The major uncertainties that affect the plume height are the regional extent of the Meyer Gas Sand (10 ± 5 km) and the transverse dispersion coefficient in the A3 (3.15 × 10^7 cm^2/sec). The horizontal velocity of the A3 ground water relates to the (one-dimensional diffusion) time (3000 ± 1000 yrs) and the width of the Meyer Gas Sand (10 ± 5 km). The flow based on this model is ~3 ± 1 m/yr, lower than the calculation of 13 ± 5 m/yr based on ^{4}He ground water age, but still in reasonable agreement given model uncertainties. If we double the width of the Meyer Gas Sand, we would double the horizontal velocity. Regardless of the uncertainties, the highest ^{4}He and CH$_4$ concentrations are found only in the deepest sample (Gulf State Park) closest to the Pensacola Clay; the other A3 well samples have only minor ^{4}He, indicating that the A3 ground water is indeed discharging into the Gulf of Mexico and suppressing the height of the upward diffusing ^{4}He and CH$_4$ plume from the Pensacola Clay. The horizontal velocity (Vx) of ~3 m/yr translates to a discharge of 5.6 × 10^7 m^3/yr. More data from a multilevel well across the sea water/fresh water transition zone would advance our understanding of the ground water resources in the A3 aquifer.

Nitrate Flux

As in most hydrologic systems, precipitation will be distributed between evapotranspiration to the atmosphere, runoff to the rivers, and recharge to the aquifer. In Baldwin County, only a small portion of recharge contributes water to the minor rivers and streams found mostly in the southern third of the county. The small river system cannot accommodate the volume of water that falls as precipitation in the region. In large regional systems such as Baldwin County, the recharged water does not travel for 100 km at the aquifer surface, but rather penetrates deeply (40 to 60 m) into the aquifer. The vertical hydraulic gradients always are downward and the horizontal gradients are very low. Such conditions approximate the simplest flow conditions for porous media; therefore, the water packet becomes older as it flows deeper (vertical velocity) in the aquifer and toward the ocean (horizontal velocity). We estimate the recharge by measuring the time (ground water age) it takes to descend to a given depth. The annual recharge that occurs over the entire region (km^3/yr) must discharge into the coastal oceans because discharge must eventually equal recharge. At present, the ground water resources of Baldwin County are underutilized in that ~5.6×10^7 m^3/yr of ground water, or 3% of our recharge estimate, is withdrawn for agricultural and domestic use (Robinson et al. 1996a). The average A2 aquifer recharge rate of 40 ± 16 cm/yr considers only that portion of ground water that flows beneath the shallow river system and discharges directly to the ocean. This flux must be balanced by the subsurface ground water discharge to the Gulf of Mexico and forms the basis for our mass transport calculations.

The recharge and flux estimates from the A2 are much simpler to calculate because they rely on $^3H/^3He$ travel time and are consistent with the recharge percentage of total precipitation. We use our estimate of travel times for ground water to establish the ground water flux from Baldwin County to the Gulf of Mexico. By using the average recharge rate (40 ± 16 cm/yr) and surface area of Baldwin County (4481 km^2), we assume a steady-state system in which flux in (recharge) = flux out (subsurface discharge).

$$\text{Surface Area } (m^2) \times \text{Recharge Rate } (m/yr)$$
$$= \text{Submarine Discharge } (m^3/yr)$$

This calculation gives an annual subsurface discharge from Baldwin County to the Gulf of Mexico of 1.9 ± 0.8 × 10^9 m^3/yr, equivalent to ~3% and 0.3% of the Mobile-Alabama River System (7.1 × 10^{10} m^3/yr) and Mississippi River System (5.8 × 10^{11} m^3/yr) water fluxes to the Gulf of Mexico, respectively. An assumption in our calculation of a ground water system in steady state is reasonable given the short residence time of the A2 aquifer and the highly conductive nature of the sediments. Our submarine flux estimate is independent of seasonality and short-term perturbations because it is based on the long-term average ground water recharge estimated from $^3H/^3He$ ground water ages (40 ± 16 cm/yr) and the average dissolved nitrate concentrations. However, our discharge estimates are significantly lower than aquifer test results that yield an average transmissivity of 253 ± 141 m^2/day (range 65 to 502 m^2/day) (Robinson et al. 1996a). These values result in the subma-

rine discharge estimate of 1.2 ± 0.6 × 10^{10} m^3/yr, 2% of the Mississippi River System input, or 1.5 times more than the annual precipitation that Baldwin County receives (7.5 × 10^9 m^3/yr). Aquifer tests, although susceptible to local heterogeneity in permeability, demonstrate that the A2 aquifer is highly conductive and support the $^3H/^3He$ recharge estimates that integrate the sediment permeability over the entire flowpath.

There are few published studies concerning submarine ground water discharge into the Gulf of Mexico (Bugna et al. 1996; Cable et al. 1996a; Cable et al. 1996b; Corbett et al. 1999; Krest et al. 1999; Pope et al. 2001). The Baldwin County site may represent one end member for submarine ground water discharge. There exists a thick (200 m) and wide (100 km) section of coarse-grained siliciclastic unconsolidated sediments that rapidly transmit water to depth (the high transmissivity of the aquifer is highlighted by Robinson et al. [1996a]). Rainfall on the wide coastal plain does not discharge to rivers, but rather predominantly enters the aquifer. This setting contrasts with other submarine ground water sites that focus on mainly shallow flow (< 10 m depth) to coastal lagoons or river-dominated systems in which major rivers collect the flow and discharge into the coastal ocean via an estuary. In these cases, if an aquitard underlies the setting at shallow depths, then the river system will capture most of the recharge. However, if the coastal aquifer is thick and extensive, even in the presence of major rivers, the surface flow will represent only a portion of the total discharge. Such is the case in the Ganges-Brahmaputra River System of Bangladesh, where $^3H/^3He$ ages indicated that a significant (99+%) amount of total recharge bypassed the surface flow system to enter the deeper aquifer and ultimately discharge to the Bay of Bengal as submarine ground water discharge (Dowling et al. 2003).

In karstic systems, the magnitude of submarine discharge will be much higher but most likely not uniform. Using ^{222}Rn concentrations in the coastal ocean, Cable et al. (1996b) have determined that the ground water discharge in their 620 km^2 study area in the Florida Panhandle is ~1.4×10^{10} m^3/yr (equivalent to 23 m of annual recharge, > 100% of precipitation), suggesting that the flow is being channeled in karst and difficult to integrate over a wide area. When their discharge rate is extrapolated over the Gulf coastline of Florida, the total discharge rate is 3.0 × 10^{11} m^3/yr. In order to integrate over a larger study area, the amount of annual precipitation, recharge, and surface area needs to be considered. Using this method, the estimated discharge from the Florida Panhandle is 1.0 × 10^{11} m^3/yr. The coastal aquifers of the Gulf of Mexico are roughly 60% siliceous and 40% karstic, so we used a weighted average of the discharge values of Baldwin County and Florida extrapolated to the Gulf Coast. The submarine ground water discharge into the Gulf of Mexico is ~2.8 × 10^{11} m^3/yr or 50% of the Mississippi flux. The water and nitrate submarine discharge values integrated over the Gulf Coast are very rough values and could either overstate or understate the magnitude of discharge to the Gulf of Mexico. The calculated discharges, based on ground water velocities determined from $^3H/^3He$, are higher than would be calculated simply using Darcy velocities and ground water heads. Due to the hydraulics of sea water intrusion (Smith

and Wheatcraft 1993), the velocity of the ground water increases as it approaches the coastal zone.

Antweiler et al. (1996) estimated the Mississippi River's total input of nitrate into the Gulf of Mexico to be 1.5×10^{10} mol/yr, and Goolsby et al. (1999) calculated a similar nitrate contribution ($1.5 \pm 0.06 \times 10^{10}$ mol/yr). The Mobile-Alabama River System, that drains ~75% of Alabama, contributes ~2.2 to 2.3×10^{8} mol/yr of nitrate into the Gulf of Mexico (Carey et al. 2003). Using the average nitrate concentrations for the A2 aquifer and the calculated discharge rate for Baldwin County, the annual submarine flux of nitrate into the Gulf of Mexico is $1.1 \pm 0.01 \times 10^{8}$ mol/yr or 0.8% and 50% of the yearly nitrate input from the Mississippi and the Mobile-Alabama rivers, respectively. This becomes significant because Baldwin County is only 1% of the entire Gulf Coast shoreline and may inject nitrate far from the known river sources.

However, ground water discharge rates and nitrate levels can vary dramatically between locations, and the elevated nitrate concentrations measured in the Baldwin County wells may not be found elsewhere. Some of the shallow wells of Florida have very low nitrate levels (0.25 $\pm$ 0.05 µM to 0.62 $\pm$ 0.48 µM) and the interstitial pore water of Florida Bay has 0.68 µM NO_3 (Bugna et al. 1996; Corbett et al. 1999). Even if the ground water and interstitial pore fluids have a low amount of nitrate, submarine discharge can still contribute a significant amount of nutrients to the coastal oceans and have a local effect on the ecosystem. Using the discharge rate for the Floridian Gulf Coast and the nitrate level found in the interstitial water, the nitrate flux from the Gulf coastline of Florida to the Gulf of Mexico is 6.9×10^{7} mol/yr or 0.5% of the nitrate flux from the Mississippi River System. However, this nitrate flux is underestimated because there are areas in Florida that have much higher dissolved nitrate in their ground water systems associated with long-term agriculture. In the Florida Keys, the ground water nitrate ranges from 15 to 50 µM (Shinn et al. 1994), and the ground waters surrounding sewage injection facilities can have nitrate as high as 2.89 mM (LaPointe et al. 1990).

Submarine discharge estimates for the different aquifer systems along the Gulf Coast need to be evaluated on an individual basis because there are such large ranges of nitrate values, recharge rates, and spatial variability in ground water discharge throughout the Gulf of Mexico. Areas with moderate discharge rates and elevated levels of nitrate (e.g., Baldwin County and wastewater injection systems) will have a significant effect on the local ecosystem and are an overlooked, but important, source of additional nitrate in the Gulf of Mexico.

Conclusions

The A2 aquifer is an active flow system characterized by anthropogenic tritium values, moderate vertical velocities, and high nitrate concentrations. From the ground water age distribution, we calculated a recharge rate of 40 ± 16 cm/yr. The A3 aquifer, physically separated from the A2 aquifer for ~40 km inland, is tritium dead and has low nitrate values. Using the helium diffusion model for the A3 aquifer,

the ground water ages range from 2000 to 7500 years, becoming progressively older as the samples become deeper and closer to the sea. The natural gas that is diffusing into the A3 aquifer from the Pensacola Clay is found only in the deepest sample, indicating that the ground water is flowing into the Gulf of Mexico and suppressing the natural gas plume in the A3 aquifer. Knowledge of this deep flux can provide important constraints when estimating the safe yield of ground water withdrawal from coastal aquifers.

The deep submarine discharge along this portion of the Gulf of Mexico is significant. The mature siliceous aquifer of Baldwin County has a ground water flux of $1.9 \pm 0.8 \times 10^{9}$ m³/yr. The submarine flux of nitrate from Baldwin County to the Gulf of Mexico is $1.1 \pm 0.01 \times 10^{8}$ mol/yr or 0.8% and 50% of the annual contributions from the Mississippi and Mobile-Alabama river systems. This flux might become substantial even though Baldwin County is only 1% of the entire Gulf Coast shoreline. If other regions with substantial long-term agriculture have significant submarine ground water discharge that bypasses the surface system, then the estimates could be underestimated by 50%. The Floridian aquifers discharge more water (1.1×10^{11} m³/yr), but less nitrate (6.9×10^{7} mol/yr), than Baldwin County. However, this nitrate discharge into the Gulf of Mexico from Florida is underestimated since there are areas that have much higher dissolved nitrate in their ground water systems. By using $^{3}H/^{3}He$ ages to establish recharge and discharge rates, and average nutrient levels in ground water, we can obtain reasonable estimates for nutrient loading over a significant section of coastline in contrast to point discharge estimates. Further studies need to be done on individual aquifer systems along the coastline to provide better estimates of the global submarine flux of nutrients into the oceans.

References

Aeschbach-Hertig, W., U. Beyerle, R. Kipfer, and F. Peeters. 1999. Interpretation of dissolved atmospheric noble gases in natural waters. *Water Resources Research* 35, 2779–2792.

Anderson, P.F., J.W. Mercer, and H.O. White. 1988. Numerical modeling of salt water intrusion at Hallandale, Florida. *Ground Water* 26, 619–630.

Anthony, S.S., F.L. Peterson, F.T. MacKenzie, and S.N. Hamlin. 1989. Geohydrology of the Laura freshwater lens, Majuro Atoll: A hydrogeochemical approach. *Geological Society of America Bulletin* 101, 1066–1075.

Antweiler, R.C., D.A. Goolsby, and H.E. Taylor. 1996. Nutrients in the Mississippi River. In *Contaminants in the Mississippi River, 1987–92*, ed. R.H. Meade. U.S. Geological Survey Circular 1133.

Ballentine, C.J., and C.M. Hall. 1999. Determining paleotemperature and other variables by using an error-weighted nonlinear inversion of noble gas concentrations in water. *Geochimica et Cosmochimica Acta* 63, 2315–2336.

Benson, D.A., A.E. Carey, and S.W. Wheatcraft. 1998. Numerical advective flux in highly variable velocity fields exemplified by saltwater intrusion. *Journal of Contaminant Hydrology* 34, 207–233.

Bokuniewicz, H., and B. Pavlik. 1990. Groundwater seepage along a barrier island. *Biogeochemistry* 10, 257–276.

Bond, L.D., and J.D. Bredehoeft. 1987. Origins of seawater intrusion in a coastal aquifer—A case study of the Pajaro Valley, California. *Journal of Hydrology* 92, 363–388.

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 northeastern Gulf of Mexico. *Geochimica et Cosmochimica Acta* 60, 4735–4746.

Burnett, W.C., J.B. Cowart, and S. Deetae. 1990. Radium in the Suwannee River and Estuary. *Biogeochemistry* 10, 237–255.

Cable, J.E., G.C. Bugna, W.C. Burnett, and J.P. Chanton. 1996a. Application of ^{222}Rn and CH_4 for assessment of groundwater discharge to the coastal ocean. *Limnology and Oceanography* 41, 1347–1353.

Cable, J.E., W.C. Burnett, J.P. Chanton, and G.L. Weatherly. 1996b. Estimating groundwater discharge into the northeastern Gulf of Mexico using Radon-222. *Earth and Planetary Science Letters* 144, 591–604.

Cant, R.V., and P.S. Weech. 1986. A review of the factors affecting the development of Ghyben-Herzberg lenses in the Bahamas. *Journal of Hydrology* 84, 333–343.

Capone, D.G., and J.M. Slater. 1990. Interannual patterns of water table height and groundwater derived nitrate in nearshore sediments. *Biogeochemistry* 10, 277–288.

Carey, A.E., C.A. Nezat, J.R. Pennock, T. Jones, and W.B. Lyons. 2003. Nitrogen budget of the Mobile-Alabama River System watershed. *Geochemistry: Exploration, Environment, Analysis* 3, 239–244.

Carey, A.E., R.J. Poreda, W.B. Lyons, and S.W. Wheatcraft. In review. The Alabama Gulf coastal aquifer system: The importance of quartz weathering. *Water Resources Research*.

Carey, A.E., and S.W. Wheatcraft. 1995. Parametric study of salt water intrusion. In *Geological Society of America-Abstracts with Programs* 27, 260. Boulder, Colorado: Geological Society of America.

Carey, A.E., S.W. Wheatcraft, R.J. Glass, and J.P. O'Rourke. 1995. Non-Fickian ionic diffusion across high-concentration gradients. *Water Resources Research* 31, 2213–2218.

Carey, A.E., S.W. Wheatcraft, R.J. Glass, J.P. O'Rourke, and J.M. Woodruff. 1993. Diffusive transport of electrolytes in multi-phase aqueous systems. In *Geological Society of America-Abstracts with Programs* 25, 246. Boulder, Colorado: Geological Society of America.

Chandler, R.V., J.D. Moore, and B. Gillett. 1985. Ground-water chemistry and salt-water encroachment, southern Baldwin County, Alabama. Alabama Geological Survey Bulletin 126.

Clarke, W.B., W.J. Jenkins, and Z. Top. 1976. Determination of tritium by mass spectrometric measurement of ^{3}He. *International Journal of Applied Radiation and Isotopes* 27, 515–522.

Contractor, D.N., and R. Srivastava. 1990. Simulation of saltwater intrusion in the northern Guam lens using a microcomputer. *Journal of Hydrology* 118, 87–106.

Corbett, D.R., J. Chanton, W. Burnett, K. Dillon, C. Rutkowski, and J.W. Fourqurean. 1999. Patterns of groundwater discharge into Florida Bay. *Limnology and Oceanography* 44, 1045–1055.

Dowling, C.B., R.J. Poreda, and A.R. Basu. 2003. The ground waters of the Bengal Basin: Their geochemistry and trace metal flux to the oceans. *Geochimica et Cosmochimica Acta* 67, 2117–2136.

Dowling, C.B., R.J. Poreda, S.L. Peters, A.R. Basu, and P.K. Aggarwal. 1999. Groundwater flux of trace elements in the Ganges-Brahmaputra flood plain. *Eos Transactions* 80, 431.

Farley, K.A. 1995. Cenozoic variations in the flux of interplanetary dust recorded by ^{3}He in a deep-sea sediment. *Nature* 376, 153–156.

Giblin, A.E., and A.G. Gaines. 1990. Nitrogen inputs to a marine embayment: The importance of groundwater. *Biogeochemistry* 10, 309–328.

Goolsby, D.A., W.A. Battaglin, G.B. Lawrence, R.S. Artz, B.T. Aulenbach, R.P. Hooper, D.R. Keeny, and G.J. Stensland. 1999. Flux and sources of nutrients in the Mississippi-Afchafalaya River Basin: Topic 3 report for the integrated assessment on hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 17, NOAA Coastal Ocean Office.

Gröning, M., C.B. Taylor, G. Winckler, R. Auer, and H. Tatzber. 2001. The Sixth IAEA intercomparison of low-level tritium measurements in water (Tric2000) report. International Atomic Energy Agency, Vienna, Austria.

Harris, P.J. 1995. Water quality impacts from on-site waste disposal systems to coastal areas through groundwater discharge. *Environmental Geology* 26, 262–268.

Hickey, J.J. 1989. An approach to the field study of hydraulic gradients in variable-salinity ground water. *Ground Water* 27, 531–539.

Hiyagon, H., and B.M. Kennedy. 1992. Noble gases in CH_4-rich gas fields, Alberta, Canada. *Geochimica et Cosmochimica Acta* 56, no. 4: 1569–1589.

Hunt, A.G. 2000. Diffusional release of helium-4 from mineral phases as indicators of groundwater age and depositional history. Ph.D. dissertation, Department of Earth and Environmental Sciences, University of Rochester, Rochester, New York.

Hunt, A.G., R.J. Poreda, and D.K. Solomon. 2000. Factors controlling the release of ^{3}He, ^{4}He, and ^{21}Ne in quartz. *Eos Transactions* 81, 447.

Isphording, W.C. 1977. Petrology and stratigraphy of the Alabama Miocene. *Gulf Coast Association of Geological Societies Transactions* 27, 304–313.

Izbicki, J.A. 1996. Seawater intrusion in a coastal California aquifer. U.S. Geological Survey Fact Sheet 125–96.

Johannes, R.E. 1980. The ecological significance of the submarine discharge of groundwater. *Marine Ecology Progress Series* 3, 365–373.

Kakinuma, T., Y. Kishi, and K. Inouchi. 1988. The behavior of groundwater with dispersion in coastal aquifers. *Journal of Hydrology* 98, 225–248.

Kashef, A.A.I. 1983. Salt water intrusion in the Nile Delta. *Ground Water* 21, 160–167.

Katz, B.G., J.K. Bohlke, and H.D. Hornsby. 2001. Timescales for nitrate contamination of spring waters, northern Florida, USA. *Chemical Geology* 179, 167–186.

Kaufman, S., and W.F. Libby. 1954. The natural distribution of tritium. *Physics Review* 93, 1337–1344.

Krest, J.M., W.S. Moore, and Rama. 1999. Ra-226 and Ra-228 in the mixing zones of the Mississippi and Atchafalaya rivers: Indicators of groundwater input. *Marine Chemistry* 64, 129–152.

LaPointe, B.E., J.D. O'Connell, and G.S. Garrett. 1990. Nutrient couplings between on-site sewage disposal systems, ground waters, and nearshore surface waters of the Florida Keys. *Biogeochemistry* 10, 289–307.

Lee, C.-H., and R.T.-S. Cheng. 1974. On seawater encroachment in coastal aquifers. *Water Resources Research* 10, 1039–1043.

Loeb, S.L., and C.R. Goldman. 1979. Water and nutrient transport via groundwater from Ward Valley into Lake Tahoe. *Limnology and Oceanography* 24, 1146–1154.

Long, S.E., and T.D. Martin. 1991. Method 200.8: Determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry. In *Methods for the Determination of Metals in Environmental Samples*, 83–122. U.S. EPA.

Mercer, J.S., B.H. Lester, S.D. Thomas, and R.L. Bartel. 1986. Simulation of saltwater intrusion in Volusia County, Florida. *Water Resources Bulletin* 22, 951–965.

Meyer, F.W. 1989. Hydrogeology, ground-water movement, and subsurface storage in the Floridian Aquifer System in southern Florida. U.S. Geological Survey Professional Paper 1403-G.

Moore, W.S. 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. *Nature* 380, 612–614.

Moore, W.S. 1997. High fluxes of radium and barium from the mouth of the Ganges-Brahmaputra River during low river discharge suggest a large groundwater source. *Earth and Planetary Science Letters* 150, 141–150.

Mooty, W. 1988. Geohydrology and susceptibility of major aquifers to surface contamination in Alabama: Area 13. U.S. Geological Survey Water Resources Investigations 88-4080.

Oberdorfer, J.A., M.A. Valentino, and S.V. Smith. 1990. Groundwater contribution to the nitrogen budget of Tomales Bay, California. *Biogeochemistry* 10, 199–216.

Panno, S.V., K.C. Hackley, H.H. Hwang, and W.R. Kelly. 2001. Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. *Chemical Geology* 179, 113–128.

Peterson, F.L., J.A. Williams, and S.W. Wheatcraft. 1978. Waste injection into a two-phase flow field: Sandbox and Hele-Shaw models study. *Ground Water* 16, 410–416.

Pope, K.O., E. Rejmankova, and J.F. Paris. 2001. Spaceborne imagine radar-C (SIR-C) observations of groundwater discharge and wetlands associated with the Chicxulub impact crater, northwestern Yucatan Peninsula, Mexico. Geological Society of America Bulletin 113, 403–416.

Poreda, R.J. 1982. Helium partitioning in basalt glass: Comments on a paper by M.D. Kurz and W.J. Jenkins. *Earth and Planetary Science Letters* 59, 437–438.

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

Poreda, R.J., and K.A. Farley. 1992. Rare gases in Samoan xenoliths. *Earth and Planetary Science Letters* 113, 129–144.

Poreda, R.J., P.D. Jenden, I.R. Kaplan, and H. Craig. 1986. Mantle helium in Sacramento Basin natural gas wells. *Geochimica et Cosmochimica Acta* 50, 2847–2853.

Portnoy, J.W., B.L. Nowicki, C.T. Roman, and D.W. Urish. 1998. The discharge of nitrate-contaminated groundwater from developed shoreline to marsh-fringed estuary. *Water Resources Research* 34, 3095–3104.

Rabalais, N.N., R.E. Turner, D. Justic, Q. Dortch, and W.J. Wiseman. 1999. Characterization of hypoxia: Topic 1 for the integrated assessment on hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 15, NOAA Coastal Ocean Program, Silver Spring, Maryland.

Raymond, D.E. 1983. Depositional sequences in the Pensacola Clay of southwest Alabama and their significance in petroleum exploration. *Gulf Coast Association of Geological Societies Transactions* 33, 195–201.

Reed, P., and J. McCain. 1971. Water availability of Baldwin County, Alabama. Geological Survey of Alabama Map 96.

Robertson, W.D., and J.A. Cherry. 1989. Tritium as an indicator of recharge and dispersion in the groundwater system in central Ontario. *Water Resources Research* 25, 1097–1109.

Robinson, J., R. Moreland, and A. Clark. 1996a. Groundwater resources data for Baldwin County, Alabama. U.S. Geological Survey Open File Report 96-487.

Robinson, J.L., R.S. Moreland, and A.E. Clark. 1996b. Potentiometric surface of the Miocene-Pliocene aquifer system of Baldwin County, Alabama, 1995. U.S. Geological Survey Open File Report 96-590.

Schlosser, P., M. Stute, C. Sonntag, and K.O. Münnich. 1989. Tritiogenic ^{3}He in shallow groundwater. *Earth and Planetary Sciences Letters* 94, 245–256.

Schmorak, S. 1976. Saltwater encroachment in the coastal plain of Israel. *International Association of Scientific Hydrology* 72, 305–318.

Shaw, T.J., W.S. Moore, J. Kloepfer, and M.A. Sochaski. 1998. The flux of barium to the coastal waters of the southeastern USA: The importance of submarine groundwater discharge. *Geochimica et Cosmochimica Acta* 62, 3047–3054.

Shinn, E.A., R.S. Reese, and C.D. Reich. 1994. Fate and pathways of injection-well effluent in the Florida Keys. U.S. Geological Survey Open File Report 94-276.

Simmons, C.T., T.R. Fenstemaker, and J.M. Sharp. 2001. Variable-density groundwater flow and solute transport in heterogeneous porous media: Approaches, resolutions, and future challenges. *Journal of Contaminant Hydrology* 52, 245–275.

Smith, C. 1991. Foraminiferal biostratigraphic framework, paleoenvironments, rates of sedimentation, and geologic history of the subsurface Miocene of southern Alabama and adjacent state and federal waters. Geological Survey of Alabama Bulletin 138.

Smith, J.L., and S.W. Wheatcraft. 1993. Groundwater flow. In *Handbook of Hydrology*, ed. D. Maidment, chapter 6, 6.1–6.58. New York: McGraw Hill.

Solomon, D.K., A. Hunt, and R.J. Poreda. 1996. Source of radiogenic helium-4 in shallow aquifers: Implications for dating young groundwater. *Water Resources Research* 32, 1805–1813.

Solomon, D.K., R.J. Poreda, P.G. Cook, and A. Hunt. 1995. Site characterization using ^{3}H/^{3}He ground water ages, Cape Cod, Massachusetts. *Ground Water* 33, 988–996.

Solomon, D.K., R.J. Poreda, S.L. Schiff, and J.A. Cherry. 1992. Tritium and helium-3 as groundwater age tracers in the Borden Aquifer. *Water Resources Research* 28, 741–755.

Speiran, G.K. 1996. Geohydrology and geochemistry near coastal groundwater discharge areas of the Eastern Shore, Virginia. U.S. Geological Survey Water Supply Paper 2479.

Sukhija, B.S., V.N. Varma, P. Nagabhushanam, and D.V. Reddy. 1996. Differentiation of palaeomarine and modern seawater intruded salinities in coastal ground waters (of Karaikal and Tanjavur, India) based on inorganic chemistry, organic biomarker fingerprints, and radiocarbon dating. *Journal of Hydrology* 174, 173–201.

Swarzenski, P.W., C.D. Reich, R.M. Spechler, J.L. Kindinger, and W.S. Moore. 2001. Using multiple geochemical tracers to characterize the hydrogeology of the submarine spring off Crescent Beach, Florida. *Chemical Geology* 179, 187–202.

Valiela, I., J. Costa, K. Foreman, J.M. Teal, B. Howes, and D. Aubrey. 1990. Transport of groundwater-borne nutrients

from watersheds and their effects on coastal waters. *Biogeochemistry* 10, 177–197.

Valiela, I., K. Foreman, M. LaMontagne, D. Hersh, J. Costa, P. Peckol, B. DeMeo-Anderson, C. D'Avanzo, M. Babione, C.-H. Sham, J. Brawley, and K. Lajtha. 1992. Couplings of watersheds and coastal waters: Sources and consequences of nutrient enrichment in Waquoit Bay, Massachusetts. *Estuaries* 15, 443–457.

Wheatcraft, S.W., and R. Buddemeier. 1981. Atoll island hydrology. *Ground Water* 19, 311–320.

Wheatcraft, S.W., and E.R. Burns. 1997. A sandbox model of seawater intrusion: Validation of density-coupled flow and transport models. *Geological Society of America-Abstracts with Programs* 29, 73.

Whitaker, F.F., and P.L. Smart. 1990. Active circulation of saline ground waters in carbonate platforms: Evidence from the Great Bahama Bank. *Geology* 18, 200–203.

Yatsevich, I., and M. Honda. 1997. Production of nucleogenic neon in the earth from natural radioactive decay. *Journal of Geophysical Research* 102, 10291–10298.

Zhang, Q., R.E. Volker, and D.A. Lockington. 2001. Influence of seawater boundary condition on contaminant transport in unconfined coastal aquifers. *Journal of Contaminant Hydrology* 49, 201–215.