Biogeochemistry **55:** 247–268, 2001.

Relationship between DOC concentration and vadose zone thickness and depth below water table in groundwater of Cape Cod, U.S.A.

WENDY J. PABICH[1,*], IVAN VALIELA[2] & HAROLD F. HEMOND[1]
[1]*Massachusetts Institute of Technology, Department of Civil and Environmental Engineering, Ralph M. Parsons Laboratory, Cambridge, MA 02138, U.S.A.;* [2]*Boston University Marine Program, Marine Biological Laboratory, Woods Hole, MA 02543, U.S.A. (*Corresponding author: Environmental Defense, 6 North Market Building, Faneuil Hall Marketplace, Boston, MA 02109; phone: (617) 723-5111 x 331; fax: (617) 723-5052; e-mail: wpabich@environmentaldefense.org)*

Key words: Cape Cod, DOC, groundwater, saturated zone, vadose

Abstract. Changes in concentration of dissolved organic carbon (DOC) reflect biogeochemical processes that determine chemical composition of groundwater and other natural waters. We found that the deeper the vadose zone, the lower the concentration of DOC in groundwater near the water table, indicating that considerable attenuation of surface-derived DOC occurred in the vadose zone. Under vadose zones <1.25 m, DOC concentrations at the surface of the water table ranged to >20 mg C l^{-1}, while for vadose zones >5.0 m, DOC never exceeded 2.0 mg C l^{-1}. DOC concentrations also decreased exponentially with increasing depth below the water table, most notably in the upper two meters, implying continued attenuation in the upper layer of the saturated zone. Ninety-nine percent of the DOC was attenuated by the time the water reached a depth of 19 m below the water table. A strong inverse relationship between DOC and nitrate concentrations suggests that nitrate is depleted where DOC supplies are high, providing evidence that some portion of the DOC losses in groundwater are due to microbial transformations, including denitrification. DOC concentrations in shallow groundwater show considerable spatial variability, but concentration of DOC at any one site is surprisingly stable over time. The largest source of variation in DOC concentration in groundwater therefore is spatial rather than temporal, suggesting that local heterogeneities play an important role in DOC delivery to shallow groundwater. Our results highlight both the importance of shallow vadose areas in DOC delivery to groundwater and the need to distinguish where samples are collected in relation to flow paths before conclusions are made about mean groundwater DOC concentrations. The substantial losses of DOC in the vadose zone and in shallow depths within the aquifer suggest quite active biogeochemical processes in these boundary environments.

Introduction

DOC alters chemical composition of surface and ground waters by acting as a substrate for microbial catabolism, an electron acceptor for anaerobic respiration, and a ligand for metal complexation, and by providing protons for acid/base chemistry, and nutrients that stimulate biological productivity. DOC is generated in soil organic horizons by microbial metabolism, root exudates, and leaching of organic matter (Schiff et al. 1997) and transported by recharge water to the saturated zone (Cronan & Aiken 1985; Thurman 1985; Clay at al. 1996) or by surface runoff (Jordan et al. 1997) to surface water bodies. Export of DOC from forested catchments depends on a complex, seasonally and spatially varying interplay of production, decomposition, sorption, precipitation, and hydrology (Cronan & Aiken 1985; Schiff at el. 1997).

DOC concentrations change as the organic matter is transported from the surface of a watershed to receiving waters. Cronan and Aiken (1985), McDowell and Likens (1988), Schiff et al. (1990), Easthouse et al. (1992), and Kookana and Naidu (1998) demonstrated that DOC in soil solutions decreased as recharge water percolates through soil horizons, from >70 mg C l^{-1} in upper soil horizons to 1–2 mg C l^{-1} in lower soil horizons. Mechanisms that may attenuate organic carbon as it percolates through soils include sorption and complexation with mineral surfaces (e.g. Fe and Al oxides and hydroxides) and clay minerals (Thurman 1985), microbial oxidation to CO_2 (Chapelle 1992), precipitation, flocculation and formation of insoluble complexes (Kookana & Naidu 1998), and filtering of organic colloids (Wan & Tokunaga 1997).

Several authors have pointed to the importance of the length or duration of hydrologic flow paths in controlling DOC delivery (Cronan & Aiken 1985). Easthouse et al. (1992) contend that work on inorganic constituents (Sullivan et al. 1986; Lawrence et al. 1988; Neal et al. 1989; Mulder et al. 1990) has demonstrated the importance of hydrologic flow paths in explaining variations in stream water chemistry. Similarly, Schiff et al. (1997) highlighted the importance of flow paths when they concluded that recently-fixed labile DOC leached from the A horizon or litter layer can only reach the stream via short flow paths that bypass locations where significant soil sorption occurs. Recharge is often spotty, and preferential flow paths, or fingers are likely to develop even in relatively homogeneous sandy soils (Parlange et al. 1999), potentially resulting in variable transport of DOC to groundwater.

Little information is available about the fate and transport of DOC either in the vadose zone or after it has reached the saturated zone. We hypothesize that 1) groundwater DOC concentrations decrease as the thickness of the vadose zone (T_{vad}) through which recharge occurs increases, and 2) DOC concentrations in the saturated zone decrease with increasing depth below the water table (D_{wt}). We tested these hypotheses by measuring DOC concentrations in groundwaters beneath a range of vadose thicknesses and at a range of depths below the water table.

Materials and methods

Study site

This work was carried out in the watershed of Waquoit Bay, a shallow estuary on the southwestern shore of Cape Cod, Massachusetts, subject to increasing eutrophication from groundwater-transported nitrogen. The watershed is underlain by an unconsolidated sole-source sand and gravel aquifer (Barlow & Hess 1993; Leblanc et al. 1986). The aquifer matrix is comprised of primarily quartz and feldspar sand (95%) with some ferromagnesian aluminosilicates and oxides (5%); sand grains are coated with hydrous oxides of aluminum and iron (Stollenwerk 1996). Groundwater flow is almost entirely in the horizontal direction, with an approximate flow velocity of 0.4 m per day (LeBlanc et al. 1991). Annual recharge is 53 cm yr^{-1} (Barlow & Hess 1993; LeBlanc 1984). Groundwater discharge to Waquoit Bay and its tributaries accounts for 89% of the total freshwater input to Waquoit Bay (Cambareri & Eichner 1998), and is the primary avenue by which land-derived nitrogen is delivered to the estuary (Valiela et al. 1997).

We sampled groundwater near South Cape Beach and Sage Lot Pond in the southern part of the watershed, and in the Crane Wildlife Management Area to the north (Figure 1). Both areas have mixed pitch pine and scrub oak forest cover and are typical of forested areas throughout Cape Cod. Other data are from USGS wells located in and near the watershed (Savoie & LeBlanc 1998).

Groundwater sample collection and analysis

At South Cape Beach, we collected groundwater using a drive-point piezometer and hand pump. Samples were taken in duplicate after multiple well volumes had been pumped and the water ran clear (generally after pumping 1–2 liters). We sampled from 12 stations on each of five sampling dates (March 27, April 11, April 29, June 4, and August 6) during 1988; we reached the water table in 56 of the 60 sampling attempts.

At Crane Wildlife Management Area, we sampled from 3 multi-level sampling devices (LeBlanc et al. 1991), installed parallel to groundwater flow direction. Each multi-level sampling well had between 9 and 15 ports spanning from just below the water table to a maximum depth of 9.3 m below

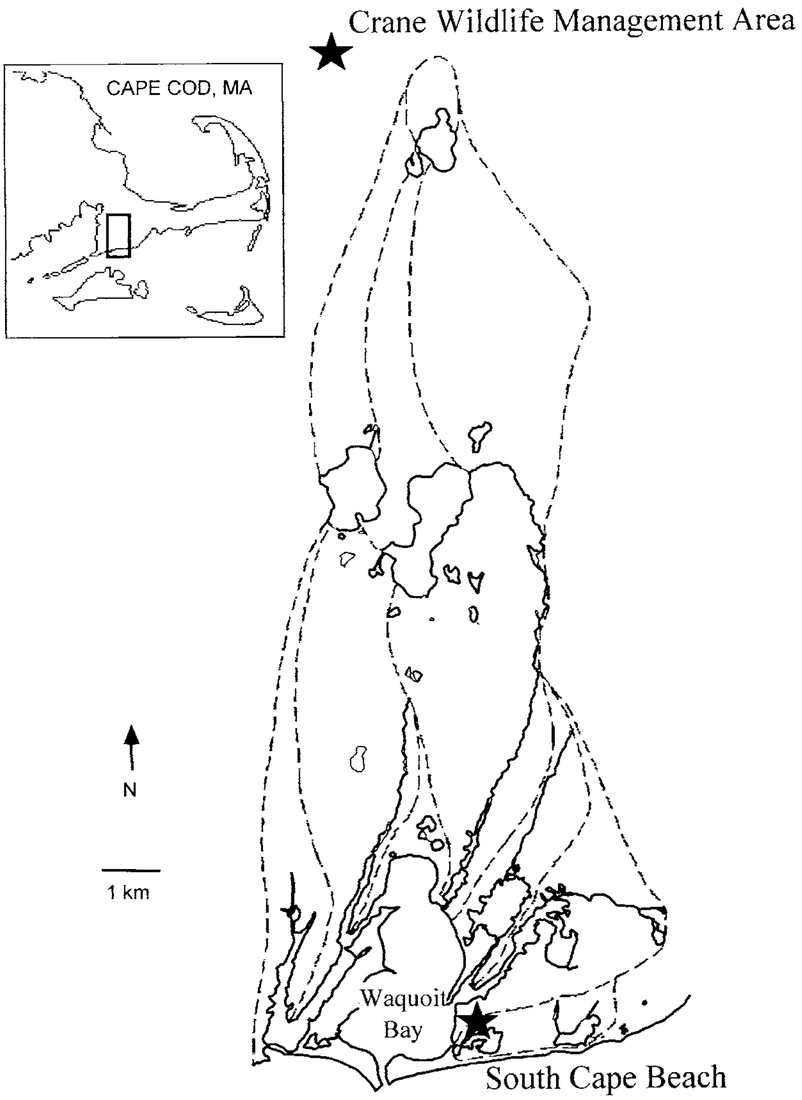

Figure 1. Location of the Crane Wildlife Management Area and South Cape Beach study sites in and near the Waquoit Bay watershed, Cape Cod, MA. Groundwater generally flows in a south-southwesterly direction toward Waquoit Bay.

the water table. At each port a 0.64 cm diameter polyethylene tube protruded through a central 3.2 cm PVC pipe and was covered with a nylon screen (Smith et al. 1991). We collected groundwater samples in duplicate using a peristaltic pump (Geopump 2, Geotech Environmental Equipment, Inc.) after purging a minimum of 3 well volumes (13.8 ml per m tube length) from each port.

All samples were collected in 15 ml amber glass vials (Supelco #27088-U) previously soaked in a 5% Extran (VWR #2300-3; sodium hydroxide, water, and trisodium nitrilotriacetate) bath to remove any traces of organic carbon. Samples from the multi-level sampling wells were filtered in-line during pumping using pre-combusted 0.7 μm Whatman GF/F filters. Samples obtained using the piezometer were vacuum filtered through the same GF/F filters upon return to the lab. All samples were acidified to pH ≈ 2 with 5N HCl and stored in a cold room (T = 4 °C) until analysis.

At South Cape Beach, we located the surface of the water table by first driving the piezometer below the water table (verified by drawing water), and then pulling it out of the ground in 0.1 m increments and attempting to pump at each position. We recorded the water table position as that depth where we could no longer draw water through the piezometer. At Crane Wildlife Management Area, we measured the thickness of the vadose zone by lowering a Fisher m-SCOPE Water Level Indicator into a nearby monitoring well (<20 m) and measured the distance of the water table from land surface. Depth to the water table was tabulated for USGS wells in Savoie and LeBlanc (1998).

We measured DOC concentrations in triplicate Ar-purged samples using high temperature catalytic oxidation (HTCO) with infrared detection of CO_2 (Shimadzu TOC 5000). Potassium acid phthalate was used as a carbon standard; deionized water (Vaponics Aries at 18 megaohms) was used as a method blank. The coefficient of variation for triplicate measurements was generally 3–7%.

DOC data for USGS wells were taken from Savoie and LeBlanc (1998). Many of the USGS wells were drilled to investigate groundwater pollution emanating from the Massachusetts Military Reservation. We collected data only from wells located in areas of clean groundwater, either outside the boundaries of mapped wastewater plumes or having methyl blue active substances (MBAS) below 0.02 mg l^{-1}. The MBAS test, which determines the concentration of surfactants in water, is commonly used as a conservative tracer for wastewater in aquifers (LeBlanc 1984). MBAS concentrations measured in the sewage plume at the Massachusetts Military Reservation ranged as high as 2.6 mg MBAS l^{-1} (LeBlanc 1984) and uncontaminated groundwater contained detergents in concentrations less than 0.1 mg MBAS l^{-1} (Savoie & LeBlanc 1998). We chose to use the detection limit for the MBAS method (0.02 mg MBAS l^{-1}) as a conservative delineation between clean and contaminated groundwater to insure that we were not including wastewater-contaminated samples in our study.

Recharge to an unconfined aquifer generally results from vertical percolation of precipitation through the unsaturated vadose zone to the surface of the water table. In this study, we refer to this water table location as the "point of recharge", at which groundwater travel time and age are zero. In the Waquoit Bay aquifer, groundwater migrates from the point of recharge primarily in the horizontal direction with some small vertical displacement over a much larger horizontal travel distance (horizontal to vertical hydraulic conductivity ∼2:1 to 5:1, LeBlanc et al. 1991). This vertical displacement, albeit small, results in stratification of water masses by age (Schlosser et al. 1988; Solomon et al. 1992), so that groundwater age increases in a predictable manner with increasing depth below the water table.

Travel times in an unconfined aquifer in which recharge is spatially uniform are described by Vogel (1967):

$$t = (aH/W) * \ln(H/h)$$

where t = time since recharge to the water table in years; a = porosity; H = total depth of aquifer in meters; W = recharge rate in meters per year; and h = height over bottom of aquifer in meters. This relationship is particularly robust in the Waquoit Bay aquifer, where the groundwater flow system is relatively simple (LeBlanc et al. 1991), and accurate predictions of groundwater flow have been made using regional water table maps (LeBlanc 1984). In fact, Solomon et al. (1995) used tritium and helium isotope analyses at the nearby Massachusetts Military Reservation (Falmouth, MA) to confirm that, in this aquifer, measured vertical groundwater age profiles agreed well with ages modeled using the Vogel equation. In our work, we therefore used the Vogel equation to estimate groundwater ages for each of our samples, and then used the estimated age of water parcels in our approximation of DOC loss rates in groundwater.

In assessing the relationship between groundwater DOC concentration and vadose thickness, we recognized that, with the exception of those samples closest to the water table, the recharge point for each sample is some distance upgradient from the actual sampling point, and that the vadose thickness above that recharge point may or may not be similar to the vadose thickness above the sample location (Figure 2). Yet, the geometry of the Waquoit Bay aquifer is fairly regular, thickest beneath the uppermost portion of the watershed (up to 60 m) and thinning north to south (Barlow & Hess 1993) to as little as 11 m thick as it nears Waquoit Bay (Cambareri & Eichner 1998). Groundwater generally flows to the south and southwest (LeBlanc 1984), parallel to the direction in which the aquifer thins. Given this geometry, the vadose thickness at the point of recharge is likely to be equal to or slightly greater than the vadose thickness at the sampling points. We assigned the vadose thickness measured above the sampling point to each sample rather than the vadose thickness at the point of recharge, because we had no values for vadose thickness at recharge points for 2 of our 3 data sets (South Cape Beach and the USGS data).

The error introduced into the analysis by use of this proxy appears to be minimal. For example, at the Crane Wildlife Management Area, we sampled groundwater from three multilevel sampling wells, installed parallel to groundwater flow direction (Figure 2). The sampling ports of the middle well (Figure 2, F605) were located between 0.5 and 9.3 m below the water table. The vadose thickness measured at this well was 5.0 m, which we assigned as the vadose thickness for all of the sampling ports on this particular well. To estimate the error associated with the assumption that the vadose thickness at the sampling point is similar to the vadose thickness at the recharge point, we used both MODFLOW (Masterson et al. 1997) projections and Vogel (1967) groundwater age estimates, developed prior to designing the well transect, to compare the estimated vadose thicknesses (those at the sampling point) with actual vadose thicknesses (those at the upgradient recharge points). Our projections suggest that the water sampled from F605, port #6 (2.3 m from the water table surface), originated at the location of the most upgradient well in the transect (Figure 2, F606), where the vadose thickness was approximately 5.6 m. Thus, our estimate of vadose thickness (5.0 m) for this well port is approximately 11% less than that measured at the actual point of recharge (5.6 m). Similar analysis suggests that the error increases as sampling depth below the water table increases, so that the error is negligible for water sampled at the shallowest ports and greatest for the deepest ports (37%). The degree of uncertainty in our vadose thickness estimates (e.g., 0.6 m for F605, port 6) is small relative to the variation in vadose thicknesses between our sites (i.e., vadose thickness at Crane Wildlife Management Area is, on average, 3.8 m greater than at South Cape Beach). The error in our estimates at South Cape Beach site are likely to be negligible, since the topography is fairly regular and groundwater is shallow, with depths to groundwater at each of our twelve sampling stations varying between 0.5 and 1.4 m. At this site, groundwater flow paths were assumed to be short and the differences between the vadose thicknesses measured at the sampling points and those at the actual recharge points minimal.

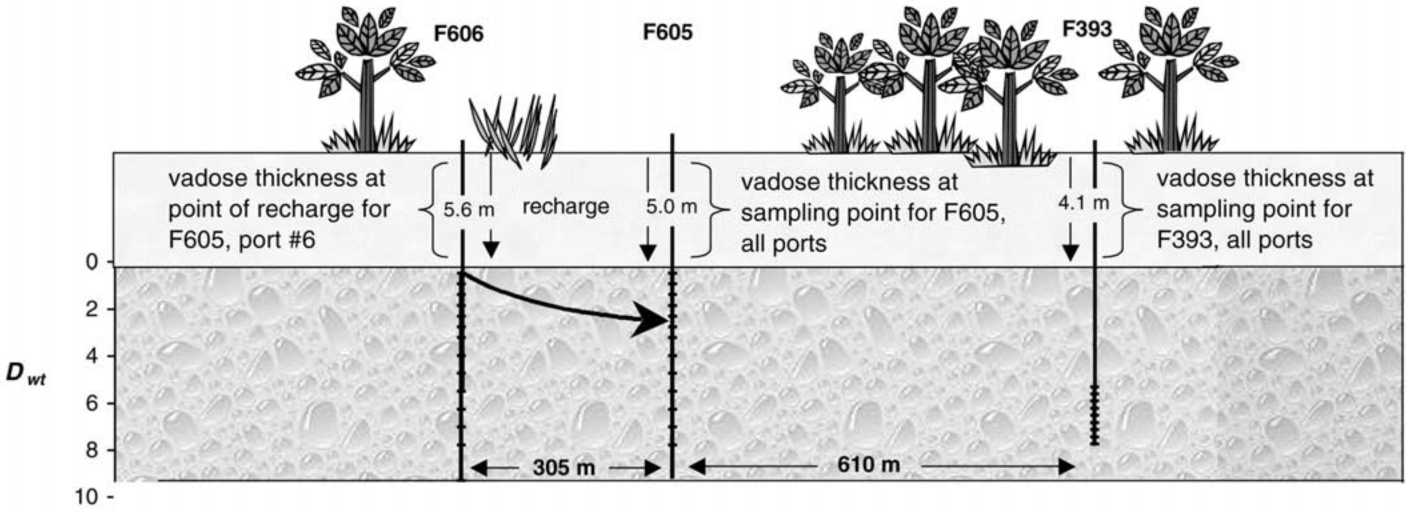

Figure 2. Multi-level sampling well transect (labeled F606, F605, and F393), installed parallel to groundwater flow direction, at Crane Wildlife Management Area. The fairly regular geometry of the aquifer implies that the vadose thickness measured at each sampling port (i.e., for F605, port #6, vadose thickness at sampling port = 5.0 m) is a reasonable proxy for vadose thickness at the point of recharge (which, for F605, port #6, occurs at approximately the location of F606, where vadose thickness = 5.6 m).

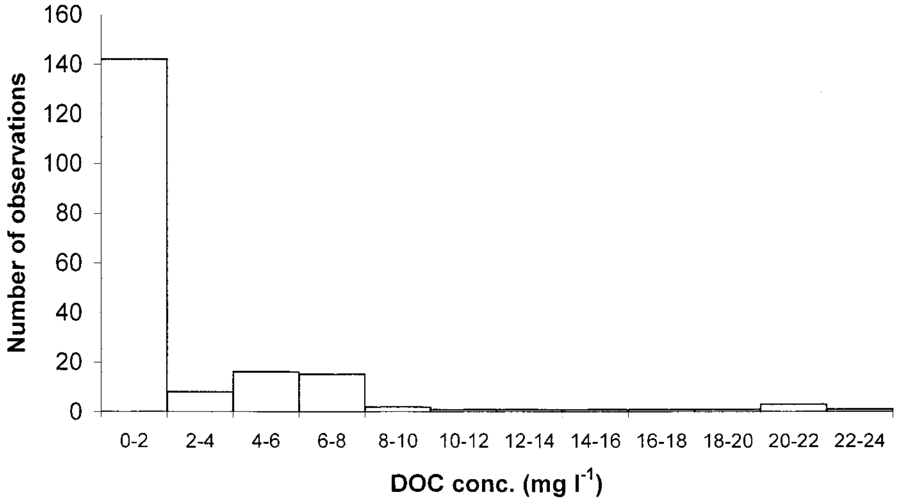

Figure 3. Frequency plot of measured groundwater DOC concentrations for South Cape Beach, Crane Wildlife Management Area, and the USGS well data. Data were highly leptokurtic.

Results and discussion

Groundwater DOC concentrations varied from 0.04 to 23.38 mg C l^{-1} and averaged 2.31 ± 0.30 mg C l^{-1}, and were highly positively skewed (Figure 3). The wells provided a range of vadose thicknesses (T_{vad}) from 0.5 m to 17.5 m, and averaging 4.7 ± 0.3 m. Water table depths (D_{wt}) ranged from 0.03 to 51.8 m, and averaged 8.7 ± 0.8. Summary statistics for the three variables are provided in Table 1.

We found, as did Cronan and Aiken (1985) and Easthouse et al. (1992), that DOC concentrations were quite variable spatially, but more consistent temporally. For example, at the 12 South Cape Beach stations, where the vadose zone was routinely less than 1.5 m thick, DOC ranged from <1 to 23 mg C l^{-1}, with a coefficient of variation of 77%. Despite this spatial variability, when we sampled on 5 sampling dates between March and August of 1988 at each of the 12 stations at South Cape Beach, we found that DOC was consistently high at some sampling points and consistently low at others. Mean coefficient of variation of the time series data for the 12 stations was 37%. The lack of a strong temporal signature in our data is not unexpected, since only some samples were taken from the surface of the water table, which is where a seasonal signal is most likely to be evident. Samples taken at some depth below the water table were recharged at a previous time that may or may not have coincided with the season during which sampling was

Table 1. Summary statistics for depth below water table (D_{wt}), vadose thickness (T_{vad}), and groundwater DOC concentration

Summary statistics	D_{wt}	T_{vad}	DOC
Mean	8.70	4.67	2.31
Standard error	0.79	0.34	0.30
Median	3.37	2.57	0.40
Mode	0.22	1.22	0.20
Standard deviation	10.98	4.76	4.21
Sample variance	120.64	22.70	17.71
Kurtosis	1.48	0.71	9.56
Skewness	1.44	1.37	2.94
Range	51.73	17.04	23.34
Minimum	0.03	0.46	0.04
Maximum	51.76	17.50	23.38
Sum	1670.70	895.93	442.83
Count	192	192	192

done. This is especially true of the Crane Wildlife Management Area and USGS groundwater samples, the majority of which were sampled at some depth below the water table, so that the recharge date does not coincide with the sampling date. The high degree of spatial variability is consistent with work by Seely et al. (1998), who suggested that differences in DON retention capacity in mineral soils at several sites within the Waquoit Bay watershed were likely related to variations in soil texture.

Concentrations of DOC were inversely related to both T_{vad} and D_{wt} (multiple regression of log transformed values, $R^2 = 0.68$, $p < 0.001$, Table 2). The two variables, T_{vad} and D_{wt}, were relatively independent: the highest variance inflation factor (VIF) (Sokal & Rohlf 1995) was 1.3, which suggests only minimal correlation between independent variables. To evaluate the relative influence of T_{vad} and D_{wt} on DOC concentration, we calculated Kruskal's index of importance (average of squared partial correlation coefficients) (Sokal & Rohlf 1995); the index was 0.58 for D_{wt}, and 0.23 for T_{vad}. This indicates that depth below the water table was relatively more important than vadose thickness in predicting DOC concentration. These analyses suggest that T_{vad} and D_{wt} were relatively independent, and both contributed significantly to DOC concentrations in the aquifer.

To examine in more detail the effect of varying vadose thickness on losses of DOC within the aquifer, we stratified the data into three categories of T_{vad}

Table 2. Analysis of variance for multiple regression of effect of depth below the water table (D_{wt}) and vadose thickness (T_{vad}) on DOC concentration. Data were log-transformed. Regression equation: log DOC = $-0.52\ D_{wt} - 0.39\ T_{vad} + 0.19$; $R^2 = 0.68$; *df* = degrees of freedom, *SS* = sum of squares, *MS* = mean squares, *F* = sample variance, and *p* = probability. For probability <0.001, *df* = 2 and 189, critical *F*-value (F_{crit}) <7.32

	df	*SS*	*MS*	*F*	*p*
Regression	2	58.58	29.29	204.9	<0.001
T_{vad}	1	4.58	4.58	32.02	<0.001
D_{wt}	1	30.86	30.86	215.89	<0.001
Residual	189	27.02	0.14		
Total	191	85.59	0.45		

(0–1.25, 1.25–5.00, and >5.00 m), and plotted DOC as a function of depth below the water table (Figures 4 and 5). DOC concentrations at the water table were highest in groundwater under areas with the shallowest vadose zones, and decreased with increasing vadose thickness. This relationship is particularly apparent when we plot DOC concentration as a function of vadose thickness for only the shallowest groundwater samples (those with $D_{wt} < 1$ m, Figure 6), supporting our hypothesis that DOC concentrations decrease as T_{vad} increases. For these shallow water samples, recharge presumably occurred nearby the sampling port so that the vadose thickness at the sampling point is very similar to that at the recharge point, and the relationship between vadose thickness and DOC concentration has been less obscured by the effect of depth.

DOC concentrations also decreased with increasing depth below the water table (Figure 4). Reductions occurred particularly within the upper few meters of the water table, and resulted in DOC losses totaling two orders of magnitude. To better examine the reduction of DOC concentration with D_{wt}, we log-transformed the data (Figure 5). The data could be reasonably well fit with an exponential curve (Figure 5, $R^2 = 0.82$ for $T_{vad} = 0$–1.25; $R^2 = 0.59$ for $T_{vad} = 1.25$–5.0 m; $R^2 = 0.10$ for $T_{vad} > 5.0$ m). For $T_{vad} = 0$–1.25 m, 99% of the DOC was lost by the time a depth of 19 m was reached. Regardless of vadose thickness, and thus of the concentration of DOC at the surface of the water table, the DOC concentration at the deepest wells was similarly low (about 0.1 mg C l^{-1}) (Figure 5).

These losses likely result from both abiotic adsorption (Thurman 1985) and microbial oxidation (Chapelle 1992). Further investigation is necessary to determine the relative role of various loss mechanisms. Abiotic sorption is

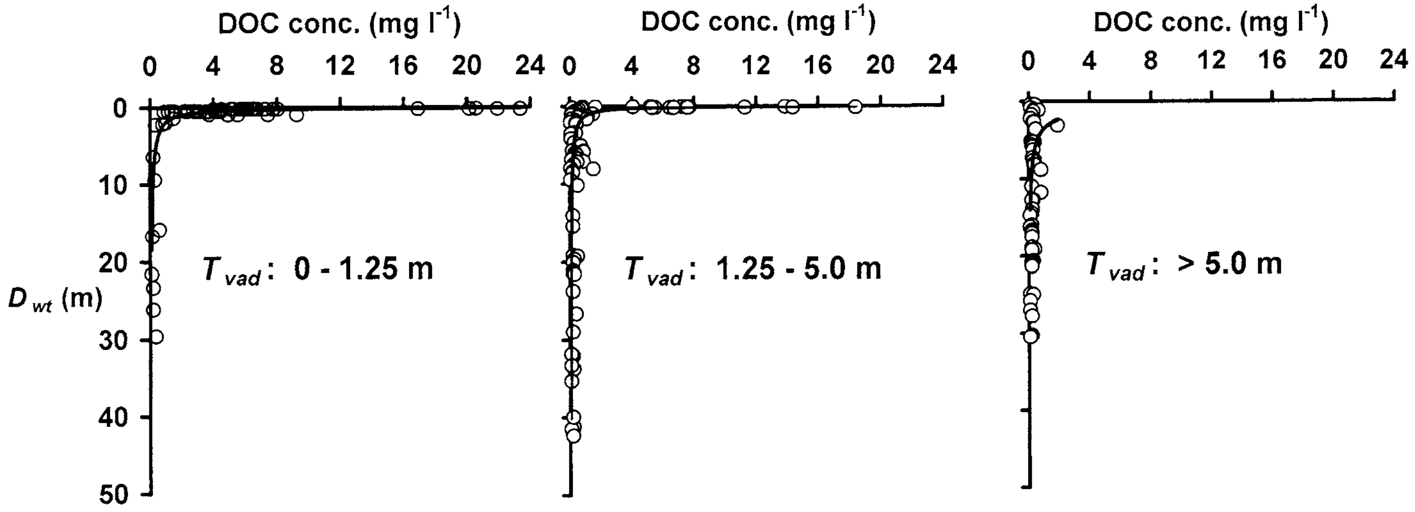

Figure 4. DOC concentration as a function of depth below water table (D_{wt}) for each of three vadose thickness (T_{vad}) strata: 0–1.25 m, 1.25–5.0 m, and >5.0 m.

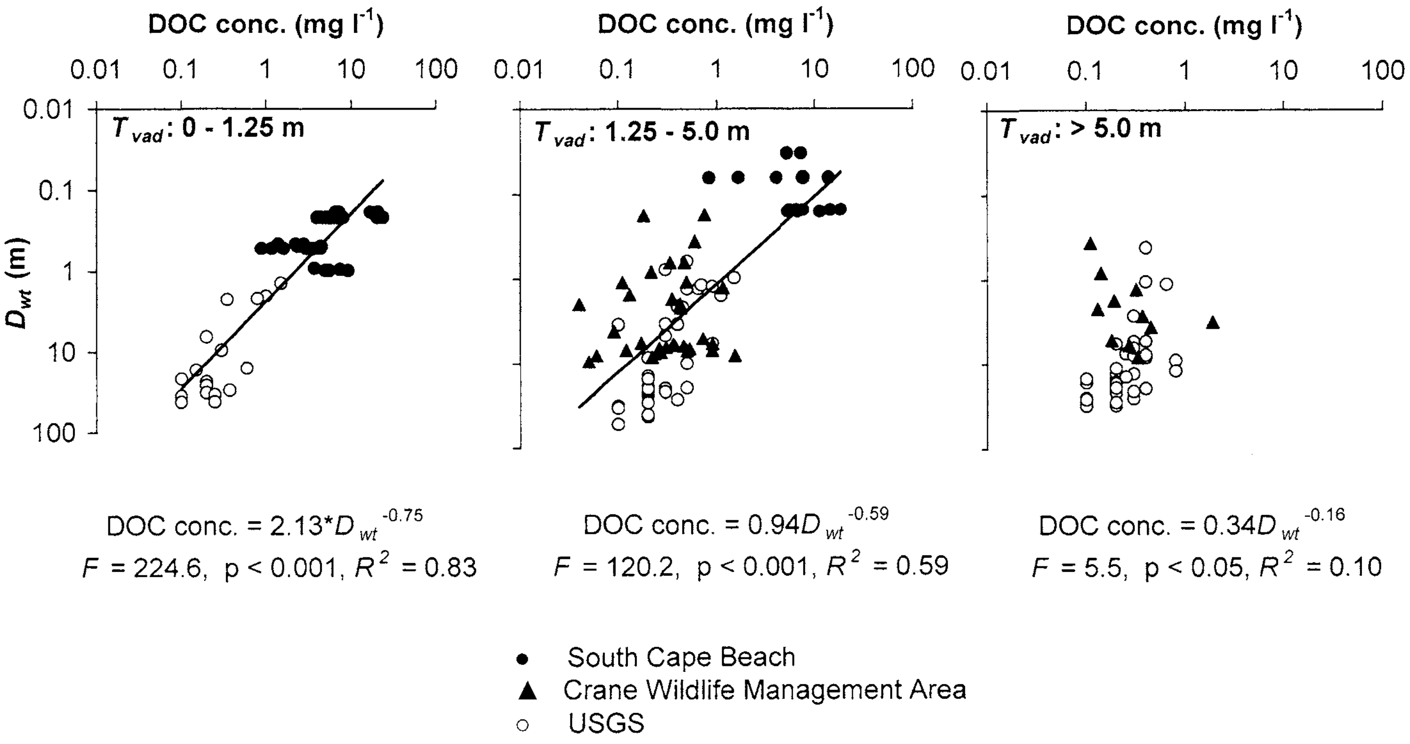

Figure 5. DOC concentration plotted as a function of depth below water table (D_{wt}) for each of three vadose thickness (T_{vad}) strata: 0–1.25 m, 1.25–5.0m, and >5.0 m for South Cape Beach, Crane Wildlife Management Area and USGS wells. Axes are logarithmic.

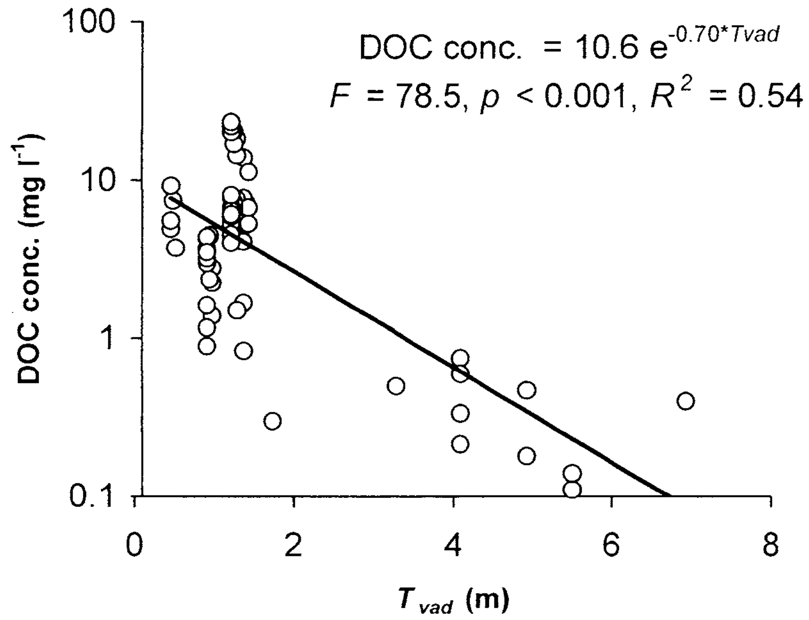

Figure 6. DOC concentration plotted as a function of vadose thickness (T_{vad}) for those samples near the water table (<1 m). Y-axis is logarithmic.

commonly invoked as a primary mechanism by which DOC concentrations are reduced during transport through mineral soil profiles (e.g., McDowell & Likens 1988). Natural dissolved organic matter adsorbs strongly to iron oxyhydroxides (Sholkovitz & Copland 1982; Tipping et al. 1981; Davis 1982), which, in this system, commonly coat the sediment grains comprising the aquifer matrix (Barber 1991; LeBlanc et al. 1991; Stollenwerk 1996) and may contribute to DOC losses beneath the water table. Adsorption of organic acids is usually accompanied by an increase in pH (Parfitt et al. 1977; Davis 1982) since compounds with more acidity sorb preferentially over those with lower acidity (Davis 1982). At the Crane Wildlife Management Area site, groundwater pH increased with increasing depth below the water table (Figure 7, data from Pabich 2001), consistent with losses of groundwater DOC due to sorption.

Microbial metabolism is also likely to contribute to DOC losses beneath the water table. Groundwater metabolism is limited by DOC availability, and hydrologic linkage between soils and groundwater represents a critical flux of DOC that supports metabolism in unconfined aquifers (Baker et al. 2000). Further, the air/water interface at the water table is a transitional environment where both changes in the sorption characteristics of the aquifer media and the presence of a different microbial consortia contribute to enhanced

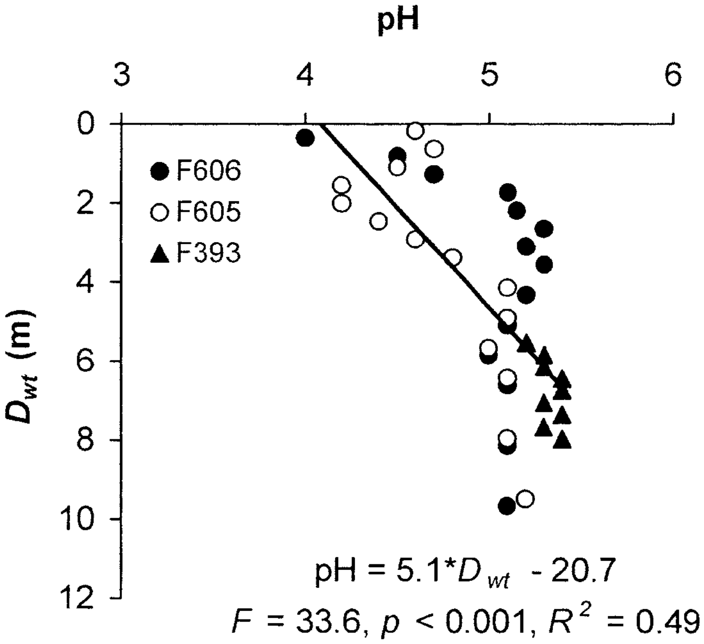

Figure 7. pH plotted as a function of depth below water table (D_{wt}) for the 3 multi-level sampling wells (F606, F605 and F393) at Crane Wildlife Management Area.

DOC losses as DOC is transported across this boundary (L. Barber, personal communication).

In a study investigating the influence of patterns of supply of electron donors and acceptors on groundwater denitrification, Hill et al. (2000) demonstrated that groundwater DOC concentrations were inversely related to oxidized nitrogen (NO_3^- and N_2O) concentrations, and suggested that oxidized forms of N are depleted in more reduced environments that have high supplies of DOC, providing evidence of microbial transformations of N. An inverse relationship between groundwater nitrate and DOC concentrations is also evident for the Waquoit Bay aquifer samples (Figure 8; $F = 182.6$, $p < 0.001$, $R^2 = 0.54$; data from Pabich (2001)), and suggests that microbial transformations, including denitrification, may contribute to DOC losses beneath the water table.

In this aquifer, depth is a remarkably close proxy for time (Solomon et al. 1995; Portniaguine & Solomon 1998). Using the Vogel (1967) model, we calculated that at a depth of 19 m, groundwater traveled approximately 15.8 years since recharge. Therefore, for T_{vad} = 0–1.25 m, the mean DOC loss rate between the surface and 19 m was approximately 1.5 mg C l^{-1} yr^{-1}. In contrast, for $T_{vad} > 5$ m, the loss rate over this same distance was about 0.12

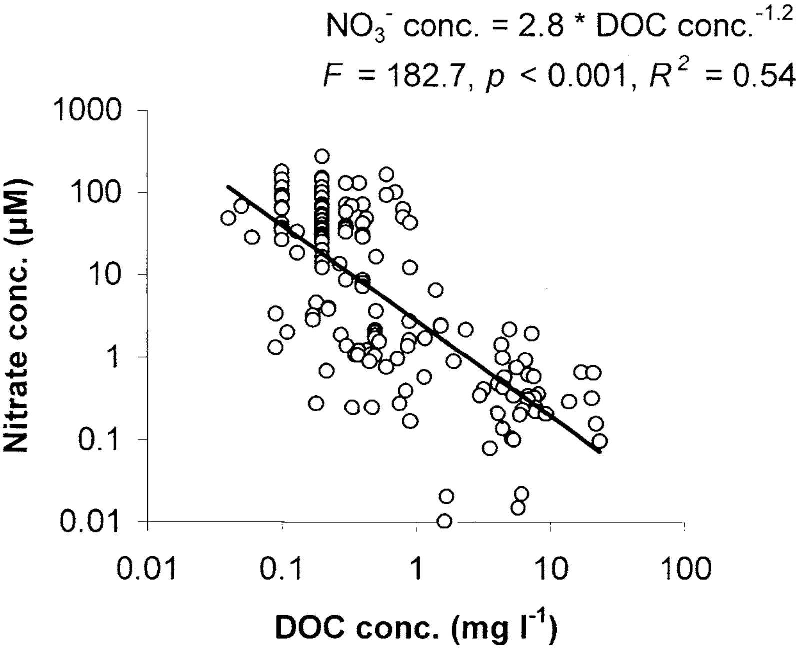

Figure 8. Nitrate concentration plotted as a function of DOC concentration for South Cape Beach, Crane Wildlife Management Area, and the USGS well data.

mg C l^{-1} yr^{-1}. We further investigated depth-dependence of DOC loss rate by taking the first derivative (*dy/dz*) of the fitted power function curve for each T_{vad} category (Figure 9). DOC loss rate quickly diminished with depth for all T_{vad} categories. At depth (~30 m), where DOC losses were small, the rate of attenuation was lowest for groundwater beneath the thickest vadose zones. The difference in attenuation rates suggests that processes in the vadose zone affect the composition or the quality of DOC reaching the water table so that DOC beneath thicker vadose zones is either less labile or less sorpable.

Our interest in understanding how DOC is distributed in groundwater stems from the larger question of how nitrogen is transported to receiving waters and to what degree denitrification in groundwater is limited by the supply of DOC. Many aquifers do not contain sufficient organic matter to produce anaerobic conditions required for denitrification (Bryan 1981; Parkin & Meisinger 1989; Thurman 1985; Barcelona 1984; Lind & Eiland 1989; McCarty & Bremner 1992; Obenhuber & Lowrance 1991). Groundwater DOC values reported in the literature from a wide range of aquifer settings and depths (Figure 10) suggest, first, that there are many places where groundwater contains significant concentrations of DOC. These concentrations may be sufficiently high to support denitrification. Our measurements

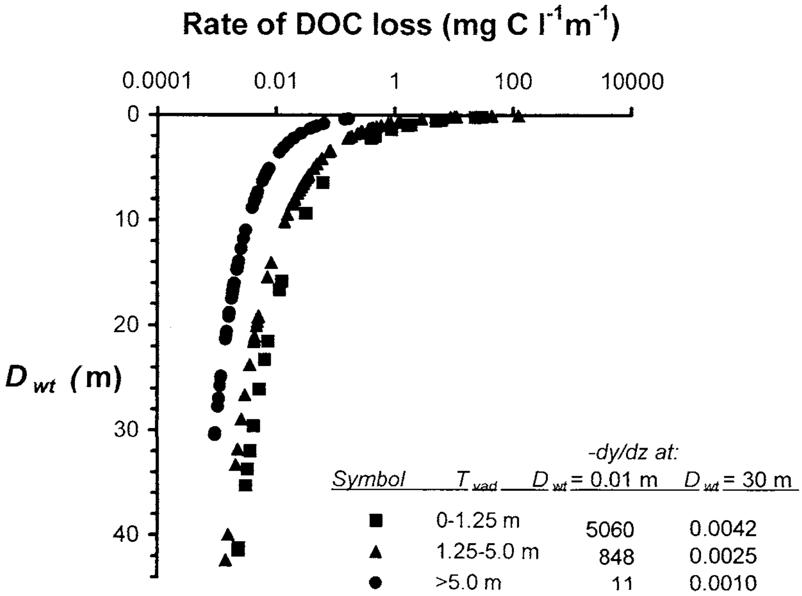

Figure 9. Instantaneous DOC loss rate as a function of depth below water table (D_{wt}) for each of three vadose thickness strata (T_{vad}): 0–1.25 m, 1.25–5.0 m, and >5.0 m. Loss rate was calculated as the first derivative (*dy/dz*) of the fitted power curve for DOC versus D_{wt} for each of the 3 T_{vad} classes, and solved at each measured depth.

of DOC concentrations fall within the wide range reported in the literature (0.014–30 mg C l^{-1}).

The data in Figure 10 can also be used to make a second point: sampling groundwater at depth may provide underestimates of DOC dynamics in aquifers. The rather steep gradient in DOC concentration that we found near the water table suggests that measurements of DOC in samples from deep groundwater wells may not only fail to describe the dynamics of DOC, but may underestimate mean groundwater DOC concentrations. The strong attenuation of DOC concentration within the vadose zone and the upper portion of the water table suggests that these sites are potentially those where biogeochemical transformations of nitrogen, as well as carbon, should be active.

The comparison of published DOC concentrations (black circles, Figure 10) relative to the values we report here (white circles, Figure 10) also makes a third point: in general, despite the scatter in the data, regression analysis suggests that DOC concentrations do decrease with increasing depth below the water table. Of course, the scatter of points from the diverse sites makes the pattern less obvious, but it is nonetheless true that the larger concentrations of DOC tend to lie in the shallower layers (Figure 10 (literature values):

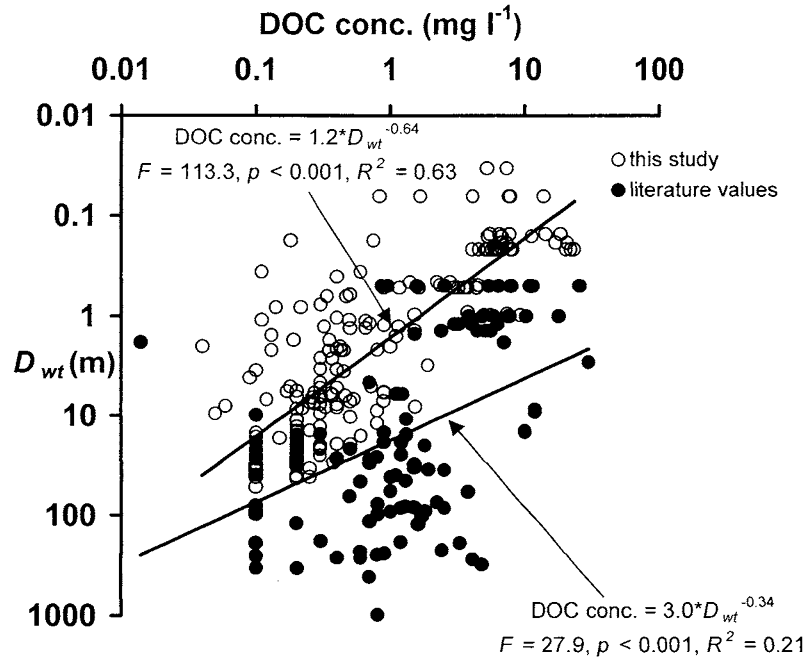

Figure 10. DOC concentrations in groundwater as a function of depth below water table (D_{wt}). White circles represent the data from this study. Black circles represent data from the literature (Aelion et al. 1997; Ellis et al. 1998; Ford & Naiman 1989; Hakenkamp et al. 1994; Hendricks & White 1995; Keller 1991; Leenheer et al. 1974; Rutherford & Hynes 1987; Schindler & Krabbenhoft 1998).

DOC conc. = $3.0{*}D_{wt}^{-0.34}$, $R^2 = 0.21$, $F = 27.9$, $p < 0.001$), as we demonstrate in our own data in some detail (Figure 10 (this study): DOC conc. = $1.2{*}D_{wt}^{-0.64}$, $R^2 = 0.63$, $F = 113.3$, $p < 0.001$).

The results we include here demonstrate that there are tight couplings among components of the below-ground ecosystems. DOC is intercepted near or in boundaries layers, either in the vadose zone or in the shallow aquifer, leaving only a small concentration of DOC for transport to open receiving waters. Such large decreases in DOC may follow significant stoichiometric relationships linking carbon dynamics to other elements. Investigation of the stoichiometry is the next step suggested by the large transformations documented in this paper.

Acknowledgements

MIT Sea Grant (#65591) and a National Estuarine Research Reserve (NERRS) Graduate Fellowship from the National Oceanic and Atmospheric Association (NA77OR024) supported this work. We thank Denis LeBlanc of the US Geological Survey, Marlborough, MA for well construction and installation, site access, and worthy advice; Paul Barlow, also at USGS Marlborough, for running a MODFLOW simulation of the Crane Wildlife Management Area site; John MacFarlane at MIT for assistance with the Shimadzu TOC analyzer; Vanessa Bhark also at MIT, who helped analyze our DOC samples as part of her summer internship; and Gabrielle Tomasky, at the Boston University Marine Program, for field and lab assistance.

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