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FLOW AND GEOCHEMISTRY OF GROUNDWATER BENEATH A BACK-BARRIER LAGOON: THE SUBTERRANEAN ESTUARY AT CHINCOTEAGUE BAY, MARYLAND, USA

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Supplemental Material

Section A: Additional Details of Methods

In August 2003 a complex subsurface field investigation was carried out to examine the occurrence and chemistry of subestuarine groundwater beneath the Maryland section of Chincoteague Bay, as a follow-up to earlier surface geophysical studies (Manheim et al., 2004). Offshore work at four sites (Figure 1, Supplemental Material, Table C.1), consisting of rotary drilling, downhole geophysical logging, and sampling of groundwater, sediments, and surface water, was performed from a spud barge platform. This was augmented with onshore logging of four existing wells (one on the mainland at Public Landing, and three on Assateague Island; Figure 1; Supplemental Material, Table C.1), and collection of surface water samples from shore at bay and ocean sites, and from four creeks that flow into Chincoteague Bay or adjacent bays (Figure 1; Supplemental Material, Table C.1). The maximum drilling depth reached offshore was 23 m beneath the sediment surface. The approach to sampling, logging, and analysis used in this investigation was similar to that employed in a previous investigation in Delaware (Böhlke and Krantz 2003; Bratton et al., 2004; Krantz et al., 2004).

A.1 Drilling

Downhole geophysical logs and groundwater or porewater samples were collected in two areas of Chincoteague Bay during this investigation: adjacent to Public Landing on the central western shore, and in a north-south transect extending offshore from South Point in the northern end of the bay, between Newport Bay and Sinepuxent Bay (Figure 1). Surface-water samples also were

collected at South Point and Public Landing to constrain the chemistry of the estuarine endmember.

Drilling was performed using 10.2-cm outside-diameter steel casing, advanced by spinning and washing with pumped bay water using a trailer-mounted drilling rig secured to a spud barge. Sediment samples were collected in the upper 6 m of each hole using either a 152-cm or a 76-cm split-barrel corer with an outside diameter of 5.1 cm. Sediment cores were collected by pushing or driving the corer in 152-cm runs (overdriving twice the length when the 76-cm corer was used), and advancing casing through the cored interval between each successive run. Sample recovery was typically 40-55% of cored length. Sediment sample depths were measured from the top of the coring interval with no attempt to correct for compaction or uneven recovery (i.e., differences between cored length and recovered length were assumed to be solely the result of incomplete recovery, and were recorded as gaps for sediment description purposes in Table C.2).

A.2 Geophysical logging

Downhole geophysical logging was performed at drilling sites to provide continuous profiles of subsurface data from which subsurface lithology and subestuarine groundwater salinity could be interpreted between actual sampling depths. Logs were obtained prior to installation of temporary monitoring wells by drilling to the maximum depth, and then inserting a blank PVC riser pipe filled with fresh water into the steel casing. The casing was then retracted allowing the formation to collapse around the blank riser pipe prior to logging. Geophysical logs of the boreholes were collected using a calibrated Mount Sopris Instruments MGX II portable digital logger running MSLog software, with a PGA-1000 gamma-logging tool (primarily sensitive to lithologic variations) and a PIA-1000 electromagnetic-induction (EM) probe (primarily sensitive to variations in groundwater salinity). The gamma and EM conductivity logs were taken through 5.1-cm PVC casing filled with fresh water. The PVC casing was pulled from the hole after the logging was completed. Gamma logs and EM logs also were obtained, using the same instruments, from four previously installed wells (Dillow and Greene 1999, Dillow et al., 2002) at Public Landing and on Assateague Island (Figures 1a, 1b, and 1d).

A.3 Sampling

A.3.1 Sediment squeezing

To extract pore fluid from sediment samples, a 10- to 50-cm³ aliquot of saturated sediment was pressed in the stainless steel chamber of a clean and dry Manheim-type hydraulic sediment squeezer (Manheim and Gieskes 1984; Manheim et al., 1994). Pore fluid was collected in syringes attached to the squeezing apparatus, and filtered with 0.2- μ m pore size syringe-tip filters. Typically a volume of 3 to 5 mL of water was recovered from pressed samples. Salinity of filtered samples was determined in the field using a handheld optical refractometer.

A.3.2 Well sampling

Subestuarine groundwater samples were collected at all drilling locations by pumping from temporary wells. This technique was used to allow collection of larger sample volumes than sediment squeezing produces, to make it possible to obtain high-quality dissolved gas samples, and to permit sampling from discrete depth intervals identified as possible groundwater conduits (zones of coarser sediments with low gamma activity and low EM conductivity). Temporary wells were installed in the bay at locations that were offset from the geophysical logging locations by several meters. Temporary wells were installed with 5.1-cm PVC riser through steel casing. The

casing was raised to approximately 1.5-2.5 m above the top of the well screen during development and sampling, allowing the formation to collapse around the screen. The screen for each well was 71 cm long with 0.25-mm slots and a 5-cm sump, except for the first well at SP-2003-03 where a 120-cm screen with a 24-cm sump was used. In the data tables and text that follow, the nominal depth for well samples used is the midpoint of the screen in centimeters below the sediment surface (Table C.3). Wells were developed using a Waterra brand inertial lift pump with the inlet held above the well screen, followed by final purging until clear using a bailer. Samples were subsequently pumped through nylon tubing from just above the level of the well screen using a submersible Bennett pneumatic piston pump. Specific conductance, pH, temperature, dissolved oxygen (O_2), and oxidation-reduction potential (ORP) were monitored during well development and sampling in the field using a calibrated Hydrolab[®] Datasonde 4 Multiparameter Water Quality Monitoring Instrument with an attached Scout 2 display. The instrument was calibrated to a conductivity standard for specific conductance, buffered pH standards for pH, and aerated water for dissolved oxygen. At three of four sites, wells were installed sequentially at three discrete depths working from shallow to deep in the same borehole. Wells were removed after sampling was completed. In some cases, water levels were allowed to equilibrate in wells after sampling and relative head differences were measured between water levels in the wells and surface water levels. These measurements were not corrected for tidal stage or salinity differences between well water and surface water.

A.3.3 Surface water sampling

To characterize water chemistry of other components of the hydrological system in the area, surface water samples were collected from three Chincoteague Bay locations, four streams that flow into the bay, and one Atlantic Ocean location (Fenwick Island) (Figure 1, Supplemental Material, Table C.1). Samples were collected by submerging and directly filling bottles, or pumping into bottles using a peristaltic pump. The open-water sample from the offshore drilling site SP-2003-01 was collected using the same Bennett piston pump that was used for groundwater sampling deployed upwind of the drilling barge. Samples of surface water were analyzed for a subset of the groundwater parameters listed below, using the same methods.

A.4 Laboratory analyses

Samples for nutrient analyses were filtered (0.2 μm pore size) in the field, placed on ice, and stored frozen prior to analysis at the University of Delaware. Dissolved ammonium (NH_4^+), nitrate + nitrite ($\text{NO}_3^- + \text{NO}_2^-$, abbreviated NO_{2+3}), phosphate (PO_4^{3-}), and reactive silicate ($\text{Si}(\text{OH})_4$, abbreviated Si) were determined by automated colorimetry using an O/I Analytical Flow Solution[®] IV Analyzer. 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-naphthyl) 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 (both Strickland and Parsons 1972). Typical precisions for analyses of low-concentration or diluted samples of NH_4^+ , NO_{2+3} , and PO_4^{3-} were approximately ± 0.2 -1, ± 1 -5, and ± 0.02 -0.05 $\mu\text{mol L}^{-1}$, respectively. Overall uncertainties may be larger for NO_{2+3} in squeezed sediment pore waters with high NH_4^+ concentrations, as a result of partial oxidation of the NH_4^+ during processing of the cores or sample storage. Some NO_{2+3} concentrations as high as 258.4 μM were obtained from porewater samples that were well within the reduced zones of the sediments where other evidence (including pumped groundwater from similar depths) indicated NO_{2+3} would not have been present.

Pumped samples collected from the temporary wells also were analyzed for major dissolved gases (Ar, N₂, O₂, CH₄), Ne, He, He isotopes, ³H, chlorofluorocarbons (CFC11, CFC12, CFC113), SF₆, δ²H, δ¹⁸O of water, and δ¹⁵N of NH₄⁺ and N₂, generally following methods described by Böhlke and Krantz (2003). Sediment core samples were analyzed for total C and N concentration, and N isotopes. Dissolved-gas samples were collected in 160-mL serum bottles, preserved with KOH (approximately 200 mg), and sealed with butyl rubber stoppers without headspace. Gas analyses were done by gas chromatography on low-pressure headspace in the USGS Dissolved-Gas Laboratory in Reston, Virginia (<http://water.usgs.gov/lab/dissolved-gas/>). Concentrations of N₂, Ar, and Ne (see below) were used to estimate atmospheric equilibrium (recharge) temperatures, concentrations of excess air (assumed to be unfractionated), and concentrations of excess N₂ in the groundwaters, as described by Böhlke and Krantz (2003) and Böhlke et al., (2007).

Samples for He, Ne, and ³H-³He age determination were collected in flow-through copper tubes that were crimp-sealed in the field. He and Ne were extracted for mass-spectrometric (MS) analysis, then degassed aliquots of the water were re-analyzed after several months to determine ³H concentrations from ³He in-growth at the Lamont-Doherty Earth Observatory (LDEO) Noble Gas Laboratory (Ludin et al., 1998). The apparent age of each groundwater 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 He (Schlosser et al., 1998) with an assumed ³He/⁴He ratio of 2 x 10⁻⁸. The surface-water samples and most of the groundwater samples were analyzed for ³H by electrolytic enrichment and liquid scintillation counting at the USGS tritium laboratory in Menlo Park, CA (MPTL; R.L. Michel, written communication). For samples analyzed both ways, results were in agreement to within ± 0.3 TU. Reported groundwater and SP surface water ³H concentrations are from ³He ingrowth measured by LDEO for consistency with the other ³He data; reported values for other surface waters are from MPTL (no ³He data).

Samples to be analyzed for chlorofluorocarbons (CFCs) were collected unfiltered with no headspace in 125-mL glass bottles with aluminum-lined caps. 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, Virginia (<http://water.usgs.gov/lab/cfc/>). For each sample, the measured concentrations of CFC11, CFC12, and CFC113 were converted to equilibrium partial pressures at sea level, adjusted for the measured salinities at the equilibration temperatures indicated by dissolved-gas data. Samples for SF₆ analysis were collected unfiltered in 2-L glass bottles with polyseal caps without headspace. In the laboratory, an aliquot was taken from each of two bottles from each sampling depth for analysis by purge-and-trap gas chromatography (Busenberg and Plummer, 2000) (<http://water.usgs.gov/lab/sf6/>). For each sample, the SF₆ 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 (Bullister et al., 2002; E. Busenberg, written communication, 2005). Concentrations of ³H, ³H/³H^o ratios, and the partial pressures of CFCs and SF₆ were compared with atmospheric records to determine apparent ages of groundwater samples, and to evaluate various types of simple age mixtures using the program Tracermodel1 (Böhlke, 2006).

The N isotopes in NH₄⁺ were analyzed by a modification of the NH₃ diffusion method (Holmes et al., 1998; Hannon and Böhlke, in press). Aliquots of water containing 3 μmol of NH₄⁺ were transferred to 60-mL acid-washed HDPE bottles. De-ionized water and NaCl (precombusted to 475°C) were added to each bottle to achieve a constant total volume of 31 mL and salinity of 40. Each bottle received a Teflon diffusion packet consisting of a 1-cm GFD filter containing 25 μL of 2N H₂SO₄ sandwiched between two PTFE membrane filters. Finally, 0.35 g of MgO (precombusted to 475°C) was added to each bottle, which was then capped and held in a rotating

hybridization-incubation oven at 45°C for 72 hours. The diffusion packets were removed and placed in individual ashed glass scintillation vials inside a dessicator containing concentrated H₂SO₄ for 24 hours, and then removed and capped. For isotopic analysis, the GFD filters were removed from the Teflon[®] packets, loaded into tin foil capsules, and analyzed by EA-IRMS. The δ¹⁵N values were calibrated by analyzing ammonium isotopic reference materials as samples and are reported with respect to atmospheric N₂ and normalized to values of +0.43‰ for IAEA-N1 and +53.7‰ for USGS26 (Böhlke and Coplen 1995), with average reproducibilities of approximately ± 0.2‰.

Sediment samples for isotopic analysis were freeze-dried, ground, and homogenized. Aliquots were loaded into tin capsules, then flash-combusted in an elemental analyzer (EA), from which the gases were flushed with He through a Porapak[®] PQS chromatographic column, and into an isotope ratio mass spectrometer operated in continuous flow mode. Sediment C and N concentrations and δ¹⁵N values were calibrated by analyses of organic reference materials USGS40 and USGS41 (Qi et al., 2003), with reproducibilities of approximately ± 0.2‰ for δ¹⁵N.

For N isotope analyses of dissolved N₂, the headspace gas remaining in 160-mL serum bottles after gas chromatography was pressurized with He, then released to a closed loop and flushed through a mol-sieve capillary column GC, to the inlet of an isotope-ratio mass spectrometer operated in continuous flow mode (Révész et al., 1999; Tobias et al., 2007). Results were calibrated against samples of N₂ in air (δ¹⁵N = 0.0‰) and laboratory-equilibrated water (δ¹⁵N = +0.65‰ ± 0.10‰) that were analyzed the same way as the samples.

Water samples to be analyzed for H and O isotopes (δ²H and δ¹⁸O) were collected in 60-mL glass bottles and analyzed at the USGS Reston Stable Isotope Laboratory (<http://isotopes.usgs.gov/>) by H₂ and CO₂ equilibration and mass spectrometry methods. Values of δ²H and δ¹⁸O were normalized to the VSMOW-SLAP scale (Coplen 1988) with uncertainties of approximately ± 1‰ and ± 0.1‰ (1σ), respectively.

A.5 Additional references not included in main article

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Section B: Figures

Captions

Figure B.1. Gamma (solid lines, 3-point moving average of data) and EM induction (dashed lines) logs from Assateague Island locations (Figure 1D). Lower gamma log values indicate coarser (sandy) deposits or peats; higher values indicate finer, clay-rich deposits. Lower EM values reflect lower salinity of groundwater. Note the larger scale on the EM axis in the middle profile (WO-Ef-26) to show the full range of brine-influenced measurements.

Figure B.2. Sediment N isotopes vs. sediment N concentration, with groundwater ammonium N isotope ranges shown for comparison, including ranges from a previous study in Indian River Bay, Delaware (Böhlke and Krantz 2003). ϵ = hypothetical isotopic fractionation factor with trend similar to some of the sediment data (shown for reference).

Figure B.1

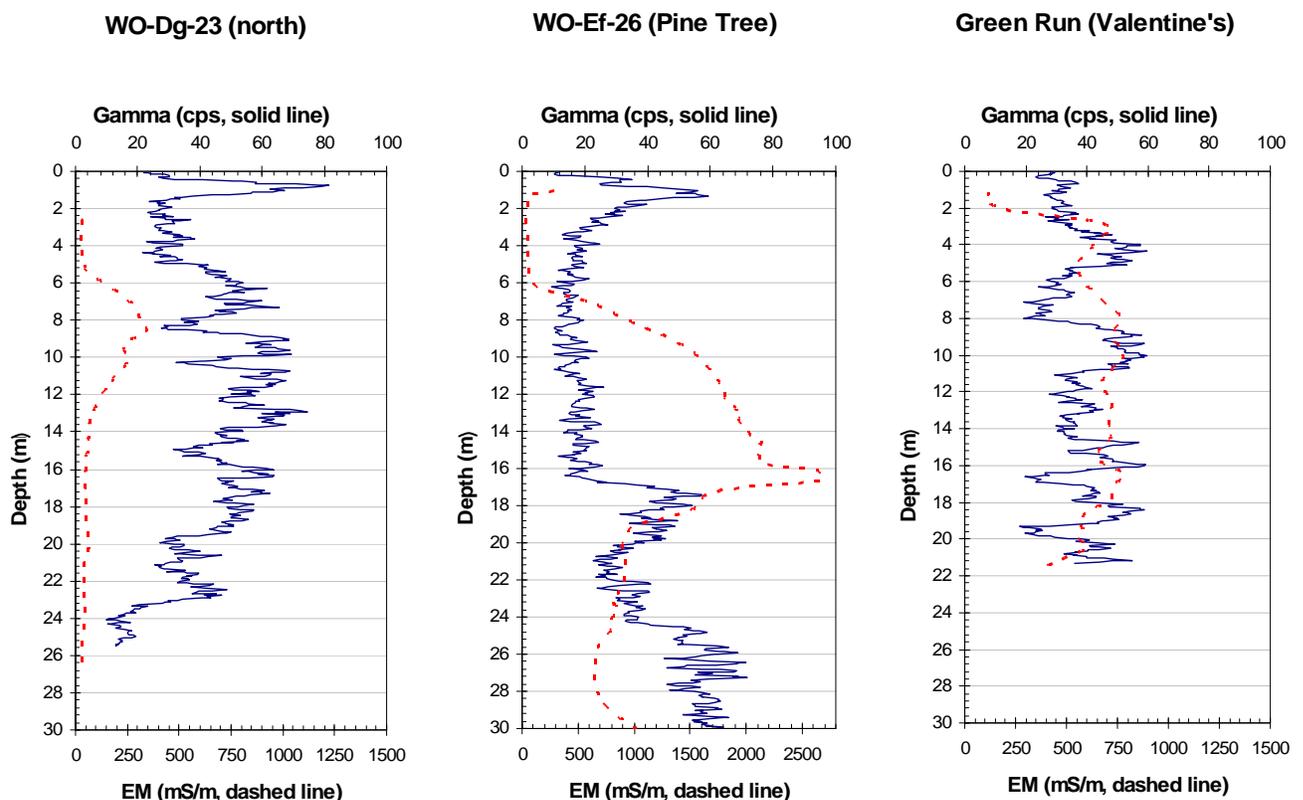
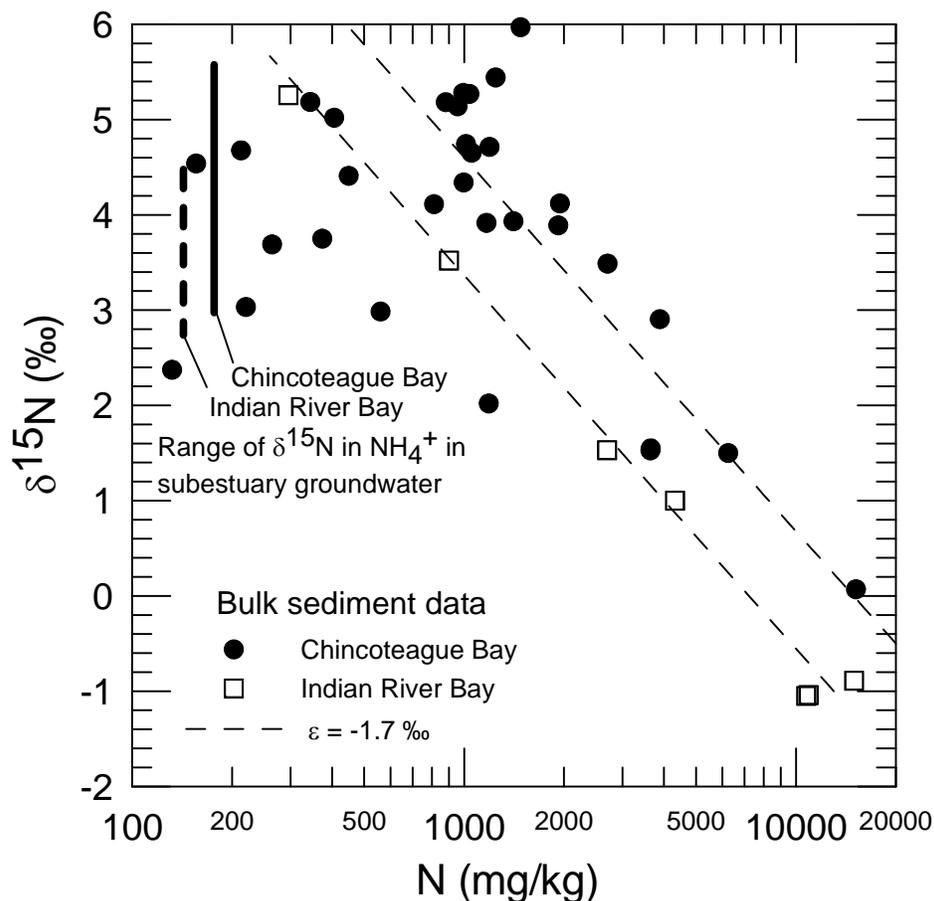


Figure B.2.

chincoteague-core-N1.grf (JKB) 2/7/08



Section C: Tables

Table C.1. Drilling, logging, and sampling locations.

Table C.2. Sediment descriptions.

Notes:

Units of measure are: cm, centimeters; cm bsf, centimeters below seafloor.

Table C.3. Nutrient, salinity, carbon, and nitrogen data for samples collected from the Chincoteague Bay area.

Notes:

Abbreviations and units of measure are: na, not analyzed; mbsf, meters below seafloor; μM, micromoles per liter; g/kg, grams per kilogram; δ¹⁵N, nitrogen isotope ratio (¹⁵N/¹⁴N) in standard delta notation; ‰ air, permil (part per thousand) relative to an air standard. Ammonium, nitrate + nitrite, phosphate, and silicate concentrations of water samples were measured at the University of Delaware. Carbon, nitrogen, and δ¹⁵N of sediment samples were measured at the USGS, Reston Stable Isotope Laboratory (RSIL).

Table C.4. Water quality, isotope, and age-related data for groundwater and surface water samples collected from offshore Chincoteague Bay sites.

Notes:

Units of measure are: m, meters; mbsf, meters below seafloor; cm, centimeters; mg, milligrams; L, liters; μM , micromoles per liter; pmol, picomoles (10^{-12} moles); fmol, femtomoles (10^{-15} moles); μS , microsiemens; mV, millivolts; VSMOW, Vienna Standard Mean Ocean Water; ccSTP, cubic centimeters of gas at standard temperature (0°C) and pressure (1 atmosphere); ‰, permil (part per thousand); pptv, parts per trillion by volume, calculated atmospheric mixing ratio of gas in equilibrium with a water sample at the estimated recharge temperature and excess air concentration (calculated from the mean of the measured aqueous concentrations); TU, tritium unit (1 atom of ^3H per 10^{18} atoms of ^1H). Chemical symbols and parameters are: ORP, oxidation-reduction potential; O_2 , molecular oxygen; CFC11, chlorofluorocarbon CCl_3F ; CFC12, chlorofluorocarbon CCl_2F_2 ; CFC113, chlorofluorocarbon $\text{C}_2\text{Cl}_3\text{F}_3$; SF_6 , sulfur hexafluoride; CH_4 , methane; Ar, argon; N_2 , molecular nitrogen; NH_4^+ , ammonium; ^3H , tritium; He, helium; $^3\text{He}^*$, tritiogenic helium; $^4\text{He}^*$ (terr.), terrigenic helium; $^3\text{H}^0$, reconstructed initial ^3H concentration at the time of recharge, corrected for decay; Ne, neon; $\delta^{15}\text{N}$, nitrogen isotope ratio ($^{15}\text{N}/^{14}\text{N}$) in standard delta notation; $\delta^{18}\text{O}$, oxygen isotope ratio ($^{18}\text{O}/^{16}\text{O}$) in standard delta notation; $\delta^2\text{H}$, hydrogen isotope ratio ($^2\text{H}/\text{H}$) in standard delta notation; $\delta^3\text{He}$, helium isotope ratio ($^3\text{He}/^4\text{He}$) in standard delta notation. Sources of data are: LDEO, Lamont-Doherty Earth Observatory (Noble Gas Laboratory); RCFC, USGS Reston Chlorofluorocarbon Laboratory; RSIL, USGS Reston Stable Isotope Laboratory. Shaded entries have relatively large uncertainties.

Annotations: [1] Samples are identified by the corehole site, followed by the depth of the well screen beneath the sediment-water interface in meters. [2] Apparent (calculated) values of $^3\text{H}^0$, $^3\text{H}/^3\text{H}^0$, and $^3\text{H}-^3\text{He}$ “age” may be affected by mixing of waters with different properties (see text).

Table C.5. Analytical data for surface-water samples collected from shore in the vicinity of Chincoteague Bay.

Notes:

Salinity, $\delta^2\text{H}$, and $\delta^{18}\text{O}$ data from USGS, Reston Stable Isotope Laboratory (RSIL); ^3H data from USGS, Menlo Park Tritium Laboratory (MPTL). Also see Table C.4 notes.