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Seasonal Dynamics in Dissolved Organic Carbon Concentrations in a Coastal Water-Table Aquifer at the Forest-Marsh Interface

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Abstract. The seasonal dynamics of dissolved organic carbon (DOC) in a subterranean estuary were examined in a coastal water-table aquifer extending across a forest-marsh interface into an adjacent tidal creek that leads to North Inlet (SC). The aquifer is characterized by groundwater flow from the forest recharge area towards the creek. DOC concentrations range from 50 to 140 mg L^{-1} in the shallow portions of the aquifer below the forest and undergo seasonal changes that are inversely related to temperature and precipitation conditions. Markedly lower DOC concentrations (<10 mg L^{-1}) in the deep portion of the aquifer are consistent with the loss of a large fraction of the original DOC along the groundwater flow paths. Mass balance estimates indicate that over 60% of the DOC losses are due to sorption reactions whereas the rest appear to be caused by heterotrophic decay. Groundwater DOC discharge from the forest, which occurs in a restricted zone of the high marsh, is 5.5 mg carbon m^{-2} d^{-1} and accounts for a minor component of the annual carbon export from North Inlet. In contrast, moderately saline (2–12 ppt) ground waters below the marsh display elevated DOC concentrations (∼20 mg L^{-1}) that appear to be the result of mixing of fresh ground waters and surface seawater during tidal seepage and concentration during evapotranspiration. The flux of DOC associated with the discharge of these saline ground waters is 600 mg carbon m^{-2} d^{-1}, which represents a significant fraction of the annual DOC budget for North Inlet.

Key words: dissolved organic carbon, coastal aquifer, subterranean estuary, ground water

1. Introduction

The discharge of continental ground waters into the ocean has been the subject of many studies (e.g., Valiela et al., 1990; Simmons, 1992; Nuttle and Harvey, 1995; Cable et al., 1996; Moore, 1996; Shaw et al., 1998; Li et al., 1999; Nowicki et al., 1999; Krest et al., 2000; Gardner et al., 2002; Cai et al., 2003). Moore (1999) recently formalized the concept of a subterranean estuary to describe the input of fresh water from continental aquifers into the ocean and the underground mixing of fresh and seawater along ocean margins. By definition, subterranean estuaries are environments in which continental and ocean waters mix and interact. Much like their surface counterparts, the balance between fresh water and tidal flow plays a critical role in the exchange of solutes across subterranean estuaries (Figure 1).

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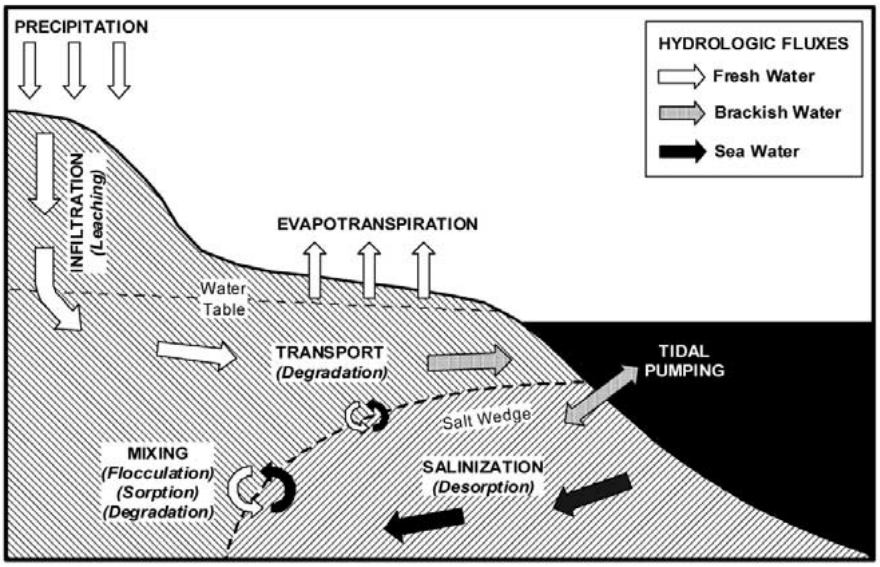

Figure 1. Illustration of important processes in subterranean estuaries.

In terms of the biogeochemical cycles of dissolved substances, subterranean estuaries share several processes with their surface counterparts, including addition from recharge regions through leaching and microbial degradation, sorption onto particles, flocculation as freshwater encounters higher ionic strength sea water, desorption of particle-bound materials in high salinity water, and exchange with the ocean due to tidal pumping (Figure 1; Moore, 1999). In spite of these parallels, there are significant differences between surface and subterranean estuaries. Most important is the fact that flow rates in subterranean estuaries are significantly slower than their surface counterparts (e.g., Gardner et al., 2002). Another important difference is the predominance of solute/particle interactions in the subterranean vs. surface estuaries. Finally, the physical characteristics of aquifers minimize the role of photosynthetic organisms and macrofauna. Instead, microbial activity is likely to dominate most chemical reactions of biogenic solutes and particle-associated materials.

In this paper, we present results from our study of the dissolved organic carbon (DOC) dynamics in a well-characterized subterranean estuary located at North Inlet, South Carolina (USA). Specifically, we describe the spatial and seasonal changes in DOC concentrations exhibited by ground waters from this shallow aquifer and relate them to the existing hydrological and geochemical data at this site.

2. Methods

2.1. SITE DESCRIPTION

2.1.1. North Inlet Basin

North Inlet is a pristine, bar-built tidal estuary located in Georgetown County, approximately 90 km north of Charleston along the northern coastline of South Carolina (Figure 2). The area has a temperate to subtropical climate with moderate precipitation ($\sim$1500 mm yr^{-1}). North Inlet has a terrestrial forested watershed of about 75 km^2 and includes 34 km^2 of salt marshes, tidal creeks, oyster reefs, and mudflats. The tides are semidiurnal and the mean range is 1.5 m (Kjerfve et al., 1978). Modern barrier islands bound the east side of the basin. The western boundary is delimited by low relief, forested, beach ridge terrain (Figure 2). The marsh in North Inlet evolved under a regime of slowly rising sea level during the late Holocene (Gardner et al., 1992; Gardner and Porter, 2001). As sea level rises, the low-lying areas (swales) between beach ridges are buried by marsh mud at a rate of about 0.2 cm yr^{-1} (Sharma et al., 1987), while the salinity increases caused by inundation gradually converts forest into marsh (Gardner et al., 1992; Gardner and Porter, 2001).

As part of this study, we sampled ground waters from different depths within a shallow aquifer that extends along transect D (Figure 2) in a northwest-southeast direction from the upland forest, across a marsh, to Crabhaul Creek, one of the tidal channels that leads to North Inlet. Additionally, we sampled surface waters from two locations within the tidal channel complex of North Inlet basin (Figure 2). The Crabhaul Creek site is located close to the forest/marsh boundary, and it is directly influenced by drainage from the upland forest. The North Inlet site, which is located at the mouth of the inlet, is most distal from the upland forest and is more strongly affected by the marsh and the open ocean.

2.1.2. Transect D

Transect D starts (at 0 m) in the upland forest and extends $\sim$90 m southeastward across the marsh towards the tidal creek (Figure 3). The change in ground elevation across transect D is almost 2 m. There are three, clearly delimited vegetation zones that are controlled primarily by soil salinity (Figure 3; Thibodeau et al., 1998): the upland forest (salt intolerant), the *Juncus* marsh (low salinity tolerant), and the *Spartina* marsh (high salinity tolerant). The vegetation in the upland forest region is composed of shrubs and trees, primarily oak (*Quercus virginiana*) and loblolly pine (*Pinus taeda*). The two botanical zones characteristic of the brackish and salt marshes contain almost exclusive monocultures of *Juncus roemarianus* and *Spartina alterniflora*, respectively.

The forest soils are sandy Spodosols and primarily receive organic inputs through litter fall with little to no mineral deposition (Gardner et al., 1992; Goñi and Thomas, 2000). The *Juncus* zone, which extends from the edge of the forest to

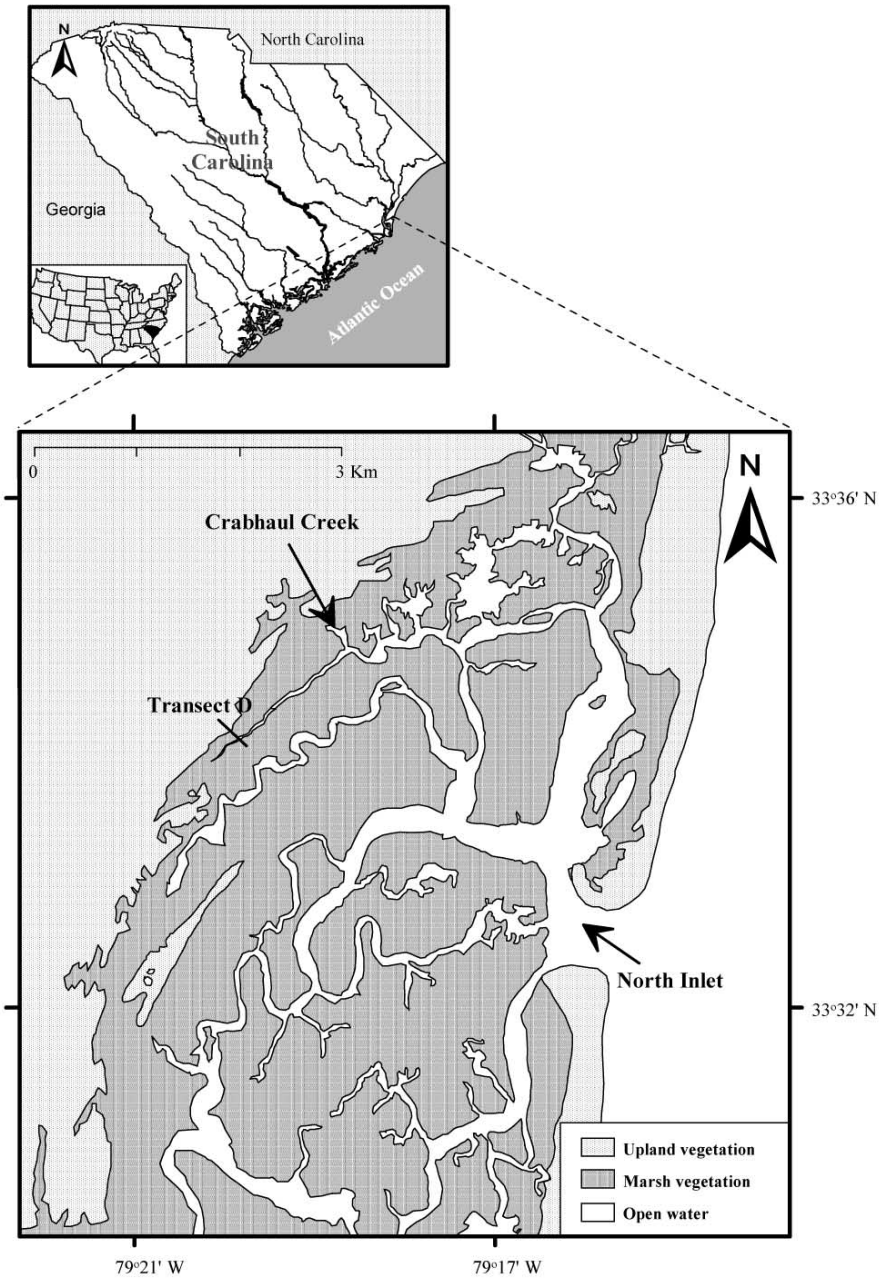

Figure 2. Location and geography of the study sites within the North Inlet basin.

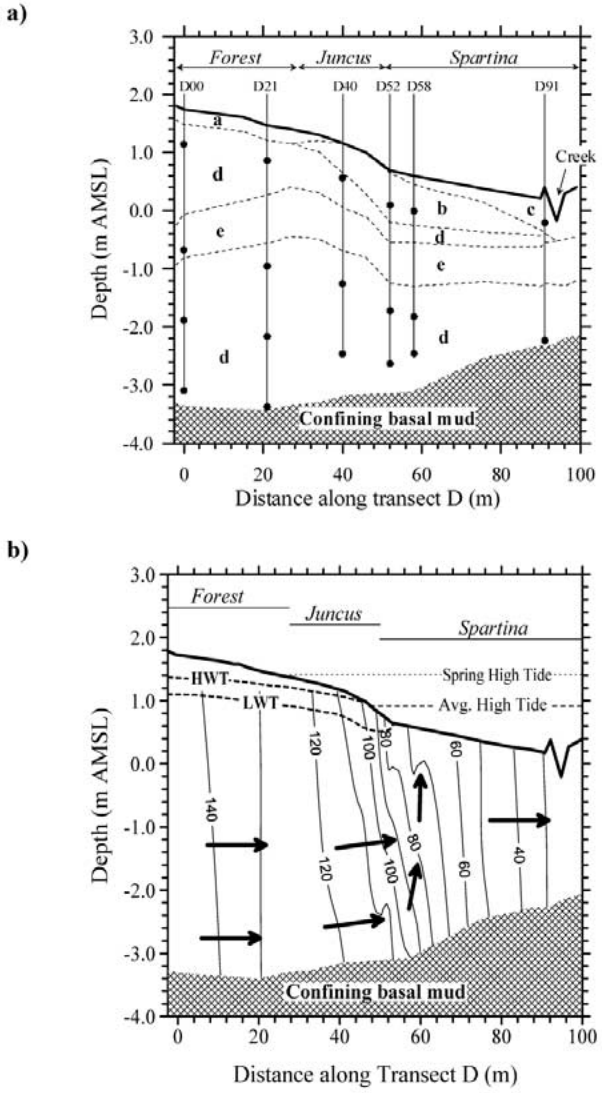

Figure 3. Cross-section along Transect D from the forest (northwest) to the tidal creek (southeast) showing (a) the elevation of the soil surface relative to average mean sea level (AMSL), the major botanical zones, and the distribution of the major soil types and (b) the contours of time-averaged hydraulic head measurements (in cm AMSL) along transect D (from Gardner et al., 2002). The code for soil types in Figure 3a are: a, forest A and E soil horizons; b, mixed sand and mud; c, marsh mud; d, fine/medium sand; e, coarse sand (after Thibodeau, 1997). Also included in this graph are the location of the piezometers sampled for this project (D00, D21, D40, D52, D58 and D91, which correspond to the distance in meters from the NW end of transect D). The depths of the piezometers at each location are indicated by the dots. Figure 3b shows the positions of the water table during periods of high precipitation (HWT) and low precipitation (LWT) and the tidal range. Finally, the arrows in this graph highlight the general direction of groundwater flow as determined from hydraulic head contours.

about mean high tide mark, receives small amounts of mud from tidal deposition (Stuckey, 1982; Gardner et al., 1992; Goñi and Thomas, 2000). Both neap and spring tides regularly inundate the *Spartina* zone and are responsible for the large accumulation of marsh mud (clays and silts), which is extensively bioturbated by fiddler crabs and other organisms (Gardner et al., 1992). Only spring tides inundate the *Juncus* zone.

2.1.3. Characteristic of the Coastal Aquifer

The aquifer along transect D consists mainly of variable textured sands and is confined at the bottom by a stratum of mud that serves as an aquitard (Figure 3a). Up to a meter of marsh mud caps the low-lying swale along the tidal channel cut by Crabhaul Creek. In order to understand the hydrology of the system, a network of piezometers was installed along transect D. Each piezometer consists of a 3.2 cm inner diameter PVC pipe, which has a slotted and screened opening at a specified depth that allows ground water from that depth to enter into the pipe. Figure 3a illustrates the depths of the aquifer in which groundwater head measurements and water samples were taken using these piezometers (for details see Thibodeau, 1997; Keenan, 1994; Gardner et al., 2002; Gardner and Reeves, 2002).

Previous studies indicate that variations in groundwater head and salinity along the transect are driven by the interaction of rainfall, evapotranspiration and tides (e.g., Keenan, 1994; Thibodeau, 1997; Wojcik, 1998; Thibodeau et al., 1998; Gardner et al., 2002; Gardner and Reeves, 2002). Hydraulic head decreases from the forest to the marsh (Figure 3b), consistent with a general easterly flow of the ground water down the topographic slope. Based on the hydraulic gradient and the average hydraulic conductivity (obtained by slug tests) for the sand horizons in the western edge of Transect D, the velocity of groundwater flow from the forest towards the marsh is about 8 m yr^{-1} (Thibodeau, 1997).

Besides the predominant lateral head gradient along the forest-marsh transect, there is a strong vertically upward component of the head gradient in the region between the forest and salt marsh (between 45 and 65 meters from the start of transect D; Figure 3b). Gardner et al. (2002) hypothesize that this vertical gradient, which indicates upward flow of ground water in this region of the transect, is the result of the easterly lateral groundwater flow being constricted by the basal mud at the bottom of the aquifer and the cap of relatively impermeable marsh mud near the creek. The height of the water table in the forest also undergoes significant seasonal variability (Figure 3b) that is related to changes in the balance between precipitation and evapotranspiration (Gardner et al., 2002). Such variations are only evident in the forest and high marsh sections of transect D, whereas tidal flooding maintains saturation all the way to the soil surface in the lower marsh.

Table I. Sample information

Date of sampling period	Cum. precip. (mm)[a]	Avg. temp. (°C)[a]	Tidal range sampled (m)	Tidal stage sampled	[b]Samples transect D	[b]Samples Crabhaul Creek	[b]Samples North Inlet
1997–1998 intensive study							
06/24/97	185.2	21.7	–0.24 to 1.36	Rising	10	n.m.	12
11/23/97	125.7	13.2	0.97 to 1.09	Rising	13	4	4
02/11/98	262.9	9.0	–0.05 to 0.91	Falling	17	5	5
05/20/98	75.9	19.5	0.18 to 1.24	Rising	19	7	5
06/25/98	88.6	26.5	–0.18 to 1.48	Falling	16	7	7
08/03/98	181.1	27.5	0.18 to 1.30	Rising	21	7	7
11/10/98	1.8	16.1	0.68 to 1.83	Rising	10	n.m.	n.m.
11/19/98	6.9	15.7	n.a.	n.a.	20	n.m.	n.m.
Additional groundwater sampling periods							
05/01/96	n.a.	n.a.	n.a.	n.a.	7	n.m.	n.m.
07/01/96	n.a.	n.a.	n.a.	n.a.	9	n.m.	n.m.
05/17/97	n.a.	n.a.	n.a.	n.a.	2	n.m.	n.m.

[a]Estimated for the 30 days prior to sampling period from NOAA's Georgetown weather station data.
[b]Samples, number of samples taken from each sampling location; n.a., not applicable; n.m., not measured; –, data not available.

2.2. SAMPLING

The piezometers were sampled by pumping the water from the pipe into acid-rinsed, pre-cleaned, opaque, one-liter Nalgene bottles. Prior to collection, the standing water in the piezometers was pumped out twice, and water from the aquifer was allowed to refill the pipes. Loosely fitted lids were placed over all piezometers between sampling periods to minimize contamination but allow venting. In order to have access to all the piezometers, ground waters were sampled within 3 hours of low tide.

Surface waters from Crabhaul Creek and North Inlet were collected at hourly intervals from the Baruch Laboratory pier and from a small boat, respectively. All surface water samples were taken from 0.5 m below the surface by hand into acid-rinsed, pre-cleaned, opaque Nalgene bottles. In most cases we were able to collect samples from a range of tidal stages, as indicated in Table I. We sampled the aquifer along transect D and the surface stations intensively during different seasons of the year in 1997 and 1998 in order to gain seasonal coverage.

2.3. ANALYSES

Immediately after collection, the temperature of all water samples was measured in the field with a hand held mercury thermometer. Salinity was measured in the field on filtered samples (0.45 μm membrane) with an Atago (S/Mill-E) refractometer. Both the thermometer and the refractometer were calibrated on a regular basis. Based on replicate analyses by different operators, the variability of the temperature and refractometer readings was $\pm 0.5\,^{\circ}$C and ± 0.75 ppt, respectively. Following these measurements, samples were packed in coolers ($\sim 5\,^{\circ}$C) and transported to the lab where they were refrigerated until further analysis. Additional salinity and temperature measurements were done in Crabhaul Creek and North Inlet using a YSI portable conductivity, temperature and salinity meter, and an Ocean Sensors 200 CTD to confirm the manual temperature and salinity measurements. The salinity and temperature profiles obtained from these measurements also showed that the water columns in these two stations were well mixed from surface to bottom. In selected cases, we were able to confirm the salinities measured with the refractometer with salinities calculated ($1.81 \times$ Cl ppt) from chlorinity measurements carried out in the lab with a Haake-Buchler chlorodiometer (Krest et al., 2000).

Dissolved organic carbon concentrations were determined for all water samples after they were filtered through 0.45 μm GF/F Acrodisc filters and acidified with 50 μL of concentrated HCl acid to drive off the inorganic carbon. DOC concentrations were measured by high temperature combustion using a Shimadzu (model TOC-500) total organic carbon analyzer (Benner and Strom, 1993). Samples, procedure blanks and instrument blanks were run in triplicate for each batch of analyses. The precision in most cases was better than 1% of the measured value.

3. Results

3.1. SEASONAL GROUNDWATER DYNAMICS

In order to understand the dynamics of the subterranean estuary along transect D, we sampled the piezometer network during several periods of contrasting conditions from 1997 to 1998 (Table I). Figure 4 illustrates the monthly average temperatures and cumulative precipitation at the Georgetown NOAA Weather Station during 1997 and 1998, when the bulk of the measurements in this study were carried out. The temperature record clearly shows the steady warming of the region from minima of about 10 °C during winter months (Dec–Feb) to maxima of over 28 °C in the summer (Jun–Aug). The precipitation record in 1998 shows the typical trend of high precipitation ($>$150 mm per month) during the winter (Dec–Feb) and a secondary peak ($\sim$ 150 mm per month) in the late summer and early fall (Jun–Sep). In contrast, the 1997 precipitation record is more erratic (Figure 3). The low rainfall during the early part of 1997 was partially due to the occurrence of a strong El Niño that year, which caused a severe drought in this area. Additionally, large

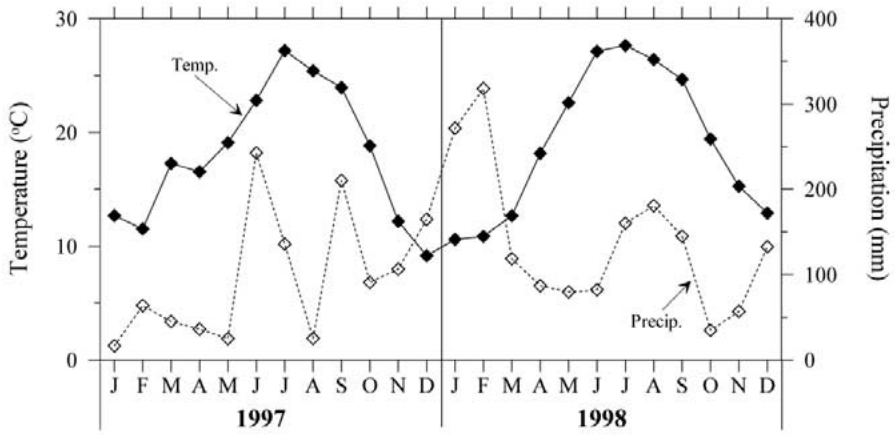

Figure 4. Monthly average air temperature and cumulative precipitation for the period covered in this study. All data are from NOAA's Weather Station in Georgetown, South Carolina (32°22′N, 79°13′W).

storms on June 6–7, 1997 and September 24–28, 1997 resulted in 130 and 155 mm of precipitation, respectively.

3.1.1. *Trends in Temperature*

Groundwater temperatures in the shallow, 0.5 to –1 m above mean sea level (AMSL), region of the aquifer display a strong seasonal cycle (Figure 5) that is consistent with climate variability in the region. Our observations show that the temperature in the top part of the aquifer gradually increased from 16 °C (Feb 98) to over 26 °C (Aug 98) as the year progressed, decreasing to ∼20 °C during the fall (Figure 5). The trend in the temperature of the near surface ground water followed the trend in atmospheric temperatures (Figure 5; Table I), indicating the close relationship between the two. In contrast the deeper (–1 to –3 m AMSL) part of the aquifer displayed a much more attenuated temperature range of 18–21 °C, indicative of its relative isolation from surface conditions.

3.1.2. *Trends in Salinity*

The distributions of groundwater salinity along transect D show marked longitudinal and depth contrasts that are seasonally variable (Figure 6). Low salinities (<2 ppt) were consistently measured in the western section (0–20 m) of transect D under the upland forest region. Higher salinities (2–10 ppt) were typically encountered in the eastern section (40–90 m) of transect D, although the extent of salt water intrusion varied significantly with season. For example, fresh water extended over most of the aquifer on February 11, 1998, which followed a period of elevated precipitation (Table I) and high recharge. This distribution contrasted markedly with those observed during the summer and fall months, in which low salinity (1–2

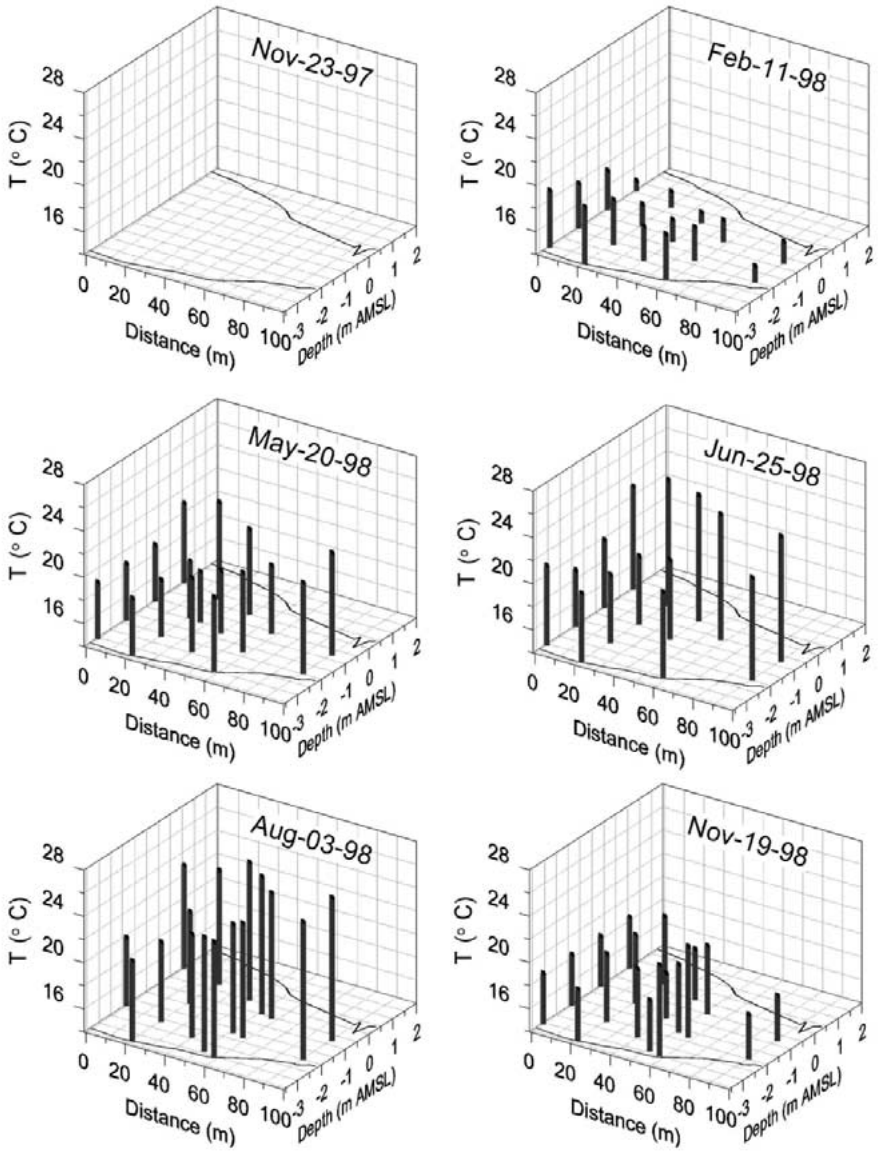

Figure 5. Groundwater temperatures along transect D for different sampling periods.

ppt) water was measured underneath the forest (0–20 m) and higher salinity water (2–10 ppt) was encountered underneath the marsh (40–90 m).

The highest salinities were consistently measured in the piezometers below the creek bed (at 91 m) and in the piezometers located in the *Juncus* zone (at 40 m) (Figure 6). With the exception of this latter site, the highest salinities in each region of the aquifer were consistently observed in the deepest piezometer. Such trend is consistent with the development of a salt wedge below the tidal creek and its

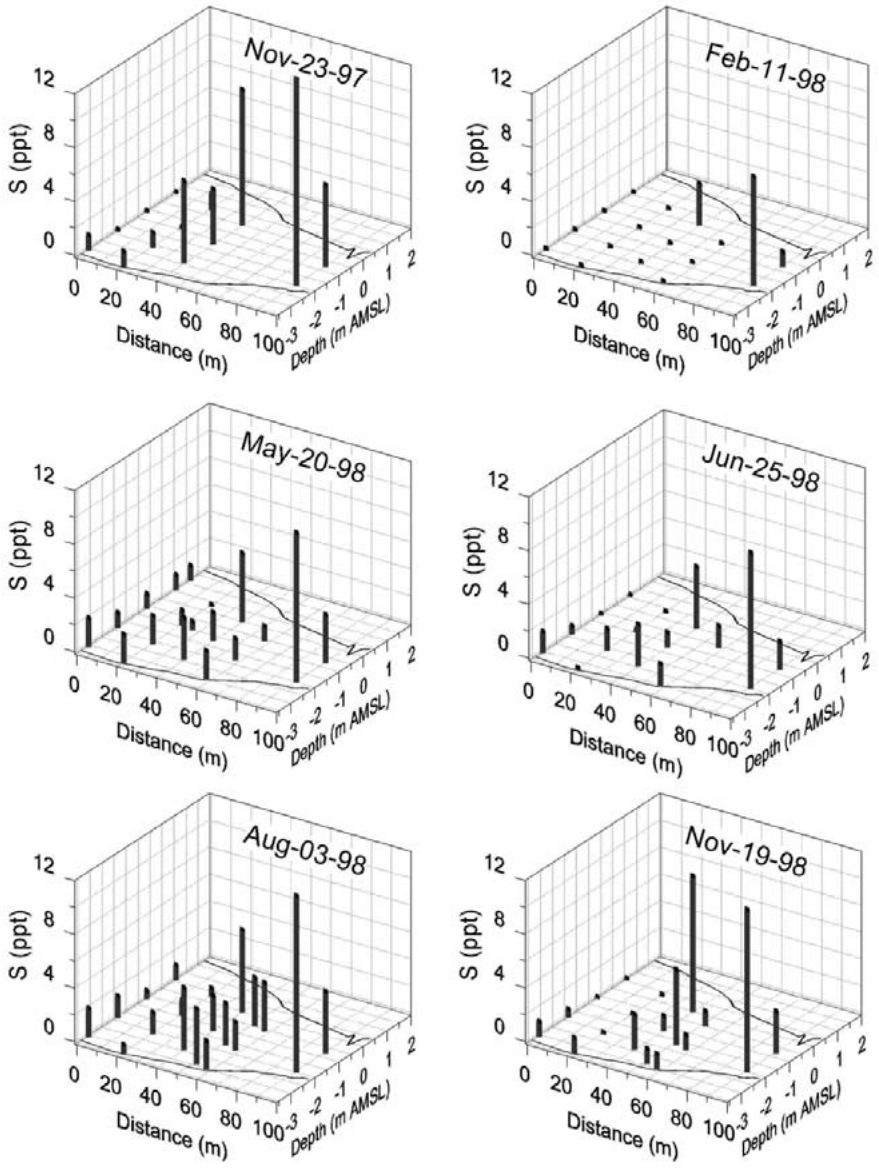

Figure 6. Groundwater salinities along transect D for different sampling periods.

migration landward during periods of low discharge (Gardner and Reeves, 2002). Enhanced salinities in the shallow piezometers from the *Juncus* zone are observed throughout the study period and are most prominent in late summer and fall. The shallow location of these high salinities coincides with a region of relatively high evapotranspiration and recharge by tides (Gardner and Reeves, 2002); suggesting

that the combination of these two processes is responsible for the trends observed in the *Juncus* zone.

Overall, the salinities measured along transect D were generally much lower than the near seawater salinities encountered most of the year in the adjacent tidal creeks (see below), indicating that the salinization of this part of the coastal aquifer, albeit significant, was impeded by the flow of fresh ground water from the forest. The low hydraulic conductivity of the marsh mud probably also contributes to this trend by limiting the exchange with the creek water in this part of transect D.

3.1.3. *Trends in DOC*

Groundwater DOC concentrations in the aquifer ranged from 6 to over 120 mg L^{-1}. DOC concentrations were highest (>50 mg L^{-1}) in the shallow regions of the forest section of the aquifer and lowest (<10 mg L^{-1}) in the regions underneath the marsh and the deeper parts below the forest (Figure 7). Consistently, we observed a sharp decrease of almost an order of magnitude in groundwater DOC concentrations with depth (between 0.5 and –3.0 m AMSL) in the forest section of transect D. DOC concentrations also decreased significantly from the forest towards the marsh edge, with the sharpest contrast between 20 and 40 m from the start of transect D. In contrast, groundwater DOC concentrations remained low and fairly constant in the portion of transect D below the *Spartina* marsh. Additionally, the deep piezometer under the marsh creek (91 m) and the shallow piezometer in the *Juncus* zone (40 m) consistently displayed relatively elevated DOC values ($\sim$20 mg L^{-1}).

The shallow ground waters from the forest displayed the highest seasonal variability in DOC concentrations (Figure 7). For example, the shallow (0.5 m AMSL) piezometer in the western edge of the forest (0 m) displayed DOC concentrations that ranged from 40 mg L^{-1} in August to 80 mg L^{-1} in February. A similar seasonal range (60–120 mg L^{-1}) was observed in the shallow piezometer located 20 m from the western end of transect D. No other set of piezometers, showed such variability in DOC. A summary of the trends in groundwater compositions described above (Figures 5–7) are summarized as annual averages in Table II.

3.2. SURFACE WATER COMPOSITIONS

The compositions of surface waters from Crabhaul Creek and the mouth of North Inlet showed significant seasonal trends that varied with tidal stage (Table III). In general, the temperature of surface waters at both locations followed the trends in atmospheric temperatures (Figure 4), with the coolest values (12–15 °C) in the winter and warmest readings in summer (28–34 °C) in summer (Table III). Salinities followed a similar trend with the lowest values (12–23 ppt) measured during the February 1998 sampling period and the highest values (28–36 ppt) detected during the summer months (June and August, 1998; Table III). The salinities measured in Crabhaul Creek during November 1997, February 1998, and May 1998, were distinctively lower than those measured at the North Inlet site. These contrasts in

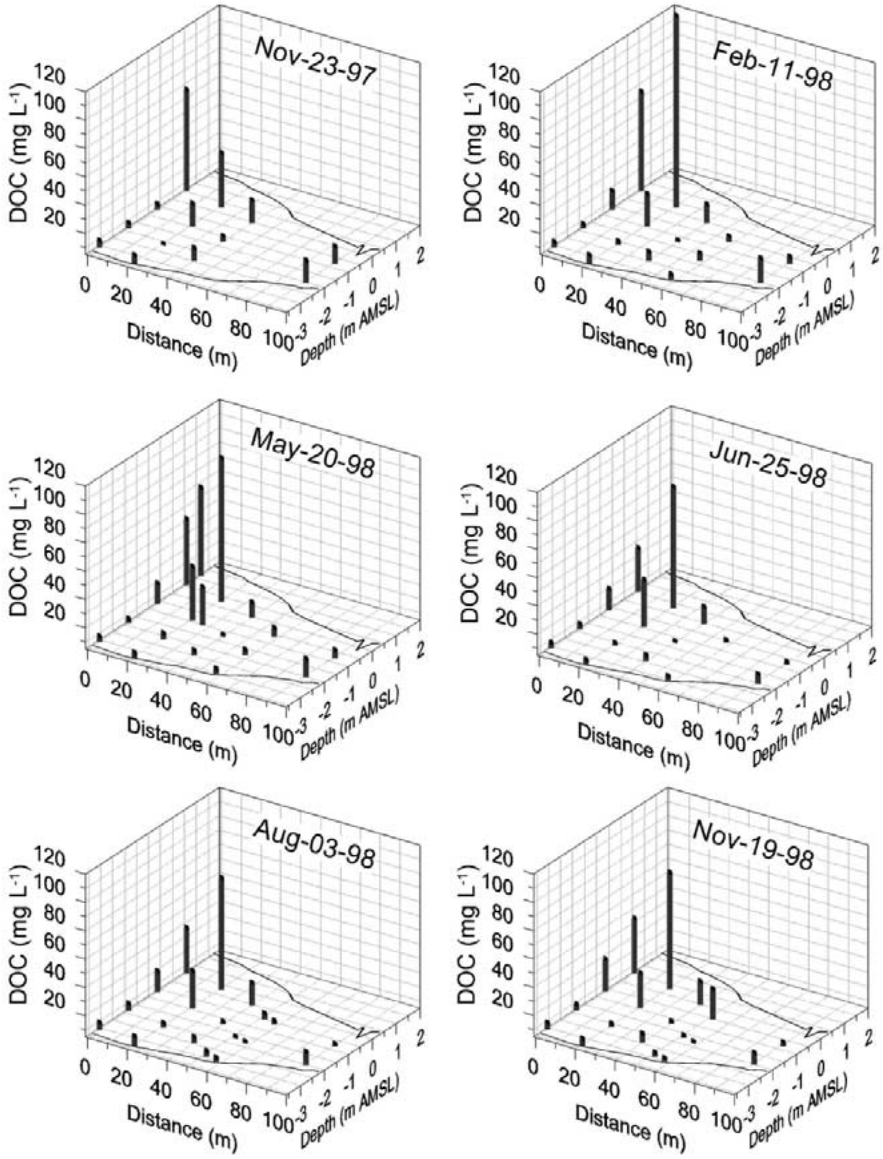

Figure 7. Groundwater dissolved organic carbon (DOC) concentrations along transect D for different sampling periods.

salinity are evidence of significant fresh groundwater and surface water input from the upland forest into the tidal creek system during this period. The fact that the lowest salinities at these times were measured during low tide (Table III) is further evidence for this process.

DOC levels in Crabhaul Creek waters ranged from 3.3 to 13 mg L^{-1}, while DOC concentrations in the North Inlet site ranged from 3.6 to 9.9 mg L^{-1} (Table III).

Table II. Average compositions of piezometer samples collected over the study period

Distance from D00 (m)	Depth (m AMSL)	Code	n	Avg. T s.d. (°C)	Avg. S s.d. (ppt)	Avg. DOC s.d. (mg L^{-1})
0	1.144	D00-2	1	1.0		68.0
0	0.538	D00-4	10	20.4 ± 3.1	0.3 ± 0.5	53.1 ± 19.1
0	–0.674	D00-8	9	18.8 ± 1.0	0.3 ± 0.4	18.5 ± 7.5
0	–1.886	D00-12	8	19.4 ± 1.4	0.4 ± 0.6	9.5 ± 1.0
0	–3.098	D00-16	6	19.4 ± 1.1	1.3 ± 0.8	9.8 ± 0.7
21	0.258	D21-4	8	21.7 ± 3.5	0.3 ± 0.4	84.8 ± 32.1
21	–0.954	D21-8	7	19.4 ± 2.2	0.4 ± 0.5	32.9 ± 7.2
21	–2.166	D-21-8	7	19.9 ± 1.3	0.9 ± 0.9	8.1 ± 1.2
21	–3.378	D21-12	6	19.5 ± 1.0	0.8 ± 0.8	10.8 ± 1.4
40	–0.042	D40-4	9	21.2 ± 4.1	6.2 ± 3.7	19.0 ± 2.7
40	–1.254	D40-8	9	18.6 ± 2.1	2.0 ± 1.5	7.8 ± 2.5
40	–2.466	D40-12	9	20.4 ± 2.2	3.1 ± 1.6	13.2 ± 7.4
52	–0.512	D52-4	2	23.0 ± 4.2	2.3 ± 1.8	18.4 ± 12.0
52	–1.724	D52-8	2	21.8 ± 2.5	4.3 ± 1.8	7.1 ± 0.6
52	–2.936	D52-12	2	21.3 ± 3.9	2.5 ± 2.1	9.3 ± 0.8
58	–0.612	D58-4	5	21.6 ± 3.8	1.6 ± 1.3	9.1 ± 1.7
58	–1.824	D58-8	5	21.0 ± 2.9	1.1 ± 0.7	9.2 ± 2.5
58	–3.036	D58-12	7	21.3 ± 2.0	1.4 ± 0.7	10.6 ± 3.7
91	–0.812	D91-4	8	21.8 ± 4.1	4.0 ± 3.4	10.0 ± 3.4
91	–2.024	D91-8	8	21.0 ± 3.7	9.3 ± 2.9	19.7 ± 11.8

n = number of samples from each piezometer. The location of each piezometers is indicated in Figure 2.

At the Crabhaul Creek site the highest concentrations were consistently detected during the low tide periods, consistent with a forest input. DOC levels decreased with increasing tidal height in the four months during which multiple measurements were made. The decreases were largest during the winter (February). With the exception of the August measurements, which revealed a peak in DOC during mid-tide, the trends in North Inlet were similar with those in Crabhaul Creek. These results are consistent with an input of DOC from the forest-marsh margin and its dilution with marine DOC from the coastal ocean (Wolaver et al., 1986). Similar patterns have been observed in nutrient concentrations (Morris, 2000), which have been interpreted as consistent with a groundwater/sediment pore water source.

Table III. Composition of surface waters in North Inlet sampling sites

Date	Crabhaul Creek[a]					North Inlet[a]				
	Time	Tide (m)	T (°C)	S (ppt)	DOC (mg L^{-1})	Time	Tide (m) (m)	T (°C)	S (ppt)	DOC (mg L^{-1})
23 Nov 97	12:40	1.00	18	32	4.7	12:00	0.97	16	35	5.5
	14:30	1.39	17	32	n.m.	13:40	1.18	15	36	6.2
	16:07	1.27	18	34	7.6	15:44	1.27	15	38	3.4
	17:33	1.18	18	32	5.9	16:44	1.09	16	36	5.9
11 Feb 98	10:00	0.91	12	23	6.8	10:04	0.91	12	30	6.3
	11:00	0.64	12	23	6.0	10:54	0.64	13	25	3.9
	12:30	0.24	12	21	7.4	12:37	0.24	14	23	5.6
	14:07	–0.05	14	16	12.6	14:00	–0.05	15	20	7.7
	15:30	0.24	14	18	10.5	15:32	0.24	13	15	7.9
20 May 98	9:45	0.01	24	21	11.3	10:30	0.18	26	22	9.7
	10:45	0.27	25	27	10.6	11:00	0.33	27	24	9.9
	11:45	0.48	25	27	10.1	13:20	0.82	25	34	6.0
	12:45	0.70	26	27	9.9	14:00	1.03	24	35	5.9
	13:45	0.91	26	27	8.9	15:00	1.24	28	34	6.5
	14:45	1.12	25	25	9.7	n.m.	n.m.	n.m.	n.m.	n.m.
	15:45	1.30	25	27	8.8	n.m.	n.m.	n.m.	n.m.	n.m.
25 Jun 98	9:45	1.48	28	34	3.65	9:56	1.48	28	34	4.4
	10:45	1.27	28	34	3.3	10:45	1.27	28	33	3.8
	11:45	0.91	29	34	3.8	11:45	0.91	28	31	3.6
	12:45	0.67	n.m.	34	4.5	12:42	0.67	29	33	4.5
	13:45	0.36	32	34	5.9	13:45	0.36	30	32	4
	14:45	–0.09	34	34	6.1	14:45	–0.09	30	31	4.5
	15:45	–0.18	35	34	6.2	15:45	–0.18	31	31	6.3
3 Aug 98	10:30	0.36	n.m.	35	7.8	10:30	0.36	27	35	9
	11:30	0.18	n.m.	35	7.5	11:30	0.18	27	36	4.6
	12:30	0.36	n.m.	35	7.8	12:30	0.36	28	35	4.5
	13:30	0.55	n.m.	36	6.7	13:30	0.55	29	36	5
	14:30	0.85	n.m.	35	7.7	14:40	0.85	29	36	8.3
	15:30	1.06	n.m.	36	6	15:30	1.06	29	35	4.8
	16:30	1.30	n.m.	36	6.2	16:30	1.30	28	35	5.6

[a]locations identified in Figure 1.
m = AMSL, meters above mean sea level; n.m. = not measured.

4. Discussion

Biogeochemical processes in estuaries can often be elucidated by plotting the concentrations of specific dissolved substances against salinity, which is commonly assumed to be a conservative tracer of mixing between fresh and ocean waters (Boyle et al., 1974). A plot of DOC concentrations vs. salinity for all the samples analyzed in this study illustrates the large spatial and temporal variability and apparent non-conservative behavior of DOC in this subterranean estuary (Figure 8). Most significant are the large decreases in DOC that occur in low salinity portion of the aquifer below the forest. Furthermore, at intermediate salinities (6–15 ppt), the aquifer waters display relatively elevated DOC concentrations that are higher than those measured in the putative low salinity (deep aquifer waters from the forest) and high salinity endmembers (surface Crabhaul Creek and North Inlet waters). In this discussion, we focus on three areas of the aquifer geochemistry that are important in the context of carbon cycling: the contrasts among the surficial and deep fresh ground waters from the forest, the seasonal changes observed in the near surface ground waters below the mid marsh, and the trends measured in the deeper ground water along the forest-marsh transect.

4.1. CARBON DYNAMICS IN THE FOREST SECTION OF THE AQUIFER

Two major patterns are evident in the compositions of the ground waters below the upland forest portion of the aquifer: (a) the marked decrease in DOC concentrations between shallow and deep piezometers; (b) the spatial and seasonal variation in DOC concentrations of the shallow D00 and D21 piezometers (Table II). Before addressing the changes in DOC with depth, we first consider the factors that control the variability observed in the near surface part of the forest aquifer. It is likely that the processes affecting these shallow forest piezometers are representative of the overall recharge area and, thus, determine the initial composition of the ground water that flows eastward towards the creek (Gardner et al., 2002).

Although we consistently measured significantly higher DOC concentrations in the shallow D21 piezometers than in the shallow D00 piezometers (Table II), we cannot find a simple reason for this contrast. Uncharacterized heterogeneities in vegetation coverage, water table dynamics, and soil composition may be responsible for the observed differences and probably reflect the natural variability we can expect across the recharge area. In spite of the spatial variability between both sites, we found negative correlations ($r^2>0.4$; $P = 0.02$) between the DOC concentrations of surface forest piezometers and the average air temperature of the 30 days prior to collection (Figure 9a, b). Not surprisingly, since temperature and precipitation inversely co-vary in our study area, we also found weak positive correlations between DOC concentrations and cumulative precipitation for the 30 days prior to collection (Figure 9c, d). Notably, none of the marsh surface piezometers or deep piezometers along transect D displayed similar statistically significant relationships.

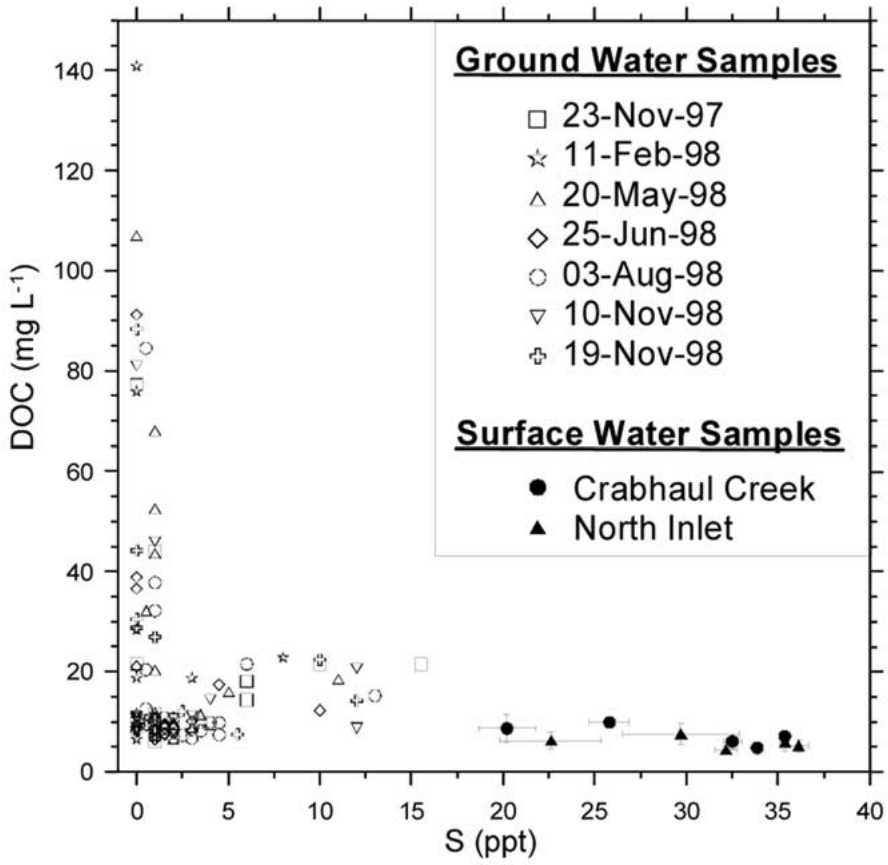

Figure 8. DOC concentrations vs. salinity for all water samples (both ground waters and surface waters) collected in the study. In the case of surface waters, the averages and standard deviations over the tidal cycles are plotted.

These correlations with temperature may be the result of enhanced microbial activity and heterotrophic degradation of DOC in the shallow forest ground waters during warmer periods. Alternatively, they could mean that DOC is preferentially leached from recently deposited litter by rains in the winter and early spring (Meyer and Tate, 1983). In any case, the trends shown in Figure 9 provide no support for enrichment of DOC by evapo-concentration (Ford and Naiman, 1989) or the dilution of DOC by precipitation (Fiebig, 1995). Overall, these trends indicate that during winter months, when precipitation is high and temperature is low, recharge results in high amounts of DOC entering the upper part of the aquifer.

The sharp decrease in DOC concentrations between shallow (40–140 mg L^{-1}) and deep forest piezometers ($\sim$10 mg L^{-1}) (Figure 10a) may be partially caused by the heterotrophic degradation of dissolved organic matter along the groundwater flow paths. Thus, using a mass balance approach we can compare the amount of DOC loss (30–130 mg L^{-1}) to increases in dissolved inorganic carbon (DIC) meas-

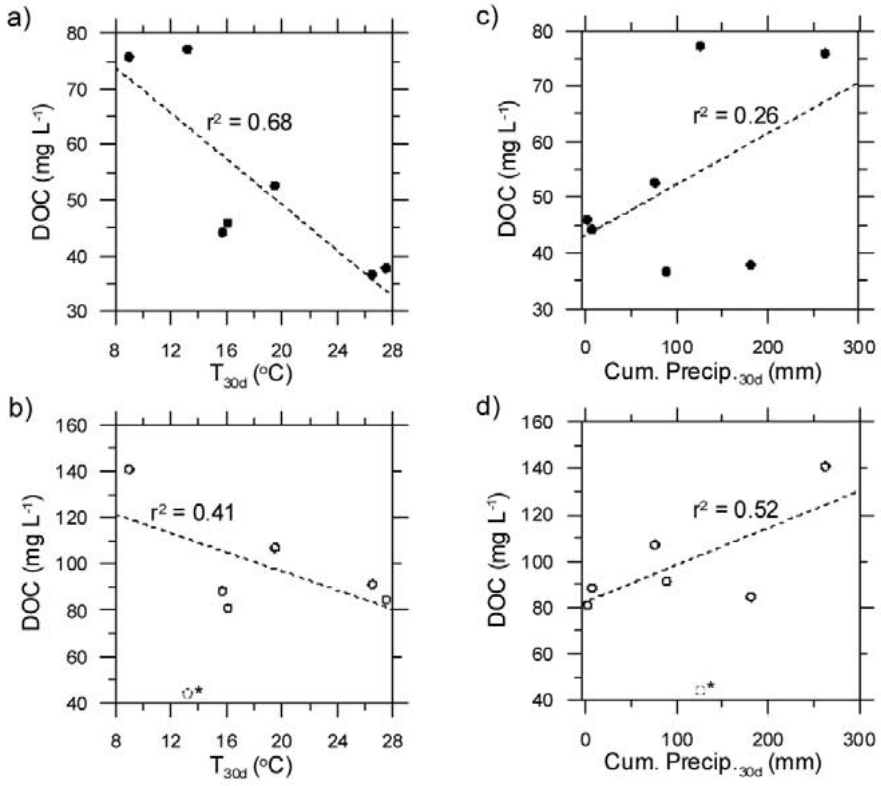

Figure 9. DOC concentrations of shallow ground waters (0.5 to 0.2 m AMSL) vs. air temperature in °C (T_{30d}) and cumulative precipitation in mm (Cum. Precip.$_{30d}$), both estimated for the 30 days prior to groundwater collection (NOAA Georgetown station): (a) D00 samples vs. T_{30d}; (b) D00 samples vs. Cum. Precip. $_{30d}$; (c) D21 samples vs. T_{30d}; d) D21 samples vs. Cum. Precip. $_{30d}$. The correlation indices are indicated on the graph. *, indicates the D21–4 sample collected on 23 November 97 with unusually low DOC values, which was excluded from the correlation calculations.

ured over the same aquifer region (Cai et al., 2002). Cai and co-workers (2002) measured a 4–6 mM increase in DIC between the low salinity (0–2 ppt) surface and deep forest ground waters. They attributed ∼2mM of that increase to organic matter decay, mainly through CH_4 generation, while the rest of the DIC increase was attributed to $CaCO_3$ dissolution. Our estimates indicate that DOC losses average 5mM and range from 3 to 10 mM, with the highest losses typically determined in the deeper piezometers. Based on these calculations, it appears that heterotrophic decay only accounts on average for 44% of the DOC losses observed between the surface and deep piezometers. In the deepest piezometer, the heterotrophic loss only represents 25% of the total measured decreased in DOC. In all likelihood, sorption and precipitation processes that do not directly contribute to the measured DIC increases are responsible for the rest of the loss (Cai et al., 2002).

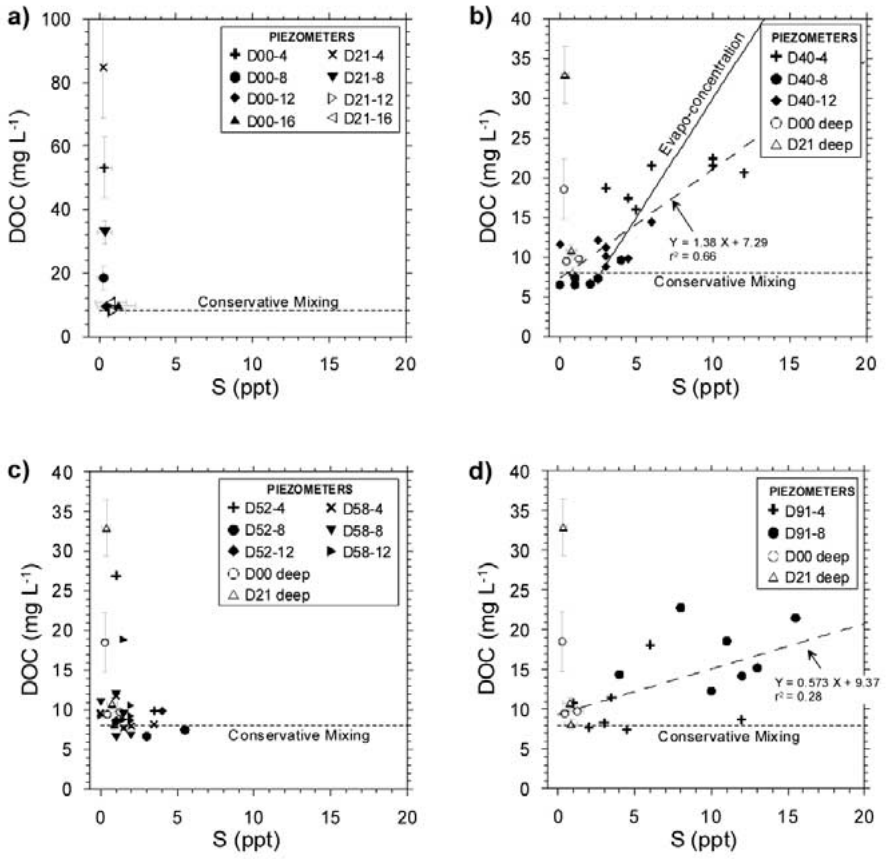

Figure 10. Graphs showing the relationship between DOC and salinity for selected piezometer samples including: (a) D00 and D21 samples, (b) D40 samples, (c) D52 and D58 samples, and (d) D91 samples. Statistical correlation relationships and coefficients are indicated in the graphs. The conservative mixing line between deep forest ground waters and surface waters from North Inlet (average of all samples in Table III) is shown in each graph. In Figure 10b, the evapo-concentration line illustrates the DOC and salinity compositions expected for the evaporation of a 90–10 mixture of deep fresh forest ground water and North Inlet surface water endmembers.

Sorption of DOC is the main process involved in the formation of the spodic (Bh) horizon in forest soils (McKeague et al., 1983). The fact that the soils in the forest section of Transect D are Spodosols (Stuckey, 1982; Gardner et al., 1992) is consistent with the estimates that 56–75% of the observed DOC losses are due to sorption. Furthermore, we have preliminary data suggesting that a large part of this DOC loss is due to decreases in the fraction of high molecular weight (>1000 Daltons) dissolved organic matter (HMW DOM) in forest ground waters. Indeed, our estimates indicate that while HMW DOM represents 20–30% of the DOC in the shallow wells below the forest, it only accounts for less than 5% of the DOC in the deep wells at this location (Goñi unpublished data).

4.2. GROUNDWATER CARBON DYNAMICS AT THE FOREST-MARSH INTERFACE

The trends in DOC concentrations with salinity across the forest-marsh boundary of the aquifer (40–60 m from D00) are not simple due to the complex nature of the water fluxes in this zone. For example, while evapotranspiration and tidal recharge dominate the water balance in the D40 piezometers, upwelling of fresh, deep ground water from the forest is most significant in the D52 and D58 piezometers (Figure 3b; Gardner and Reeves, 2002). Because of the contrast in groundwater flow paths and mixing processes, it is useful to consider the trends in the D40 piezometer separately from those in D52 and D58.

Figure 10b shows a general positive correlation between salinity and DOC for the D40 piezometers, with the highest values (S of 6–12 ppt; DOC $\sim$20 mg L^{-1}) measured in the shallow samples (D41–4). Tidal recharge alone cannot account for this trend because conservative mixing with surface waters, which display S and DOC values that range from 20–35 ppt and 5–10 mg L^{-1}, does not explain the elevation in DOC. Thus, we need to invoke other processes in order to explain these results. It is likely that the increases in DOC are due to concentration during evapotranspiration (Ford and Naiman, 1989). As an example, the evapoconcentration line plotted in Figure 10b illustrates the expected S and DOC trend for the concentration of a 90–10 mixture of deep ground water and average surface water. The variability observed in the D40–4 samples may reflect the combined seasonally variable effects of evapotranspiration and tidal recharge. Additionally, the elevated DOC levels observed in these piezometers could also reflect variable lateral seepage from shallow forest waters located upslope (Gardner et al., 2002) and non-conservative mixing with surface waters. Analyses of DOC composition are needed in order to elucidate which of these processes is most significant.

Comparable increases in DOC with increased S are not evident in the D52 and D58 piezometers (Figure 10c). Instead, the compositions of most of these samples suggest conservative mixing of deep forest ground waters and surface inlet water. Such interpretation is consistent with the upwelling of ground water at this site (Figure 3; Gardner et al., 2002; Gardner and Reeves, 2002). We can estimate the annual carbon flux from the subterranean to the surface estuary associated with this process by multiplying the average concentration of DOC in upwelled ground waters (10 mg L^{-1}) by the average groundwater upwelling rate (20 cm y^{-1}; Gardner and Reeves, 2002) and the total area of the forest-marsh transition zone where upwelling occurs (area $= 3 \times 10^9$ cm^2; 20 m wide, 7 km long). The resulting estimate is a daily flux rate of 5.5 mg DOC m^{-2} d^{-1} and a total flux of 2.8×10^2 Kg DOC y^{-1}, which represents a minor fraction of the annual discharge of DOC from North Inlet to the coast (7.8×10^6 Kg y^{-1}; Dame et al., 1986). However, this calculation is a conservative estimate of the total groundwater DOC flux into North Inlet because it only includes forest-derived DOC brought in by the upwelling of deep ground waters at the forest-marsh margin. It does not include direct input of high DOC shallow ground waters from the forest during periods when the water

table exceeds the ground surface, nor inputs from the saltier part of the aquifer due to tidal pumping and deeper groundwater circulation (Krest et al., 2000), both of which may be significant (see below).

4.3. GROUNDWATER CARBON DYNAMICS IN THE MARSH AQUIFER

The salinity distribution in the piezometers located below the creek (D91) and in the deepest piezometers to the west (Figure 6) suggests that a wedge of dense salty water exists in the deepest part of the aquifer (Gardner et al., 2002). The salt wedge migrates westward during periods of low recharge and low hydraulic head while it is pushed eastward when the aquifer is recharged by high precipitation. DOC concentrations display weak positive relationship with salinity, with the highest values measured in the deep piezometers below the creek (Figure 10d). Clearly, such a trend cannot be explained by conservative mixing of deep ground water and surface waters. Instead, as we saw in the forest-marsh zone, other processes such as concentration due to evapotranspiration and/or desorption in the eastern part of transect D must be responsible for the doubling of DOC concentrations at S ranges of 6–16 ppt. An additional source of DOC at elevated salinities must be viewed in the context of increased DIC concentrations over the same salinity ranges (Cai et al., 2002). Cai and co-workers associated the increase in DIC in the high salinity region of the aquifer with SO_4^{2-} reduction. Since we measured an increase of DOC with salinity, our results suggest that the substrate of this heterotrophic reaction must be a different carbon source besides DOC, such as for example CH_4.

Overall, the fact that ground waters of intermediate salinity (6–16 ppt) have doubled DOC concentrations relative to deep low-salinity ground waters means that discharges from the salty region of the aquifer may be responsible for significant fluxes of dissolved organic matter in addition to dissolved nutrients (e.g., Krest et al., 2000). Using 30 L m^{-2} d^{-1} as the saline groundwater discharge into North Inlet (Krest et al., 2000) and 20 mg L^{-1} as the DOC concentration in this ground water, we estimate a DOC export rate of 600 mg m^{-2} d^{-1} or 50 mmol m^{-2} d^{-1}. The magnitude of this flux is about 30% of the DIC export estimated by Cai et al. (2002). It is likely that the discharge of this saline ground water occurs primarily through the banks and beds of the tidal creeks, which incise the aquifer and lack the cap of low hydraulic conductivity mud present on the marsh surface. Given an estimated tidal creek surface area of 7.14 km^2 (Krest et al., 2000), we calculate the annual flux of DOC from saline ground water to be 1.6×10^6 Kg y^{-1}, a value that represents 20% of the annual discharge of DOC from North Inlet to the ocean (7.8×10^6 Kg y^{-1}; Dame et al., 1986). In spite of the uncertainties associated with this estimate, our calculations indicate that the DOC discharge of saline ground water may account for a significant fraction of the net DOC export from North Inlet. Because of its unique diagenetic history, the composition and characteristics (e.g., age) of this subterranean source of DOC are likely to be different (Goni unpublished data) from the surface sources traditionally considered. Dissolved organic

matter in saline ground waters discharging in continental margins may, therefore, be an important but yet uncharacterized component of the ocean's carbon cycle (e.g., Bauer and Druffel, 1998).

5. Summary

The subterranean estuary present in the coastal aquifer underlying the North Inlet basin is characterized by several salient processes including (a) seasonally variable inputs of DOC from overlying forest soils in the recharge area, (b) large decreases in the concentrations of DOC along the groundwater flow paths within the fresh portion of the aquifer, (c) conservative mixing of DOC as upwelled fresh ground water mixes with surface waters, and (d) increases in DOC concentration in areas of the marsh where evapotranspiration exceeds groundwater seepage or tidal recharge. Our results indicate that the lower temperature and high precipitation typical of late winter early spring conditions favor the input of high amounts of DOC from the forest soils into the water-table aquifer. Carbon mass balance shows that heterotrophic decay accounts for $\sim$40% of the DOC losses measured before the fresh ground water reaches the forest-marsh interface; the rest (over 60% of the DOC decrease) appears to be caused by sorption/precipitation. Although our estimates suggest that the upwelling of fresh, deep ground water at the forest-marsh interface only accounts for a small fraction of the annual DOC export from North Inlet, this carbon flux is likely to be significant during high recharge periods when groundwater discharge from the aquifer below the forest is high. Finally, the relatively elevated DOC concentrations and the high discharge of saline ground water at our study site indicate that this poorly characterized endmember may contribute significantly to the overall carbon budget in North Inlet and potentially represent an important source of DOC to the coastal ocean.

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