

Stable Isotope Studies in Groundwater in the Northeastern United States and Associated Recharge of Glacial Meltwaters during the Last Glacial Maximum

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Freshwater has been observed in confined aquifers extending over 100 km offshore from the northeastern coastal U.S.A., much greater distances than can be explained by groundwater models using contemporary hydrologic boundary conditions. In order to investigate the origin and residence times of these groundwaters, a total of 25 groundwater samples were collected on Nantucket Island and Martha's Vineyard, MA, Long Island, NY, and along the coastal plain of southern New Jersey. Sample sites were believed to contain remnant glacial meltwaters of the LGM. Samples were analyzed for stable isotopes (^{18}O , D) and major and minor ion chemistry. A U.S.G.S. monitoring well on Sandy Hook, N.J., had a chloride concentration of 15,151 mg/l. This well was determined to be intruded by saltwater.

Observed groundwater $\delta^{18}\text{O}$ and δD values were similar to those of modern meteoric waters in the recharge area. Other studies interested in LGM waters in Atlantic Coastal Plain aquifers have also found $\delta^{18}\text{O}$ values representative of modern meteoric water. These studies used noble gases and ^{14}C to confirm the presence of glacial age groundwater. Interestingly, their $\delta^{18}\text{O}$ values did not correlate with colder recharge temperatures ($\sim 5^\circ\text{C}$ cooler) as indicated by noble gas analyses. The absence of ^{18}O -depleted groundwaters may be explained by (1) a poor correlation of $\delta^{18}\text{O}$ to temperature along the Atlantic Coast, (2) conflicting effects of boundary conditions at the LGM (e.g. cooling accompanied by changes in atmospheric vapor origin or

increases in evaporation), (3) sampling of modern Holocene waters believed to be LGM (4) inadequate sampling of aquifers.

Future work will involve noble gas and ^{14}C analyses of the groundwater samples. This will allow for the determination of recharge temperatures and groundwater ages, further building an understanding of the behavior of stable isotope values in the Atlantic Coastal Plain aquifer system.

I. INTRODUCTION

Ocean drilling on the North Atlantic Continental Shelf has indicated that the saltwater-freshwater mixing zone within Pleistocene to Cretaceous age coastal-plain sediments is far out of equilibrium with modern sea-level (Kohout et al., 1977; Hathaway et al., 1979). Anomalous volumes of freshwater have been observed beneath Nantucket, Martha's Vineyard, and the North Atlantic Continental Shelf up to 100 km off New Jersey. The Ghyben-Herzberg relationship states that, in equilibrium, for every meter of freshwater above sea level there is 40 meters below sea level. On Nantucket, for example, groundwater elevations reach up to 3 m a.s.l., which according to the Ghyben-Herzberg principle would indicate approximately 120 m of freshwater below Nantucket. However, a 514-m deep borehole (well USGS 6001; Figs. 1 & 2) penetrating through the entire Cretaceous sedimentary package had pore-water salinities of less than 1 ppt within the permeable intervals (Fig. 1). In addition, a deep borehole located about 150 km offshore Long Island, New York (well 6009), had a salinity level as low as 3000 mg/l within a Miocene/Pliocene sand unit (Fig. 1).

Kohout et al. (1977) proposed that unusually fresh water within the permeable units of the Atlantic continental shelf could be the result of lateral inflow of meteoric recharge into these confined aquifers during Pleistocene sea-level lowstands. Marine $\delta^{18}\text{O}$ records and precise dating of shoreline facies and corals suggest that Pleistocene sea level varied by ~120 m with a period of between 40 k.y. and 100 k.y. (Shackleton and Opdyke, 1973; Hays et al., 1976). However, cross sectional models of variable-density flow and solute transport constructed by Person et al. (2003) showed that sea-level fluctuations alone could not drive freshwater as far out on the continental shelf off Long Island as observed in the USGS well 6009.

Groen et al. (2000) proposed that local flow systems associated with secondary topography of the subaerially exposed and incised continental shelf are essential to emplace meteoric water far out onto the continental shelf. Person et al. (2003) emphasized the role of sub-ice-sheet recharge from adjacent Long Island Ice sheets and/or recharge from associated pro-glacial lakes, respectively. Figure 3 presents illustrations of the current conceptual models used to explain the presence of freshwater off the North Atlantic Continental Shelf.

Stable isotopes are an important tool in deciphering between groundwaters of different origins. Modern meteoric water can be distinguished from glacial meltwaters of the Last Glacial Maximum (20 k.y. B.P.) by its isotopic signature. Modern meteoric and river water in the northeastern coastal plain of the United States on average has a $\delta^{18}\text{O}$ composition between -6‰ and -8‰ as indicated by USGS NASQAN (Coplen and Kendall, 2000) and IAEA-WMO (<http://www.waterisotopes.org>) isotope data (Figure 4). Several studies have shown that groundwaters of the late Pleistocene and associated Laurentide Ice Sheet (e.g. pro-glacial lake/sub-glacial meltwater) are significantly more depleted in ^{18}O ($\delta^{18}\text{O} \sim -20\text{‰}$; Remenda et al.,

1994; Hendry and Wassenaar, 1999; Grasby et al., 2000). Stable isotope values will prove valuable in deciphering between Holocene and LGM groundwaters.

The purpose of this study is to compile and assess a data set of stable isotopes (^{18}O and D; Table 1 & 2-see Figures and Tables section) from groundwaters in confined aquifers in the northeastern United States. The stable isotope information will then be used to identify latitudinal and/or spatial isotopic trends representative of recharge from the Laurentide Ice Sheet and associated glacial meltwaters that resulted from the Last Glacial Maximum. A total of 25 groundwater samples, believed to contain remnant meltwaters of the LGM, were collected on Nantucket Island and Martha's Vineyard in MA, Long Island, NY, and along the coastal plain of New Jersey.

II. BACKGROUND OF STABLE ISOTOPES

A. Expression of isotopes

Isotopic concentrations are expressed as the difference between the measured ratios of the sample and reference over the measured ratio of the reference standard. This is expressed using the delta (δ) symbol. Because fractionation processes do not create large variations in isotopic concentrations, δ -values are expressed as the permil (‰) difference from the reference standard, reproduced in equation (1):

$$\delta^{18}\text{O}_{\text{sample}} = \left(\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{reference}}} - 1 \right) * 1000 \text{‰ VSMOW} \quad (1)$$

VSMOW (Vienna Standard Mean Ocean Water) is the internationally accepted reference for ^{18}O and D. 2.0052×10^{-3} and 1.5575×10^{-4} are the reference numbers for ^{18}O and D, given in terms

of the natural abundance ratios for $\frac{{}^2\text{H}}{{}^1\text{H}}$ and $\frac{{}^{18}\text{O}}{{}^{16}\text{O}}$.

B. Fractionation

Isotope fractionation occurs in any thermodynamic reaction due to differences in the rates of reaction for different molecular species which contain different isotopes of a given element. Isotopic fractionation in the case of the hydrological cycle occurs when water changes from a gas to a liquid or from a solid to a liquid phase. Fractionation causes the relative abundance of the individual isotopes to change because the heavier isotopes (^{18}O and D) tend to be more concentrated in the liquid phase while the lighter isotopes are more concentrated in the gaseous phase. Fractionation factors provide a quantitative look at the amount of isotopic fractionation that occurs in a given setting. The fractionation factor α represents the ratio of the isotope ratios for the reactant and product in a thermodynamic reaction for both equilibrium and kinetic processes (equation 2).

$$\alpha = \frac{R_{\text{reactant}}}{R_{\text{product}}} \quad (2)$$

$$\text{e.g. } \alpha^{18}\text{O}_{\text{water-vapor}} = \frac{({}^{18}\text{O}/{}^{16}\text{O})_{\text{water}}}{({}^{18}\text{O}/{}^{16}\text{O})_{\text{vapor}}}$$

C. Temperature effect on fractionation

For many systems, isotope fractionation is strongly dependent on the temperature of the reaction. Experimental studies have shown that fractionation factors for ^2H and ^{18}O decrease with

increasing temperature (Dansgaard, 1961; Craig et al., 1963; Majoube, 1971; Horita and Wesolowski, 1994). The fractionation factor is close to 1 at high temperatures. With decreasing temperature, α departs from unity, and isotope partitioning between the reactants and products occurs. Horita and Wesolowski (1994) developed a set of equations (3 and 4) that relate the fractionation factors (expressed as $10^3 \ln \alpha$) of ^{18}O and D to temperature:

$$10^3 \ln \alpha(^{18}\text{O}) = -7.685 + \frac{6.7123 \times 10^3}{T} - \frac{1.6664 \times 10^6}{T^2} + \frac{0.35041 \times 10^9}{T^3} \quad (3)$$

$$10^3 \ln \alpha(^2\text{H}) = \frac{1158.8T^3}{10^9} - \frac{1620.1T^2}{10^6} + \frac{794.84T}{10^3} - 161.04 + \frac{2.9992 \times 10^9}{T^3} \quad (4)$$

where T is expressed in kelvins (K).

The fractionation factor for ^{18}O between water and vapor is approximately 1.012 (11.5 ‰) at freezing, and decreases to about 1.005 (5 ‰) at 100°C. The fractionation factor for D decreases from about 1.112 (106‰) at 0°C to only 1.027 (27‰) at 100°C (Table 3).

Table 3. Fractionation factor values for ^{18}O and ^2H between -10°C and 100°C

Exchange Reaction	T(°C)	$\alpha(^{18}\text{O})$	$\alpha(^2\text{H})$
Water-Vapor ^{1,2}	-10	1.013	1.130
	0	1.012	1.112
	5	1.011	1.105
	10	1.011	1.097
	15	1.010	1.091
	20	1.010	1.085
	25	1.009	1.079
	30	1.009	1.074
	40	1.008	1.064
	50	1.008	1.057
	70	1.006	1.043
	75	1.006	1.040
	90	1.006	1.031
100	1.005	1.027	

1 Majoube (1971)

2 Horita and Wesolowski (1994)

D. Rainout and Rayleigh Distillation

An air mass that follows a trajectory from its initial vapor source area (e.g. Atlantic Ocean) to higher latitudes and over continents will progressively cool and lose its water vapor along the way through condensation & precipitation. This process is known as “rainout”. Equilibrium fractionation between vapor and the condensing phases preferentially partitions ^{18}O and ^2H into the rain or snow. As the air mass moves through its trajectory the process of rainout distills the heavy isotopes from the vapor. Because the air mass keeps moving, no back reactions between the vapor and liquid reservoir occur. Therefore, isotopically enriched rain is forming and falling from a diminishing vapor mass. The residual vapor becomes more and more isotopically depleted. Each subsequent rain will be depleted of the heavy isotopes with respect to earlier rains. Rainout is an evolution towards colder, more isotopically-depleted precipitation. The Rayleigh distillation equation (5) is an exponential function that describes the progressive partitioning of heavy isotopes from the air mass:

$$R = R_o f^{(\alpha-1)} \quad (5)$$

where R = isotope ratio of O or H of vapor remaining in an air mass in which condensate is forming

R_o = isotope ratio of O or H in vapor before any condensate has formed

α = isotope fractionation factor of ^{18}O or D defined as in Equation 3

f = fraction of water vapor remaining in the air mass

E. Latitude effect

Global studies have shown that precipitation at higher latitudes is relatively depleted in ^{18}O and D in comparison to samples from lower latitudes. High latitude regions tend to be farther away from the source of moisture; therefore air masses experience greater amounts of rainout by the time precipitation falls in these areas. Temperatures are significantly colder at

higher latitudes as well. The temperature and latitude effects are the primary concerns of this investigation. Table 4 provides evidence of the modern relationship between latitude and stable isotopes in precipitation.

Table 4. Mean $\delta^{18}\text{O}$ and δD (VSMOW) distribution in precipitation on the Earth (data from GNIP, IAEA-WMO database.)

Latitude(°)	Weighted Annual $\delta^{18}\text{O}$ (‰)	Weighted Annual $\delta^2\text{H}$ (‰)
82.30	-28.68	-216.58
80.00	-26.25	-205.42
71.30	-17.39	-127.89
69.46	-15.64	-106.07
64.58	-12.90	-92.38
52.10	-8.12	-57.15
41.38	-5.50	-31.00
38.01	-5.87	-34.30
28.12	-5.65	-32.14
18.28	-4.26	-26.40
6.54	-3.42	-17.76
-24.78	-5.86	-40.78
-33.45	-9.84	-67.65
-54.78	-11.02	-85.13
-67.57	-13.76	-111.09

F. Meteoric Water Line

Craig (1961) demonstrated a strong correlation between $\delta^{18}\text{O}$ and δD from meteoric waters on a global scale. This relationship was termed the Meteoric Water Line and originally was the following equation (6):

$$\delta\text{D} = 8\delta^{18}\text{O} + 10 \text{‰} \quad (6)$$

Subsequent studies have shown the MWL varies from region to region; however this relationship generally applies in most parts of the world. A more accurate regression for the

Global Meteoric Water Line (GMWL) was developed by Rozanski et al. (1993) (Fig. 7) and is the following:

$$\delta D = 8.13\delta^{18}O + 10.8\text{‰ VSMOW} \quad (7)$$

Deviations of $\delta^{18}O$ and δD from the MWL and the associated causes for these isotopic shifts are found in Figure 8 (Schwartz & Zhang, 2003). High temperatures will tend to push $\delta^{18}O$ and δD values further away from the MWL towards more positive (less negative) values. Evaporation of water from lakes, ponds, and rivers will occur when water resides in these reservoirs for an extended period of time. The lighter isotopes are removed in water vapor and the water bodies become enriched in the heavier isotopes. Condensation events will cause the opposite effect of evaporation, moving $\delta^{18}O$ and δD values towards greater negative values.

A positive shift in $\delta^{18}O$ from the meteoric water line is observed for geothermal waters. Due to the low content of H in most rock-forming minerals, no shift for H is seen on the MWL for thermal water. Groundwater is highly depleted in ^{18}O in comparison to the surrounding minerals. In most aquifers, the temperature is too low and circulation rates too high for there to be significant isotopic alterations of the groundwater by mineral exchange. However, the high temperatures (greater than 100°C) of geothermal systems do not allow for equilibrium fractionation of ^{18}O between minerals and water which results in a shift of $\delta^{18}O$ towards more enriched values. In contrast to high-temperature water-rock interactions, the hydration of silicate minerals at temperatures below 300°C cause waters to be enriched in D and depleted in ^{18}O relative to the MWL.

III. STABLE ISOTOPES AND PALEOGROUNDWATERS

A. Relationship between climate and stable isotopes

Because aquifers are recharged by meteoric water, a strong correlation exists between the isotopic composition of precipitation and groundwater. As a result, climate change should be recorded in paleogroundwaters of confined aquifer systems (Loosli et al., 1998). Temperate latitudes have experienced significant changes in temperature since the late Pleistocene (Clark and Fritz, 1999). Climate changes are seen by a shift in the stable isotope content of precipitation and associated groundwater. This shift can be observed on the meteoric water line.

B. Influence of late Pleistocene glaciation on climate of northeastern United States

Climatic differences between the late Pleistocene and Holocene have important implications for stable isotope values of precipitation. The equator to pole temperature gradient was much greater during the LGM (Bush and Philander, 1999). In comparison to the present day, the interior of Antarctica was up to 11°C cooler, while the tropics were around 4°C cooler (Bush and Philander, 1999). Noble gas and stable isotope studies in confined aquifers have shown that temperatures during the LGM were ~5°C cooler than present in the southwestern United States, Brazil, and western and central Europe (Stute et al., 1992a; Stute et al., 1995a; Stute et al., 1995b; Andrews and Lee, 1979; Beyerle et al., 1998).

A study of noble gas and stable isotope records in the Aquia Aquifer in Maryland (Aeschbach-Hertig et al., 2001) showed greater cooling of approximately 9.0 ± 0.6 °C during the late Pleistocene. Climate models based on pollen data collected from lakes in the northeastern United States (Webb et al., 1998) indicate temperatures around the LGM to be 2-10° C cooler

than present. The results of the study in Maryland (Aeschbach-Hertig et al., 2001) fall within the more extreme values of the temperature range estimated from pollen data. The pollen-based climate reconstructions (Webb et al., 1998) and the study in Maryland (Aeschbach-Hertig et al., 2001) both indicate that sites close to the Laurentide ice sheet experienced a larger LGM-Holocene temperature decrease than observed at sites further south.

C. LGM and Holocene Meteoric Waters

Predictions can be made for stable isotope values of LGM waters. This can be done by looking at existing proxies for LGM precipitation and/or by using the relationship between isotopes in precipitation and temperature. Analysis of the isotopic composition of proglacial lake clays (Remenda et al., 1994; Hendry and Wassenaar, 1999) and aquifers from the Williston Basin (Grasby et al., 2000) show a large depletion in ^{18}O ($\delta^{18}\text{O} \sim -20\text{‰}$) for Pleistocene glacial meltwaters. It is possible water that fell as local precipitation in the northeastern United States would have a different isotopic signature than glacial meltwaters, which originated as snow much further north. The estimates of temperature change local to the field area would therefore provide a better estimate of ^{18}O -precipitation values.

Quantified estimates of temperatures changes during the LGM have been made using a variety of terrestrial and marine paleoclimate indicators. On-shore pollen data from studies in the northeastern United States indicate July temperatures of about 15°C at 18 k.y. B.P., approximately 6°C cooler than modern July temperatures for the field area (Webb et al., 1998). Using a dense network of foraminifera-based paleo-sea-surface temperature studies, Macintyre et al. (1976) showed SST declines were particularly large (8 to 14°C) in coastal waters between Cape Hatteras and Newfoundland owing to the southward migration of the Gulf Stream at that

time. Temperature data from the AES (1982) displays modern mean annual temperature gradients across the Eastern Canadian Arctic. A maximum mean annual temperature change of 14°C between the northeastern U.S. of the LGM and present (Macintyre et al., 1976) correlates with temperatures found today in the Eastern Canadian Arctic (0-2.5°C; AES, 1982) at roughly 58°-60°N latitude. $\delta^{18}\text{O}$ values in sampled lake waters on Baffin Island (Sauer, 1997) that lie within the temperature range of LGM temperatures for the northeastern U.S. show $\delta^{18}\text{O}$ values of approximately -14‰. Based on this evidence, meteoric waters in the northeastern U.S. during the LGM should exhibit $\delta^{18}\text{O}$ values of approximately -14‰, in contrast to -7‰ of current meteoric waters in the study area (Fig. 4).

IV. STUDY AREA

A. Brief overview of North Atlantic Continental Shelf

The study area consists of confined aquifers of the southern New England mid-Atlantic coastal plain region extending southward to New Jersey and Maryland (Fig. 9). The sediments of the Atlantic continental margin thicken seaward from coastal plain outcrops on the mainland across the continental shelf to the continental slope (Kohout et al. 1988). Pleistocene through Cretaceous age sediments, generally called coastal plains sediments, typically dip seaward to form a thick wedge overlying crystalline basement rocks. Miocene and younger aquifers are exposed along the continental shelf in submarine canyons allowing groundwater discharge directly to the ocean (Person et al., 2003). Numerous Mesozoic and Cenozoic unconsolidated-sand and sandstone aquifers extend for hundreds of kilometers offshore before grading into finer-grained, less permeable facies. The deepest part of the sedimentary wedge consists of carbonates

with minor amounts of evaporates (Manheim and Hall, 1976). The Cretaceous aquifers of the Atlantic continental shelf do not crop out on the mainland over much of New England and therefore are not receiving freshwater recharge today. For an extensive review, see Sheridan and Grow (1988).

B. Geology and Hydrogeology of Study Sites

Nantucket and Martha's Vineyard

Nantucket and Martha's Vineyard are underlain by a basement complex of crystalline schist, gneiss, and igneous rocks whose surface slopes southeastward from approximately sea level on the New England mainland to as much as 490 m below sea level at Nantucket (Oldale, 1969; Oldale and others, 1974) and to 7.6-9.1 km near the edge of the continental shelf (Sheridan, 1974). Coastal plain Cenozoic and Cretaceous sediments overlie the basement rocks, forming a wedge that thickens seaward from an initial feathered edge to about 365 m at Nantucket and to more than 2000 m at the edge of the shelf (Kohout et al., 1988). Cretaceous and Cenozoic sediments are composed of sands, silts, clays, and gravels and make up part of the Atlantic coastal plain sedimentary rock belt that extends westward to Long Island, NY. During the LGM, both Nantucket and Martha's Vineyard were overlain by the Laurentide Ice Sheet (Fig. 10). The ice-sheet thickness is estimated to have been 600-1000 m near the toe of the glacier (Denton and Hughes, 1981).

On Nantucket and Martha's Vineyard freshwater from unconsolidated Pleistocene outwash sands supplies the inhabitants with drinking water. These sands have an average permeability of $10^{-10.3} \text{ m}^2$ and an average hydraulic conductivity of $10^{-3.3} \text{ m/s}$ (Person et al.,

2003). Below the overlying Pleistocene sands lay poorly consolidated silty clay sediments that are Pliocene-Oligocene in age and have an average permeability and hydraulic conductivity of $10^{-6.5} \text{ m}^2$ and $10^{-9.5} \text{ m/s}$ (Person et al., 2003). Cretaceous sandstone units lie below the Tertiary sediments. These sediments have an average permeability of $10^{-9.3} \text{ m}$ and an average hydraulic conductivity of $10^{-2.3} \text{ m/s}$ (Perlmutter and Geraghty, 1963). Estimated recharge rates for the Nantucket aquifer units are based on regional groundwater-flow models (Person et al., 1998) and tritium groundwater dating (Knott and Olimpio, 1986). These studies have shown that ~ 40% of the annual precipitation, or 0.5 m/yr, recharges the shallow freshwater Pleistocene aquifer. This percentage is similar to recharge estimates for Martha's Vineyard, Long Island, and Cape Cod (Guswa and Leblanc, 1981).

Long Island

Long Island is capped with unconsolidated Pleistocene outwash sands that supply freshwater to its inhabitants. Deeper Cretaceous aquifers are also used as a freshwater resource as the shallow-aquifers have become increasingly contaminated. The water table on Long Island reaches a maximum height of about 24 m above sea level (Buxton and Modica, 1992). The absence of recharge to produce the freshwater below Nantucket contrasts with the circumstances found on Long Island (noted by Collins, 1978). Recharge on Long Island occurs from surficial glacial deposits downward through clay deposits into the Magothy Formation and the Lloyd Sand Member of the Raritan Formation (Fig 11; Lusczynski and Swarzenski, 1962, 1966). Recharge rates for Long Island are estimated to be approximately 0.5 m/yr. A study by Buxton and Modica (1992) found that 62% of the recharge flows no deeper than the upper glacial (water-table) aquifer, 38% enters the underlying Magothy Aquifer, and only 3.1% enters the Lloyd

Aquifer. The recharge area of the Magothy aquifer is 5.4 miles wide, while that of the Lloyd Aquifer is less than 0.5 miles.

The Magothy Aquifer is bounded above by Pleistocene glacial outwash sands and below by the clay member of the Raritan Formation (Fig. 11) and is characterized by a distinctive basal gravel zone approximately 30m thick. These deposits are of Cretaceous age and are near the northern extent of the Atlantic Coastal Plain.

The Lloyd Aquifer is Cretaceous in age and is present throughout Long Island except in small areas in western and northwestern Queens and Kings Counties. It is a continental deposit consisting of very fine to very coarse, rounded to subrounded, quartzose sand with gravel and interbedded clay, clayey and silty sand, and minor amounts of heavy minerals. The Lloyd Aquifer correlates with the Middle Potomac-Raritan-Magothy Aquifer system in New Jersey. The thickness of the Lloyd Aquifer ranges from a pinch-out at its northern extent to as much as 168 m along the south shore. Depth to the Lloyd Aquifer ranges from less than 30 m in Queens County to about 457 m in the central part of Fire Island.

New Jersey

The New Jersey Coastal Plain is part of the Atlantic Coastal Plain Aquifer system (Fig. 12) of which is comprised of a seaward-dipping wedge of unconsolidated sediments that range in age from Cretaceous to Holocene. These sediments consist of clay, silt, sand, and gravel deposited in alternating sequences of high- and low-permeability strata that represent interfingering deltaic and marine-shelf deposits. The thick sand units found between silt or clay units typically are confined aquifers. The Delaware River and Estuary, Sandy Hook Bay, the Atlantic Coast and the older, harder rocks of the Piedmont province constitute the recharge

boundaries of the New Jersey Coastal Plain aquifers. Natural recharge occurs primarily through direct precipitation on the outcrop area of the geologic formations. A smaller component of natural recharge to the deeper confined aquifers of the system occurs by vertical leakage from the upper layers. Recharge rates to unconfined aquifers and the unconfined (outcrop) areas of confined aquifers are about 0.4-0.5 m/yr; however, recharge rates via vertical leakage are at least 2-3 orders of magnitude lower (Emmanuel Charles, USGS New Jersey Water District Hydrologist, personal communication). The New Jersey Atlantic Continental Shelf aquifer system is remarkable in that it hosts large volumes of freshwater over 100 km offshore in some confined sands.

The aquifers of concern in this study include the Englishtown, Piney Point, and the Lower Kirkwood-Cohansey and confined Kirkwood aquifers (Fig. 13).

The Englishtown is generally less than 30 m thick; however its greatest thickness is 70 m in southern Monmouth and northeastern Ocean counties. The Englishtown aquifer is overlain everywhere except in its outcrop area by the Marshalltown-Wenonah confining unit. Most of the recharge to the Englishtown aquifer is from the overlying Wenonah-Mount Laurel aquifer near ground-water highs in Camden and Gloucester Counties and western Monmouth County. Almost one-third of the recharge occurs where the Wenonah-Mount Laurel aquifer crops out. Flow from the confined part of the Wenonah-Mount Laurel aquifer is more than 0.013m/yr in Gloucester and Camden Counties, near the ground-water high. Dwindip flow from the unconfined part of the Englishtown aquifer accounts for very little of the recharge. Hydraulic conductivity of the aquifer ranges from 1.2 to 3 m/d. The transmissivity of the aquifer is generally less than 46 m²/d in the southern, permeable part of the aquifer.

The Piney Point aquifer does not crop out because it is overlain entirely by the basal clay of the Kirkwood Formation (Zapeczka, 1984). The Piney point aquifer thins to pinch-out and is not present several miles downdip of the Atlantic coast. The aquifer is thickest in western Cumberland County where it is over 5 m thick. The aquifer thins to the northeast where it is less than 12 m thick in Atlantic County but thickens again to over 37 m in Burlington and Ocean Counties. Recharge for the Piney Point aquifer is primarily flow from the overlying unconfined lower Kirkwood-Cohansey and confined Kirkwood aquifers. Flow in the Piney Point aquifer differs from that in other confined coastal plain aquifers of New Jersey because less of the water that recharges the aquifer updip flows downward to underlying aquifers (Pope and Gordon, 1999). Transmissivity in this aquifer is $130 \text{ m}^2/\text{d}$ (Martin, 1998).

The Miocene Kirkwood Formation forms the “lower” Kirkwood aquifer and “composite” confining units that enclose the Atlantic City 800-foot sand. The Kirkwood Formation crops out over a broad area of the southwestern New Jersey coastal plain and following the regional trend, dips to the southeast. The updip extent of the Atlantic City 800-foot sand is based on the updip limit of the overlying “lower” confining unit. Northwest of this demarcation, the Kirkwood formation is hydraulically connected to the overlying Cohansey Sand, forming a thick water-table aquifer that serves as a region of lateral recharge. The confined Atlantic City 800-foot sand aquifer is the major source of potable water along the southern New Jersey coastline. Recharge to the confined Kirkwood aquifer is primarily by horizontal flow from the unconfined part of the lower Kirkwood-Cohansey aquifer. The underlying Piney Point aquifer contributes more inflow than do the overlying unconfined parts of the upper Kirkwood-Cohansey aquifer. The average value for transmissivity of the lower Kirkwood-Cohansey and confined Kirkwood aquifers is approximately $327 \text{ m}^2/\text{d}$.

Maryland

The Aquia Formation previously studied by Aeschbach-Hertig et al. (2001) is a Paleocene layer in the sequence of unconsolidated sediments of the Atlantic Coastal Plain. Aeschbach-Hertig et al. (2001) focused on the part of the Aquia located in southern Maryland to the west of the Chesapeake Bay (Fig. 14). In this region, the Aquia outcrops between Washington D.C. and Annapolis and dips southeast toward the ocean. Groundwater flow is in an easterly direction. Average annual precipitation ranges from 1.06-1.19 m in eastern Maryland (USGS WSP 2275). About one-fourth to one-third of precipitation reaches the water table (~0.25-0.33 m/yr). A very small part of this ground water moves into the deeper aquifers; most discharges to nearby streams. The stratigraphy of the region consists of a sequence of sandy layers acting as aquifers and silty to clay layers acting as aquitards (Hansen, 1974). In the majority of the area studied by Aeschbach-Hertig et al. (2001) the Magothy aquifer (Cretaceous) underlies the Aquia, which are separated by the confining beds of the Monmouth, Matawan (both are Cretaceous), and Brightseat (Paleocene) Formations. The confining unit underlying the Aquia is the Marlboro clay (Paleocene/Eocene). The confining unit overlying the Aquia consists of the silty and clayey part of the Nanjemoy formation (Eocene). The upper, sandy part of the Nanjemoy Formation acts as an aquifer and is hydraulically connected to the overlying Piney Point aquifer (Eocene), which is also present in New Jersey.

V. METHODS

Groundwater samples were collected from coastal New Jersey, Nantucket Island, MA, Martha's Vineyard, MA, and Long Island, NY (Fig. 9) during the months of July and August, 2005, as part of a National Science Foundation Research Experience for Undergraduates (REU) program to study the isotope hydrology and noble gas composition of the Atlantic Continental Shelf Aquifer System. The project was led under the direction of Dr. Mark Person of Indiana University and Dr. Zoltan Szabos of the USGS, New Jersey Water Resources Division. Samples were collected for stable isotopes ($\delta^{18}\text{O}$, δD), ^{14}C , and noble gases. ^{14}C and noble gas analyses have not yet been completed and only stable isotope analysis will be considered for this study.

Samples from 10 USGS observation wells were collected in New Jersey (Fig 12). In order to find groundwaters most representative of the Late-Pleistocene, three deep confined aquifers most likely to contain paleowaters were sampled. Well depths ranged from ~ 84 m to 275 m. Screens were approximately 2-4 meters long near the bottom of the wells. Three samples were collected from the Englishtown Aquifer; three from the Piney Point Aquifer; and four from the Lower Kirkwood formation (Lower Kirkwood-Cohansey and Kirkwood Confined aquifers). Samples for stable isotopes were collected in 125 ml clear and amber glass bottles and capped with polyseal caps. Caps were then wrapped with electrical tape to ensure no gas exchange with air.

Groundwater samples (Figs. 15 & 16) were collected on Nantucket and Martha's Vineyard under the direction of Dr. Mark Person along with his graduate student, Andee Marksamer. Samples were collected from 8 USGS observation wells on Nantucket in shallow unconfined and deeper confined aquifers (Fig. 2). Well depths ranged from ~ 8 m to 115 m.

Samples were collected from 2 sites on Martha's Vineyard, one a public supply well and the other a USGS well (Fig. 16). Well depths ranged from ~38 to 47 m. Samples were collected in 10 ml clear plastic bottles. Samples PW 13, PT 12, PT 13, and USGS 6001 were collected in the summer of 2003 by Dr. Person et al. and are used for comparison in this study.

Groundwater samples were collected on Long Island (Fig. 17) under the direction of the USGS Water Resources Division, Long Island. Samples were collected from 5 different sites, 2 USGS wells and 3 public supply wells all within the Lloyd Aquifer except N-6701.2 which was screened in the Raritan clay (Fig. 11). Well depths ranged from ~ 233 to 517 m. Samples were collected in 10 ml clear plastic bottles.

The sampling procedure for all locations was the same. Three casing volumes were purged from each well before initial sampling. Water temperature, electrical conductivity, turbidity, dissolved oxygen, eH, and pH were repeatedly measured before and during sampling to ensure that conditions for sampling remained stable.

Water samples were analyzed for $\delta^{18}\text{O}$ and δD in the Department of Geological Sciences, Indiana University, using a Thermo Finnigan Delta Plus XP Mass Spectrometer under the direction of Dr. Peter Sauer. The instrument was fitted with a chromium reduction furnace at 800°C for D. A Gas Bench CO_2 equilibration device was used at 32°C for ^{18}O . Isotope ratios were converted to the VSMOW scale by comparison with two well constrained internal lab standards (Boulder and Miami water).

VI. RESULTS

A. Latitudinal effect

Because of the poleward shift in mean annual temperature, it is expected to see an increase in isotopic depletion in ^{18}O and D from Maryland (38°N Latitude) to Nantucket Island (41° N Latitude) as a result of the latitude effect on isotopic fractionation. This is assuming all groundwater samples are of the same age and no longer part of the modern hydrological cycle. The only age dates (^{14}C) for the study area are from Maryland (Aeschbach-Hertig et al., 2001) in which the waters are believed to be paleowaters but cannot be confirmed to be from the LGM. Nevertheless, general observations for isotopic trends can be made that may be better explained with further data.

Figures 12, 14-17 present map views of the stable isotope ($\delta^{18}\text{O}$ and δD) distribution in each study area. Observations indicate that the entire suite of isotope values fall within the same range of values of one another with the exception of three wells on Long Island. With the exception of these 3 wells, all of the isotope values for $\delta^{18}\text{O}$ lie between -6‰ and -8‰ (± 0.23 -0.30) and for δD between -39‰ and -48‰ (± 0.7) (Table 1). These values match the values of modern meteoric water. Wells N-6701.2, N-2597, and N-12218 on Long Island have $\delta^{18}\text{O}$ values between -8‰ and -9‰ (± 0.22) and δD between -53‰ and -59‰ (± 0.7) (Table 1).

A boxplot of $\delta^{18}\text{O}$ values vs. latitudinal positions of collected groundwater samples from southeastern Maryland to Nantucket Island. Figure 18 shows the median value contained within the box with the bars representing the high and low values. There are no apparent isotopic trends and slightly more negative $\delta^{18}\text{O}$ values exist at 40°N latitude for the three wells mentioned on

Long Island. Figure 19 displays a boxplot of δD values vs. latitudinal positions for collected groundwater samples from southeastern Maryland to Nantucket Island. Again there are no isotopic trends to be noted and slightly more negative δD values exist at $40^{\circ}N$ latitude for the three wells mentioned on Long Island

B. Stable isotopes along flowpaths of confined aquifers

The cross-section for New Jersey (Fig. 13) was comprised using well data provided by the USGS New Jersey Water Resources Division, Pope and Gordon (1999), and Kohout et al. (1988). Cross-sections were not created for Long Island, Martha's Vineyard, or Nantucket as samples were either not collected along the flowpath or there was not enough data points from an individual aquifer. A cross-section for the Aquia formation (Fig. 23; Aeschbach-Hertig et al., 2001) is also shown.

New Jersey

Figures 20-22 show negligible isotopic variation along the flowpaths of three confined aquifers in New Jersey. All of the isotopic values are representative of modern meteoric water, falling between -6 and -8‰ (± 0.23 - 0.30) for $\delta^{18}O$ and -44‰ and -52‰ (± 0.7) for δD (Table 1). The isotope value for well Sandy Hook ($\delta^{18}O = -2.4\text{‰}$) is an anomaly. It has been noted that saltwater/freshwater mixing is taking place in this well and most likely has affected the isotope results.

Maryland

Aeschbach-Hertig et al. (2001) confirmed the presence of paleowater in the Aquia formation from ^{14}C and noble gas data. Figure 23 displays mean $\delta^{18}O$ and NGT values for two

data sets (labeled 1 and 2) indicative of a “cold” and “warm” period. The correlation between Noble Gas Temperatures (NGTs) and chloride concentrations indicates that the wells of data set 1 (Fig. 23) may tap water that infiltrated at times around the Last Glacial Maximum. Wells 4, 5, 6, 9, 17, and 18 do not fit into these data clusters; however, disregarding these wells there is a weak climate signal in the $\delta^{18}\text{O}$ data when compared with the NGT's. Nonetheless, $\delta^{18}\text{O}$ and δD values (unlike NGT's) do not indicate glacial meltwater representative of the LGM. The stable isotope ratios between $\delta^{18}\text{O}$ and δD do not provide a clear record of past climatic change and there are no significant isotopic trends that were observed in the Aquia formation.

VII. DISCUSSION

A. Climatic factors on LGM groundwaters

The noble gases in groundwater can be used to determine temperature of recharge. Concentrations of dissolved atmospheric noble gases in groundwater reflect the temperature during groundwater infiltration (Stute and Schlosser, 1993, 2000). This is based on the simple physical principle involving the temperature dependence of the solubility of noble gases in water. In effect, noble gases can be used for paleoclimate studies (Stute et al., 1995a; Byerle et al., 1998).

Based on noble gas analyses from confined aquifers, the study by Aeschbach-Hertig et al. (2001) found approximately a 9°C drop in temperature within the Aquia Aquifer during the LGM to present. It was previously discussed (see section, “III. Stable Isotopes and Paleogroundwaters”) that a maximum 14°C drop in temperature during the LGM obtained from foraminifera-based paleo-SST studies corresponds to a 14‰ difference in $\delta^{18}\text{O}$ in precipitation

between LGM and Holocene meteoric water in the northeastern United States (Macintyre et al., 1976; AES, 1982; Sauer, 1997). Rosanski et al. (1993) developed a relationship between modern ^{18}O in precipitation and surface air temperatures with a slope of $0.58\text{‰}/^{\circ}\text{C}$. Based on this relationship, a 9°C lowering in temperature thought to be during the LGM (Aeschbach-Hertig et al., 2001) corresponds to a 5.22‰ difference between Holocene and LGM meteoric waters. The slope value determined by Rosanski et al. (1993) was based on a very large number of IAEA-WMO stations with limited data in the northeastern U.S. and the North Atlantic. However, if this were to be considered the minimum estimated ‰ difference between LGM and Holocene meteoric waters in the northeastern U.S., then the $\delta^{18}\text{O}$ values for the sampled groundwaters in this study and the Maryland study (Tables 1 and 2; Aeschbach-Hertig et al., 2001) do not fall within the minimum and maximum ‰ differences in ^{18}O (5.22‰ to 14‰ difference) predicted between LGM and Holocene meteoric waters. The sampled groundwaters clearly do not represent isotopic depletion in ^{18}O characteristic of LGM glacial meltwaters ($\delta^{18}\text{O} \sim -20\text{‰}$).

Aeschbach-Hertig et al. (2001) present three climate related factors that may have influenced the $\delta^{18}\text{O}$ -values in their study which include the following: i) ice-volume effect; ii) continental effect; iii) temperature effect. These climatic factors would have influenced the entire North Atlantic coastal plain aquifer system and therefore further discussion is relevant to this study.

The ice volume effect is the result of the storage of isotopically depleted water in glacial ice sheets which led to a $\sim 1.3\text{‰}$ increase of the $\delta^{18}\text{O}$ of sea water during the LGM (Fairbanks, 1989). If Aeschbach-Hertig et al. (2001) assume their groundwater samples with low NGTs are of Pleistocene age, their $\delta^{18}\text{O}$ values should be corrected by subtracting up to 1.3‰ . In order to

substantiate this correction reliable dating should be combined with a chronology of ice-volume changes.

The continental effect involves the decrease of $\delta^{18}\text{O}$ -values with distance from the coast (Rozanski et al., 1993). This should have resulted in a lowering of the $\delta^{18}\text{O}$ -values during the Pleistocene when sea-level was lower and the recharge areas to major confined aquifers was increased in relation to the coast. Aeschbach-Hertig et al. (2001) estimated that the continental effect could have had a similar magnitude as the ice-volume effect.

Weak $\delta^{18}\text{O}$ -temperature relationships are typical for the Atlantic Coastal Plain region, as indicated by the data from several weather monitoring stations near the east coast of North America (IAEA, 1992), as well as isotope studies in coastal aquifers (Purdy, 1991; Plummer, 1993; Clark et al., 1997). Aeschbach-Hertig et al. (2001) interpreted their stable isotope results by concluding that the continental and sea-level related ice-volume effects practically cancelled each other, and the remaining $\delta^{18}\text{O}$ signal reflects a temperature comparable to the modern $\delta^{18}\text{O}$ -temperature relationship.

It is possible that the above mentioned climatic factors may play a role in the stable isotope values in this study. Nonetheless, without age dates it is difficult to assess these climatic factors on this investigation. Further mechanisms may be at work in the absence of isotopically light groundwaters.

B. LGM Meltwaters Offshore

The groundwaters sampled during summer 2005 may in fact be Holocene in age and would not be isotopically light (i.e. LGM waters). Holocene meteoric recharge may have pushed glacial meltwaters offshore on the North Atlantic Continental Shelf (Fig. 5). A study by

Marksamer, Person, and Brown (2005) done on Nantucket Island did however conclude that the absence of glacial meltwaters within a glacio-lacustrine sediment was the result of advective flushing by modern meteoric water. It is possible then that isotopically light groundwater will be found further offshore along the North Atlantic Continental Shelf.

C. The Role of Permafrost

Several studies in Europe (Andrews and Lee, 1979; Purtschert et al., 2001; Walraevens, 1990.) under the PALAEAUX project (Edmunds et al., 2001) have recognized age gaps in aquifers that indicate the absence of recharge during the Last Glacial Maximum. In the UK East Midlands aquifer (Andrews and Lee, 1979), where there is excellent ^{14}C control, no water ages are found between 20 and 10 k.y. B.P. and this timescale for an absence of recharge is found elsewhere in Europe (Beyerle et al., 1998). These age gaps have been determined to be the result of effective permafrost cover that sealed the aquifers from recharge during the LGM. Extensive evidence of periglacial features (i.e. permafrost) from the Laurentide Ice sheet (Wisconsin Age) have been noted in North America (Pewe, 1983). Figure 24 shows the extent of continuous and discontinuous permafrost cover south of the Laurentide Ice Sheet during Wisconsin time. New Jersey is the only area in this investigation that displays remnant periglacial features from the Laurentide Ice Sheet (Fig 24).

The role of cold climate processes in shaping the surficial geology and geomorphology of the New Jersey coastal plain has been an ongoing topic. Wolfe (1956) noted widely distributed fields of enclosed depressions and shallow basins reminiscent of patterned ground, dormant sand dunes, and near surface deformation of Tertiary and Quaternary deposits across New Jersey. She attributed her observations to the work of permafrost in the late Pleistocene. Walters (1978)

described a patterned ground signature in thin surficial deposits on Triassic red beds of the Newark basin in northern New Jersey. During the late Pleistocene northern New Jersey was in an ice-marginal position and permafrost certainly existed (Walters, 1978). Other studies suggest cold-climate landscape modification as well (Stanford, 2002a, 2002b).

Periglacial phenomena have been reported from central and southern New Jersey (Newall et al., 1989, 2000). In the last few years there has been a recent renewal in cold climate surficial deposits in New Jersey (French and Demitroff, 2001, French, et al, 2003, 2005). These studies have produced definitive work that confirms the cold climate interpretation of the surficial geology and deposits of the mid-Atlantic region. French et al., (2003, 2005) have used thermal luminescence to date wind blown sand and interpreted frost wedge fillings. The results show deposition during the last glacial maximum.

The study area of New Jersey in this investigation was indeed overlain by permafrost during the Last Glacial Maximum as shown by numerous field observations and recent TL dating methods. All 10 sampled wells displayed isotopic values of modern meteoric waters (Fig. 12) and it is possible that permafrost cover from the Laurentide Ice sheet limited and/or prevented recharge during the LGM (Figs. 6a & 6b).

VIII. CONCLUSIONS AND FUTURE WORK

There were no ground waters on Long Island or coastal Massachusetts representative of LGM glacial meltwater found during summer 2005. In New England (including Martha's Vineyard and Nantucket) it is possible that glacial meltwaters may be found further offshore. Dr. Mark Person and colleagues have proposed a targeted drilling campaign to the IODP off the

coast of Martha's Vineyard on the North Atlantic Continental Shelf to document the distribution of the anomalous freshwater plumes. The objective of this drilling campaign will be to understand the distribution of freshwater, fluid pressure, environmental isotopes, noble gases, and temperatures across on the North Atlantic Continental Shelf to reconstruct the paleo-transport mechanisms associated with the emplacement of the freshwater plumes. Onshore data collected from summer 2005 will be used in conjunction with offshore data from the proposed IODP project to assemble an extensive data set characterizing the North Atlantic coastal plain and continental shelf confined aquifer systems.

The groundwater samples from summer 2005 will provide the first onshore data set of noble gases and ^{14}C from New Jersey, Long Island, NY, and Nantucket. ^{14}C will provide much needed age dates that will reveal whether the sampled waters are in fact late Pleistocene or younger. The noble gases in groundwater will be used to determine the ground surface temperature of the study area during groundwater recharge.

In addition to providing the temperature of recharge, noble gas analyses will provide discrimination among the three water types that might have been displaced on the Atlantic Continental Shelf aquifer system during the Pleistocene (meteoric, glacial lake, sub-ice sheet). Table 5 shows concentrations of Ne (ccSTP/kg) and % excess air (Heaton and Vogel, 1981) indicative of meteoric, glacial lake, and sub-ice sheet waters.

The stable isotope information presented in this investigation in combination with future noble gas and ^{14}C data will enable a greater understanding of the recharge mechanisms that took place during the Pleistocene on the North Atlantic Continental Shelf. In addition, this ongoing investigation of the northeastern U.S. (38°N-41°N Latitude) combined with studies in Maryland, New Mexico, Georgia, Colorado, and Kansas (Aeschbach-Hertig et al., 2001; Stute et al., 1992a,

1995a; Clark et al., 1997, 1998) will further build a data set that will provide discussion of the latitudinal temperature gradient during the LGM and the influence of the Laurentide Ice sheet on North America.

IX. REFERENCES

- AES. (1982) Climatic Atlas Climatique-Canada. Canada Department of the Environment (Environment Canada), Ottawa, Ontario.
- Aeschbach-Hertig, W., Peeters, F., Beyerle, U., and Kipfer, R. (1999) Interpretation of dissolved atmospheric noble gases in natural waters. *Water Resources Research* **35**(9), 2779-2792.
- Aeschbach-Hertig, W. S., M., Clark, J.F., Reuter, R.F., and Schlosser, P. (2002) A paleotemperature record derived from dissolved noble gases in groundwater of the Aquia Aquifer (Maryland, USA). *Geochimica et Cosmochimica Acta* **66**(5), 797-817.
- Andrews, J. N., and Lee, D.J. (1979) Inert gases in groundwater from the Bunter Sandstone of England as indicators of age and palaeoclimatic trends. *Journal of Hydrology* **41**, 233-252.
- Beyerle, U., Purtschert, R., Aeschbach-Hertig, W., Imboden, D.M., Loosli, H.H., Wieler, R., and Kipfer, R. (1998) Climate and groundwater recharge during the last glaciation in an ice-covered region. *Science* **282**, 731-734.
- Boulton, G. S., and Caban, P. (1995) Groundwater flow beneath ice sheets: part II - its impact on glacier tectonic structures and moraine formation. *Quaternary Science Reviews* **14**(25), 563-587.
- Bush, A., and Philander, S.G. (1999) The Climate of the Last Glacial Maximum: Results from a coupled atmosphere-ocean circulation model. *Journal of Geophysical Research* **104**(D20), 24509-24525.
- Buxton, H. T., and Modica, E. (1992) Patterns and rates of ground-water flow on Long Island. *Ground Water* **30**, 857-866.
- Clark, I. and Fritz, P. (1999) *Environmental Isotopes in Hydrogeology*. Lewis Publishers.
- Clark, J. F., Stute, M., Schlosser, P., Drenkard, S., and Bonani, G. (1997) A tracer study of the Floridan aquifer in southeastern Georgia: Implications for groundwater flow and paleoclimate. *Water Resources Research* **33**, 281-289.
- Clark, J. F., Davisson, M.L., Hudson, G.B., and Macfarlane, P.A. (1998) Noble gases, stable isotopes, and radiocarbon as tracers of flow in the Dakota aquifer, Colorado and Kansas. *Journal of Hydrology* **211**, 151-167.
- Collins, M. A. (1978) Comment on "Fresh ground water stored in aquifers under the continental shelf: Implications from a deep test, Nantucket Island,

- Massachusetts, " by Kohout and others, 1977. *American Water Resources Bulletin* **14**(4), 484-485.
- Coplen, T. and Kendall, C. (2000) Stable Hydrogen and Oxygen Isotope Ratios for Selected Sites of the U.S. Geological Survey's NASQAN and Benchmark Surface-water Networks. *U.S.G.S. Open File Report 00-160*.
- Craig, H. (1961b) Isotopic variations in meteoric waters. *Science* **133**, 1702-1703.
- Craig, H. and Gordon, L. (1965) Deuterium and oxygen-18 variation in the ocean and the marine atmosphere. In *Stable Isotopes in Oceanographic Studies and Paleotemperatures* (ed. E. Tongioli), pp. 9-130. Spoleto.
- Dansgaard, W. (1961) The isotopic composition of natural waters with special reference to the Greenland Ice Cap. *Meddelelser om Gronland* **165**, 1-120.
- Denton, G. H., and Hughes, T.J. (1981) *The last great ice sheets*. John Wiley and Sons.
- Edmunds, W. M., Hinsby, K., Marlin, C., Melo, T., Manzano, M., Vaikmae, R., and Travi, Y. (2001) *Palaeowaters in Coastal Europe: evolution of groundwater since the late Pleistocene*. Geological Society.
- Edmunds, W. M. (2001) Paleowaters in European coastal aquifers - the goals and main conclusions of the PALEAUX project. In *Paleowaters in Coastal Europe: Evolution of groundwater since the Late Pleistocene* (ed. W. M. a. M. Edmunds, C.J.), pp. 1-16. The Geological Society.
- Fairbanks, R. G. (1989) A 17,000-year glacio-eustatic sea level record: influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation. *Nature* **342**, 637-642.
- Folger, D. W., Hathaway, R.A., Christopher, R.A., Valentine, P.C., and Poag, C.W. (1978) Stratigraphic test well, Nantucket Island, Massachusetts. *U.S. Geological Survey Circular* **773**, 28.
- French, H. M., and Demitroff, M. (2001) On the Cold-Climature Origin of the Enclosed Depressions and Wetlands ['Sprungs'] of the Pine Barrens, Southern New Jersey, USA. *Permafrost and Periglacial Processes* **12**, 337-350.
- French, H. M., Demitroff, M., and Forman, S.L. (2003) Evidence for Late-Pleistocene Permafrost in the New Jersey Pine Barrens (Latitude 39°N), Eastern USA. *Permafrost and Periglacial Processes* **14**, 259-274.
- French, H. M., Demitroff, M., and Forman, S.L. (2005) Evidence for Late-Pleistocene Thermokarst in the New Jersey Pine Barrens (Latitude 39°N), Eastern USA. *Permafrost and Periglacial Processes* **16**, 173-186.
- GNIP (Global Network of Isotopes in Precipitation). *IAEA-WMO Database* (<http://www.waterisotopes.org>).
- Grasby, S., Osadetz, K., Betcher, R., and Render, F. (2000) Reversal of the regional-scale flow system of the Williston Basin in response to Pleistocene Glaciation. *Geology* **28**(7), 635-638.
- Groen, J., Velstra, J., and Meesters, A.G.C.A. (2000b) Salinization processes in paleowaters in coastal sediments of Suriname: evidence from $\delta^{37}\text{Cl}$ analysis and diffusion modeling. *Journal of Hydrology* **234**(1-2), 1-20.
- Guswa, J.H. and Leblanc, D.R. (1981) Digital models of ground-water flow in the Cape Cod aquifer system, Massachusetts. *Water Resources Investigations Open File Report* **80-67**, 127.

- Hansen, H. J. (1974) Sedimentary facies of the Aquia formation in the subsurface of the Maryland Coastal Plain. *Report of Investigations No. 21, Maryland Geological Survey*.
- Hathaway, J. C., Poag, C.W., Valentine, P.C., Millerk, R.E., Schultz, D.M., Manheim, F.T., Kohout, F.A., Bothner, M.H., and Sangrey, D.A. (1979) U.S. Geological Survey core drilling on the Atlantic Shelf. *Science* **206**, 515-527.
- Hays, J.D., Imbrie, J., and Shackleton, N.J. (1976) Pacemaker of the ice ages. *Science* **194**, 1121-1132.
- Heaton, T. H. E., and Vogel, J.C. (1981) "Excess air" in groundwater. *Journal of Hydrology* **50**, 201-216.
- Hendry, M.J. and Wassenaar, L.I. (1999) Implications of the distribution of δD in pore waters for groundwater flow and the timing of geologic events in a thick aquitard system. *Water Resources Research* **35**(6), 1751-1760.
- Horita, J. and Wesolowski, D.J. (1994) Liquid-vapor fractionation of oxygen and hydrogen isotopes of water from the freezing to the critical temperature. *Geochimica et Cosmochimica Acta* **58**, 3425-3437.
- Kipfer, R., Aeschbach-Hertig, W., Peeters, F., Stute, M. (2002) Noble gases in lakes and groundwaters. *Reviews in Mineralogy and Geochemistry* **47**, 615-700.
- Knott, J. F., and Olimpio, J.C. (1986) Estimation of recharge rates to sand and gravel aquifer using environmental tritium. *U.S. Geological Survey Water Supply Paper* **2297**, 26.
- Kohout, F. A., Hathaway, J.C., Folger, D.W., Bothner, M.H., Walker, E.H., Delaney, D.F., Frimpter, M.H., Weed, E.G.A., and Rhodehamel, E.V.C. (1977) Fresh groundwater stored in aquifers under the continental shelf, Implications from a deep test, Nantucket Island, Massachusetts. *Water Resources Bulletin* **13**, 373-386.
- Kohout, F. A., Meisler, H., Meyer, F.W., Johnston, R.H., Leve, G.W., and Wait, R.L. (1988) Hydrogeology of the Atlantic continental margin. In *Sheridan, R.E., and Grow, J.A., eds., The Atlantic Continental Margin: Geology of North America*, Vol. I-2, pp. 463-480. Geological Society of America.
- Loosli, H. H., Lehmann, B., Aeschbach-Hertig, W., Kipfer, R., Edmunds, W.M., Eichinger, L., Rozanski, K., Stute, M., Vaikmäe, R. (1998) Tools used to study paleoclimate help in water management. *EOS Transactions* **79**, 576-582.
- Luszczynski, N. J. a. S., W.V. (1962) Fresh and salty ground water in Long Island, New York, American Society of Civil Engineers, Journal of the Hydraulics Division **38** (HY4) 173-194.
- Majoube, M. (1971) Fractionnement en oxygene-18 en deuterium entre l'eau et sa vapeur. *Journal of Chemical Physics* **197**, 1423-1436.
- Manheim, F. T., and Hall, R.E. (1976) Deep evaporitic strata off New York and New Jersey-Evidence from interstitial water chemistry of drill cores. *U.S. Geological Survey Journal of Research* **4**(4), 697-702.
- Martin, M. (1998) Ground-water flow in the New Jersey coastal plain. *U.S.G.S. Professional Paper* **1404-H**.
- McIntyre, A., Kipp, N.G., Be, A.W.H., Crowley, T., Kellogg, T. Gardner, J.V., Prell, W., and Ruddiman, W.F. (1976) Glacial North Atlantic 18,000 years ago: a CLIMAP reconstruction. In *Investigations of Late Quaternary Paleoceanography and*

- Paleoclimatology* (ed. R. M. C. a. J. D. Hays), pp. 43-76. Geological Society of America.
- Meisler, H., Leahy, P.P., and Knobel, L.L. (1984) Effect of eustatic sea-level changes on saltwater-freshwater relations in North Atlantic Coastal Plain. *U.S. Geological Survey Water Supply Paper 2255*, 1-26.
- National Water Summary-Ground Water Resources, Maryland and the District of Columbia. *U.S. Geological Survey Water supply Paper 2275*.
- Newall, W. L., Powars, D.S., Owens, J.P., Stanford, S.D., and Stone, B.D. (2000) Surficial geologic map of Central and Southern New Jersey. In *Miscellaneous Investigations Series*. United States Geological Survey.
- Newell, W. L., Wyckoff, J.S., Owens, J.P., and Farnsworth, J. (1989) Cenozoic geology and geomorphology of the Southern New Jersey Coastal Plain. *Southeast Friends of the Pleistocene, 2nd Annual Field Conference*.
- Oldale, R. N. (1969) Seismic investigations on Cape Cod, Martha's Vineyard, and Nantucket, Massachusetts, and a topographic map of the basement surface from Cape Cod Bay to the islands. *U.S. Geological Survey Professional Paper 650-B*, B122-B127.
- Oldale, R. N., Uchupi, Elazar, and Prada, K.E. (1973) Sedimentary framework of the western Gulf of Maine and the southeastern Massachusetts offshore area. *U.S. Geological Survey Professional Paper 757*, 10.
- Oldale, R. N., Hathaway, J.C., Dillon, W.P., Hendricks, J.D., and Robb, J.M. (1974) Geophysical observations on northern part of Georges Bank and adjacent basins of Gulf of Maine. *American Association of Petroleum Geologists Bulletin* **58**(12), 2411-2427.
- Oldale, R. N. a. O. H., C.J. (1984) Glaciotectonic origin of the Massachusetts coastal end moraines and a fluctuating late Wisconsin ice margin. *Geological Society of America Bulletin* **95**, 61-74.
- .Perlmutter, N. M., and Geraghty, J.J. (1963) Geology and ground-water conditions in southern Nassau and southeastern Queens Counties, Long Island, New York. *U.S. Geological Survey Water Supply Paper 1613-A*, A1-A39.
- Person, M., Taylor, J., and Dingman, S.L. (1998) Sharp interface models of salt water intrusion and well head delineation on Nantucket Island, Massachusetts. *Ground Water* **36**, 731-742.
- Person, M., Dugan, B., Swenson, J., Urbano, L., Stott, C., Taylor, J., and Willett, M. (2003) Pleistocene hydrogeology of the Atlantic continental shelf, New England. *GSA Bulletin* **115**(11), 1324-1343.
- Pewe, T. L. (1973) *The periglacial environment in North America during Wisconsin time, In Late-Quaternary Environments of the United States*. University of Minnesota Press.
- Plummer, L. N. (1993) Stable isotope enrichment in paleowaters of the southeast Atlantic Coastal Plain, United States. *Science* **262**, 2016-2020.
- Pope, D.A. and Gordon, A.D. (1999) Simulation of ground-water flow and movement of freshwater-saltwater interface in the New Jersey Coastal Plain. *U.S. Geological Survey Investigations Report* (98-4216).

- Prentice, I. C., Bartlein, P.J., and Webb, T., III. (1991) Vegetation and climate change in eastern North America since the last glacial maximum. *Ecology* **72**, 2038-2056.
- Purdy, C. B. (1991) Isotopic and chemical tracer studies of groundwater in the Aquia Formation, southern Maryland: Including ^{36}Cl , ^{14}C , ^{18}O and ^2H , University of Maryland.
- Purtschert, R., Beyerle, U., Aeschbach-Hertig, W., Kipfer, R., and Loosli, H.H. (2001) Palaeowaters from the Glatt Valley Switzerland. In *Palaeowaters in Coastal Europe: evolution of groundwater since the late Pleistocene*, Vol. Special Publications 189 (ed. W. M. Edmunds, and Milne, C.J.), pp. 155-162. Geological Society.
- Remenda, V. H., Cherry, J.A., and Edwards, T.W.D. (1994) Isotopic composition of old groundwater from Lake Agassiz: Implications for late Pleistocene climate. *Science* **266**, 1975-1978.
- Rozanski, K., Araguas-Araguas, L. and Gonfiantini, R. (1993) Isotopic patterns in modern global precipitation. In *Continental Isotope Indicators of Climate*. American Geophysical Union Monograph.
- Sauer, P. E. (1997) Records of climate and late Quaternary paleoclimate from stable isotopes in lakes and lake sediments, Eastern Canadian Arctic, University of Colorado, Boulder.
- Schafer, J. P., and Hartshorn, J.H. (1965) The Quaternary of New England. In *The Quaternary of the United States* (ed. H. E. Wright, Jr., and Frey, D.G.), pp. 113-128. Princeton University Press.
- Schwartz, F.W., and Zhang, H. (2003) *Fundamentals of Groundwater*. 592 pgs.
- Shackleton, N.J., and Opdyke, N.D. 1973, Oxygen isotope and paleomagnetic stratigraphy of equatorial Pacific core V28-238: Oxygen isotope temperatures and ice volumes on a 10^5 year and 10^6 year scale. *Quaternary Research* **3**, pp.39-55.
- Sheridan, R. E. (1974) Atlantic continental margin of North America. In *The geology of continental margins* (ed. C. A. Burke, and Drake, C.L.), pp. 391-407. Springer-Verlag.
- Stanford, S. (2002a) Surficial geology of the Freehold Quadrangle, Middlesex and Monmouth Counties, New Jersey. In *Open File Map 43*. New Jersey Geological Survey.
- Stanford, S. (2002b) Surficial geology of the Rocky Hill Quadrangle, Somerset and Mercer Counties, New Jersey. In *Open File Map 48*. New Jersey Geological Survey.
- Stute, M., Schlosser, P., Clark, J.F., and Broecker, W.S. (1992a) Paleotemperatures in the Southwestern United States derived from noble gases in ground water. *Science* **256**, 1000-1003.
- Stute, M., and Schlosser, P. (1993) Principles and applications of the noble gas paleothermometer. In *Climate Change in Continental Isotopic Records*, Vol. 78 (ed. P. K. Swart, Lohmann, K.C., McKenzie, J., and Savin, S.), pp. 89-100. American Geophysical Union.

- Stute, M., Clark, J.F., Schlosser, P., and Broecker, W.S. (1995a) A 30,000 yr continental paleotemperature record derived from noble gases dissolved in groundwater from the San Juan Basin, New Mexico. *Quaternary Research* **43**, 209-220.
- Stute, M., Forster, M., Frischkorn, H., Serejo, A., Clark, J.F., Schlosser, P., Broecker, W.S., and Bonani, G. (1995b) Cooling of tropical Brazil (5°C) during the Last Glacial Maximum. *Science* **269**, 379-383.
- Stute, M., and Schlosser, P. (2000) Atmospheric noble gases. In *Environmental tracers in subsurface hydrology* (ed. V. P. Cook, and Herczeg, A.L.), pp. 349-377. Kluwer Academic Publishers.
- Walraevens, K. (1990) Natural isotope research on groundwater from the semi-confined Ledo-Paniselian aquifer in Belgium: application of ¹⁴C correction methods. *Natuurwetenschappelijk Tijdschr* **72**, 79-89.
- Walters, J. C. (1978) Polygonal patterned ground in central New Jersey. *Quaternary Research* **10**, 42-54.
- Webb III, T., Anderson, K.H., Bartlein, P.J., and Webb, R.S. (1997) Late Quaternary climate change in eastern North America: a comparison of pollen-derived estimates with climate model results. *Quaternary Science Reviews* **17**, 587-606.
- Wolfe, P. E. (1956) Pleistocene periglacial frost-thaw phenomena on the New Jersey Coastal Plain. *Transactions, New York Academy of Sciences* **18**, 507-515.
- Zapeczka, O. S. (1984) Hydrogeologic Framework of the New Jersey Coastal Plain. *U.S.G.S. Geological Survey Open-File Report 84-730*, 61.

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XI. FIGURES AND TABLES

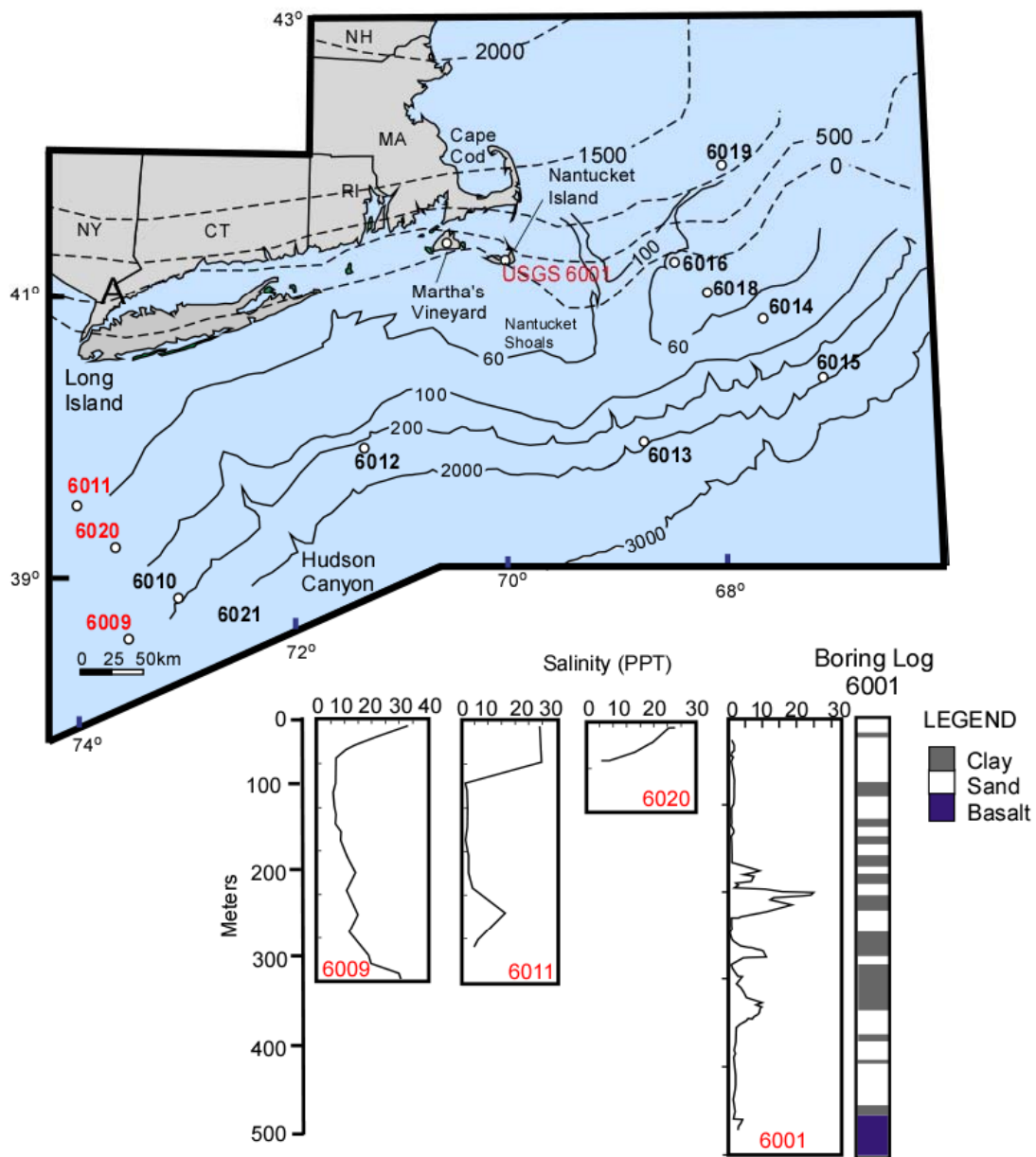


Figure 1. Location of AMCOR boreholes on Atlantic continental shelf (circles) and associated salinity profiles of select AMCOR wells (Hathaway et al., 1979).

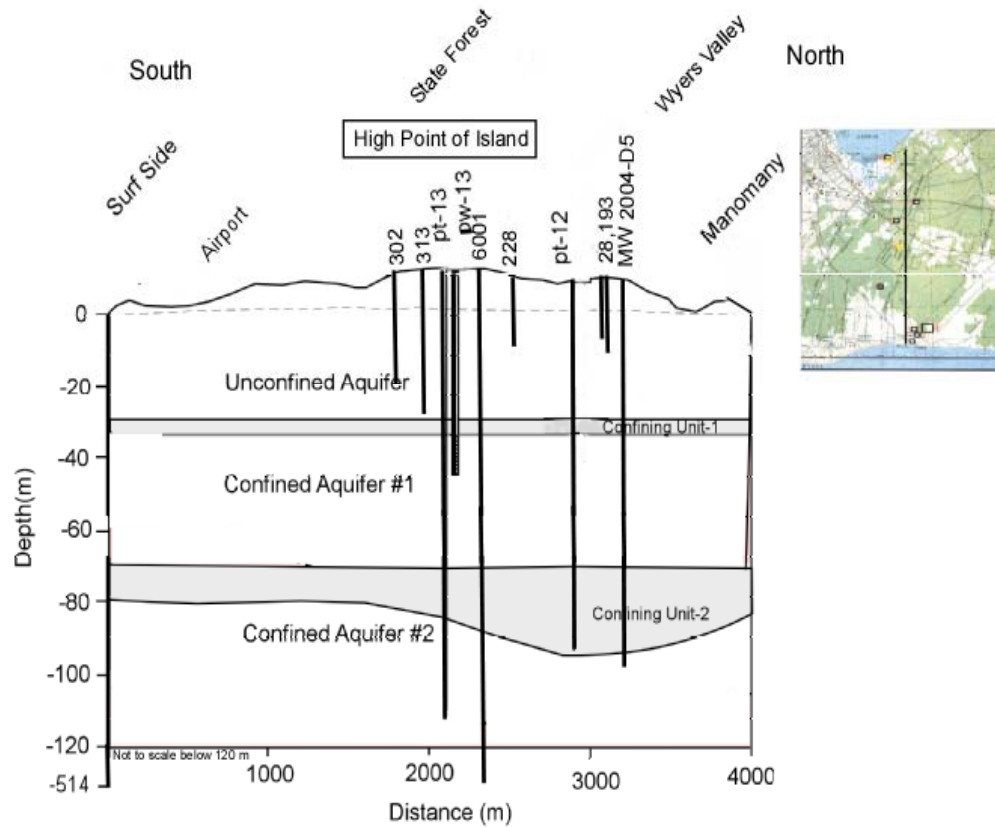


Figure 2. Cross section of shallow confined and unconfined aquifers on Nantucket Island and locations of sampled wells. Note: well 6001 goes to a depth of 514-m.

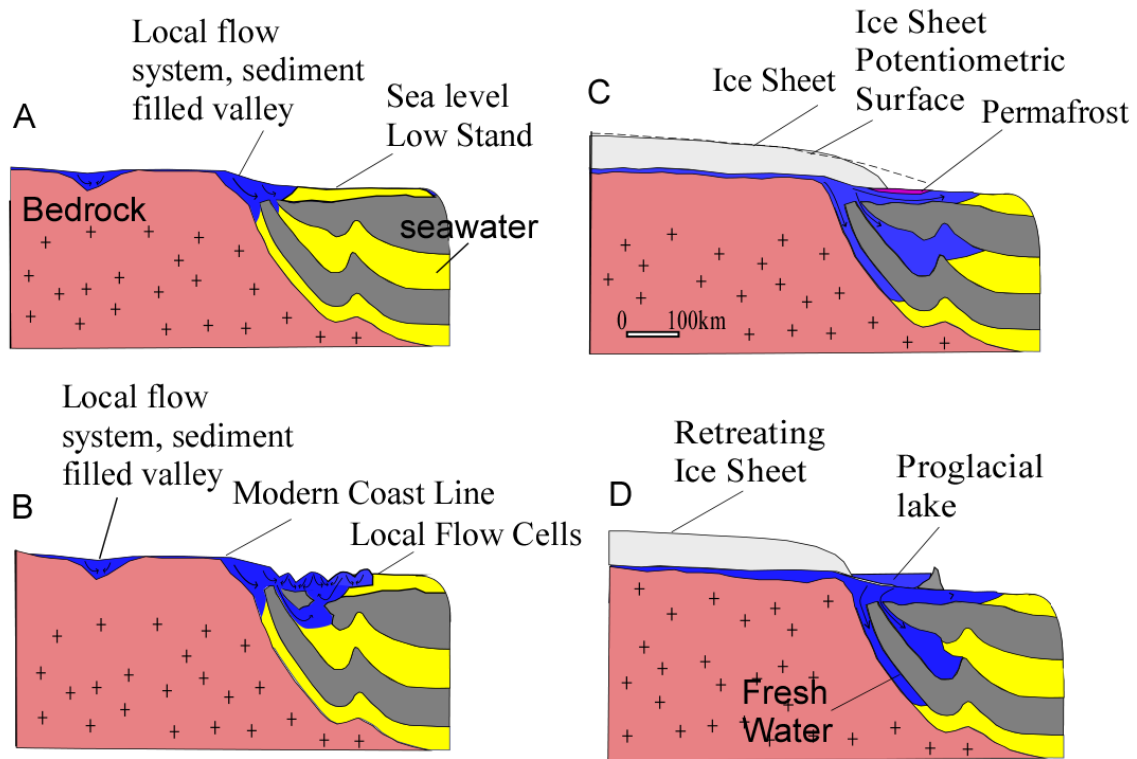


Figure 3. Conceptual models for freshwater plumes: (A) lateral incursion of freshwater during the Pleistocene sea-level low stands; (B) vertical infiltration of meteoric water induced by local flow cells; (C) sub-ice-sheet recharge from the Laurentide ice sheet; (D) infiltration beneath proglacial lakes.

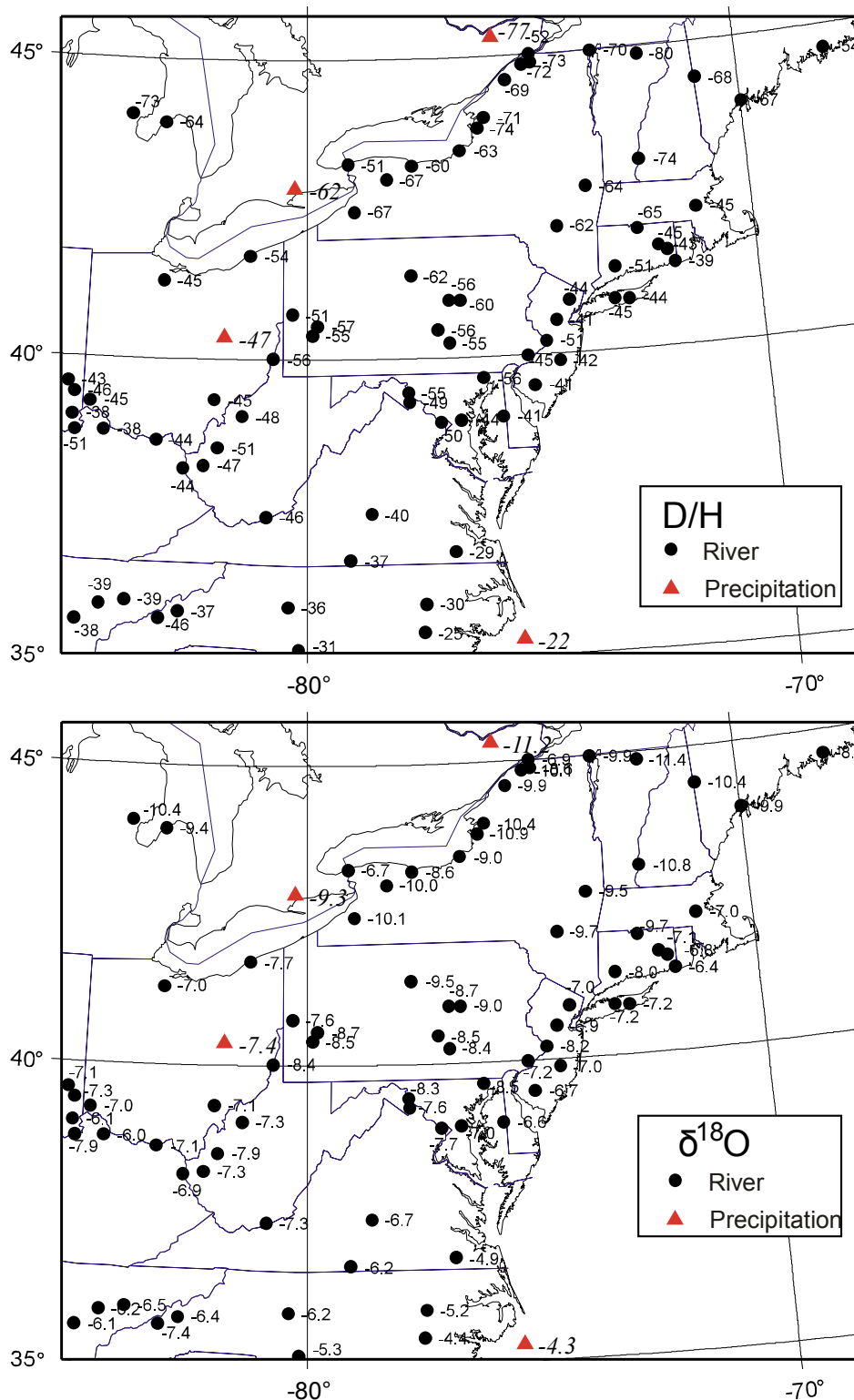


Figure 4. Plot of average river isotope and precipitation values of δD and $\delta^{18}O$ along the northeastern United States (River data obtained from Coplen and Kendall, USGS Open File Report 2000-160, <http://pubs.usgs.gov/of/ofr00-160>; Precipitation data obtained from the GNIP, IAEA-WMO database, <http://www.waterisotopes.org>).

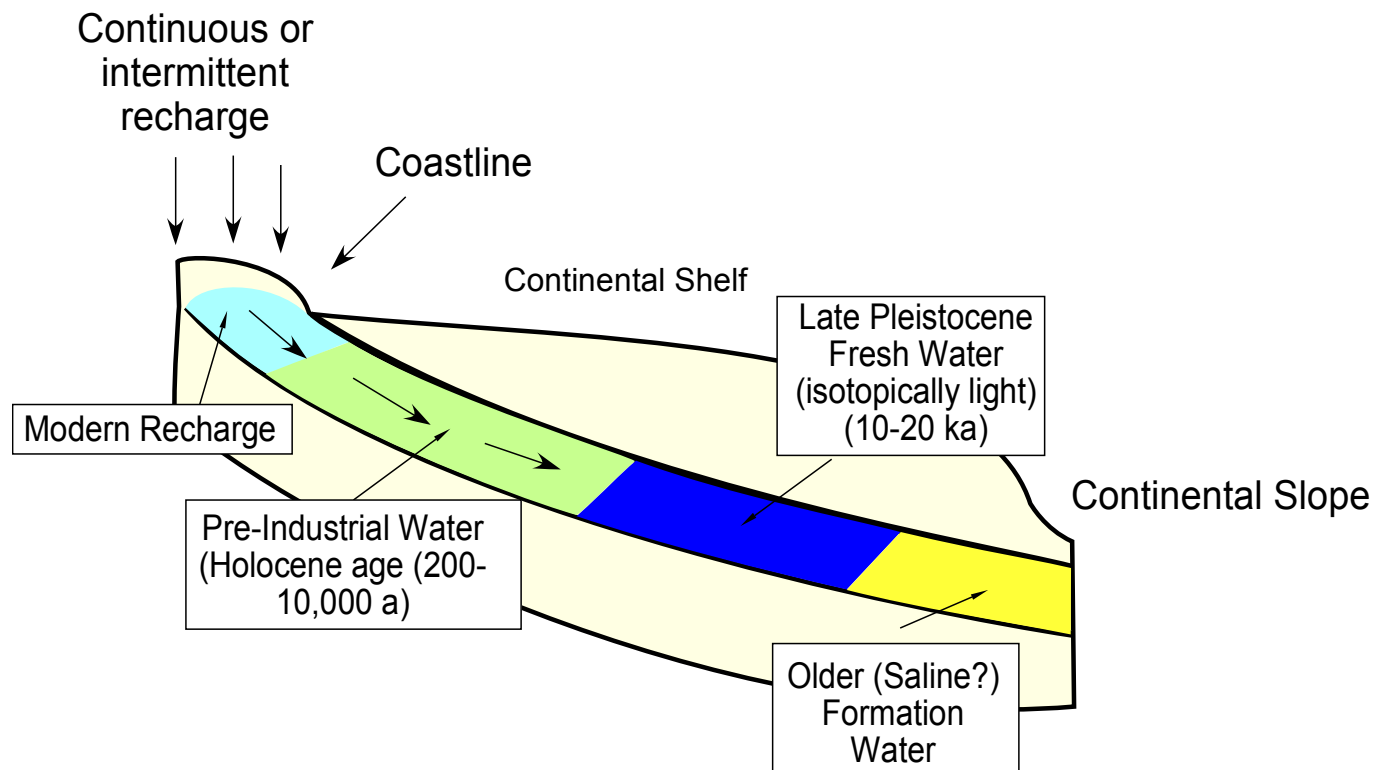


Figure 5. Flow path of aquifers on the North Atlantic continental shelf showing the presence of late Pleistocene glacial meltwaters offshore (Edmunds, 2001).

Last Glacial Maximum (~20 k.a.)

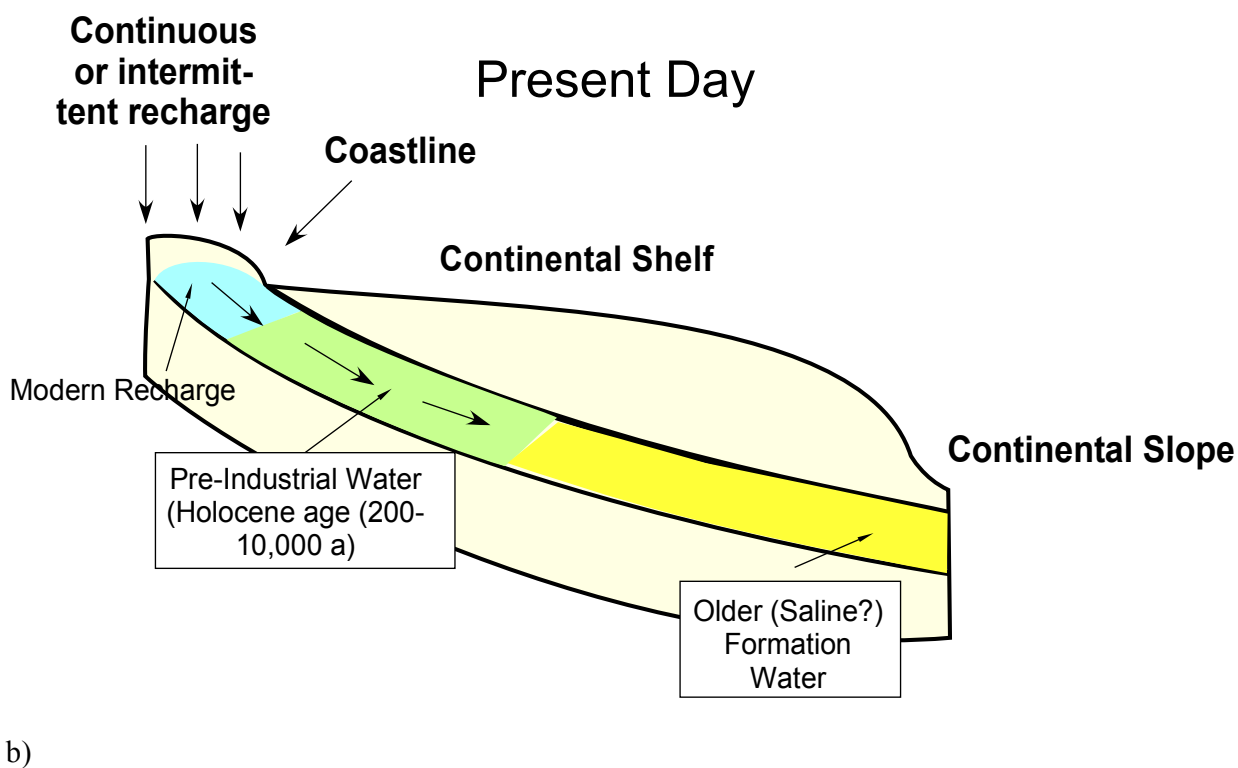
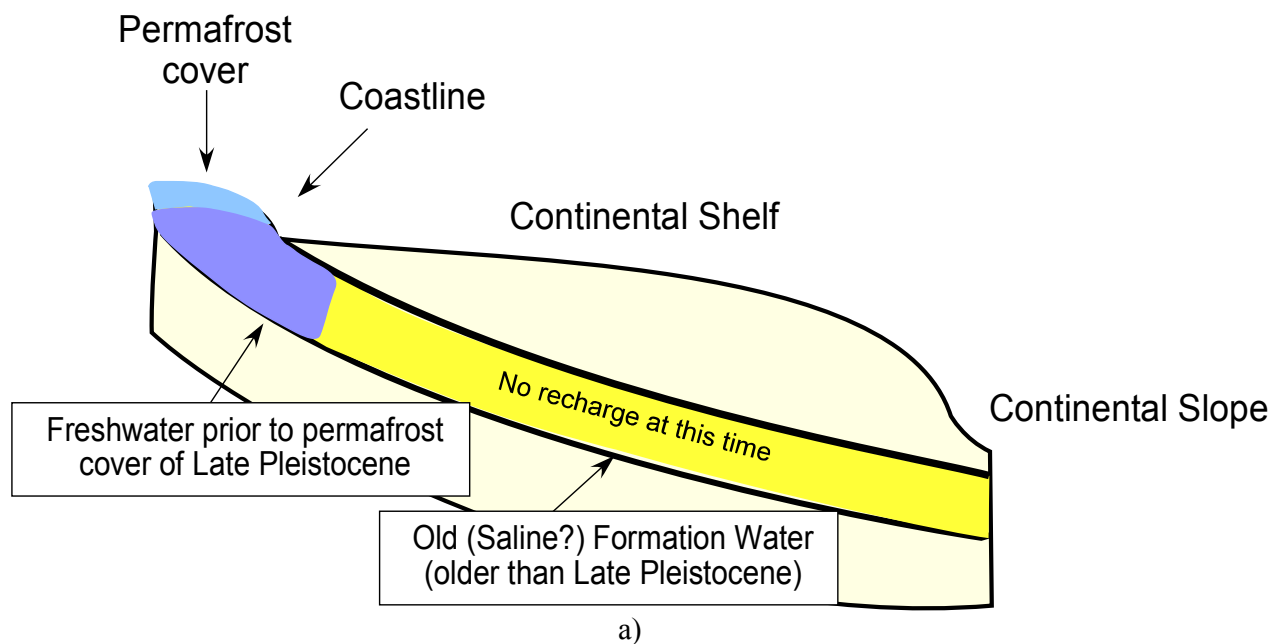


Figure 6. a) Permafrost cover south of the Laurentide Ice Sheet during the LGM. b) Absence of Pleistocene glacial meltwaters as a result of permafrost.

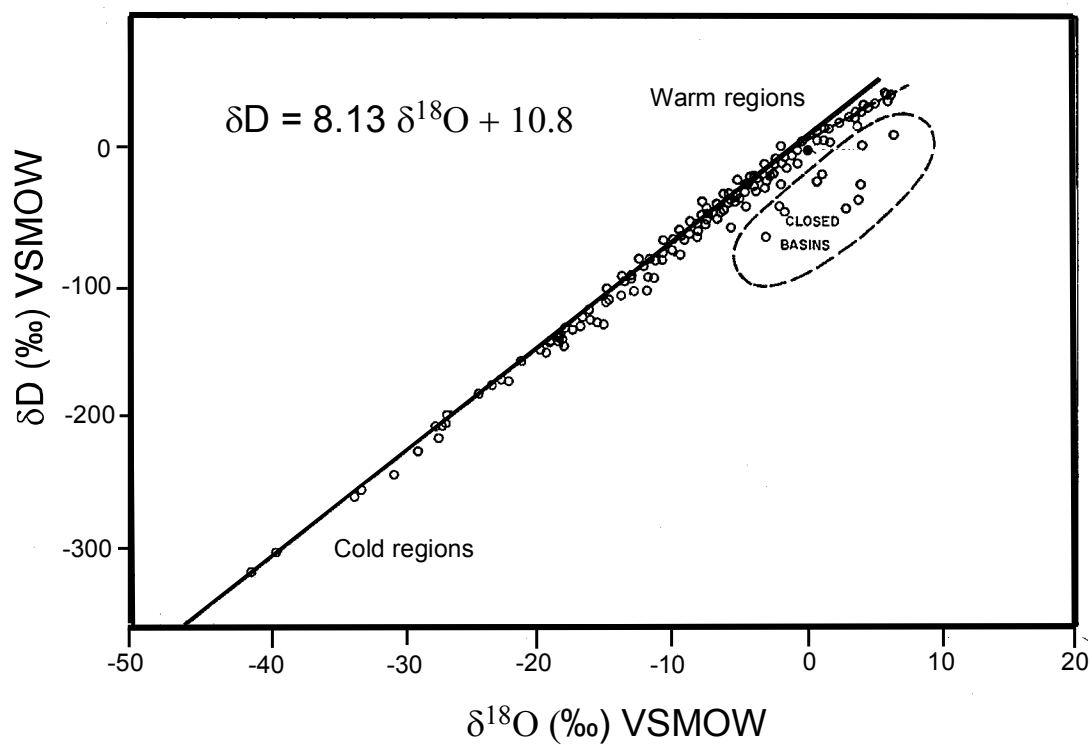


Figure 7. The meteoric relationship for ^{18}O and D in precipitation based on the Vienna Standard Mean Ocean Water (VSMOW; Modified from Craig, 1961b).

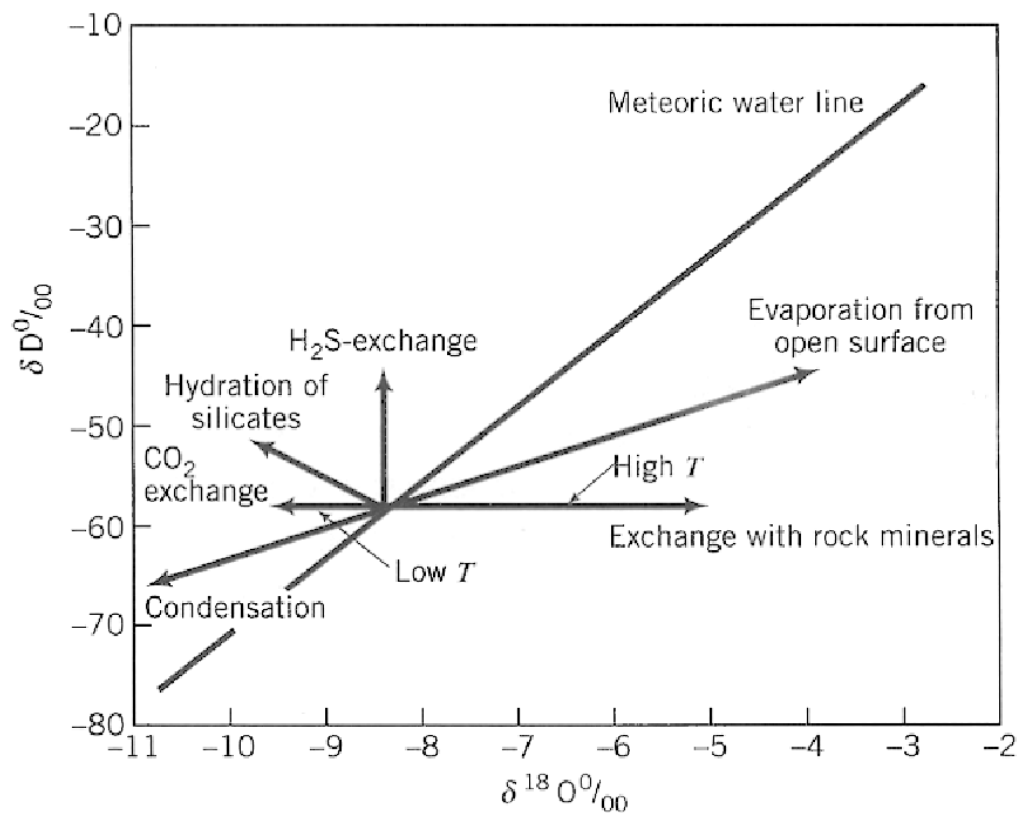


Figure 8. Various processes which cause deviations in isotopic compositions away from the meteoric water line (Schwartz and Zhang, 2003).



Figure 9. Study area along the North Atlantic coastal plain. See Figure insets for site maps.

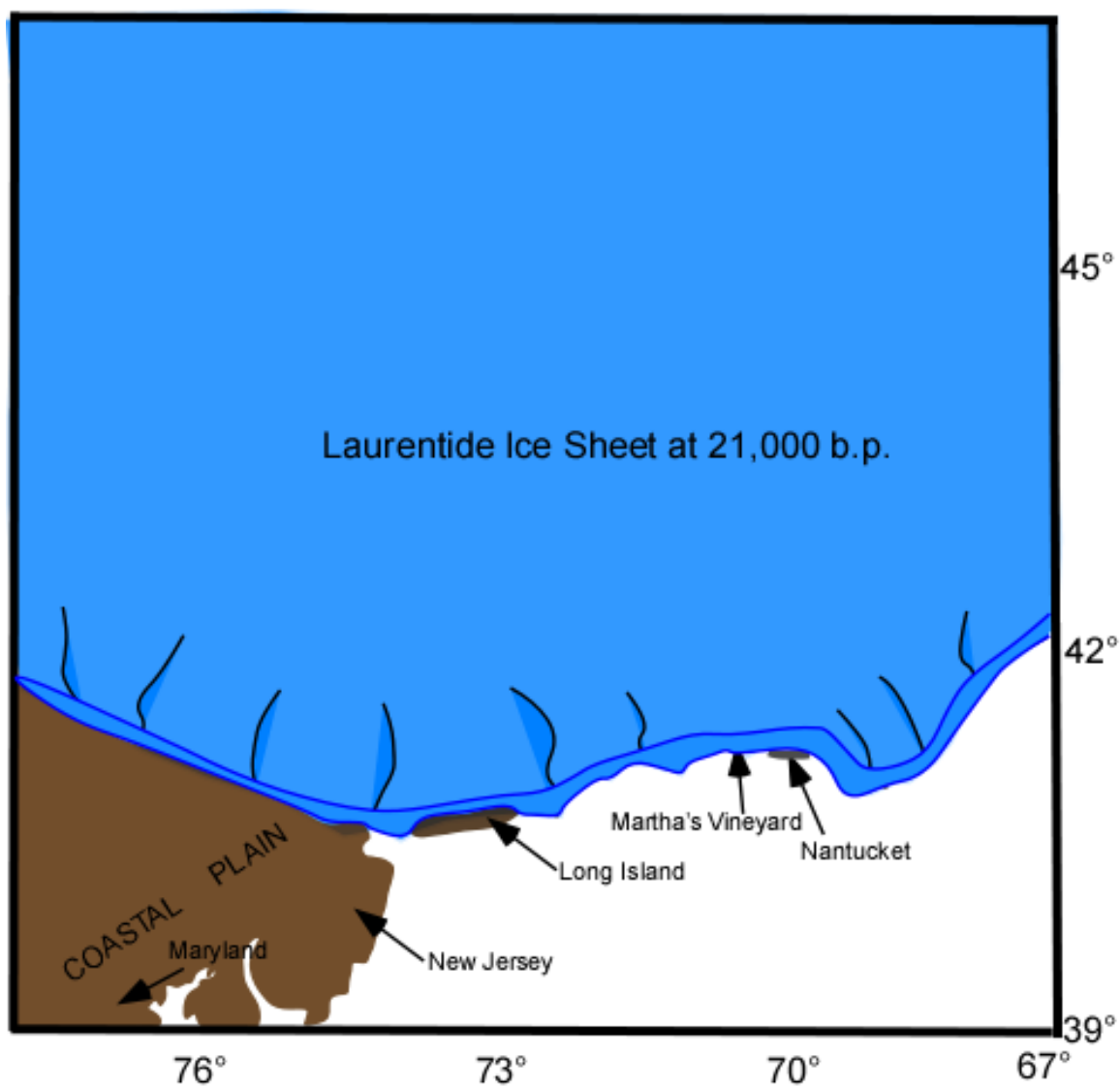


Figure 10. Extent of Laurentide Ice Sheet in northeastern United States during the LGM at 21k.y. B.P.

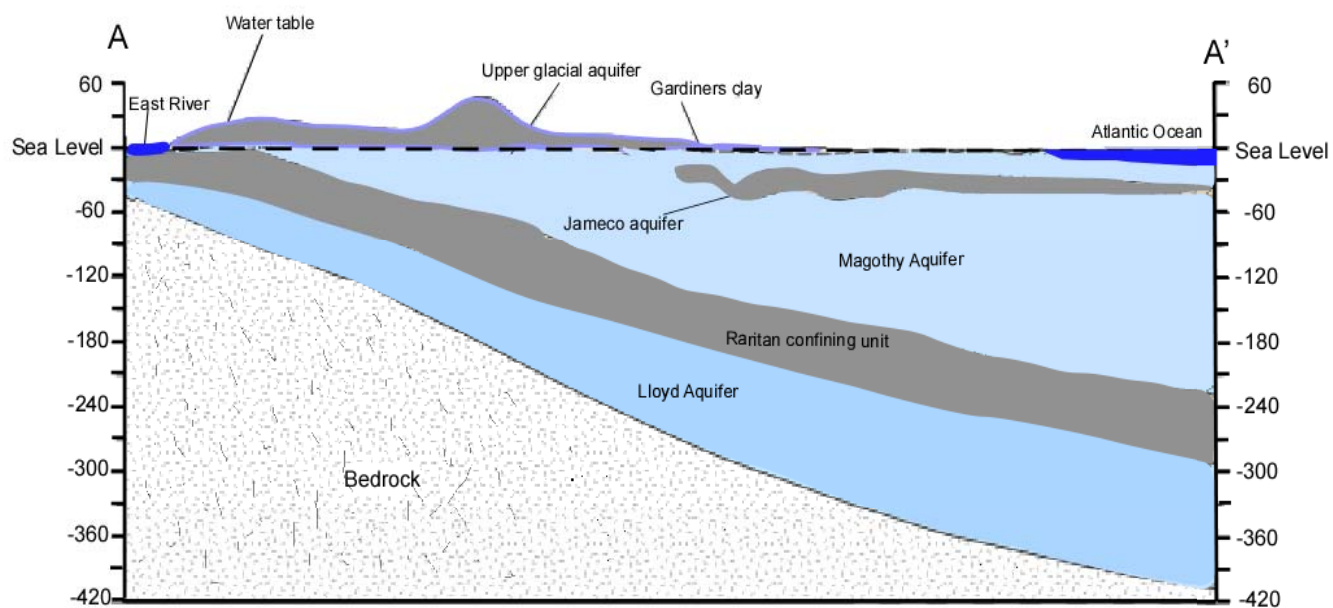
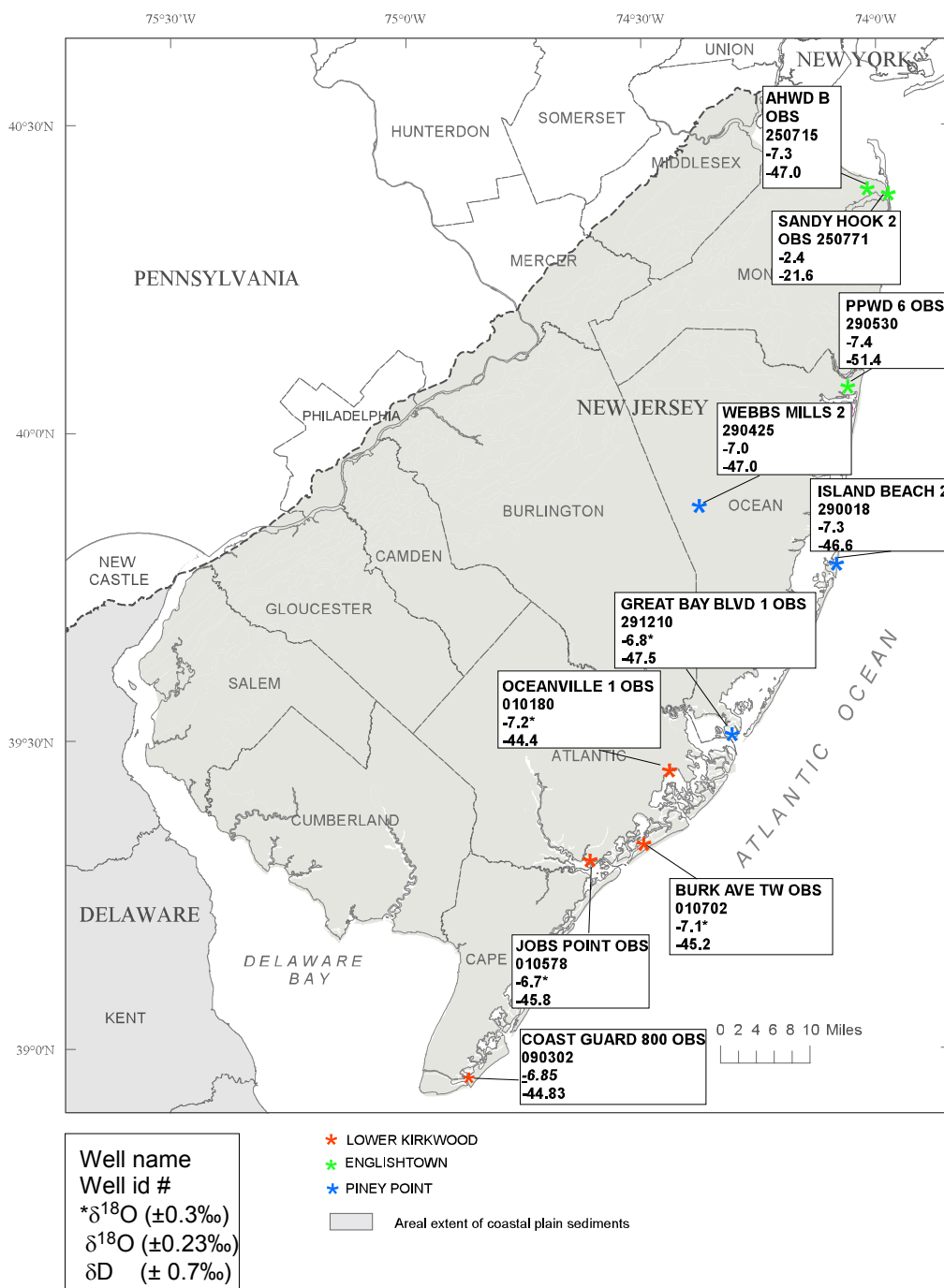


Figure 11. Long Island Aquifer system. (Modified from Buxton and Shernoff, 1999). Vertical exaggeration is 30X.



$\delta^{18}\text{O}$ value for well COAST GUARD 800 OBS was obtained from the MWL using corresponding δD value

Figure 12. $\delta^{18}\text{O}$ and δD values in New Jersey from sampling campaign, summer 2005.

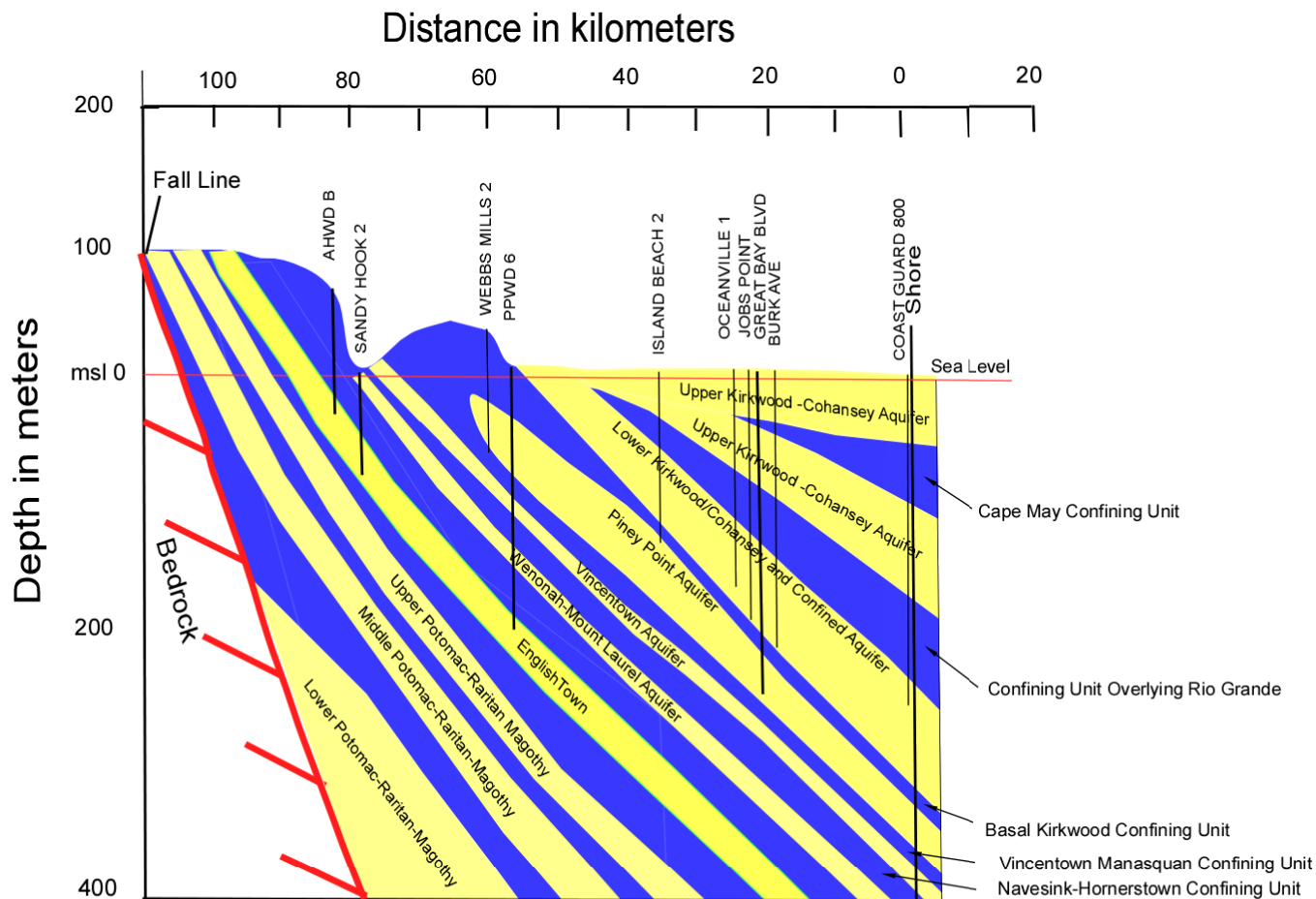


Figure 13. Hydrogeologic Section of the coastal plain of New Jersey and the locations of sampled wells (relative to the Fall Line).

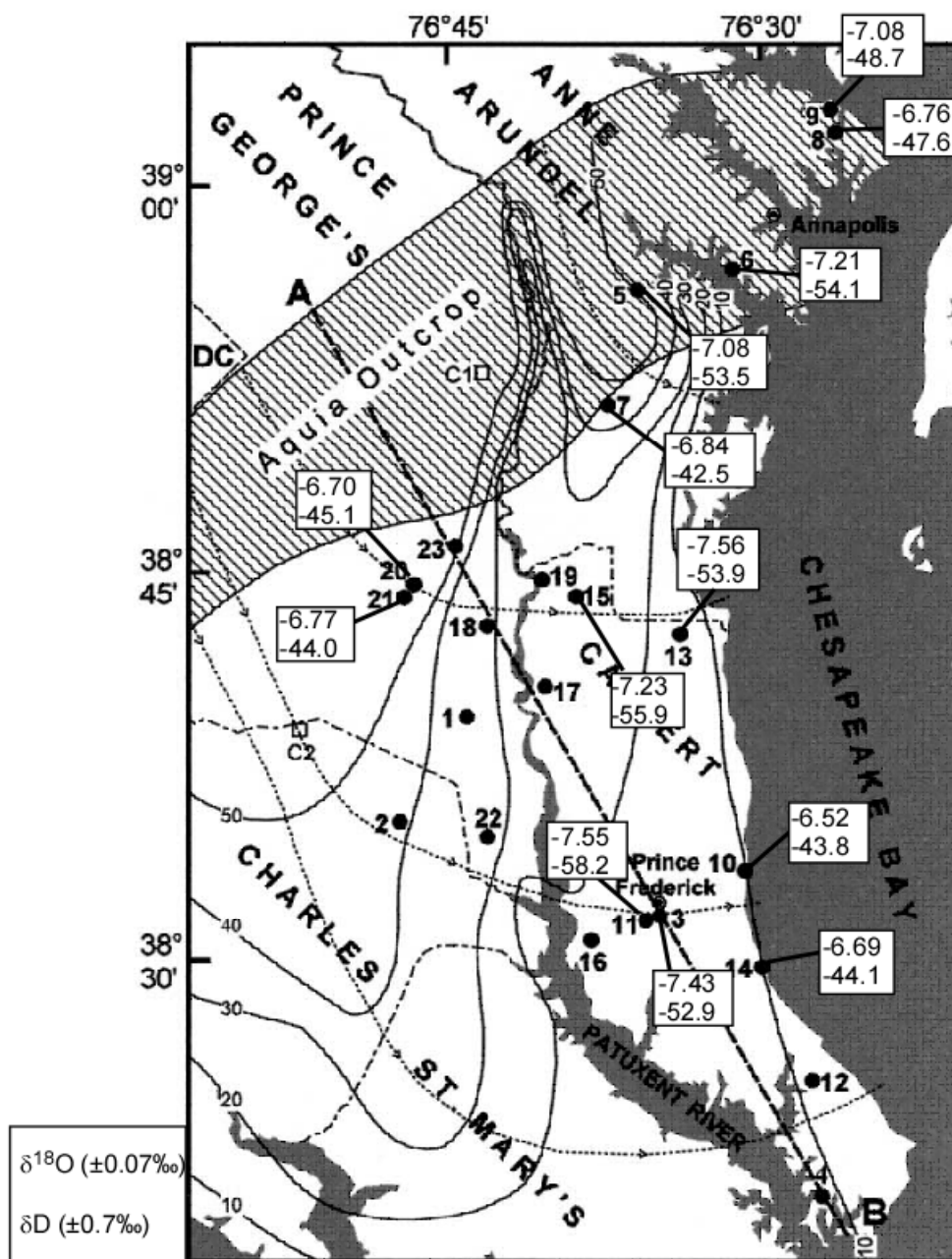


Figure 14. Map of the study area for the Aquia aquifer in southeastern Maryland (Aeschbach-Hertig et al. 2001) displaying $\delta^{18}\text{O}$ and δD values for selected wells.

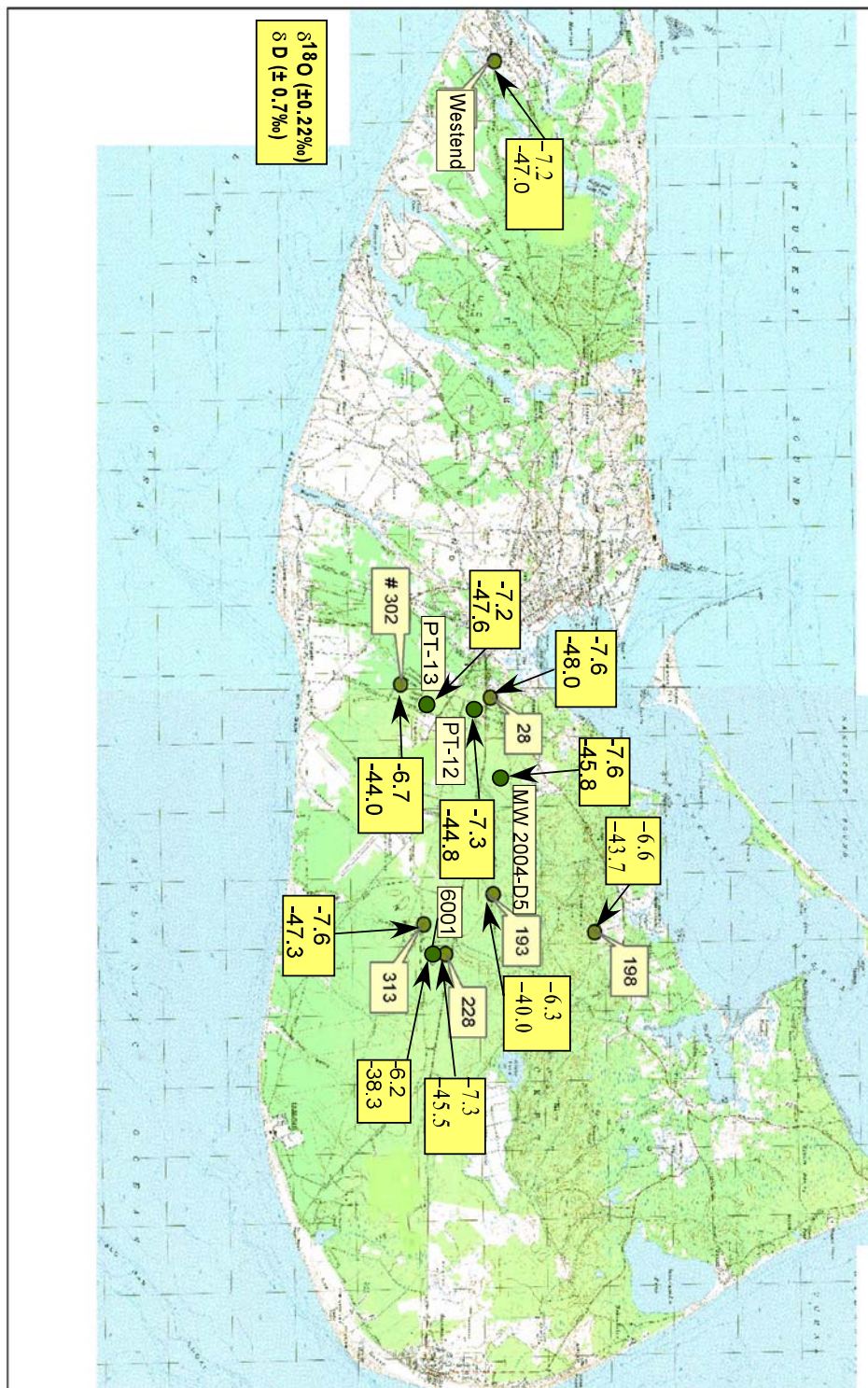


Figure 15. $\delta^{18}\text{O}$ and δD values on Nantucket Island from sampling campaign, summer 2005.

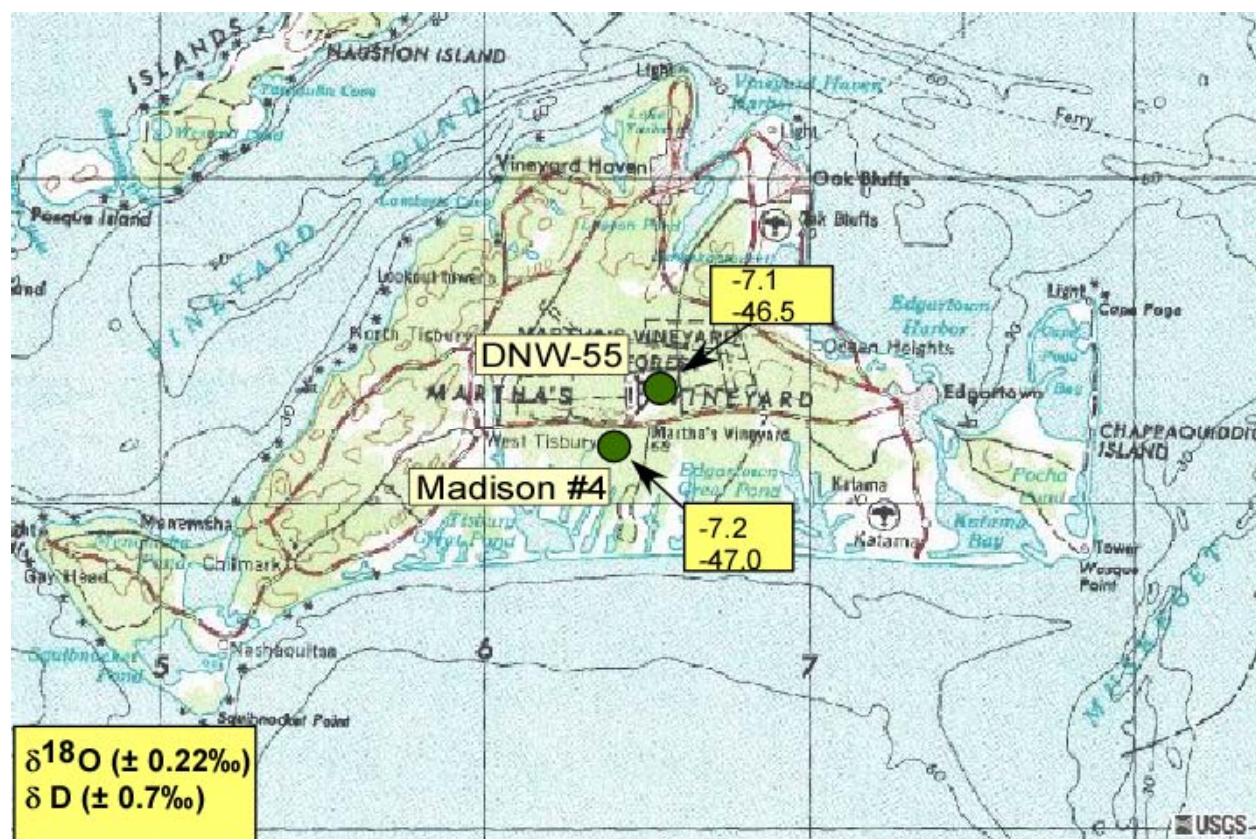


Figure 16. $\delta^{18}\text{O}$ and δD values on Martha's Vineyard from sampling campaign, summer 2005

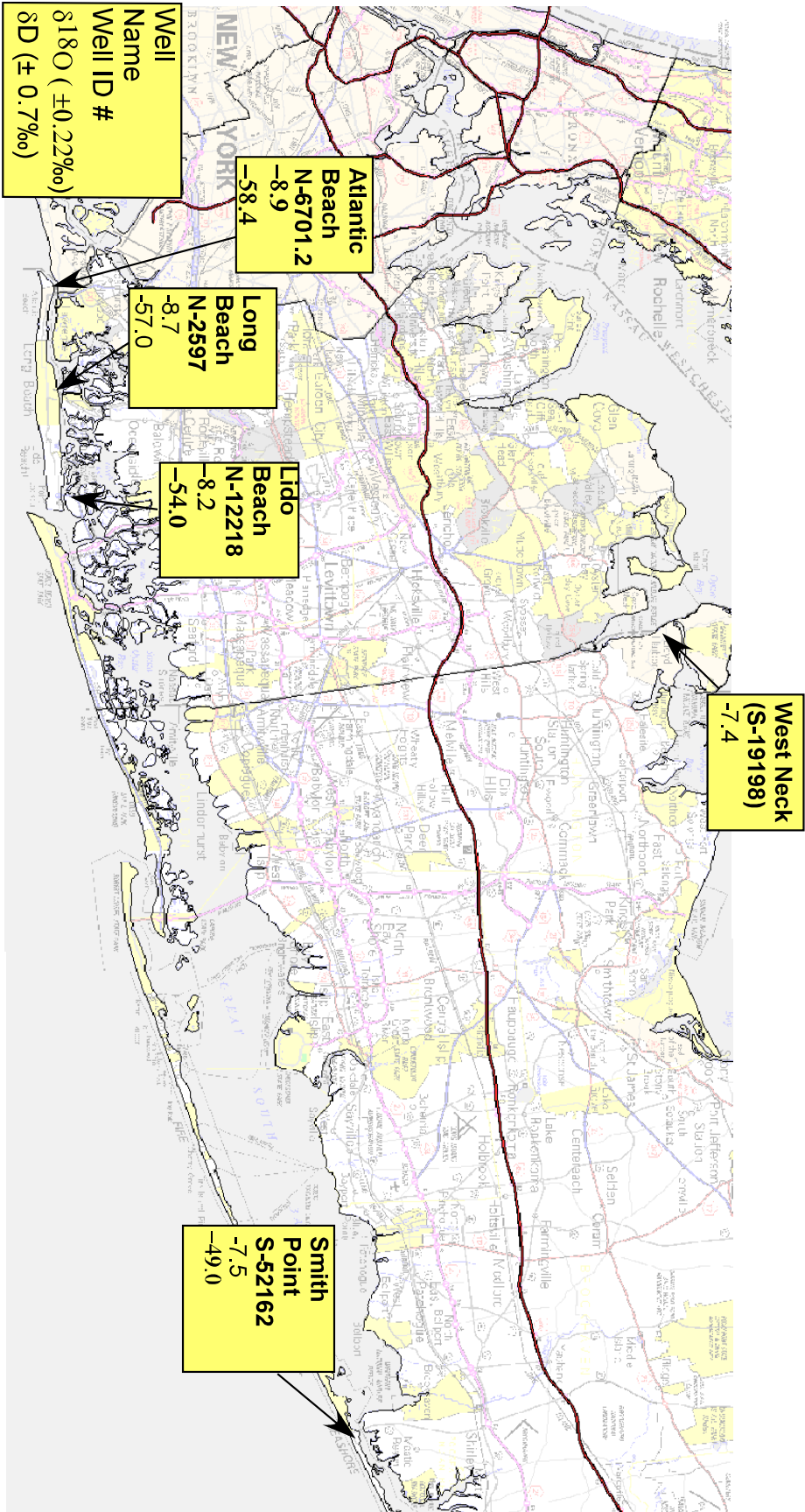


Figure 17. $\delta^{18}\text{O}$ and δD values for Long Island from sampling campaign, summer 2005.

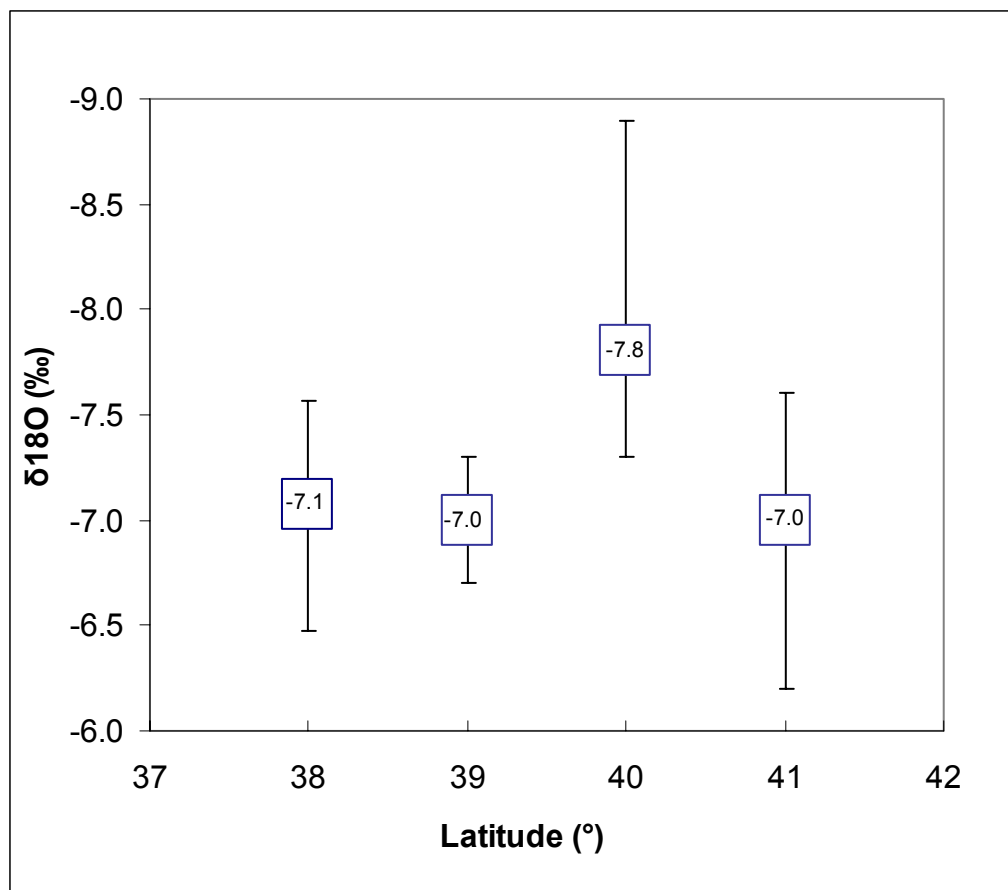


Figure 18. Compilation of $\delta^{18}\text{O}$ data from Maryland (Aeshbach-Hertig et al., 2001) to Nantucket Island showing boxplot of $\delta^{18}\text{O}$ values vs. latitude.

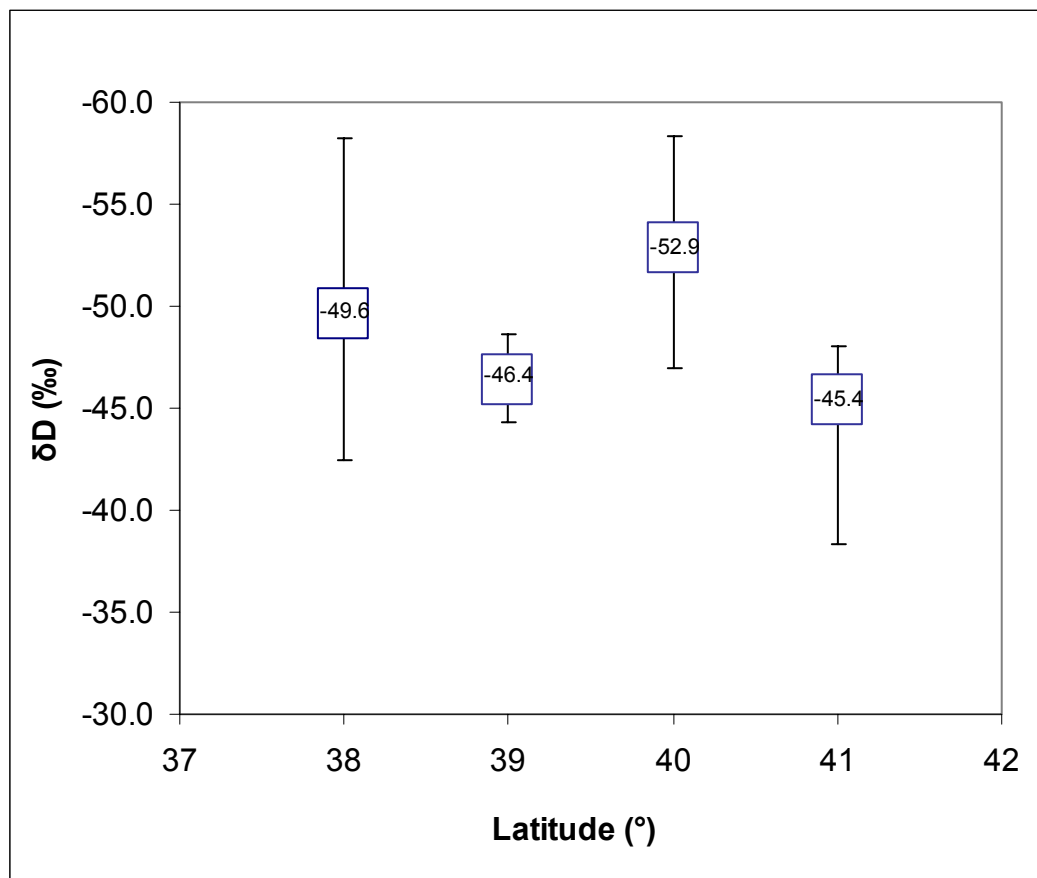


Figure 19. Compilation of δD data from Maryland (Aeschbach-Hertig et al., 2000) to Nantucket Island showing boxplot of δD values vs. latitude.

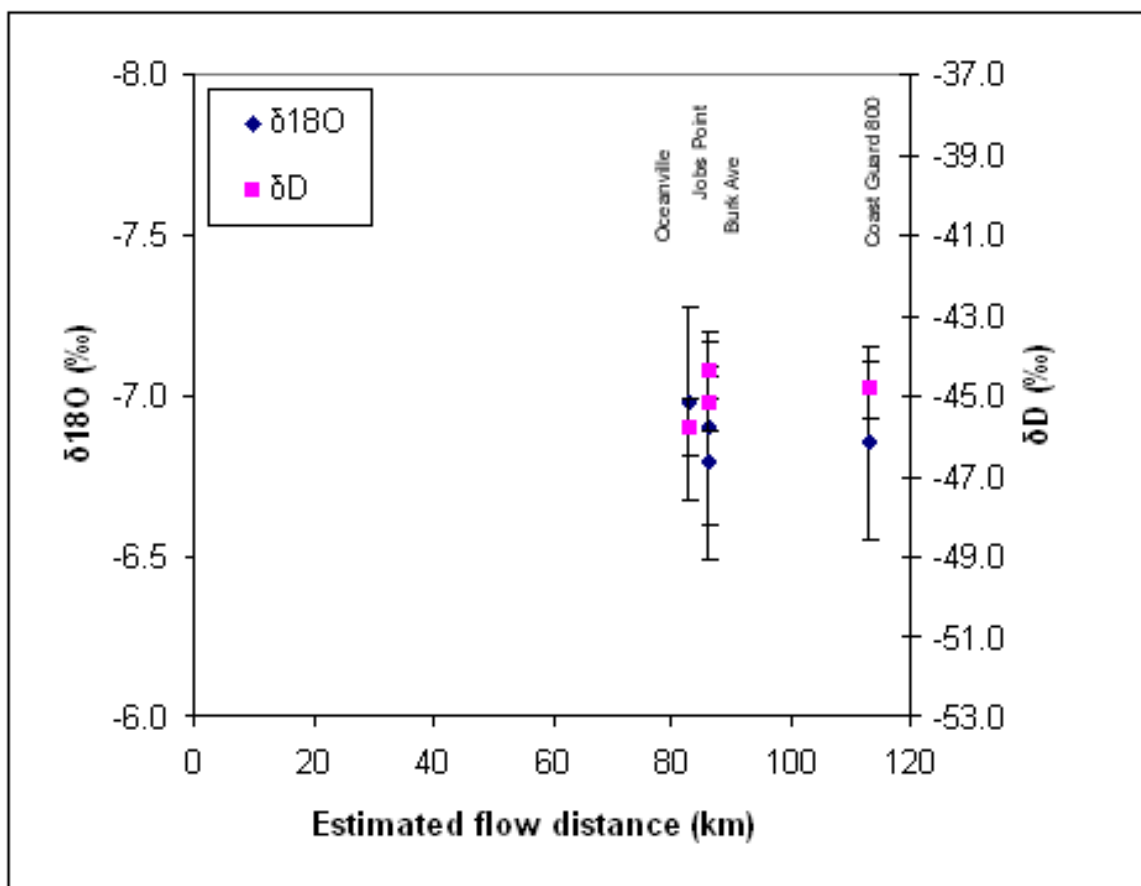


Figure 20. Variation of isotope data with flow distance in the Lower Kirkwood Aquifer, New Jersey.

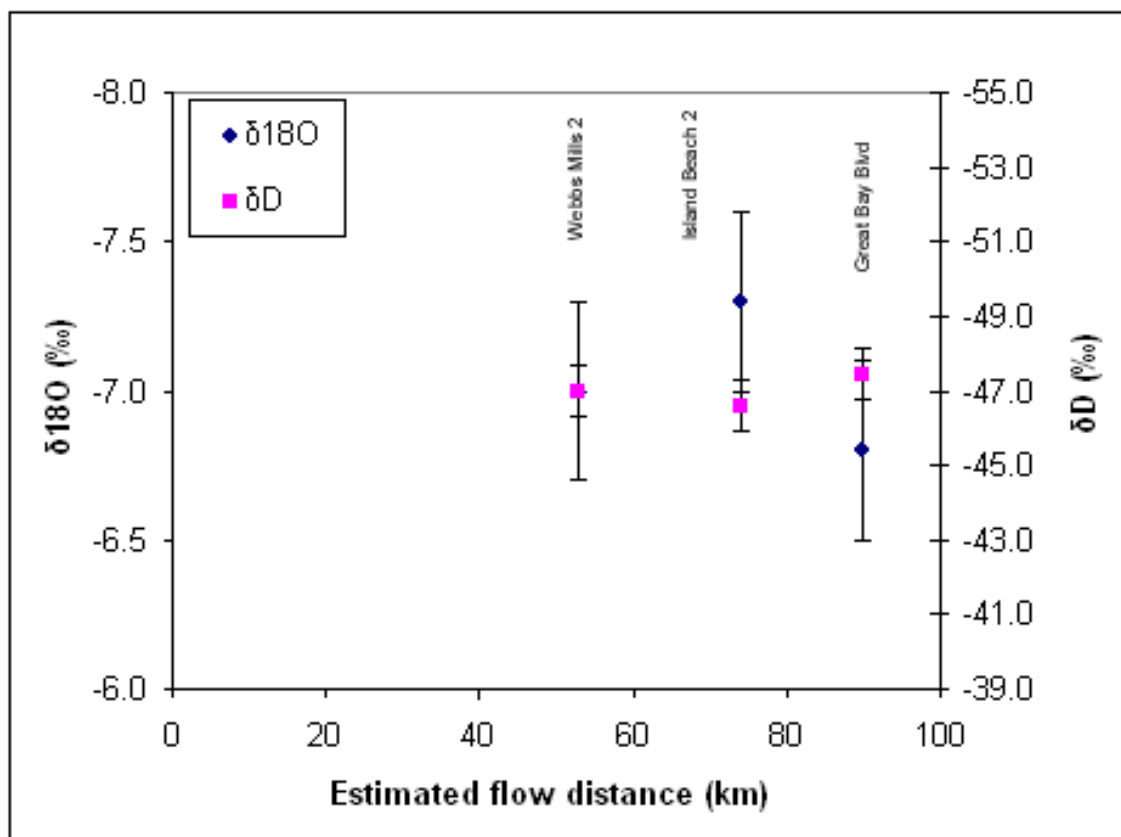


Figure 21. Variation of isotope data with flow distance in the Piney Point Aquifer, New Jersey.

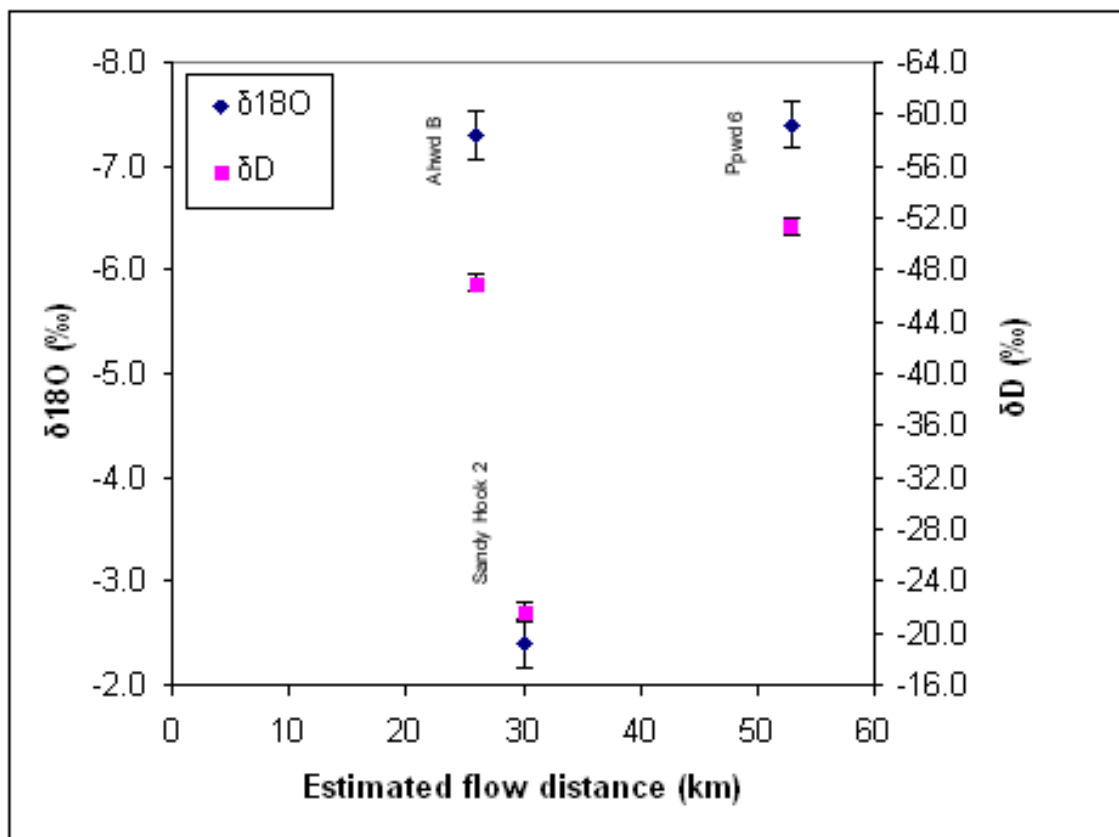


Figure 22. Variation of isotope data with flow distance in the Englishtown Aquifer, New Jersey.

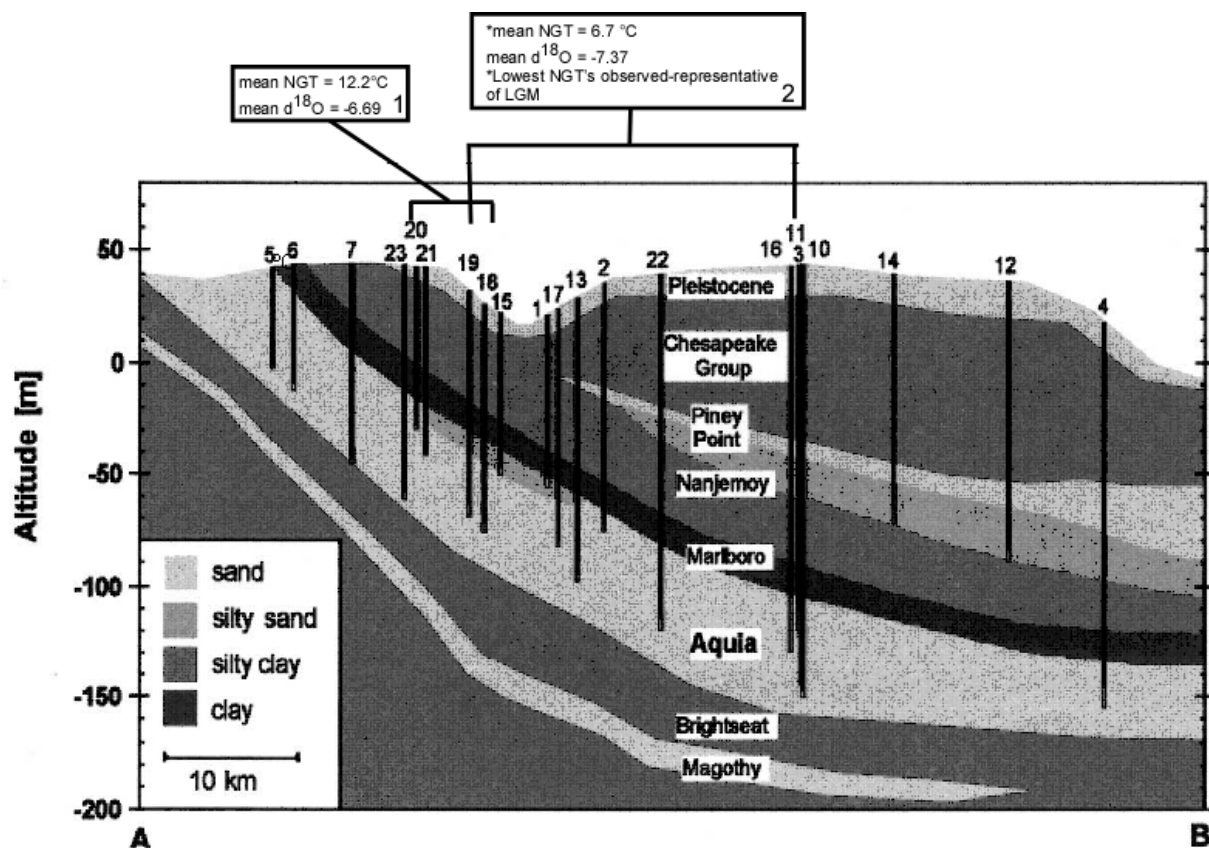
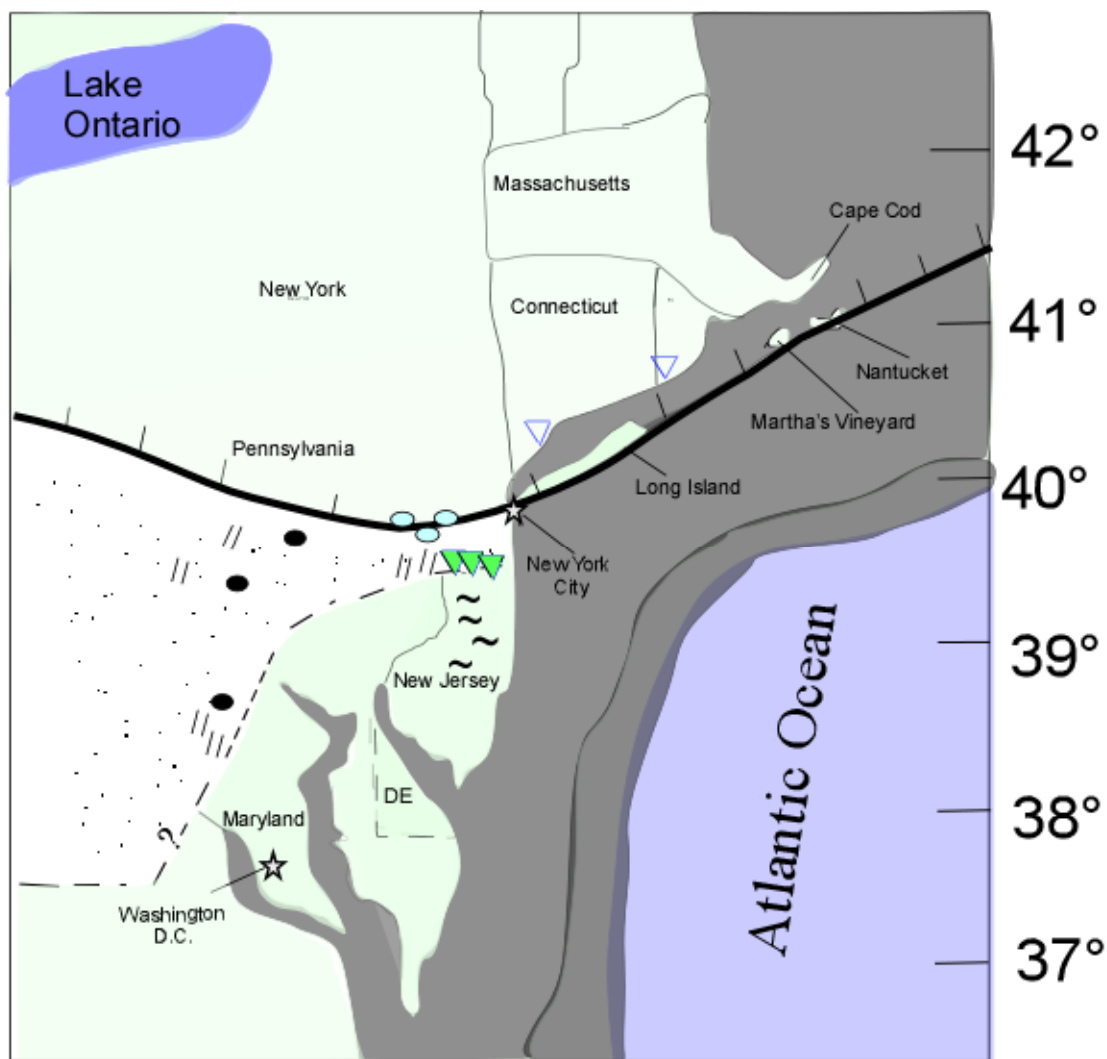


Figure 23. Cross-section of Aquia formation along line A-B indicated in Figure 14. Mean $\delta^{18}\text{O}$ values and Noble Gas Temperatures (NGT's) are shown for data sets 1 and 2. Note: all wells except MD12 and 14 tap the Aquia formation.



Explanation

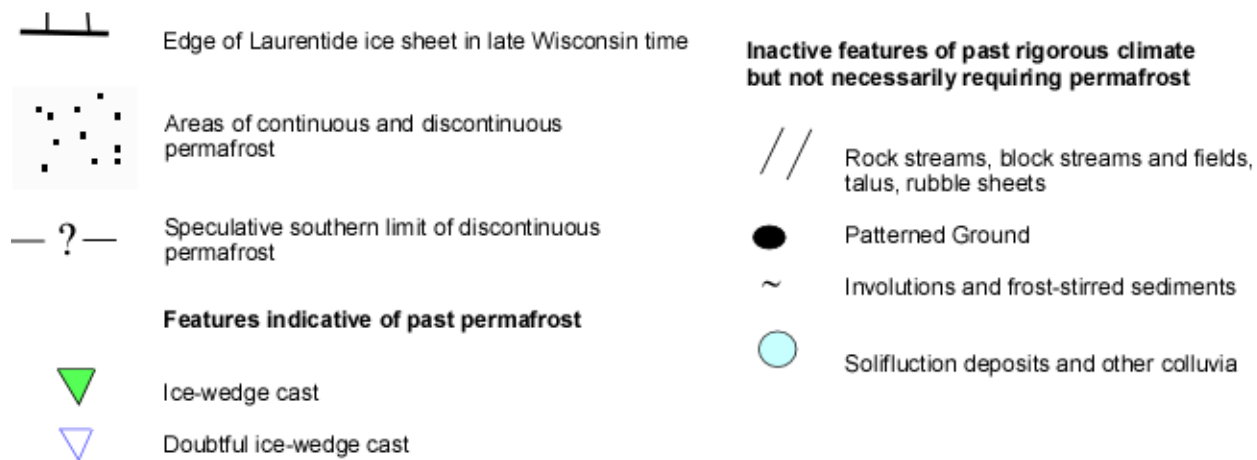


Figure 24. Maximum extent of permafrost at the LGM in the northeastern U.S. and locations of geological evidence for the influence of permafrost.

Table 1. Stable isotope data from sampling campaign, summer 2005.

Sample Location	Well Name	* $\delta^{18}\text{O}$ (‰)	* δD (‰)
Nantucket			
	¹ USGS 28	-7.6	-48.0
	¹ USGS 313	-7.6	-47.3
	¹ USGS 198	-6.6	-43.7
	¹ USGS 193	-6.3	-39.8
	¹ USGS 302	-6.7	-44.0
	¹ USGS 228	-7.3	-45.5
	¹ West End	-7.2	-47.0
	¹ MW 2004-D5	-7.6	-45.8
	¹ USGS 6001	-6.2	-38.3
	¹ PW 13	-7.1	-43.1
	¹ PT 12	-7.3	-44.8
	¹ PT 13	-7.2	-44.4
Martha's Vineyard			
	¹ DNW-55	-7.1	-46.5
	¹ Madison #4	-7.2	-47.0
Long Island			
	¹ Smith Point (S-52162)	-7.4	-49.0
	¹ Lido Beach (N-12218)	-8.2	-53.9
	¹ West Neck (S-19198)	-7.4	-49.9
	¹ Atlantic Beach (N-6701.2)	-8.9	-58.4
	¹ Long Beach (N-2597)	-8.6	-56.9
New Jersey			
	² AHWD B	-7.3	-47.0
	³ COAST GUARD 8	-6.9	-44.8
	³ BURK AVE TW	-7.1	-45.2
	² WEBBS MILLS 2	-7.0	-46.9
	² ISLAND BEACH 2	-7.3	-46.6
	² SANDY HOOK 2	-2.4	-21.6
	³ OCEANVILLE 1	-7.2	-44.4
	³ GREAT BAY BLVD 1	-6.8	-47.5
	³ JOBS POINT	-6.7	-45.8
	² PPWD 6	-7.4	-51.4
	Errors	$\pm 0.22^1$ $\pm 0.23^2$ $\pm 0.30^3$	± 0.7
*Relative to internal lab standards at Geosciences Department, Indiana University (Boulder and Miami Water)			

Table 2. Stable isotope data from Aquia Aquifer, Maryland (Aeschbach-Hertig et al., 2001).

Sample Location	Well Name	$\delta^{18}\text{O}$ (‰)	δD (‰)
Maryland	MD9	-7.08	-48.7
	MD8	-6.76	-47.6
	MD5	-7.08	-53.5
	MD6	-7.21	-54.1
	MD7	-6.84	-42.5
	MD20	-6.70	-45.1
	MD23	-7.00	-48.1
	MD21	-6.77	-44.0
	MD18	-7.06	-48.5
	MD19	-7.21	-50.6
	MD15	-7.23	-56.0
	MD1	-7.05	-50.6
	MD2	-6.73	-45.7
	MD17	-6.92	-46.7
	MD22	-7.39	-58.3
	MD13	-7.56	-53.9
	MD16	-7.31	-50.0
	MD11	-7.55	-58.2
	MD3	-7.43	-52.9
	MD10	-6.52	-43.8
	MD14	-6.69	-44.1
	MD12	-7.37	-51.8
	MD4	-6.78	-44.2
*wells in bold represent $\delta^{18}\text{O}$ and δD values shown on Figure 11	Errors	± 0.07	± 0.7

Table 5. Noble Gas Characteristics

	Composition reflects	Ne (ccSTP/kg)	"Excess air" Δ Ne	Recharge Temperature Reflects
Meteoric groundwater	Solubility + some atmosphere	2e-5 - 5e-5	30-100%	Water table
Subglacial Meltwater	Atmosphere + minor effect gravitational fraction	6e-4 - 2e-3	>500%	Analysis does not have unique solution
Proglacial lake/ surface water	Solubility	2e-5	1 - 5%	Lake surface