DISSOLVED ORGANIC AND INORGANIC ^{14}C CONCENTRATIONS AND AGES FOR COASTAL PLAIN AQUIFERS IN SOUTHERN MARYLAND

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ABSTRACT. The Aquia (Paleocene) and Magothy (Late Cretaceous) Formations of the Atlantic Coastal Plain represent two well-characterized (hydrodynamically and geochemically) aquifers in southern Maryland. ^{14}C measurements of the dissolved organic (DOC) and inorganic carbon (DIC) of Aquia and Magothy groundwaters have been made using accelerator mass spectrometry (AMS). Both DI^{14}C and DO^{14}C concentrations in the initial flow path are unexpectedly low. As the water progresses farther from the recharge area, the DI^{14}C percent modern carbon (pMC) is consistently lower than the DO^{14}C pMC; this difference stays constant for all samples. The ^{14}C-derived ages for an Aquia water sample downgradient at Site 4 are 17 ka and 12 ka for DI^{14}C and DO^{14}C, respectively. Radiocarbon ages have been compared to ages determined by two other independent dating methods: computer-simulated hydrodynamic modeling and age estimates based on changes in Cl$^-$, ^{18}O and ^{2}H distributions, which are interpreted to be influenced by sea level and climate.

INTRODUCTION

A study of ^{14}C measurements of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) in the groundwater of two Coastal Plain aquifers of southern Maryland has been initiated to evaluate the potential of ^{14}C dating of these waters. ^{14}C values of both fractions of dissolved carbon provide a better understanding of the carbon sources to the groundwater in the recharge zone and throughout the aquifer flow path. This information can be used to determine to what extent ^{14}C dating using DIC and/or DOC concentrations can be a reliable assessment of age of the water.

The DIC in groundwater is primarily in the form of bicarbonate in the pH range of 6.4 to 9.0, which is characteristic of Coastal Plain aquifers (Back 1966). The HCO$_3^-$ forms in the unsaturated zone by the following reaction:

$$CaCO_3(s) + CO_2(g) + H_2O \rightarrow Ca^{2+}(aq) + 2\ HCO_3^-(aq) . \tag{1}$$
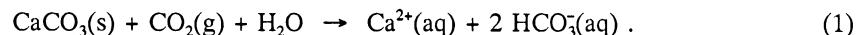
Soil CO_2(g) from root respiration and, to a much lesser extent, from the atmosphere accounts for the remaining source of inorganic carbon in the recharge zone. The ^{14}C activity in percent modern carbon (pMC) is expected to be ~100 and ~0 for the CO_2 and the $CaCO_3$, respectively. Based on the above equation, the HCO$_3^-$ should contain ~50 pMC, as it forms in the unsaturated, organic-rich zone. However, Tamers (1975) has shown that additional CO_2(g) in groundwater samples can account for the average of ~70 pMC in DI^{14}C measured in 90 samples from several aquifers. Tamers (1975), Pearson and Hanshaw (1970), Mook (1980) and Fontes and Garnier (1979) developed models to explain further the DI^{14}C activities observed in groundwater that begins to penetrate a confined aquifer. These values represent the initial DI^{14}C activities of the groundwater system, and is frequently referred to as $A_{(o)}$.

The DOC in recharge groundwater is expected to derive from the decomposition of plant and, to a lesser extent, animal material in the soil horizon and thus, to contain a modern ^{14}C signature. This carbon fraction would not be subject to the same type of correction factors necessary to characterize the pMC in DIC in the recharge zone. However, Murphy *et al.* (1989a, b), Schiff *et*

al. (1990), and Wassenaar *et al.* (1990, 1991) have shown that the $DO^{14}C$ pMC can be unexpectedly low (75–92 pMC) in surface groundwater. Kerogen from the aquifer matrix with a 0 pMC has been designated as the source of "dead" organic carbon in the DOC (Murphy *et al.* 1989a). Murphy *et al.* (1989 a, b) characterized the DOC as high molecular weight (HMW) or low molecular weight (LMW), whereas Wassenaar *et al.* (1990) and Schiff *et al.* (1990) characterized it as humic and fulvic fractions to determine which fraction contains the source of modern and old carbon. Schiff *et al.* (1990) suggested that DOC is subject to extensive cycling in the upper soil zone and the aquifer, and thus, does not represent a sole vegetation source breaking down at the surface.

The aquifer sediments can contain organic and inorganic carbon, the latter consisting of carbonate minerals, mainly $CaCO_3$. The DIC can be augmented by carbon from either of these pools, in the first case, by microbial oxidation or bacterially mediated sulfate reduction, and in the second case, by simple dissolution. However, the DOC in the water is likely to be augmented only from the organic pool. Once the $DO^{14}C$ activity has been established in the recharge zone, the loss of $DO^{14}C$ in the water passing downgradient in a confined, piston-type flow aquifer system would be due to decay only, unless there is a continuous flux or cycling of DOC to or in the aquifer.

HYDROGEOLOGY AND GEOCHEMISTRY

Both the Aquia (Paleocene) and Magothy (Upper Cretaceous) aquifers lie in the continental shelf portion of the Atlantic Coastal Plain Province (Fig. 1). The geological formations of this region consist of unconsolidated sediments gradually dipping southeast with gradients of 2–4 m km⁻¹ toward the sea. These layers generally outcrop toward the land and thicken towards the distal seaward extensions, forming wedged-shaped layers. The gravel, sand and silty sand deposits are the valuable productive aquifers of the coastal states. The sand layers are bounded by packed clay and silt/clay formations, creating confined aquifers at various depths. These aquifers are primarily recharged in the outcrop regions by precipitation, and are characterized by laminar flow downgradient. Before exploitation, these aquifers were generally artesian where overlain by confining beds, and were expected to discharge upward through the overlying confining beds to cause vertical mixing between aquifers in some regions. Vertical recharge has been suggested as a significant source of recharge to these aquifers (Kapple & Hansen 1976; Chapelle & Drummond 1983). Very low chloride concentrations (0.02–0.30 mM) suggest that these aquifers have been flushed of their original connate water (Back 1966; Wood 1981; Purdy 1991).

The Aquia and the Magothy aquifers are separated by the Brightseat, Monmouth and Matawan Formations, which together form approximately 30 m of confining bed. The Marlboro Clay, a pink kaolinitic unit, and the ocherous kaolinite and illite Patapsco clays, serve as aquitards overlying the Aquia and underlying the Magothy, respectively. The Magothy outcrops farther inland relative to the Aquia outcrop (Fig. 1), and both aquifer systems flow in the same direction in the study region with piston-flow hydrodynamics (Mack & Mandle 1977; Knobel & Phillips 1988). Average linear velocities of 0.010 and 0.015 m day⁻¹ have been estimated for the Aquia and Magothy aquifers, respectively, based on a steady-state computer simulation using prepumping potentiometric surfaces (Fleck & Vroblesky, in press).

The Aquia is a marine unit, comprised predominantly of quartz sand (50–75%), glauconite (20–40%), and shell (calcite and aragonite) and other calcareous materials (5–25%) (Hansen 1974). The Magothy, however, is of fluvio-marine origin containing strand-zone deposits (Hansen 1972). These deposits are composed largely of quartz sand and gravel (~75–86%), interbedded with kaolinite and montmorillonite layers (~14–25%) (Force & Moncure 1978). This aquifer has minor
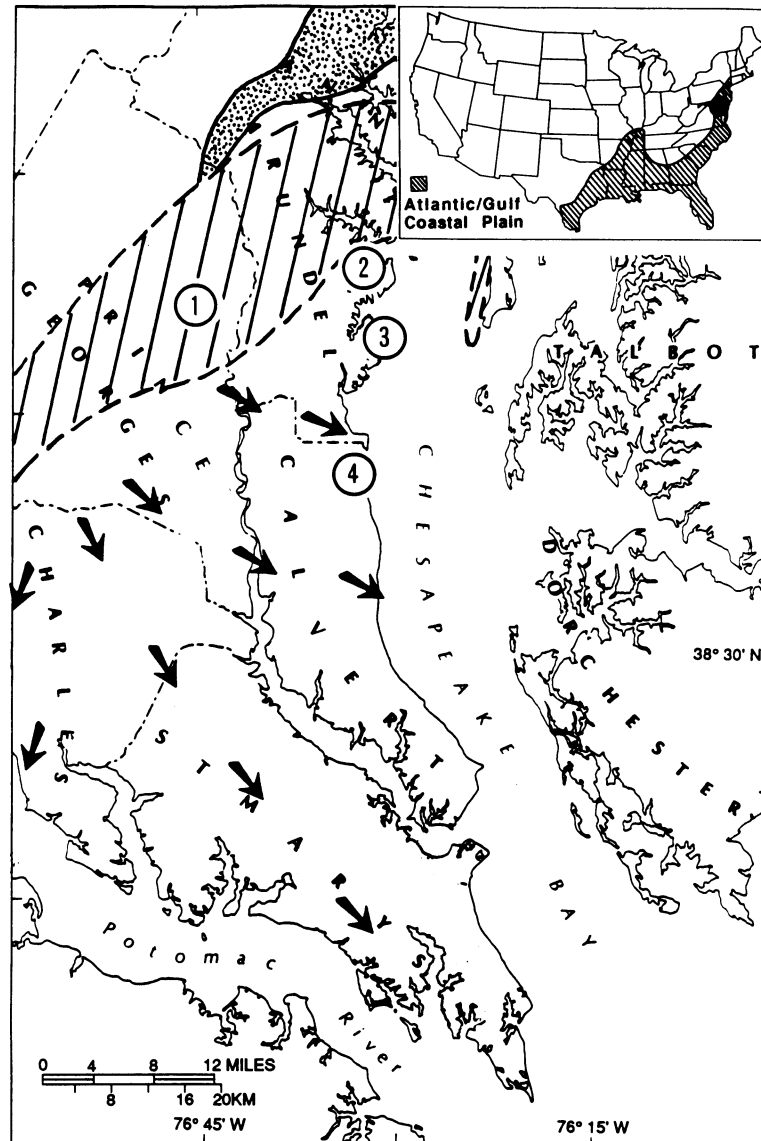
Fig. 1. Plan view of study area with numbers indicating sampling sites. Arrows show direction of groundwater flow in Aquia aquifer. Hatched and dotted areas represent the recharge region of Aquia and Magothy aquifers, respectively. ● on US map (inset) indicates the location of the study area in the Atlantic Coastal Plain.

amounts of lignite and pyrite, and trace amounts of feldspar, mica and iron minerals (Glaser 1969; Trapp *et al.* 1984).

The geochemistry of the Aquia aquifer system can be essentially described by ion exchange reactions with glauconite and dissolution/precipitation of $CaCO_3$ (Chapelle 1983; Chapelle & Knobel 1983). The Magothy geochemistry is influenced by CO_2 and H_2O reactions with silicate minerals (biotite and plagioclase) to produce kaolinite and the ions Na^+, Mg^{2+}, Ca^{2+}, HCO_3^-, and aqueous SiO_2 (Knobel & Phillips 1988). Both systems are expected to be open, with respect to CO_2, based on microbial processes. Sulfate-reducing bacteria have been observed in both aquifers

(Chapelle *et al.* 1987), and sulfate-reducing bacteria are expected to produce CO_2 from carbonaceous material, such as lignite (Knobel & Phillips 1988; McMahon & Chapelle 1991).

Chapelle and Knobel (1985) reported a range of groundwater $\delta^{13}C$ values from $-13.0‰$ in the outcrop to $-11.4‰$ about 80 km downgradient for 8 samples from the Aquia aquifer collected in the same region as this study. In this region of the Magothy aquifer, Chapelle *et al.* (1987) reported groundwater $\delta^{13}C$ values of (-12.3) to $(-11.9)‰$ for 3 sites. Due to different depositional histories, the organic material is characterized as an algal source in the Aquia and a terrestrial plant source in the Magothy (Chapelle, personal communication 1991).

METHODS

Filtered samples were collected at each site and stored in treated 20-liter polyethylene carboys. Each well was pumped continuously for 15 min prior to sampling. The precleaned carboys were rinsed several times with well water before collection. $HgCl_2$ was added to the water to inhibit microbial activity. Samples were later processed at the USGS Radiocarbon Laboratory.

Two-liter aliquots of each sample were used in the analyses. Each was placed in a vessel on a vacuum line, and 20 ml of 70% H_3PO_4 was added to liberate the DIC fraction as CO_2. A photo-chemical oxidation method (Armstrong, Williams & Strickland 1966) was used to separate the DOC fraction in which each sample was irradiated with a 1200-watt UV mercury lamp for 45 min. Samples passed through a helix of 6-mm OD quartz tubing to allow continuous exposure to the UV source. To facilitate oxidation of the exposed organic fraction, analytical-grade potassium persulfate was added to each sample. Oxygen was used as the carrier gas to collect the DOC as CO_2.

The DIC- and DOC-derived CO_2 was converted to graphite using the method of Vogel *et al.* (1984). The graphite targets were brought to the University of Arizona NSF Accelerator Facility for Radioisotope Analysis, and ^{14}C measurements were made by AMS (Linick *et al.* 1986).

DATA AND INTERPRETATION

This preliminary ^{14}C study of Maryland's groundwater includes four sites near the recharge regions of the Aquia and Magothy aquifers (Fig. 1). Two limitations of the study are the absence of ^{13}C measurements and characterization of the DOC fraction. We have interpreted the data by measuring $DO^{14}C$ and $DI^{14}C$ in water in the recharge zone (which provides a baseline for the initial water penetrating the aquifer), and by comparing this water with samples downgradient. Samples from both aquifers can establish the relative $DO^{14}C$ and $DI^{14}C$ systematics of these aquifers, and further characterize the sources and variations to the dissolved carbon system.

Two isotopes that can identify modern water by their atmospheric increases caused by nuclear weapons testing in the 1950s and 1960s are ^{36}Cl and ^3H. Bomb pulses of both these isotopes (83.4×10^6 atoms ^{36}Cl liter^{-1} and 61.2 TU ^3H) have been documented at Site 1 (Purdy 1991). The water from Site 1 (well depth 15.2 m) is expected to represent the beginning of the Aquia flowpath, based on a confining bed indicated on a geophysical log for a well within 5 km. Figure 1 shows Site 1 in the general region suggested as the recharge zone by Chapelle and Drummond (1983). The water is expected to have recharged the aquifer between the mid-1950s to late 1960s (Purdy 1991).

The well at Site 2 is in the Aquia aquifer (21.3 m). However, based on the sulfate concentrations and hydraulic heads, Purdy (1991) suggested that Magothy water is recharging the Aquia aquifer at this site, and that the water sampled here contains about 50% Magothy-derived water. The well at Site 3 is in the Magothy aquifer, and at Site 4, the well is in the Aquia aquifer (Fig. 1). Since

Site 4 is downgradient from Site 1 in the Aquia aquifer, these two sites represent, generally, one flow line.

Table 1 gives $DO^{14}C$ and $DI^{14}C$ values. The value of 34 pMC for the $DI^{14}C$ at Site 1 is lower than expected, suggesting carbonate dissolution, and perhaps significant fractionation effects (isotopic exchange reactions) due to $CaCO_3$ dissolution and precipitation reactions. Chapelle (1983) suggested postdepositional calcite cementation occurs throughout the recharge zone and the region directly downgradient within 30–40 km. The $DO^{14}C$ value of 40 pMC is also unexpectedly low, and is consistent with a significant contribution of "dead" organic carbon to water at the beginning of the flowpath. Murphy et al. (1989a, b) suggested that the source of old organic carbon in groundwater is kerogen in the aquifer matrix. Wassenaar et al. (1990) suggested that the source is the hydrophilic fraction of the DOC in the soil zone but is aquifer material at depth. Whatever the source, this "dead" organic material must be introduced to the DOC at shallow depths (<15m) in the Aquia aquifer.

TABLE 1. Total and ^{14}C Concentrations* of DOC and DIC in Aquia and Magothy Groundwater

Site	Formation	Total DOC (mg C liter^{-1})**	DOC^{14}C (pMC)[†]	HCO$_3^-$ (mM)	DIC^{14}C (pMC)[†]	O$_2$ (ppm)
1	Aquia	0.57 ± 0.01	40.4 ± 0.5	2.39 ± 0.05	33.9 ± 0.4	4.09 ± 0.05
2	Aquia/Magothy[‡]	1.06 ± 0.02	28.5 ± 0.4	4.07 ± 0.08	25.2 ± 0.4	0.01 ± 0.05
3	Magothy	1.03 ± 0.02	13.2 ± 0.9	2.85 ± 0.06	6.8 ± 0.2	0.15 ± 0.05
4	Aquia	0.62 ± 0.01	9.1 ± 0.2	2.97 ± 0.06	3.1 ± 0.2	0.07 ± 0.05

*^{14}C concentrations are computed assuming $\delta^{13}C = -25‰$. Quoted errors are counting error and machine error, combined quadratically.
**Total DOC measured independently from ^{14}C DOC using $Na_2S_2O_8$ oxidation method
[†]DOC used for ^{14}C analyses removed by UV radiation in the presence of oxygen. ^{14}C determined by AMS analyses (see text).
[‡]Water from Site 2 is expected to be a mixture of water from the Aquia and Magothy aquifers (see text).

The $DI^{14}C$ and $DO^{14}C$ values (pMC) for all sites are plotted as a function of flow distance in Figure 2A. Flow distance has been derived assuming the water originated at the northern edge of the outcrop band. (This convention was used in order to make direct comparisons with previous Aquia aquifer studies.) This is a simplification, however, since water that enters the aquifer flowpath might represent a mixture of water penetrating anywhere upgradient in the outcrop band. The $DI^{14}C$ decreases from 34 to 3 pMC and the $DO^{14}C$ from 40–9 pMC for samples from Site 1–4, respectively (Table 1). The $DI^{14}C$ is less than the $DO^{14}C$ for the same sample in all cases. More importantly, the difference in the $DI^{14}C$ and $DO^{14}C$ concentrations (~6 pMC) stays nearly constant for all samples, regardless of the aquifer or sampling distance from the respective recharge zones.

Sites 1 and 4

Using water from Sites 1 and 4 to characterize the evolution of water down one general flowpath in the Aquia aquifer, we consider the following explanations for the changes observed in both the $DI^{14}C$ and $DO^{14}C$ concentrations. If the reduction in ^{14}C activity from Site 1 to 4 was due only to radioactive decay, the age differences for the DOC and DIC fractions would stay the same (or the pMC values would eventually merge to the same value). This is not the case (Fig. 2). The DIC becomes increasingly older compared to the DOC. The simple explanation for this result would be that the ^{14}C activity in the DOC is reduced by decay only, but in the DIC, it is reduced by decay and an additional mechanism. The HCO$_3^-$ increases from 2.4 to 3.0 mM from Site 1 to 4. This is consistent with dissolution of $CaCO_3$ in this aquifer. A 20% increase in DIC from carbonate
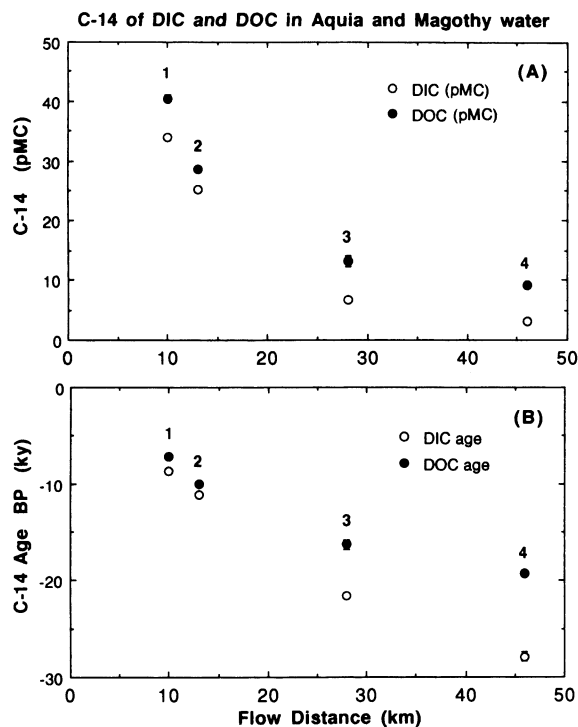
C-14 of DIC and DOC in Aquia and Magothy water

Fig. 2. ^{14}C concentrations in pMC (A) and ^{14}C uncorrected ages (B) for DIC and DOC fractions at each sampling site. Numbers on graph indicate sampling sites. Groundwater collected at Sites 1, 2 and 4 is from the Aquia aquifer, and at Site 3, from the Magothy aquifer. Based on chemical evidence, water collected at Site 2 is expected to be a mixture of water originating from the Magothy and Aquia aquifers. Magothy water is expected to recharge the Aquia at Site 2 (Purdy 1991). Flow distance for each site was determined assuming water originated at the northern edge of the outcrop band. However, the water at each site is likely a mixture of water originating anywhere upgradient in the ~20 km outcrop band. Thus, the distance position represents the maximum flow distance to each site. The uncertainty of the distance position could shift it left up to 20 km (see text). Vertical uncertainties are determined by counting error and machine error, combined quadratically. For most data points, this uncertainty is included in the circle, except where indicated.

dissolution (0 pMC) would dilute the DI^{14}C in the sample by 20%. Fractionation effects, removing the ^{14}C in the dissolved bicarbonate (increasing the ^{14}C in the CaCO$_3$ sediments), would further dilute the ^{14}C in the DIC as the water passes downgradient. Therefore, the loss of DI^{14}C from Site 1 to 4 could be attributed to decay, dilution from CaCO$_3$ sources and fractionation effects.

Another possible explanation for the ^{14}C pMC results is an addition of "dead" carbon to both the DOC and DIC. However, the DIC must be affected to a greater extent by this addition. Microbial processes might affect both the DI^{14}C and DO^{14}C. Aerobic bacteria, in the oxygenated zone, and anaerobic bacteria, in the oxygen-depleted zone, can convert sediment organic material, such as lignite, to inorganic carbon *via* oxidation and sulfate reduction, respectively. This process would account for the increase in the HCO$_3^-$ and the constant total DOC observed as the water passes from Site 1 to 4 (Table 1). Since the organic material in aquifer sediments have 0 pMC, this transformation of organic carbon to DIC would account for the lower DI^{14}C activity downdip. However, this process also assumes that organic aquifer sediments are also breaking down to DOC and replacing the original DOC in the groundwater, which would lower the ^{14}C activity in the DOC system. McMahon and Chapelle (1991), using a core from Coastal Plain sediments, have suggested that simple organic acids accumulate in aquitards due to microbial fermentation while they become depleted in the adjacent aquifer due to respiration. Thus, a concentration gradient results, causing a net diffusive flux of organic acids from aquitards to aquifers. This process would account for a constant cycling of old DOC to the aquifer.

Sites 2 and 3

Water at Sites 2 and 3 is not expected to receive water from Site 1. However, these samples demonstrate the consistent loss of ^{14}C downgradient in these aquifers and help characterize the

$DI^{14}C$ and $DO^{14}C$ systematics in these aquifers. Sample 3, containing Magothy water, is plotted on Figure 2, based on distance from its recharge (Fig. 1), whereas the Site 2 sample, with a mixture of Magothy- and Aquia-derived water, is based on distance from the Aquia recharge. Essentially, all samples are ordered, based on the time the water lost contact with the atmosphere (or age). Both these samples progressively decrease in ^{14}C as expected, regardless of aquifer system.

Magothy and Aquia water have approximately 0.8 to 1.4 and 0.6 to 0.7 mg of total organic carbon liter^{-1}, respectively, in this region of Maryland (C. Bond, unpublished data; Purdy 1991, respectively). The higher levels of DOC at Sites 2 and 3 reflect the higher DOC concentrations observed in the Magothy water. However, the $DO^{14}C$ and $DI^{14}C$ values at these sites appear to follow the same trend as observed in the Aquia, *i.e.*, lower ^{14}C activity in the DIC compared to the DOC, and a constant difference in the ^{14}C activity of the DIC and DOC fraction. Thus, the overall ^{14}C systematics appear to be similar in both aquifers, suggesting similar mechanisms controlling the carbon sources to the dissolved carbon system in both aquifers.

Age of the Aquia Water

Without a clear understanding of the sources of carbon to the groundwater in an aquifer system, uncertainty remains in the ^{14}C dating technique. However, comparing a ^{14}C estimated age with other independent dating methods can provide some insights into the limits of the dating techniques. Uncorrected ^{14}C ages for all samples are plotted against flow distance in Figure 2B. Table 2 lists the uncorrected and corrected ^{14}C age for Site 4 groundwater. Since one general flow path is from Site 1 to 4, and the Site 1 sample represents the ^{14}C concentration in water from the beginning of the flowpath, Site 1 values are used for the initial $DI^{14}C$ and $DO^{14}C$ activities. Thus, the age at Site 1 has been subtracted from Site 4 for both the DIC and DOC fractions. An additional correction factor has been applied to Site 4's $DI^{14}C$ age, based on mass balance dissolution reactions downgradient. This corrects for the 20% increase in HCO_3^- assumed to be from $CaCO_3$. The DIC reflects an age of 17.4 ka and the DOC, an age of 12 ka for Site 4 water. An additional source of "dead" carbon appears to be incorporated in the DIC fraction, possibly due to the fractionation effects discussed in this section or conversion of old DOC to DIC.

This method of dating water assumes that the ^{14}C activity of water in the recharge zone can be used to correct for addition of "dead" carbon sources to the water before it penetrates the aquifer and, in a sense, "reset the clock" for comparisons with the ^{14}C activities in water downgradient. But, in this case, both bomb ^{36}Cl and ^{3}H have been observed in the Site 1 sample. Therefore, thermonuclear ^{14}C might also be present. If this additional ^{14}C is present, it is masked by the "dead" carbon sources to the water. The maximum atmospheric ^{14}C concentration was twice the normal level in 1963 and 1964 (Nydal & Lövseth 1983) as compared to increases on the order of

TABLE 2. $DI^{14}C$ and $DO^{14}C$ Ages* of Aquia Groundwater

Formation	Site	Carbon fraction	^{14}C age (yr BP)
Aquia	1	DIC	8700 ± 100**
	1	DOC	7300 ± 100**
Aquia	4	DIC	19,200 ± 500
	4	DIC	17,400 ± 700[†]
	4	DOC	12,000 ± 200

*All ages are computed assuming $\delta^{13}C = -25‰$. Quoted errors are counting error and machine error, combined quadratically. Additional errors are discussed in the text.
**Values used as initial ^{14}C activities of DIC and DOC for the flowpath.
[†]$DI^{14}C$ age corrected for mass balance dissolution reactions downgradient.

10^2 and 10^3 over normal for ^{36}Cl and ^{3}H. Moreover, the ^{14}C bomb pulse delivery to the surface of the earth is attenuated and delayed on the order of 10–20 years, due to atmospheric exchange processes (Lal & Suess 1983). The amount of bomb ^{14}C that might be present in the Site 1 sample is difficult to quantify based on one sample and the difficulties of comparing ^{14}C with ^{36}Cl and ^{3}H maximum bomb inputs. But this effect would increase the age of Site 1 water (perhaps as much as 5 ka) and thus, assign a younger age to Site 4 water compared to the age in Table 2. This younger age is not supported by other dating techniques.

Computer-simulated hydrodynamic modeling of the Aquia aquifer has predicted an average linear velocity of 4.0 m yr^{-1} averaged over the entire aquifer for prepumping steady-state conditions (Fleck & Vroblesky, in press). This flow rate would result in an age of 11.5 ka for water at Site 4. This age is similar to the DO^{14}C-derived age (Table 3).

A third method of dating the Aquia water establishes an age of ~18 ka to the water at Site 4. Purdy (1991) discussd this method in detail, which is related to groundwater Cl$^-$ variations reflecting sea-level fluctuations. Based on distance downgradient, the gradual change in the chloride concentration reflects a minimum at approximately 40 km from the outcrop (3.23–0.73 ppm), and a gradual increase farther downdip to 2.2 ppm. The minimum has been interpreted to represent the latest low stand in sea level. During the most recent minimum in sea level, the recharge zone for this aquifer would have been 180 km farther from the coast, resulting in less chloride in precipitation. Thus, groundwater with the lowest chloride concentration is expected to have penetrated the Aquia aquifer during the documented low stand in seas, approximately 18 ka BP (Chappell & Shackleton 1986). ^{18}O and ^{2}H values further confirm this interpretation of the Cl$^-$ variations (Purdy 1991).

The age of ~18 ka for water at Site 4 is ~6 ka older than both the DO^{14}C and hydrodynamically derived ages (Table 3). The ^{14}C age represents an upper limit, since old carbon is expected to augment the carbon derived from the recharge zone. If the water is actually younger than the ^{14}C age, then the discrepancy in the ages determined by the different methods becomes greater.

Two explanations might resolve these differences. In the first case, the minimum in the Cl$^-$, ^{18}O and ^{2}H concentrations might represent a climate change occurring in this region, which may have coincided with deglaciation during the late Wisconsin. This effect would assign a younger age to Site 4 water. A climate change at 11–12 ka BP would be consistent with the DO^{14}C age of Site 4.

A second possible explanation for the age differences of these independent dating methods comes from the age of the water at Site 1. ^{3}H and ^{36}Cl bomb pulses are measured in this sample. However, their concentrations in this water do not represent maximum bomb deliveries (Purdy 1991). If older water in the flowpath is mixing with vertically recharged water at this site near the recharge zone, the sample represents a mixture of source waters. The water at Site 1 may be older than the predicted modern age, and this would make the DO^{14}C age older at Site 4. The low DO^{14}C pMC at Site 1 might be partially due to a mixture of modern and older water, not only due to a source of old carbon to the water.

TABLE 3. Summary of Ages of Aquia Water at Site 4

Dating technique	Age of Site 4 water (ka)	Flowrate (m yr^{-1})
Sea-level fluctuations expected to be reflected in Cl$^-$ variations in water	~18	2.6
DO^{14}C	~12	3.8
Hydrodynamic modeling	~11.5	4.0

CONCLUSION

Many questions remain about the geochemical organic and inorganic carbon cycle in these Coastal Plain aquifers. However, some overall conclusions can be drawn from this limited study:

1. The $DI^{14}C$ and $DO^{14}C$ values (34–41 pMC) are lower than expected for the recharge zone. The low $DI^{14}C$ is likely due to the dissolution of $CaCO_3$, as well as to fractionation effects during the dissolution/reprecipitation processes of the carbonates. The source of the "dead" organic carbon to the DOC is less clear. This source must be mixing with the DOC in the recharge zone or near the beginning of the flowpath.
2. In all samples the $DI^{14}C$ is consistently lower by ~6 pMC than the $DO^{14}C$. This suggests that the DOC may be a conservative tracer throughout the flowpath.
3. Both the Magothy and the Aquia aquifers seem to be influenced by the same dissolved carbon processes. Although the depositional history and geochemistry of both formations are different, the ^{14}C systematics in the dissolved carbon fractions reflect the same trends. This implies that similar carbon dissolution processes occur in both aquifers, resulting in similar sources of DOC and DIC.
4. The ^{14}C-derived age of the Aquia water at Site 4 is ~17 ka and ~12 ka, based on $DI^{14}C$ and $DO^{14}C$ results, respectively. This inconsistency may be due to fractionation effects during the dissolution of the carbonates. The process removes ^{14}C from the DIC, which reflects an older $DI^{14}C$ age. Further, the $DO^{14}C$ ages are not consistent with the age derived from groundwater Cl^-, ^{18}O and ^2H variations, which have been interpreted to be influenced by sea-level fluctuations. This method of dating would assign an age of ~18 ka to water at Site 4.

Inconsistent groundwater ages obtained using independent dating methods illustrate the need for a more thorough understanding of the inorganic and organic carbon sources to aquifers. The potential for using $DO^{14}C$ ages for dating groundwater might be promising once the recharge or modern water for Coastal Plain aquifers is thoroughly characterized using both $\delta^{14}C$ and $\delta^{13}C$.

ACKNOWLEDGMENTS

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