ground water

Ground Water Beneath Coastal Bays of the Delmarva Peninsula: Ages and Nutrients

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Abstract

To complement a large-scale geophysical investigation of occurrence and discharge of fresh water beneath Delaware, Maryland, and Virginia (Delmarva) coastal bays, we measured (1) salinity and nutrient concentrations in ground water samples from several offshore coring sites and (2) a suite of chemical and isotopic parameters, including age tracers, in ground water samples from a Delaware site. Samples were collected in a variety of Holocene and Plio-Pleistocene sediments in nearshore and offshore areas of the bays. Ground waters that were significantly fresher than overlying waters were found in plumes up to at least 15 m thick extending to more than 500 m offshore in some areas. Steep salinity and nutrient gradients occur within a few meters of the sediment surface in most locations studied. The zone of transition from deeper fresher waters to shallower brackish waters is generally thin near shore, but thickens and becomes more gradual offshore. Ground water ages at the Delaware site were mostly < 50 yr in both fresh waters and brackish waters up to 22 m below the bay bottom. Water chemistry and age data indicate that fresh water plumes beneath the estuary are active extensions of the surficial aquifer carrying nitrate from recharge areas on land, whereas brackish ground water surrounding the fresh water plumes is recharged beneath the estuary and contains ammonium and phosphate released by diagenesis of shallow estuarine sediments. Denitrification affects some of the fresh water nitrate before it mixes with brackish ground water or discharges to surface water.

Introduction

Fresh or brackish ground water has been shown to exist in submarine sediments on a range of scales and in a variety of geologic settings (Moore 1996; Church 1996). Areas on the Atlantic coast of the United States where this phenomenon has been studied most intensively include the outer continental shelf (Hathaway et al. 1979; Kohout et al. 1988), as well as areas closer to shore in Florida (Corbett et al. 2000a; Corbett et al. 2000b; Swarzenski et al. 2001), South Carolina (Moore and Shaw 1998), New Jersey (Paulachok et al. 1985), New York (Bokuniewicz and Pavlik 1990), and Massachusetts (Valiela and Teal 1979; Charette et al. 2001).

An issue of particular environmental concern along much of the Atlantic Coast, especially in the Delmarva Peninsula, is the relative contribution of submarine ground water discharge to the total flux of nutrients (especially nitrate) to coastal bays and estuaries, because eutrophication is the primary environmental problem in many of these settings. Bachman and Phillips (1996) and Dillow and Greene (1999) estimated nitrate loads from ground water discharging to streams and directly to the shallow Maryland coastal bays (Newport, Sinepuxent, Isle of Wight, and parts of Chincoteague and Assawoman bays) (Figure 1) using large datasets of nitrate concentrations from wells and streams, and a qualitative flow-net analysis and water budget. Andres (1987, 1992), Cerco et al. (1994), and authors cited in these publications made similar estimates for Indian River Bay and Rehoboth Bay in Delaware, but used different techniques. In these studies, assumptions were made concerning the location of ground water discharge and the microbial transformation of nitrogen species en route to discharge. These assumptions are as follows. (1) All ground water recharged in the watershed discharges directly into streams

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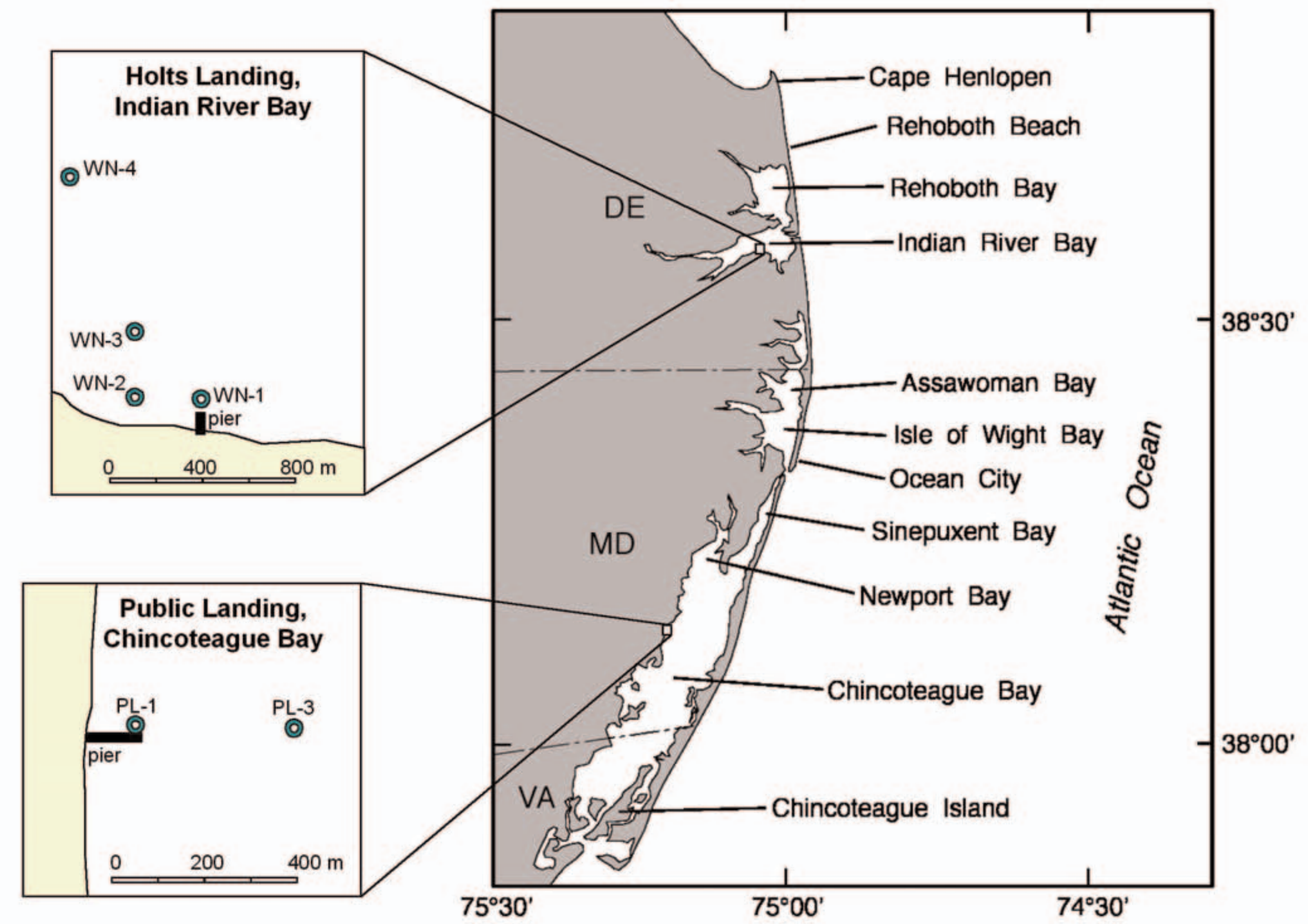

Figure 1. Location maps for Delmarva coastal bays and sketch maps showing coring and sampling locations at the Indian River Bay (Holts Landing) and Chincoteague Bay (Public Landing) study sites.

or coastal bays (i.e., no ground water passes under bays and barriers and discharges directly into the Atlantic Ocean). 2) All discharge to the bays comes from the surficial aquifer. (3) Nitrate concentrations in discharging water are the same as those measured in onshore wells (i.e., no denitrification takes place in anoxic aquifers and shallow sediment pore waters prior to discharge). Our investigation evaluates and refines some of these assumptions. The ultimate aim of this work is to complement the modeling approaches by better constraining the general conceptual framework within which model estimates are made of nutrient loading from discharge of ground water to coastal bays.

Previous geophysical and coring studies (Belknap et al. 1994; Kerhin et al. 1999) have shown that filled paleochannels underlie the axes of many coastal bays found on the Delmarva Peninsula. Rivers eroded these channels during low stands of sea level during previous glacial periods. Stillstands of sea level, both below and above modern sea level, have also left ridges of beach sand parallel to the modern shoreline exposed at the ground surface or buried in the shallow subsurface. Both sand ridges and paleochannels are likely to influence submarine transport and discharge of ground water in the coastal zone. Streaming and downhole resistivity investigations (Manheim et al. this issue; Krantz et al. this issue) detected subsurface occurrence of fresh and brackish ground water associated with such features underlying Delmarva coastal bays.

We provide new data here on subbay hydrostratigraphic relationships, ground water flow systems, and chemical transformations of dissolved nutrients prior to discharge. Ground water sampling from cores and drive-point samplers permits calibration of geophysical data from these sites. By measuring salinity, nutrient concentrations, isotopic composition of nitrogen species, dissolved gases, and age indicators in ground waters, we test multiple hypotheses about the geometry, geochemistry, and style of submarine discharge of nutrients into the Delmarva coastal bays. The results of this investigation have broader application to coastal nutrient studies in other regions, as well as to marine nutrient and elemental cycling on a global scale.

Methods

Samples of ground waters (also referred to as pore waters or pore fluids in shallow submarine sediments) were collected in two coastal bays during this investigation—Chincoteague Bay, Maryland (adjacent to Public Landing), and Indian River Bay, Delaware (adjacent to Holts Landing State Park on White Neck) (Figure 1). Coring was done first in Chincoteague Bay in June 2000 to test the capabilities of a hovercraft-mounted vibracoring rig (Hoverprobe 2000, Hovertechnics Inc., Eau Claire, Michigan) and to provide an offshore transect of subsurface samples perpendicular to both the shoreline and an onshore scarp located ~1.5 km inland. The second study area, cored in October 2001, adjoined Holts Landing State Park along the southern shore of Indian River Bay in Delaware. Sampling locations there were selected in order to (1) verify results of previous resistivity surveys by targeting paired low-resistivity (brackish) and high-resistivity (fresh) sites, as well as to (2) determine the influence of paleotopography on ground water flow by choosing nearshore and offshore targets in a known incised paleovalley imaged in previous seismic surveys. The Indian River Bay cores were collected using a vibracoring rig similar to that mounted on the Hoverprobe 2000, but in this case a trailer-mounted rig was secured to the deck of a shallow-draft barge. Coring locations are shown on the site maps in Figure 1.

Sediment Squeezing and Analysis

Most subsurface fluid samples were obtained using manual or hydraulic press methods to separate fluids from saturated sediments. To extract pore fluid with minimal drying, subsamples were collected either from cores through small holes cut in the core liners prior to longitudinal splitting or from exposed core faces shortly after the splitting of core sections. Saturated samples were either pressed immediately or placed in sealed containers until they could be pressed. Samples were closely spaced (10 to 50 cm) in the upper few meters of most cores and more widely spaced (1 to 2 m) with increasing depth. Sampling depths were determined iteratively by considering the most recent salinity measurements and downcore lithologic changes.

To extract pore fluid, a 10 to 100 cm^3 aliquot of wet sediment either was compressed in a dedicated plastic syringe with a ratcheting caulking gun or was pressed in the stainless steel chamber of a clean and dry piston-type sediment squeezer (Manheim and Gieskes 1984; Manheim et al. 1994). Syringe samples were filtered through a 0.2 µm syringe-tip filter prior to transfer to sample containers. Each chamber sample was sealed with a Teflon® disk and butyl rubber gasket, and a stainless steel piston was inserted into the top of the cylinder. The chamber was placed in a hydraulic press and compressed, forcing pore fluid through a filter and conduit and into a 10 or 30 mL syringe attached to the squeezing apparatus. The syringe was removed after no more fluid was produced from the squeezer and fitted with a 0.2 µm syringe-tip filter. The contents of the syringe were injected through the filter into either screw-top sample vials or sections of polyethylene tubing that were sealed by heating with a torch and then crimping with pliers. Typically, recovery of water was 3 to 25 mL from chamber samples and 1 mL or less from syringe samples.

Salinity of filtered samples was determined in the field using a handheld optical refractometer calibrated to deionized water (precision = ± 0.5‰). Salinity of a subset of the samples was later verified in the laboratory using a Buchler Model 4-2500 Digital Chloridometer (Labconco Buchler Instruments, Kansas City, Missouri) with a sacrificial silver electrode and gelatin reagent. The chloridometer results were calibrated with measurements of IAPSO Standard Seawater (Ocean Scientific International Ltd., Petersfield, Hampshire, Unied Kingdom; Batch P138, prepared February 7, 2000, with a reported salinity of 34.998 psu). Chloridometer data were in good agreement with refractometer results, so only refractometer values are reported here.

Pore-fluid samples for nutrient analyses were filtered (0.2 µm pore size) in the field, as previously described, and stored frozen prior to analysis at the University of Delaware. Dissolved ammonium (NH_4^+), nitrate + nitrite ($NO_3^- + NO_2^-$, abbreviated NO_{2+3}), phosphate (PO_4^{3-}), and reactive silicate ($Si(OH)_4$, abbreviated Si) were determined by automated colorimetry using an O/I Analytical Flow Solution® IV Analyzer (O.I. Analytical, College Station, Texas). Concentrations of NH_4^+ were determined by the phenol hypochlorite method (Glibert and Loder 1977; Grasshoff and Johansen 1972). NO_{2+3} concentrations were determined by the sulphanilamide/N(1-napthyl) ethylene diamine method after cadmium reduction of NO_3^- to NO_2^- (Glibert and Loder 1977). PO_4^{3-} was determined by the phospho-molybdenum blue method and Si by the silicomolybdate blue method (Strickland and Parsons 1972). Typical precisions for analyses of NH_4^+, NO_{2+3}, PO_4^{3-}, and Si were ~ ± 0.2 to 1, ± 1 to 5, ± 0.02 to 0.05, and ± 0.5 to 1 µmol/L, respectively (Savidge 2001).

Drive-Point Sampling and Analysis

At some coring locations, submarine ground water samples were collected from discrete depths below the bay bottom by pumping from a drive-point sampler constructed with either small, screened sampling ports in the drive-point itself (Chincoteague Bay) or a short (~30 cm) section of well screen located immediately above the drive-point (Indian River Bay). The drive-point technique was used (1) to allow collection of larger sample volumes than sediment squeezing permits, (2) to permit sampling from discrete depth intervals identified from downhole gamma and induction logging as possible ground water conduits (coarse, low electrical conductivity zones), and (3) to permit sampling from below the maximum depths from which continuous sediment cores could be recovered.

The drive-point sampler was emplaced using either a hovercraft-mounted (Phelan et al. 2000) or barge-mounted vibracoring rig. The sample port drive-point used in Chincoteague Bay was connected to Teflon tubing through which samples were drawn from depth using a peristaltic pump. At Indian River Bay, the drive-point piezometers were advanced with threaded steel drill rods (which also served as risers), and developed and purged using a Hydrolift II Inertial Pump (Wattera USA Inc., Bellingham, Washington) with the inlet held above the screen. Samples were subsequently pumped through parallel nylon and copper tubing from the level of the well screen using either a submersible piston pump (Bennett Sample Pumps Inc., Amarillo, Texas) or a peristaltic pump.

Nutrient analytical methods were the same as those previously described for squeezed samples. Chloride concentrations were analyzed for pumped samples in the field with a Hach® field-testing kit by silver nitrate titration (Hach Co., Loveland, Colorado). Specific conductance, pH, and dissolved oxygen (O_2) were determined using WTW brand pH/conductivity and pH/O_2 meters (WTW Measurement Systems Inc., Woburn, Massachusetts). One Winkler titration was done to check performance of the dissolved O_2 meter. Specific conductance, pH, O_2, and temperature

Table 1
Data for Drive-Point Ground Water Samples Collected from Indian River Bay Sites WN-1, WN-2, and WN-3

Coring Site	Depth (m)	Salinity (g/kg)	O_2 (µmol/L)	NH_4^* (µmol/L)	NO_{2+3} (µmol/L)	Denitrified NO_{2+3}^a (µmol/L)	$\delta^{15}N$ of NH_4^+ (‰ air)	$\delta^{15}N$ of NO_{2+3} (‰ air)	^3H (TU)	Apparent ^3H-^3He Age (years[b])	Apparent SF_6 Age (years[b])	Apparent CFC-12 Age (years[b])
WN-1	3.0	17.6	2	52	5	< 40	NA	NA	3.2	NA	NA	NA
WN-1	7.6	25.1	2	57	1	< 40	4.5	NA	4.3	NA	contam.	26
WN-1	21.6	28.5	1	76	1	< 20	3.6	NA	4.7	2	2	28
WN-2	10.7	1.4	2	3	1	58	NA	NA	9.3	34	23	28
WN-2	16.2	0.1	115	1	108	< 20	NA	6.4	4.4	37	23	contam.
WN-2	20.7	24.5	2	63	6	< 20	13.0	NA	4.5	16	9	33
WN-3	10.4	1.0	26	2	51	< 40	NA	5.3	5.6	25	22	32
WN-3	18.6	10.6	1	49	< 1	< 40	2.8	NA	0.3	56	24	53

Information in this table is based on Böhlke and Krantz (2003).
NA = not analyzed
[a] Calculated from excess N_2 and supported by anomalously high $\delta^{15}N$ of N_2
[b] Ages are relative to the sample collection year (2001).

were measured in a flow-through chamber to avoid contact with air.

At Indian River Bay, additional pumped samples were collected from the piezometers for analysis of major element chemistry, dissolved gases (argon, N_2, O_2, CH_4), neon, helium, helium isotopes, ^3H, chlorofluorocarbons (CFC–11, CFC–12, CFC–113), SF_6, and nitrogen isotopes of NO_3^-, NH_4^+, and N_2. A more detailed description of these analyses and results is available in Böhlke and Krantz (2003).

Dissolved-gas samples were collected in serum bottles and preserved with KOH. Gas analyses were done by gas chromatography on low-pressure headspace in the U.S. Geological Survey (USGS) Dissolved-Gas Laboratory in Reston, Virginia. Recharge temperatures and concentrations of excess air and excess nitrogen in ground water were calculated from argon, neon, and N_2 data (Stute and Schlosser 1999; Böhlke and Krantz 2003).

Samples for helium, neon, and ^3H-^3He age determinations were collected in crimp-sealed copper tubes. Helium and neon were extracted for mass spectrometric analysis, then degassed aliquots of the water were reanalyzed after several months to determine ^3H concentrations from ^3He ingrowths at the Lamont-Doherty Earth Observatory Noble Gas Laboratory (Ludin et al. 1998). The age of each ground water sample (in years since the time it left contact with air) was assumed to be equal to the time indicated by decay of ^3H to ^3He in a closed system, after adjustments for atmospheric gas contributions and for excess terrigenic helium (Schlosser et al. 1998). Temperatures used in the age calculations were determined from the concentrations of argon and neon, assuming those gases had only atmospheric sources.

Samples to be analyzed for chlorofluorocarbons (CFCs) were collected in flame-sealed glass ampules under pure N_2 headspace (Busenberg and Plummer 1992). CFCs were extracted by a purge-and-trap procedure and analyzed by gas chromatography with an electron-capture detector in the USGS CFC Laboratory in Reston. For each sample, the measured concentrations of CFC–11, CFC–12, and CFC–113 were converted to equilibrium partial pressures at sea level, adjusted for the measured salinities at the equilibration temperatures indicated by the dissolved-gas data. Partial pressures were compared to the atmospheric record to determine the apparent year of recharge (Plummer and Busenberg 2000). Samples for SF_6 analysis were collected unfiltered in 2 L glass bottles with polyseal caps without headspace. In the laboratory, aliquots were taken from the bottle for analysis by purge-and-trap gas chromatography (Busenberg and Plummer 2000). For each sample, the SF_6 concentration was converted to an equilibrium partial pressure at sea level after accounting for the measured salinity and for the equilibration temperature and excess air concentration indicated by the dissolved-gas data.

Isotope analyses of NH_4^+ were done by the ZymaX Isotope Laboratory, San Luis Obispo, California, for the USGS National Water Quality Laboratory. These samples were prepared by steam distillation and chemical oxidation of NH_4^+ to N_2, with reported uncertainties of ± 0.2‰. For nitrogen isotope analyses of NO_3^-, filtered fresh water samples were freeze-dried and the salts were baked in evacuated sealed glass tubes with Cu + Cu_2O + CaO to produce N_2 gas, which was analyzed on a dual-inlet isotope-ratio mass spectrometer in the USGS Stable Isotope Laboratory in Reston (Böhlke and Denver 1995). Data were normalized to values of + 0.4‰ for IAEA-N1 and + 180‰ for USGS–32 (Böhlke and Coplen 1995). For nitrogen isotope analyses of dissolved ground water N_2, the headspace gas remaining in serum bottles after gas chromatography was sealed into evacuated glass tubes with reagents, baked, and analyzed like the NO_3^- samples. Results were standardized against samples of N_2 in air ($\delta^{15}N = 0.0‰$) and laboratory-equilibrated water ($\delta^{15}N = + 0.65 \pm 0.10‰$). Sediment core samples were freeze-dried, ground, and homogenized, then baked and analyzed like the NO_3^- samples. The overall uncertainties of the normalized nitrogen isotope analyses performed in Reston are estimated to be ~ ± 0.2‰ for NO_3^- and sediment, and ± 0.1‰ for N_2.

Results

Data collected at the Chincoteague Bay and Indian River Bay coring sites are described here. Salinity measurements are presented first, followed by gas and nutrient

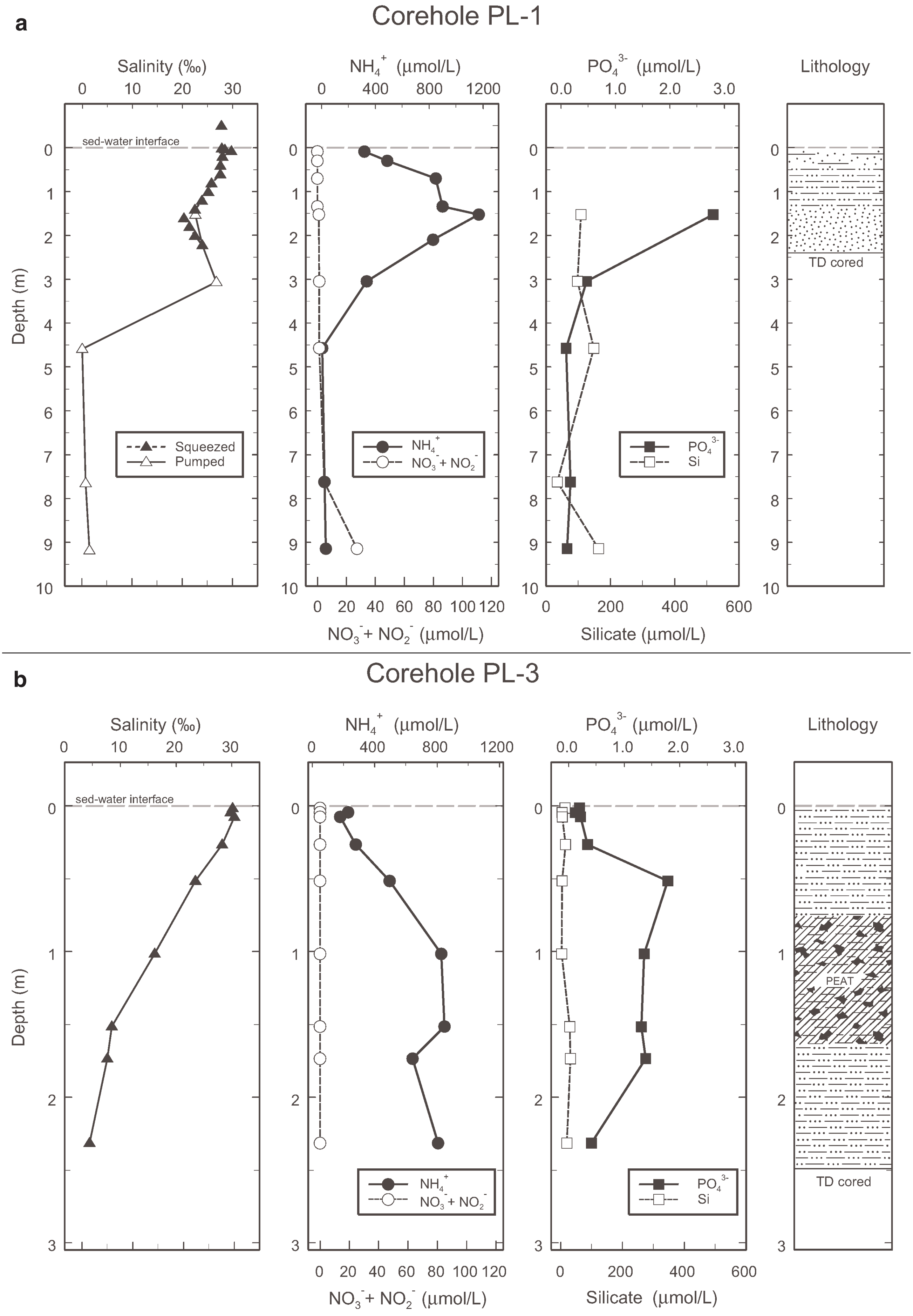

Figure 2. Profiles of salinity, NH_4^+, NO_{2+3}, PO_4^{3-}, and reactive silicate (abbreviated as Si in text) from the Chincoteague Bay coring sites (2a = PL–1, 2b = PL–3 [note expanded vertical scale relative to 2a]).

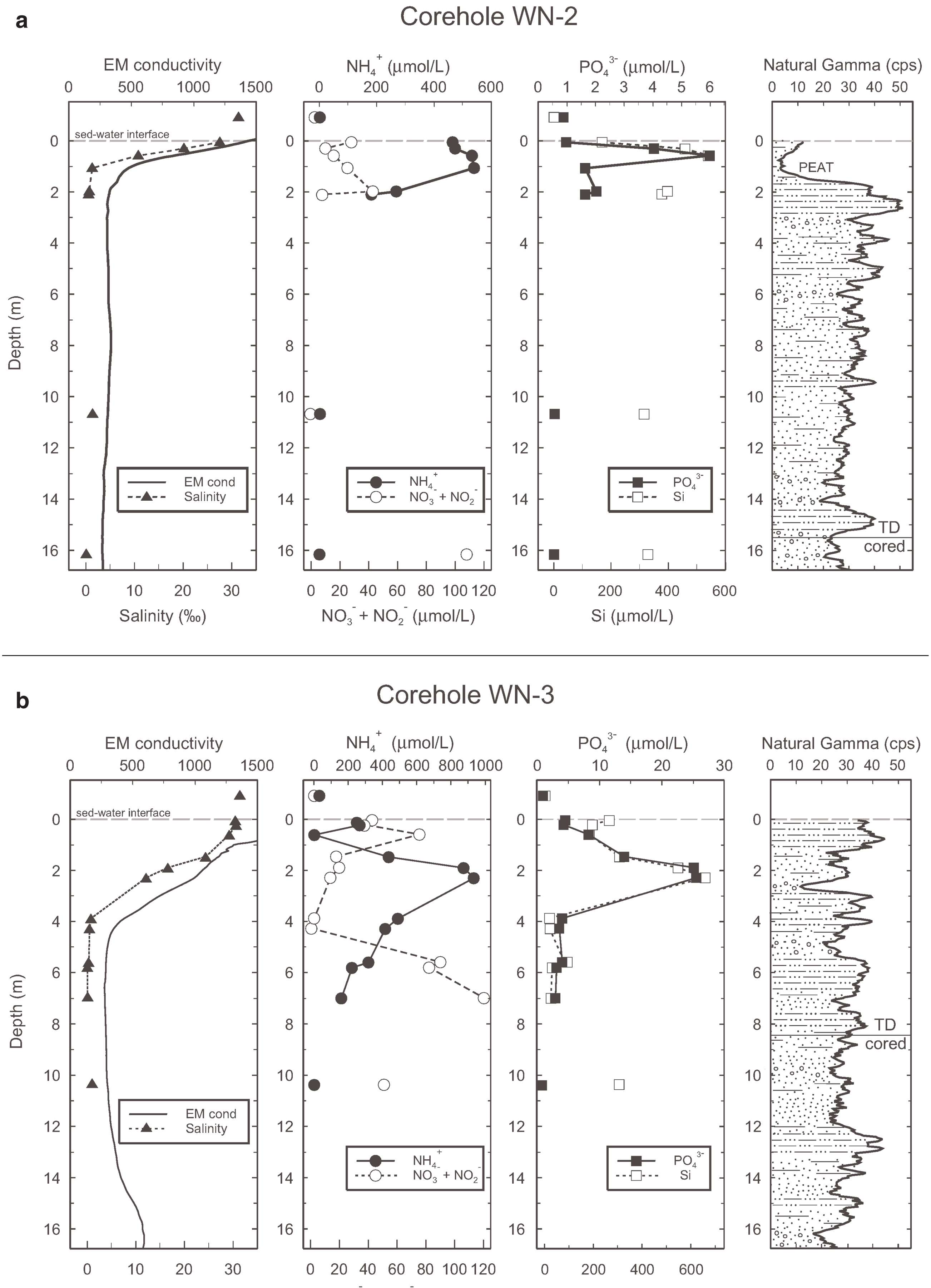

Figure 3. Profiles of salinity, electromagnetic conductivity (Krantz et al. this issue), NH$_4^+$, NO$_{2+3}$, PO$_4^{3-}$, and reactive silicate (abbreviated as Si in text) from two of the Indian River Bay coring sites (3a = WN–2, 3b = WN–3).

analyses (including nitrogen isotopes), and age dating results and calculations (^{3}H, CFCs, SF_6, and ^{3}H–^{3}He). Selected results for the drive-point samples from Indian River Bay are compiled in Table 1 (extracted from Böhlke and Krantz 2003). The sample numbering scheme used for these samples is White Neck site number (WN-#), followed by sampling depth in meters below the sediment surface (e.g., WN–2–16.1). Profiles of chemical data are shown along with stratigraphic information derived from cores and geophysical logs in Figures 2 and 3.

Salinity Profiles

A pair of nearshore and offshore coring locations sampled adjacent to Public Landing in Chincoteague Bay were separated by more than 300 m and produced somewhat different salinity profiles. Data from the first location (site PL–1, 110 m offshore [moored to pier]) (Figures 1 and 2a) show a zone of slightly reduced salinity (20‰) at ~2 m depth bounded above and below by water of higher salinity. (For comparison, 26‰ to 29‰ = average surface water salinity of central Chincoteague Bay [Maryland Department of Natural Resources 2004]; average salinity of central Indian River Bay is about 24‰ to 29‰ [Delaware Department of Natural Resources and Environmental Control 2004]). Below the sediment-water interface, ~ 3 to 4 m, a sharp (< 2 m thick) interface exists between overlying brackish ground water and underlying fresh water. The fresh water zone is at least 5 m thick. The data from the second location (site PL–3, ~450 m offshore in open water) (Figure 1) yielded a profile that differed from that of PL–1 (Figure 2b [different vertical scale from Figure 2a]). Drive-point samples were not recovered at this site, so the maximum depth reached is only ~25% of that penetrated in PL–1 (2.3 m vs. 9.1 m). The salinity decreased gradually over the length of the PL–3 core, but completely fresh waters were not reached at the core bottom. It is interesting to note, however, that the shallow brackish zone immediately underlying the bay at the offshore site (PL–3) appears to be thinner (~3 m) than the brackish zone at the site closer to shore (PL–1, ~4 m).

Indian River Bay salinity profiles and correlative electromagnetic conductivity logs (Figure 3a and 3b) (Krantz et al. this issue) show decreasing salinities with depth, as in the Chincoteague Bay cores, but the greater depth penetration and spatial resolution reveal much additional detail. Specifically, one of the nearshore sites (WN–1) (Figure 1) has a very thin zone of freshened water near the sediment surface, underlain by consistently brackish ground water (29‰ at a depth of 21.6 m). The other nearshore site (WN–2) has a thick fresh water zone (presumably a plume as described by Krantz et al. [this issue]) underlain at depth by brackish water (25‰ at a depth of 20.7 m). Both Chincoteague Bay and Indian River Bay cores show sharp transitions in the nearshore sites from brackish to fresh water in their upper few meters associated with nearshore peats. At the WN–3 site, directly offshore from WN–2, fresh water was encountered deeper and the transition back to brackish conditions at depth was more gradual than at WN–2. The WN–4 site, located ~1 km offshore, showed a gradual freshening with depth based on electromagnetic conductivity logs (Krantz et al. this issue). The general nearshore-offshore trend at the Indian River Bay site is an increased mixing of fresh water with brackish water along the upper and lower boundaries of the fresh water plume with increased distance from shore, resulting in smearing of the boundaries of the offshore plume.

Nutrients, Dissolved Gases, and Nitrogen Isotopes

At coring site PL–1 in Chincoteague Bay, deep NO_{2+3} concentrations are low or nondetectable in the shallow brackish zone and mixed zone, with a significant detection only in the deepest fresh sample recovered (Figure 2a). Conversely, NH_4^+ is not detectable in the deepest sample, but NH_4^+ concentrations increase to a peak of 1130 µmol/L 1.5 m below the sediment surface in the brackish zone in, and slightly below, black organic-rich sediments in the upper part of the core. Phosphate peaks in the same interval as NH_4^+, while Si is fairly constant to slightly decreasing from deep to shallow. In the brackish PL–3 core (Figure 2b), NH_4^+ concentrations also peak 1.5 m below the sediment surface, within a peat, and NO_{2+3} is not detectable in the mixed/brackish zone. A broad PO_4^{3-} peak coincides with the NH_4^+ peak, and Si is low over the length of the core.

The coring investigation in Indian River Bay yielded data consistent with some of the results from Chincoteague Bay (shallow NH_4^+ and PO_4^{3-} peaks, deep NO_{2+3} maximum in fresh water). Nitrate-nitrite concentrations generally are moderately high in fresh submarine ground water (Figures 3a and 3b, Table 1). In the mixing zone in the upper 1 to 6 m of the sediment column, NO_{2+3} decreases to near zero and NH_4^+ becomes the dominant nitrogen species as salinity increases toward the sediment surface. The maximum concentrations of NH_4^+ in the shallow brackish ground waters generally are at least an order of magnitude greater than the maximum NO_{2+3} concentrations in the underlying fresh ground waters. Phosphate concentrations also peak in the upper mixing zone or brackish zone in WN–2 and WN–3 ~0.5 to 2.5 m deep, consistent with PO_4^{3-} being generated from decomposition of organic matter in shallow estuarine sediments. Silicate concentrations are relatively high in fresh water and decrease in the mixed zone, which could indicate more time for silicate dissolution in the fresh waters or silicate precipitation during mixing (Rimstidt and Barnes 1980). The sharp Si peak in the upper part of the WN–3 core (also suggested in WN–2) may reflect local dissolution of biogenic Si in diatoms, which would be coincident with production of NH_4^+ and PO_4^{3-} from organic matter that includes algal biomass. Because nitrogen species are the dominant nutrients of concern in the coastal bays, Si and PO_4^{3-} results are not discussed further.

In samples that were pumped from temporary piezometers at Indian River Bay, concentrations of NH_4^+ were 49 to 76 µmol/L in the brackish ground waters, but < 3 µmol/L in the fresh ground waters. Similarly, concentrations of CH_4 were 0.3 to 0.7 µmol/L in the brackish ground waters, but < 0.1 µmol/L in the fresh ground waters. Total nitrogen concentrations of sediment samples from WN–1 and WN–3 ranged widely from ~50 to 12,000 ppm in the Holocene section, but were consistently < ~20 ppm in the Pleistocene section, from which the pumped samples were obtained (Böhlke and Krantz 2003). The δ^{15}N values of the Holocene sediments range from about –1‰ to +5‰, whereas three of the deep brackish ground water samples had similar $\delta^{15}N_{NH_4^+}$ values of ~ +3‰ to + 5‰. The overall distributions of NH_4^+ concentrations and isotopic compositions in the water and sediment samples are consistent with the brackish ground waters having acquired NH_4^+ (and possibly CH_4) from degrading sedimentary organic matter at relatively shallow depths during recharge beneath the estuary (Berner 1971; Demas and Rabenhorst 2001). One brackish ground water sample had a relatively high value of $\delta^{15}N_{NH_4^+}$ (+13‰ in WN–2–20.7), which is unexplained, but could indicate a different source of NH_4^+ or partial oxidation and isotopic fractionation of the NH_4^+ (Hübner 1986).

Two pumped ground water samples from Indian River Bay had measurable concentrations of O_2 and NO_{2+3}; WN–2–16.1 and WN–3–10.3 had O_2 = 26 to 115 µmol/L, NO_3^- = 51 to 108 µmol/L, and $\delta^{15}N_{NO_3^-}$ = 5.3‰ to 6.4‰. Both of these samples were fresh water and neither appears to have had excess N_2; thus, these samples provide evidence for transport of NO_3^- from terrestrial recharge areas to subestuarine positions in the aquifer without substantial chemical reaction. The $\delta^{15}N_{NO_3^-}$ values are within the range of values commonly observed in NO_3^- beneath fertilized agricultural fields in the Mid-Atlantic Coastal Plain, but lower than most values observed in areas dominated by manure or septic system sources of NO_3^- (Böhlke and Denver 1995; Kendall and Aravena 2000; Böhlke 2003).

The fresh water sample from WN–2–10.6 had no measurable O_2 or NO_3^-, but rather yielded an estimate of 29 µmol/L of excess N_2 (equivalent to 58 µmol/L of denitrified NO_3^-). This sample also had an anomalously high value of $\delta^{15}N_{N_2}$ (+1.1‰) compared to the other samples (+0.6‰ to +0.9‰, similar to air-saturation values), confirming that WN–2–10.6 had a substantial component of nonatmospheric N_2. This sample provides evidence that some of the NO_3^- transported beneath the estuary was reduced (denitrified) within the anoxic upper layer of the aquifer before mixing with brackish ground water or discharging. The $\delta^{15}N$ value of the nonatmospheric excess N_2 is poorly defined because of the much larger component of atmospheric N_2 in the sample, but it could be consistent with the $\delta^{15}N$ values of the NO_3^- in the oxic samples, indicating a similar source of NO_3^- in the corresponding recharge. In the WN–2 profile, denitrified ground water occurred above undenitrified ground water within the fresh water wedge; however, the location of active denitrification and the primary electron donor(s) involved are not known. It is possible that the reduced chemistry in the upper part of the fresh water plume at this site is related to the presence of the marsh located immediately behind the beach, or to other lithostratigraphic features of the aquifer. There is no convincing evidence for excess N_2 attributable to denitrification in any of the brackish ground waters, given a detection limit of ~10 to 20 µmol/L (20 to 40 µmol/L of NO_3^- equivalent).

Ground Water Dating by ^3H

Of the ground water dating methods tested in this study, the one based on tritium (^3H) concentrations alone is the least vulnerable to contamination, degradation, and degassing problems, but it may have relatively large uncertainties owing to its input history. Concentrations of ^3H in the pumped ground waters ranged from 0.3 to 9.3 tritium units (TU); however, six of the eight samples had a narrow range of ^3H concentrations between 3.2 and 5.6 TU (average = 4.6 ± 0.7 TU) (Table 1). Though there are no long-term records of ^3H concentrations in waters near the Delaware coast, there is evidence that 4 to 5 TU may be approximately equal to the average values of modern precipitation and recent ground water recharge in the study area.

The long-term record of ^3H precipitation at Washington, D.C. (International Atomic Energy Agency 2003) provides a basis for interpreting the Indian River Bay ground water data, but may require adjustments to account for recharge seasonality or proximity to the coast (Michel 1989; Dunkle et al. 1993). Lindsey et al. (2003) report that ^3H concentrations in fresh ground water recharge in the Pocomoke River Basin, near the coast south of Indian River Bay, were ~4 to 6 TU in the late 1990s, about half as high as the annual mean values in precipitation at Washington, D.C. Similarly, ground water recharge near Fairmount, Delaware (on the inland side of Rehoboth Bay) also had ^3H concentrations less than those of precipitation in Washington, D.C. (Dunkle et al. 1993). Assuming the local ^3H concentrations in recharging meteoric water near Indian River Bay were correlated with those in precipitation in Washington, D.C., but lower by a factor of two, it can be shown that ground waters recharged from local precipitation in the Indian River Watershed since about the mid-1970s and transported through the surficial aquifer in a piston-flow mode would have had ~5 TU when sampled in 2001 (Böhlke and Krantz 2003). In addition, four samples of surface water collected in 2001 and 2002 from Indian River Bay and Rehoboth Beach had ^3H concentrations averaging 4.9 ± 1.8 TU, indicating that the brackish ground waters recharged beneath the bay may have had a similar history of ^3H concentrations as the fresh ground waters. Thus, for six of the pumped ground water samples, including both fresh and brackish end members, comparison of the measured ^3H concentrations (3 to 6 TU) with the Washington, D.C., time series values ($\times$ 0.5) could indicate apparent ages of ~0 to 30 yr (postbomb peak), 45 to 50 yr (prebomb peak), or possibly mixtures of the two (Böhlke and Krantz 2003).

The highest ^3H concentration (9.3 TU) was obtained for the fresh water sample from WN–2–10.6. This value is consistent with recharge by precipitation that fell in the early 1970s, perhaps slightly earlier than some of the other samples with 3 to 6 TU. The lowest ^3H concentration (0.3 TU in the brackish sample from WN–3–18.5) is substantially lower than modern values in precipitation or estuarine surface water in the mid-Atlantic region. This low ^3H concentration indicates that the brackish ground water beneath the fresh water plume at the offshore site was dominated by water that recharged before about 1952, when large-scale atmospheric testing of thermonuclear bombs began; that is, the bulk of the water in this sample was more than 50 yr old.

Ground Water Dating by ^3H–^3He

In comparison to the other environmental gas tracer methods used for ground water dating, the ^3H–^3He method is not affected by chemical contamination and degradation, but it is relatively susceptible to errors caused by degassing in pumps and discharge tubing. Concentrations of ^3H and tritiogenic ^3He in ground water samples indicate apparent radioactive decay ages ranging from ~2 to 37 yr (corresponding recharge dates from 1965 to 1999). The sample from WN–3–18.5 had a substantial amount of terrigenic He (29% of the total helium in the sample) and yielded an adjusted apparent age of 56 yr, but should be considered undatable by this method owing to its low (prebomb) ^3H concentration. Analyses of replicate brackish samples collected from the deepest sampling point (WN–1–21.6) yielded surprisingly young ages of only 2 ± 1 yr. Other replicates were also in good agreement. For most of the samples, the apparent ^3H–^3He ages are concordant with both the measured ^3H concentrations and the reconstructed initial ^3H concentrations ($^3H = ^3H$ + tritiogenic ^3He), allowing for minor dispersion of the 1960s bomb peak (Böhlke and Krantz 2003). If the ^3H–^3He apparent ages are assumed to be correct, they would imply that CFC–12 was degraded by 50% or more in WN–1–21.6, WN–2–20.7, and possibly WN–3–10.3, and that SF_6 had a background or low contamination level equivalent to an atmospheric mixing ratio of ~0.6 ppt in WN–2–10.6, WN–2–16.1, WN–2–20.7, and WN–3–18.5.

Ground Water Dating by CFCs

Concentrations of CFC–12 indicate ground water apparent ages of ~26 to 53 yr (recharge dates from 1949 to 1976), except for WN–2–16.1, which was contaminated with CFC–12. CFC–11 and CFC–113 generally indicate relatively old recharge ages and were not detected in some samples that had substantial concentrations of CFC–12. These results are consistent with partial degradation of CFCs, beginning with CFC–11 and CFC–113, as is commonly observed in chemically reduced environments elsewhere (Oster et al. 1996; Rowe Jr. et al. 1999; Plummer and Busenberg 2000). Despite evidence for selective CFC–11 and CFC–113 degradation, the CFC–12 apparent recharge dates of fresh waters from samples WN–2–10.6 and WN–3–10.4 are roughly consistent with the corresponding ^3H–^3He ages and ^3H concentrations in those samples. The CFC–12 apparent recharge date of the late 1940s for brackish water from WN–3–18.5 is qualitatively consistent with the low (prebomb) concentration of ^3H in that sample. Furthermore, in each of the three Indian River profiles, CFC–12 apparent ages increase downward, and the CFC–12 apparent ages of the deep brackish samples increase slightly with distance offshore, as do the CFC–12 apparent ages of the fresh water samples. Based on these data and comparisons, it is concluded that CFC–11 and CFC–113 were partially to completely degraded and should not be used in the evaluation of the ground water ages. The CFC–12 data may be informative, with the caveat that CFC–12 may also be partially degraded.

Ground Water Dating by SF_6

Concentrations of SF_6 indicate ground water apparent ages of ~2 to 24 yr (recharge dates from 1977 to 2000), except for WN–1–7.6, which was contaminated with SF_6. The SF_6 ages were slightly to moderately younger than the CFC–12 and ^3H–^3He ages in two fresh water samples, and much younger in three brackish ground water samples. Mixing ground waters of varying ages could account for the relatively small discrepancies in the fresh water samples, but cannot account for the larger discrepancies in the brackish samples. Other possible reasons for SF_6 ages being younger than CFC–12 ages include CFC–12 degradation and the presence of excess SF_6. Observations that could be interpreted as evidence for CFC–12 degradation include the following. (1) The apparent age discrepancies are largest in brackish samples with higher concentrations of NH_4^+ and CH_4 (Oster et al. 1996). (2) The other analyzed CFCs (CFC–11 and CFC–113) generally appear to have been degraded relative to CFC–12, as previously described.

Observations that could be interpreted as evidence of excess SF_6 include the following. (1) CFC–12 has been shown to be relatively stable in many other aquifers under reducing conditions, even when CFC–11 and CFC–113 have been largely degraded. (2) At least one of the samples had a SF_6 concentration substantially higher than that of a modern water equilibrated with uncontaminated air. (3) Low levels of natural or anthropogenic background SF_6 have been observed elsewhere in some types of hydrogeologic settings (Busenberg and Plummer 2000). Four samples had relatively uniform SF_6 concentrations averaging 0.33 ± 0.06 fmol/L, indicating apparent recharge dates in the late 1970s. Water in one of those samples (WN–3–18.5) had $^3H = 0.3$ TU indicating recharge mainly before intensive thermonuclear bomb testing in the early 1950s. Accounting for this low concentration by mixing is not consistent with other age tracer results (Böhlke and Krantz 2003). Therefore, the data appear to indicate that there was a consistent low background or contaminant level of SF_6 in the samples, and that the SF_6 apparent ages of ~22 to 24 yr should be considered as minimum ages.

Discussion

The results for salinity, nutrient characteristics, and ground water age as reported previously have significant implications for understanding the general process of ground water and dissolved nutrient movement beneath, and ultimately into, an estuary. We now analyze results further, examine uncertainties and underlying assumptions, and identify deviations from previous interpretations of the bays' ground water systems. Schematic cross sections integrating the primary geochemical features of a submarine ground water plume typical of those investigated in Delaware and Maryland are shown in Figure 4 (see also the related figure in Krantz et al. [this issue]). It is important to qualify the results of this study. First, they represent only snapshots of submarine conditions at the times the sites were investigated (June 2000 for Chincoteague Bay, October 2001 for Indian River Bay). The results provide no information on temporal variability in the systems caused by diurnal, monthly, and annual tidal cycles; storm surges and changes in atmospheric pressure or surface water temperature; or seasonal and interannual variations in recharge and runoff. Second, the 5 to 10 m drive-point spacing and small volumes of water pumped or squeezed limited spatial resolution of the sampling. This means that interpretations

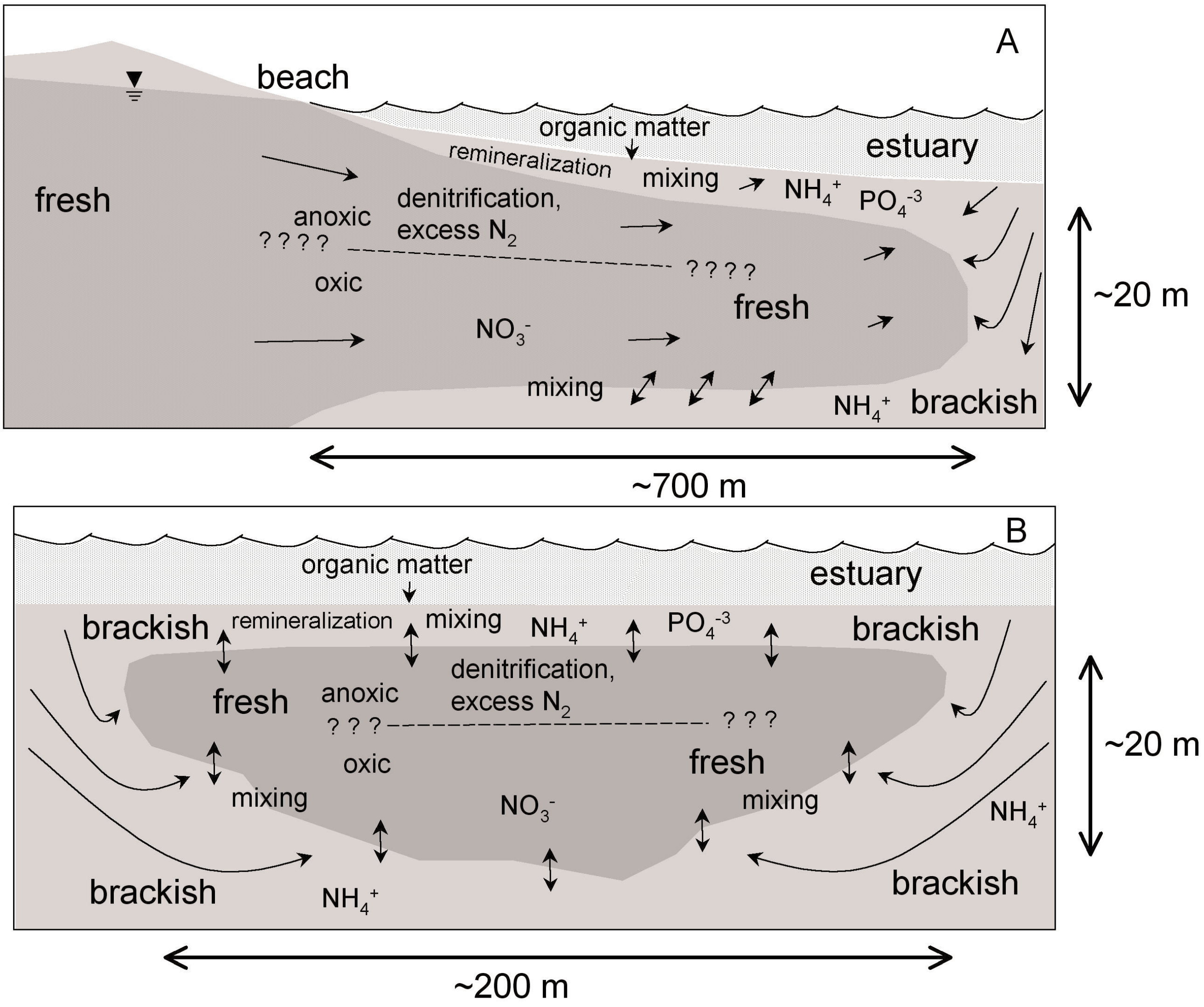

Figure 4. Schematic cross sections (a) perpendicular to and (b) parallel to the shore of a typical subestuarine plume of fresh water such as the one studied at Holts Landing in Indian River Bay.

cannot take into account fine-scale processes such as formation of salt fingers in shallow pore water, or flow through deep, thin, permeable zones between pumping depths. Conditions encountered, however, are believed to be representative of typical conditions at the study sites, and at similar estuarine sites in the mid-Atlantic region. Although surface conditions in coastal areas can change rapidly, submarine aquifer response is generally muted or dampened relative to the primary signals.

Salinity

Manheim et al. (this issue) and Krantz et al. (this issue) show that the hydrogeologic conditions required to produce offshore flow and eventual discharge of freshened ground water a significant distance from a marine shoreline are present at the coring sites studied. These conditions include (1) low-permeability sediments at or near the shoreline and seafloor to prevent nearshore discharge of fresh ground water, (2) higher-permeability units beneath the lower-permeability sediments to carry ground water horizontally under the brackish surface water body, and (3) sufficient heads in onshore aquifers to drive offshore flow. In addition to the cored sites, these conditions are present at many other locations imaged in the Delmarva coastal bays by electrical resistivity techniques (Manheim et al. this issue).

The salinity profiles produced from shallow ground water measurements show that the zone of mixing between fresh water and brackish water at these sites thickens with increasing distance from shore. This indicates that as submarine fresh water moves offshore in the subsurface, its boundaries become more diffuse, and mixing with surrounding brackish waters on all sides eventually makes it indistinguishable as a discrete subsurface water mass. Fresh ground water commonly discharges at or near the shoreline in Delmarva coastal bays and other similar settings. In relatively rare cases, based on aerial infrared imaging of Delaware bays (McKenna et al. 2001), offshore plumes may discharge as distinct low-salinity springs beneath the estuaries. Diffuse discharge characterized by slightly to moderately freshened fluids, however, may be more significant quantitatively in the open Delmarva estuaries based on the scarcity of thermal hotspots and the salinity gradients encountered during coring. These results are important for assessing the net influence of ground water on the coastal bays, especially the chemical transformations that take place in the shallow subsurface shortly before discharge. The presence of freshened water at a distance of > 1 km from shore in Indian River Bay suggests that some water recharged to the surficial aquifer in the watershed may flow under the estuary and barrier completely, eventually discharging directly to the ocean and bypassing the coastal bay.

Age Dating of Submarine Ground Water

Although it is not possible to give a definitive summary of the age distribution of the pumped ground waters because of potential mixing and observed discordance among the various ground water dating techniques, the age data indicate that, with the exception of WN–3–18.5, all samples (fresh and brackish) primarily contain water that recharged within the last 50 yr. The most consistent results were obtained from the fresh waters, where apparent age discordance is minimal. For example, WN–2–10.6 yielded apparent ages of ~30 to 40 yr from ^3H, 28 yr from CFC–12, 23 yr from SF_6, and 34 yr from ^3H–^3He. Data from all three fresh water samples indicate ages at depth that are at least qualitatively consistent with those of fresh water in surficial aquifers beneath the Delmarva Peninsula (Dunkle et al. 1993). The two fresh water samples from WN–2 appear to be stratified, with the deeper sample older than the shallower sample; WN–3 shows similar stratification. Therefore, the age data support the hypothesis that the fresh water underlying Indian River Bay is essentially a continuation of the surficial aquifer that was, and is being, recharged onshore. More detailed sampling would be required to better constrain age gradients and discharge patterns within the subestuarine fresh water plumes.

For some of the brackish ground waters, which contain relatively high concentrations of CH_4 and NH_4^+, substantial discordance among the dating techniques is not completely understood. The most important discrepancies are in the deep brackish samples from WN–1–21.6 and WN–2–20.7. If the ^3H–^3He data for these samples are correct, then it would appear that CFC–12 was degraded by ~64% to 73% and SF_6 had a low natural or anthropogenic background concentration. Anthropogenic contamination could have resulted from drilling and sampling or it could have been present in Indian River Bay when the brackish ground waters were recharged. If the CFC–12 results are assumed to be reliable, as they are in many other ground water systems, then the SF_6 would appear to be substantially derived by contamination and the measured concentrations of tritiogenic ^3He would be too low by a factor of ~4 to 20. There is no obvious reason to suspect such a bias in the helium isotope data, and it is concluded that the ^3H–^3He ages are the most reliable.

One of the most interesting results of the environmental tracer compilation is that the deep brackish ground waters at locations WN–1 and WN–2 beneath Indian River Bay appear to be relatively young. According to the ^3H–^3He data, the apparent ages of all three deep brackish samples increase offshore, and in WN–2 the deep brackish water appears to be younger than the overlying fresh water. If these age interpretations are even qualitatively correct, they imply relatively rapid downward movement of brackish water between the fresh water plumes, with the most rapid apparent recharge rate (e.g., WN-1) perhaps indicating an area of preferential downwelling. The apparent age of 2 yr for WN–1–21.6 would imply an overall net downward vertical velocity of ~10 m/yr for brackish recharge around the edge of a fresh water plume. The pattern of ^3H–^3He ages could indicate that downwelling of estuarine recharge is relatively rapid between the fresh water plumes near shore where the salinity gradients are relatively sharp (WN–1) and not so rapid farther off shore where the salinity gradients are more dispersed (WN–3).

Despite uncertainties in the interpretation of the age results, they indicate that (1) both fresh and brackish ground waters between 0 and 22 m below the sediment-water interface were recharged within the last 50 yr; (2) the fresh water beneath the bay can be considered as a continuation of the surficial aquifer with sources of both water and other constituents (e.g., NO_3^-) beneath the upgradient land surface; and (3) there is an active flow system connecting the surface water in the bay with the brackish ground water surrounding the fresh water plumes beneath the bay. More sampling of this type is warranted, though care will be required to minimize effects of degassing and eliminate sources of contamination in the drilling and sampling equipment. Further evaluation of multiple dating approaches will be helpful to establish ages reliably. Applying these approaches to other estuaries should make it possible to distinguish subsurface zones of fresh water that are being actively recharged, from trapped and stagnant pockets of fresh water that may be relict and associated with lower stands of sea level or freshening of bays during earlier closure of inlets.

Nutrient Sources and Transformations

One of the most important results derived from the nutrient data presented, including data from both Chincoteague Bay and Indian River Bay, is that the speciation of dissolved nitrogen beneath the estuary is largely related to the source of the water. That is, the simplest interpretation of the data is that the dominant inorganic nitrogen species other than N_2 in the brackish submarine ground waters (NH_4^+) is primarily derived from an offshore sediment source, whereas the NO_3^- in the underlying fresh water is derived from ground water recharge on land. Moreover, at all sites investigated in this study, the offshore fresh water plumes containing NO_3^- are overlain by anoxic NH_4^+-bearing brackish ground waters. The fate of the fresh water NO_3^- is not completely known, but our data give no evidence for discharge of NO_3^- directly to the estuarine surface water. Denitrification was indicated by dissolved-gas analyses at one site (WN–2) and is presumed to be common elsewhere as discharging ground water containing NO_3^- moves into shallow reducing sediments (see Böhlke et al. [2002] for a non-estuarine analog). Reduction of discharging NO_3^- to NH_4^+ cannot be ruled out, but it is not required to explain the distribution of nitrogen species, it cannot account for the high NH_4^+ concentrations in the shallow ground waters, and the available evidence supports a shallow sediment source for this NH_4^+.

In contrast, some other studies have reported measured or inferred direct discharge of NO_3^- to estuaries from ground water (Capone and Bautista 1985; Staver and Brinsfield 1996; Nowicki et al. 1999). This may be the case where ground water discharging through sandy beach shorefaces and nearshore zones, or various types of localized conduits offshore, does not encounter organic-rich sediments and is not reduced. It is probably also true, however, that studies of nitrogen discharge in estuaries that employ only shallow coring and benthic flux chambers often fail to adequately characterize fresh ground water chemistry, hydrogeologic framework, and transformations taking place deeper within subestuarine aquifers, or farther offshore. Shallow recycling of pore fluids due to tidal pumping and coupled nitrification/denitrification at the sediment water interface that converts shallow-sourced NH_4^+ to NO_3^- and then N_2 (Kemp et al. 1990; Lamontagne and Valiela 1995; Nowicki et al. 1999) are likely to obscure some of the larger-scale features of nutrient sources and transport.

In the Delmarva sites examined, the majority of the nitrogen in shallow ground water, in the form of NH_4^+, is considered to be derived from remineralization of organic matter deposited with the estuarine sediments and buried peats produced in, or adjacent to, the estuary in the past. Based on regional sampling of surface sediments in northern Chesapeake Bay and Chincoteague Bay (Kerhin et al. 1988; Wells and Conkwright 1999), typical values of total organic carbon (TOC) in coastal bay sediments range from 1% to 3%, with a maximum of ~10%, except in the case of peats. Recent sedimentation rates in the finer-grained areas of the coastal bays are 1.0 cm/yr or less (Chrzastowski 1986) or up to 0.8 g/cm^2/yr assuming a porosity of 70% and a typical grain-specific density of 2.6 g/cm^3. Assuming that nitrogen is present in sediment organic matter at the Redfield ratio (C:N = 6.6) and that TOC ranges from 1% to 3%, this would yield a range of nitrogen flux to the floors of the bays of 0.001 to 0.004 g N/cm^2/yr or 71 to 290 μmol N/cm^2/yr. Assuming that even a small fraction of this nitrogen were remineralized to NH_4^+, and that a significant amount were lost due to nitrification/denitrification, this particulate flux would still be more than sufficient to produce the aqueous NH_4^+ concentrations measured in shallow sediment (maximum = 1137 μmol/L or only 0.8 μmol NH_4^+/cm^3 of sediment with 70% porosity), especially when combined with nitrogen from slowly decomposing buried peats. Stated differently, little or no contribution of nitrogen from deeper ground water (maxima = 76 μmol/L of NH_4^+ or 108.1 μmol/L of NO_{2+3}) is necessary to generate these concentrations in shallow sediments; remineralization of organic matter in sediments alone is adequate to account for the nitrogen inventory in pore waters. Release back to the water column as NH_4^+ would likely result in reassimilation and redeposition back to sediments (Kemp et al. 1990). This implies that organic-rich sediments of the bays not only have electron donors and microbes capable of denitrifying land-derived nitrate in submarine ground water prior to discharge, but that the sediments also act as a sink for storage of excess nitrogen that reaches the surface waters from rivers and airfall.

Deep brackish water underlying fresh water plumes in Indian River Bay (WN–1, WN–2, and WN–3) has salinities similar to those of shallow pore waters and also contains NH_4^+ (and CH_4) and little or no NO_{2+3}. These features indicate that the deep brackish ground water may have acquired its NH_4^+ when it recharged directly from the estuary and passed through the organic-rich NH_4^+ generating zone of the near-surface sediments. This interpretation is consistent with age data, previously discussed, that indicate deep brackish water recharged from the estuary may be younger in some areas than overlying fresh water recharged on land at some distance from the coast.

Summary and Conclusions

As part of a study of potential ground water discharge of nutrients to Delmarva coastal bays, offshore submarine ground water was sampled by squeezing water from saturated core samples and by pumping water from temporary drive-point piezometers at depths ranging from 0 to 22 m below the sediment-water interface. In Chincoteague Bay and Indian River Bay, relatively fresh ground water plumes up to at least 5 m thick extend out from shore as far as 500 m (or more) and are surrounded by brackish ground water similar in salinity to the overlying estuary waters. The fresh submarine ground waters generally contain NO_3^- or N_2 produced by denitrification, with little or no NH_4^+, except where they have been influenced by reduced environments such as nearshore wetlands. The brackish ground waters consistently contain NH_4^+ and little or no NO_3^-. Ground water dating at Indian River Bay indicates that most of the sampled ground waters recharged within the last 50 yr. Although different dating techniques yield somewhat discordant results that are not completely understood, there is evidence from ^3H-^3He analyses that some brackish ground waters are younger than adjacent or overlying fresh ground waters.

The submarine fresh water plumes are interpreted as continuations of surficial aquifers that acquired NO_3^- from onshore recharge areas. The surrounding brackish ground waters are considered to have recharged from the overlying estuaries and to have acquired NH_4^+ from near-surface organic-rich estuarine sediments. Despite the presence of an extensive active flow system beneath the estuary, there is no direct evidence from this study for discharge of fresh water containing NO_3^-. It is considered likely that much of the NO_3^- present in fresh ground waters is denitrified before discharging through shallow organic-rich sediments of the type encountered offshore, except perhaps locally in areas of rapid focused discharge or where organic-rich sediments are absent. Recycling of nutrients (nitrogen, phosphorus, and Si) from decomposition of organic matter in the upper few meters of sediment may be the dominant submarine nutrient process operating in offshore areas of Delmarva coastal bays and other similar settings, rather than offshore submarine discharge of ground water carrying land-derived nutrients. Release of recycled nitrogen as ammonium may be a substantial, or even dominant, mode of nitrogen flux from offshore sediments to the coastal bays.

Acknowledgments

Field assistance was provided by B. Sturgis (National Park Service, Assateague Island National Seashore, Maryland); D. Phelan (USGS, Baltimore, Maryland); D. Queen,

W. Newell, R. Frasier, and M. Herder (USGS Hoverprobe team); W. Daisy and his barge crew (Delaware Department of Natural Resources and Environmental Control); H. Scott (MPI Drilling); P. Haywood and O.D. Sojinka (University of Toledo); M. Crawford (USGS, St. Petersburg, Florida); J. Moore (USGS, ECO, Woods Hole, Massachusetts); and D. Wells (Maryland Geological Survey). Laboratory analyses were done by K. Savidge (University of Delaware, nutrients), P. Widman (USGS, major dissolved gases), M. Doughten (USGS, inorganic chemistry), D. Wandee (USGS, SF_6), J. Wayland (USGS, CFCs), J. Hannon (USGS, nitrogen isotopes), and J. Moore (USGS, chlorinity). Primary funding was provided by the USGS Coastal and Marine Geology Program and Ground-Water Resources Program with additional financial or material support from U.S. Environmental Protection Agency-CISNet, National Park Service, University of Toledo, and Delaware Department of Natural Resources and Environmental Control. P. Barlow, M. Charette, J. Harvey, J. Martin, and an anonymous reviewer provided helpful comments on drafts of this manuscript. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. government.

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