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Distribution of terrestrially derived dissolved organic matter on the southeastern U.S. continental shelf

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Abstract

Dissolved lignin-derived compounds in seawater indicate the presence of organic matter originating from vascular plants and therefore from terrestrial (upland and coastal marsh) ecosystems. We used a hydrophobic resin to concentrate lignin-rich humic substances and to determine concentrations of lignin oxidation products (vanillyl lignin phenols) for waters of the continental shelf of the southeastern U.S. Lignin phenol concentrations ranged from 0.05 to 4.2 μg liter^{-1} and accounted for 0.002–0.13% of the total dissolved organic carbon (DOC) pool in continental shelf waters. Dissolved lignin concentrations were generally highest near the shore and in those areas receiving greatest river and marsh discharge. Concentrations varied on both short-term (weekly) and seasonal time scales, however, indicating that the contribution of terrestrially derived dissolved organic matter to the C budget of the shelf is quite variable. Salinity (>31‰) was significantly correlated (negatively) with lignin phenol concentrations during three of four cruises, suggesting largely conservative mixing of lignin-derived material on the shelf.

In selected rivers and salt marshes contributing terrestrially derived organic matter to the continental shelf, lignin phenol C accounted for 0.14–1.0% of the DOC. A simple mixing model which assumes no biological or physical sinks of lignin-derived material during transport from terrestrial sources to the shelf predicts that an average of 6–36% of nearshore DOC derives from terrestrial ecosystems, depending on whether the terrestrial end-member (lignin source) is assumed to be a river or a salt marsh, while 5–26% of inner shelf DOC and 3–18% of mid- to outer-shelf DOC is of terrestrial origin.

The importance of riverine- and salt-marsh-derived organic matter to the carbon and energy budgets of coastal waters has been a focus of marine ecological research for the past 30 yr. Questions regarding the magnitude and ecological significance of organic matter subsidies to the nearshore are particularly relevant for the southeastern coast of the U.S., where extensive salt-marsh and river systems empty into coastal waters, setting up turbid plumes visible many kilometers offshore (Blanton 1980). The phenomenon of "outwelling" from such marshes was examined initially by Teal (1962) and Odum and de la Cruz (1967), and more recently by Haines (1977), Peterson and Howarth (1987), and others. On the basis of energy budgets, C flux measurements, and stable isotope ratios, these studies implicated marsh detritus as an important, al-

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though not always dominant, source of organic matter within the marshes and adjacent estuaries.

However, data on the contribution of exported marsh and riverine organic matter to productivity farther offshore remain equivocal. Recent measurements of the flux of dissolved and particulate organic C from a Georgia salt marsh showed little evidence of movement of detrital material from the marsh surface but measurable export from marsh tidal creeks (Chalmers et al. 1985). Hopkinson (1985) compared gross primary production and community respiration in the Georgia nearshore and found evidence that at least some portions of the continental shelf are heterotrophic, presumably supplemented by outwelled marsh and riverine organic matter.

Organic matter originating in terrestrial ecosystems and coastal marshes is derived in large part from vascular plants. In Georgia salt marshes, for example, the grass *Spartina alterniflora* accounts for 84% of the total primary production (Pomeroy et al. 1981) and is the likely precursor of the bulk of particulate and dissolved marsh detritus (Moran and Hodson 1990). Because vascular plant material contains lignin, a structural biopolymer with unique chemical composition, it is possible to trace the fate of terrestrial organic matter in marine ecosystems based on the presence of lignin-derived compounds. Lignin is found only in vascular plants, making up a few percent of the weight of nonwoody tissue (e.g. 6% of *S. alterniflora* dry wt) and up to 30% of wood (Sarkanen and Ludwig 1971). Identification and quantification of characteristic phenolic compounds produced from controlled chemical oxidation of lignin can thus provide information on the presence and quantitative importance of land-derived vascular plant detritus in marine systems.

Analysis of lignin oxidation products to indicate terrestrial input to the shelf was first used by Gardner and Menzel (1974), who found traces of phenolic lignin derivatives in coastal sediments up to 24 km offshore from the Georgia coastline. Since their initial study, methodologies for analyzing lignin phenols have been improved (Hedges and Parker 1976; Hedges and Mann 1979) and adapted for analysis of dissolved organic matter (DOM) after passage of seawater through hydrophobic resins to concentrate and isolate lignin-rich humic materials (Ertel et al. 1984, 1986). In this study, we present data on concentrations of lignin phenols in seawater samples from transects across the shelf. Our data set, consisting of 71 samples collected over a 2-yr period, provides information on the dynamics of organic matter input from terrestrial sources, defined here to include all systems dominated by vascular plants, including salt marshes, and the transport of this material on the shelf.

Methods

Study area—The coastlines of Georgia and South Carolina are highly indented with inlets connecting rivers and coastal marshes to the ocean. Within our study area, approximately between the latitudes of Savannah, Georgia (32°N), and Cape Canaveral, Florida (28°N), the Savannah River (draining the southeastern piedmont), the Altamaha River (draining the piedmont and southeastern coastal plain), and the Ogeechee, Satilla, and St. Johns Rivers (draining the coastal plain) account for most of the freshwater discharge, with additional inputs from smaller rivers and creeks (Blanton 1980). Freshwater input is not evenly distributed along the north–south axis of the study area, but is concentrated in the northern half, where the Savannah and Altamaha Rivers discharge (Atkinson and Menzel 1985). Extensive salt marshes, located behind the barrier islands of Georgia and South Carolina, are in contact with coastal water during the approximately twice-daily flooding.

Sample collection—Seawater samples were collected from surface waters (1–2-m depth) between 28 and 32°N and 80 and 81.5°W. During a cruise of RV *Blue Fin* in July 1987, we collected six 40-liter seawater samples. During a FLEX cruise of RV *Columbus Iselin* in October and November 1987, we collected thirty-nine 40-liter samples from the study area and a single sample from the Gulf Stream at 32°19.85′N, 79°56.62′W. During *Blue Fin* cruises in Sep-

tember 1988 and April 1989, we collected twenty-two and three 30-liter samples.

Water samples were collected in acid-washed Nalgene carboys, immediately filtered through ashed, large-diameter (293 mm) Gelman A/E glass-fiber filters, and acidified to pH 2 with 6 N HCl. Subsamples of water were removed and frozen for later determination of dissolved organic C (DOC) concentration with an OI 700 TOC analyzer after persulfate digestion (1987 *Blue Fin* cruise only) or a Shimadzu TC500 by high-temperature combustion (all other cruises).

Humic substances isolation—Humic substances were isolated from freshly collected seawater samples by pumping water (50 ml min^{-1}) through a 2.2 × 40-cm column of Amberlite XAD-8 resin which had been previously cleaned sequentially with ether, acetonitrile, methanol, and ether (24 h Soxhlet extraction for each solvent) and prepared with repeated rinses of HCl, NaOH, and distilled/deionized water (Aiken 1985). Columns were washed with 100 ml of distilled water and humics were then eluted with 200 ml of 0.1 N NaOH followed by 100 ml of distilled water. The humic eluant was pumped through a 2.2- × 40-cm column of BioRad AG-MP50 cation exchange resin, previously cleaned with methanol and prepared with repeated rinses of NH_4OH and HCl. Humic materials were concentrated by rotary evaporation, freeze-dried, and stored frozen until oxidation. Carbon content of humic materials was determined on a Perkin-Elmer 240C CHN analyzer.

Humic isolation procedures differed slightly among cruises. For the 1987 *Blue Fin* cruise, cation exchange of the humic eluant was carried out onboard ship and humic concentrate was stored frozen until further processing in the laboratory. For the 1988 *Columbus Iselin* and the 1988 *Blue Fin* cruises, humic eluant from the XAD-8 column was acidified and stored frozen or preserved with mercuric chloride (1 mg $liter^{-1}$) until postcruise cation exchange. For the 1989 *Blue Fin* cruise, humic substances were left on the XAD-8 resin and stored at 4°C until postcruise elution and cation exchange.

Carbon budgets were calculated (for *Blue Fin* cruises only) to check for quantitative processing of samples and to determine the efficiency of humic substance recovery from the XAD-8 resin. Seawater eluant from the XAD-8 column was collected and analyzed for DOC concentration. Budgets were calculated by summing the C per unit volume of this eluant (nonhumic C) and the humic C recovered per unit volume of seawater processed. This sum was compared to the DOC content per volume of original seawater sample. C recovery averaged 113±2% for 1987 *Blue Fin* samples, 104±7% for 1988 *Blue Fin* samples, and 120±6% for 1989 *Blue Fin* samples. Recovery of humic substances from XAD-8 resin has generally not been 100% efficient (Aiken 1985), so recovery values >100% may represent organic matter leaching from the resin.

Lignin analysis—Lignin-derived compounds in seawater were quantified by gas chromatographic analysis of cupric oxide oxidation products of humic substances (Hedges and Ertel 1982; Ertel et al. 1984). The oxidation procedure involved reacting 5–30 mg of freeze-dried humic substances with alkaline cupric oxide for 3 h at 170°C to produce a suite of simple lignin phenols. The phenols fall into three categories: vanillyl phenols (*V*; vanillic acid, vanillin, and acetovanillon), syringyl phenols (*S*; syringic acid, syringealdehyde, and acetosyringone), and cinnamyl phenols (*C*; ferulic acid and *p*-coumaric acid). Phenols were extracted from the oxidation mixture with ether and converted to trimethylsilyl derivatives.

Quantification of lignin phenols was carried out on an HP 5890 gas chromatograph. Because of the complexity of gas chromatographic traces and coelution of nonlignin cupric oxide oxidation products with lignin phenols, subsamples were analyzed independently on both Supelco SE-30 (100% dimethyl polysiloxane) and J&W DB-1701 (86% dimethyl polysiloxane and 14% cyanopropylphenyl polysiloxane) silica capillary columns (Hedges et al. 1988), and normalization of lignin phenol concentrations between the two columns was based on vanillic acid concentrations. Even with this analysis procedure, quantification of two of the *S* phenols and both *C* phenols was difficult, and ratios of the various *S* and *C*

phenols to one another varied significantly among some samples. All final analyses were therefore based only on the more abundant vanillyl phenols, which accounted for ~70% of the total lignin phenols. Ratios of the concentrations of the three component *V* phenols to one another (acid : aldehyde; keytone : aldehyde; keytone : acid) were consistent among the samples (Table 1). Concentrations of vanillyl lignin phenols were summed and expressed as μg liter^{-1}.

We checked reproducibility of oxidation and GC analysis to determine whether the weight of humic material used in the oxidation affected the suite of products produced. Humic substances from three 1987 *Columbus Iselin* samples, two 1988 *Blue Fin* samples, and two 1989 *Blue Fin* samples were split into two portions of different weights and each portion was separately oxidized and analyzed. The average difference in the sum of *V* phenols between replicate analyses was 11±4% and the average difference in the acid : aldehyde (vanillic acid : vanillin) ratio between replicate analyses was 15±3%. To determine whether the XAD-8 resin itself could serve as a source of spurious lignin phenols leading to an overestimation of lignin phenol concentrations in the event of resin bleed, we oxidized 30 mg of resin at 170°C according to standard procedures. The resulting oxidation mixture contained two compounds eluting at the approximate positions of *p*-coumaric acid and acetovanillon in a 9 : 1 ratio. Even assuming all apparent *p*-coumaric acid in natural samples to be an unidentified resin-derived contaminant—a worst-case scenario—maximum possible overestimation of vanillyl lignin phenol content of seawater samples due resin bleed would be only 1–10%.

Characterization of lignin source material—Dissolved lignin phenols on the continental shelf may derive from coastal marshes or from rivers draining the coastal plain and piedmont. Water samples from a salt-marsh tidal creek, a river, and several estuaries were also analyzed for content of lignin phenols. In August 1988, water samples (28‰) were collected from the Duplin River, a large tidal creek draining the Sapelo Island, Georgia, salt marshes, on two consecutive days at high slack. In August 1990, two additional samples were collected from the Duplin on a single day, one at high slack and one at low slack. The tidal freshwater section of the Altamaha River, 16 km from the river mouth, was sampled in August 1988 with the collection of two replicate water samples on a single day at high slack. In September 1988, water samples were collected from three estuaries: Ossabaw Sound (17.8‰), the Savannah River estuary (10.9‰), and a largely freshwater section (3.5‰) of the Hampton River at its intersection with the Intracoastal Waterway. All water samples were filtered and acidified, and humic substances were isolated and analyzed for lignin phenols as described above.

Results

RV Columbus Iselin *cruise*—The October 1987 cruise represents our most intensive sampling effort, yielding 40 determinations of lignin phenol concentrations over a 15-d period. The concentrations of lignin phenols (sum of concentrations of three vanillyl phenols) were highest in nearshore and inner shelf areas, ranging from 0.2 to 4.2 μg liter^{-1}. Concentrations decreased gradually with distance from shore and at the edge of the shelf ranged from 0.05 to 0.5 μg liter^{-1}. From the coast to the shelf break, decreases in concentrations of dissolved lignin-derived phenols averaged 10-fold (Fig. 1), and concentrations were negatively correlated with salinity ($r = -0.90$, $P < 0.01$; Figs. 2 and 3). The single Gulf Stream sample contained 0.05 μg liter^{-1} lignin phenols.

A latitudinal pattern of lignin phenol concentrations was also evident. Seawater samples from the northernmost cruise tracks, at the latitudes of Savannah and Brunswick, had high concentrations of lignin-derived material relative to the southernmost tracks, at the latitudes of St. Augustine and Cape Canaveral. This north–south decrease in concentrations is most evident in the nearshore, where concentrations of lignin-derived phenols differ as much as ninefold between northerly and southerly stations; it is least evident near the shelf break, where concentrations are not consistently different along a north–south gradient (Fig. 1). This observed pattern in lignin phenol concentrations is likely a reflection of the clustering

Table 1. Concentrations of DOC (mg liter^{-1}), humic C (mg liter ^{1}), and vanillyl lignin phenols (μg liter^{-1}) and ratio of vanillic acid to vanillin in humic substances isolated from continental-shelf water samples. Percentage of terrestrially derived DOC is calculated separately for a salt-marsh (Duplin River) and a river (Altamaha River) source of lignin phenols. N—Nearshore (0–10-m depth); I—inner shelf (11–20 m); M—middle shelf (21–40 m); O—outer shelf (41–61 m). (Not determined—N.D.)

Sta.	DOC	Humic C	Lignin	Ad : Al *V*	Terrestrially derived (%)		Location
					Marsh	River	
			October 1987 RV *Columbus Iselin*				
Gulf Stream	1.62	0.06	0.054	1.10	1	<1	
1	1.60	0.05	0.045	0.89	1	<1	O
10	1.72	0.10	0.335	1.14	7	1	I
11	1.89	0.22	0.744	0.77	14	3	I
26	1.70	0.11	0.362	0.84	7	1	M
27	1.05	0.11	0.332	0.82	11	2	M
32	1.73	0.15	0.352	1.18	7	1	I
37	2.06	0.28	1.43	1.68	24	4	I
39	2.58	0.45	3.05	1.56	41	8	N
40	1.14	0.16	0.218	0.81	7	1	M
51	1.81	0.32	2.23	1.52	42	8	I
52	1.40	0.17	0.265	0.80	7	1	M
58	1.32	0.20	1.10	1.72	29	5	I
67	2.33	0.48	3.51	1.39	52	10	I
68	1.72	0.11	0.367	0.91	7	1	M
83	2.25	0.35	3.85	1.14	59	11	I
84	1.12	0.18	0.459	0.35	14	3	O
89	2.00	0.20	0.837	0.93	14	3	I
93	1.87	0.25	1.25	1.07	23	4	I
94	1.95	0.15	0.309	0.87	6	1	M
99	1.52	0.15	0.560	1.29	13	2	I
104	1.78	0.24	1.41	1.51	27	5	I
106	2.86	0.43	4.16	1.08	50	9	N
107	3.17	0.32	2.59	1.38	28	5	N
116	1.38	0.13	0.496	0.87	13	2	I
120	1.16	0.10	0.321	0.61	9	2	M
128	1.36	0.13	0.765	1.39	19	4	I
133	1.80	0.19	0.826	1.25	16	3	I
136	1.39	0.06	0.172	0.61	4	<1	M
142	2.12	0.12	0.243	0.62	4	<1	I
147	1.56	0.17	0.609	1.00	14	3	I
151	2.08	0.26	1.38	1.46	23	4	I
152	1.77	0.11	0.228	0.70	4	<1	I
158	1.96	0.21	0.922	0.81	9	3	I
162	2.56	0.27	1.95	0.89	26	5	I
163	1.41	0.11	0.182	0.89	4	<1	M
169	1.37	0.13	0.376	1.39	9	2	I
174	1.85	0.19	1.29	1.55	24	4	I
179	0.91	0.24	1.92	1.74	72	13	I
183	3.26	0.38	3.53	1.13	37	7	N
			July 1987 RV *Blue Fin*				
3	1.50	0.29	1.25	0.68	29	5	N
4	1.05	0.27	1.09	0.77	36	7	I
5	1.05	0.25	1.00	0.60	33	6	I
6	0.76	0.21	0.54	0.46	24	4	I
7	0.71	0.16	0.52	0.96	25	5	M
8	0.78	0.20	0.63	0.73	28	5	O
			September 1988 RV *Blue Fin*				
1	3.06	0.39	1.25	1.34	14	3	N
2	2.22	0.43	1.68	1.15	26	5	I
3	2.13	0.20	1.88	1.10	30	6	I
4	1.71	0.22	1.69	0.79	34	6	M

Table 1. Continued.

Sta.	DOC	Humic C	Lignin	Ad : Al *V*	Terrestrially derived (%) Marsh	River	Location
5	1.24	0.24	1.14	0.92	31	6	M
6	1.66	0.27	2.05	0.81	42	8	O
7	2.04	0.15	0.88	0.64	15	3	M
8	2.36	0.25	1.20	0.77	18	3	N
9	2.15	0.21	1.91	1.31	30	6	N
10	1.90	0.16	1.78	0.77	32	6	I
11	1.90	0.15	3.08	0.49	55	10	I
12	2.69	0.22	3.26	1.20	42	8	I
13	2.02	0.28	2.06	1.27	35	7	I
14	1.78	0.17	2.74	1.34	53	10	M
15	1.59	0.13	0.98	1.86	21	4	M
16	2.11	0.46	2.17	1.45	35	7	I
17	2.40	0.23	1.95	2.11	28	5	I
18	3.26	0.21	1.15	1.81	12	2	M
19	1.79	0.21	2.47	1.16	47	9	M
20	2.23	0.25	2.05	1.52	12	2	I
21	2.32	0.31	3.20	1.71	47	9	N
22	2.13	N.D.	1.88	1.41	30	6	I
			April 1989 RV *Blue Fin*				
1	2.53	0.39	3.77	1.09	51	9	N
2	1.84	0.44	3.07	1.14	57	11	N
3	1.96	0.33	2.04	1.17	36	7	I

of salt marshes and rivers in the northern section (Savannah/Brunswick region) of the study area (Atkinson and Menzel 1985).

Lignin phenol concentrations in shelf waters also changed temporally during the 15-d cruise. During the initial stages (23–31 October) while moderate southwestward winds prevailed, lignin phenols increased in concentration in coastal waters from 3 μg liter^{-1} to >4. Gale-force westward winds from 1 to 4 November coincided with a decrease in lignin phenol concentrations along the coast (to 1 μg liter^{-1}), suggesting southward transport and removal of coastal water during the gale and replacement with shelf water of lower lignin content and higher salinity (Figs. 1 and 2). Following the storm, concentrations again increased to >3 μg liter^{-1}.

Concentrations of both bulk DOC and humic C decreased in seawater samples with distance from shore and were negatively correlated with salinity ($r = -0.75$, $P < 0.01$ and $r = -0.88$, $P < 0.01$). DOC concentrations ranged from 3.3 mg liter^{-1} nearshore to 0.9 at the shelf break, and dissolved humic C concentrations ranged from 0.48 to 0.05 mg liter^{-1} (Table 1). Lignin phenol concentrations were positively correlated with bulk DOC concentrations ($r = 0.72$, $P < 0.01$) and humic C concentrations ($r = 0.94$, $P < 0.01$). However, lignin phenols did not account for a constant proportion of either DOC (0.002–0.13%) or humic C (0.06–0.69%) and decreased in quantitative importance within these C pools as salinity increased ($r = -0.78$, $P < 0.01$ and $r = -0.87$, $P < 0.01$). These data are consistent with there being both terrestrial and oceanic sources of DOC and humic substances to the shelf, but only a terrestrial source of dissolved lignin-derived organic matter.

RV Blue Fin *cruises*—During the July 1987 cruise, a low-salinity plume, probably originating from the Savannah River, stretched across the shelf (Fig. 4). Concentrations of both DOC and humic C generally decreased with distance from shore and were negatively correlated with salinity ($r = -0.99$, $P < 0.01$ and $r = -0.86$, $P < 0.01$). DOC concentrations ranged from 0.7 to 1.5 mg liter^{-1} and dissolved humic C from 0.16 to 0.29 mg liter^{-1} (Table 1). Lignin phenols varied in concentration from 0.5 to 1.3 μg liter^{-1} (Fig. 4) and were significantly correlated with salinity ($r = -0.92$, $P < 0.01$;

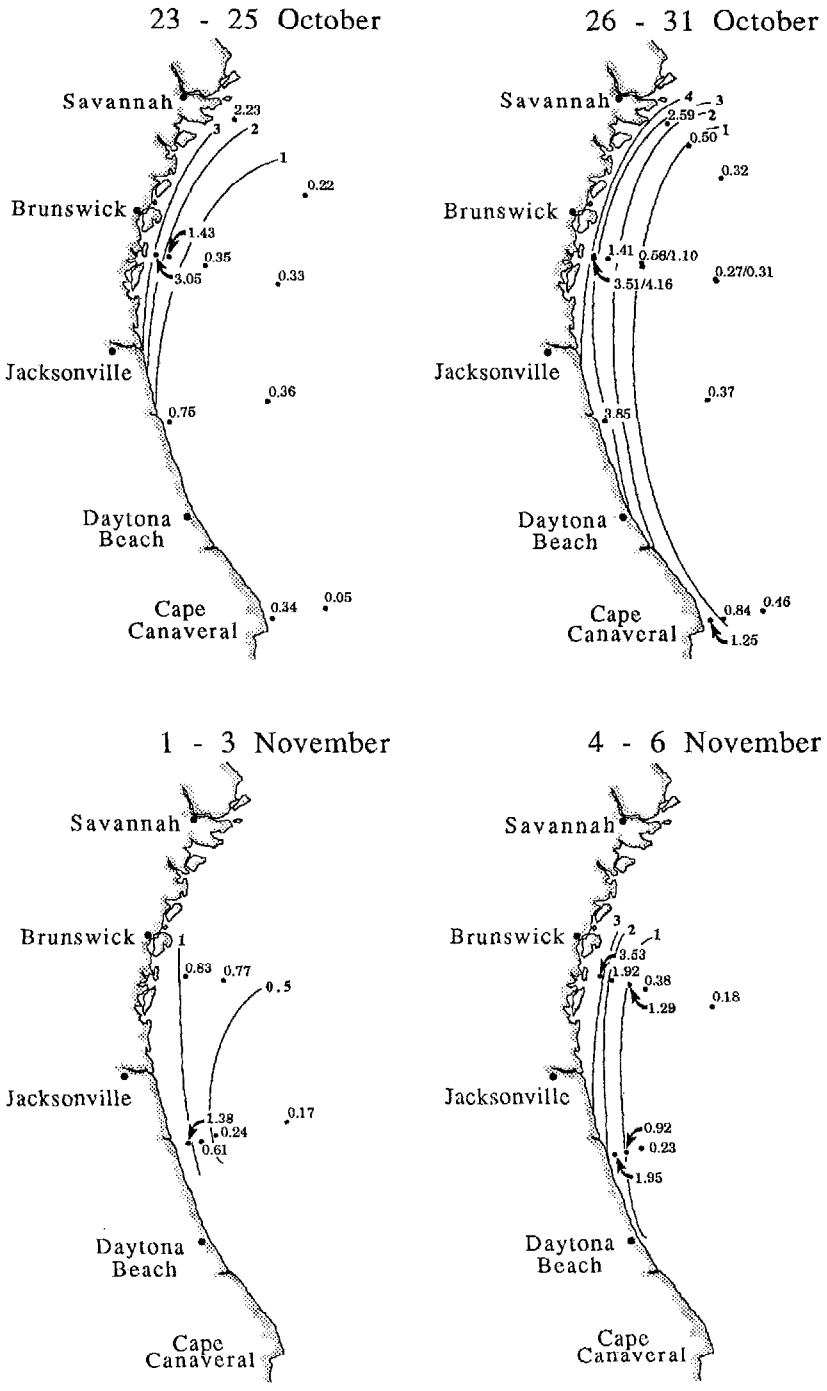

Fig. 1. Lignin phenol concentrations (μg liter^{-1}) on the continental shelf in October and November 1987 (RV *Columbus Iselin* cruise). Stations with two values (26–31 October map) were sampled twice, 3 d apart.

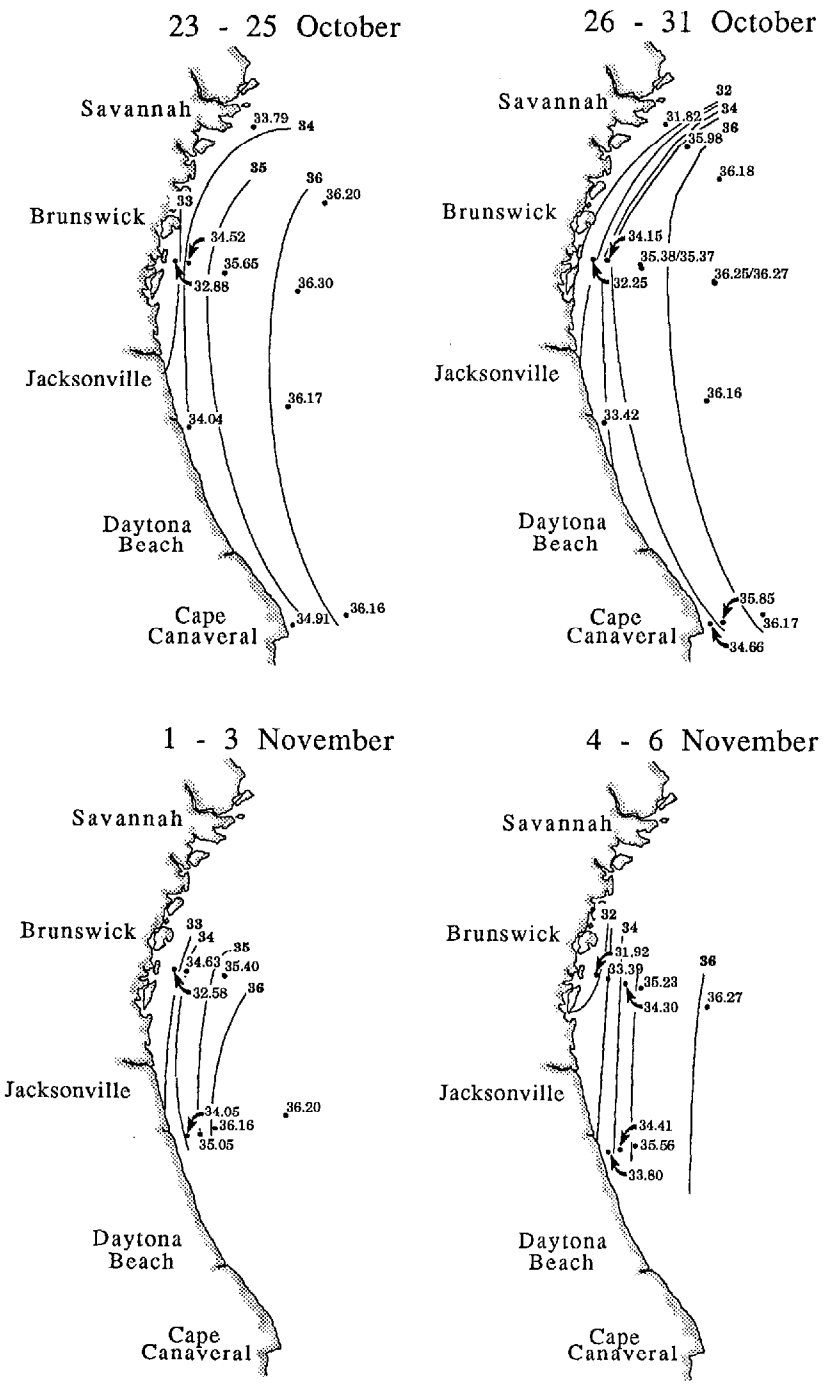

Fig. 2. As Fig. 1, but of salinity (‰).

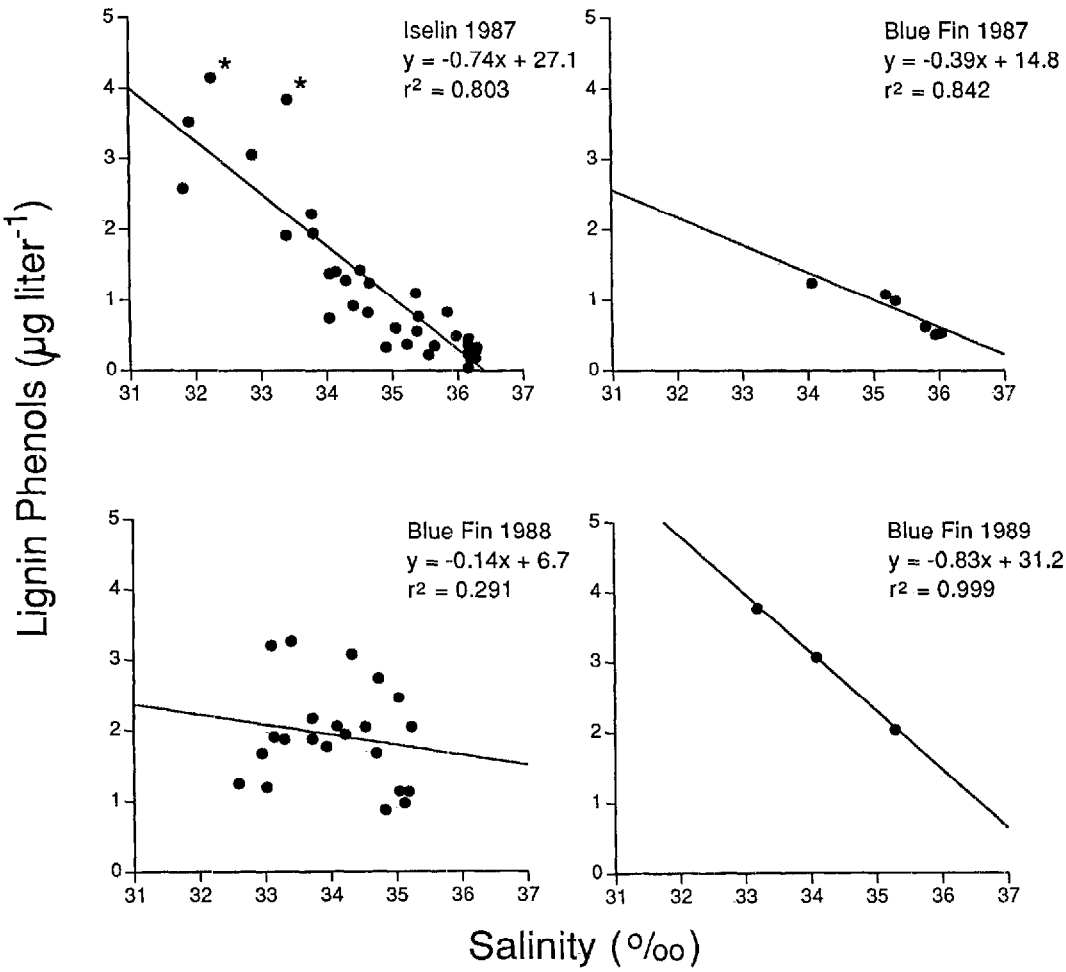

Fig. 3. Relationship of lignin phenol concentrations to salinity during four cruises on the continental shelf. Asterisks on top left panel indicate St. Simons Inlet samples (*see text*).

Fig. 3), DOC concentration ($r = 0.94$, $P < 0.01$), and humic C concentration ($r = 0.95$, $P < 0.01$). Lignin phenols accounted for 0.04–0.07% of bulk DOC and 0.16–0.27% of humic C.

The 1988 cruise was in September during a weather pattern typical of summer conditions in the area. No vertical gradients were evident for salinity, temperature, or density across the width of the shelf. However, calm winds and pulsed rainfall allowed the entrainment of two distinct water masses: a low salinity (32.6–35.2‰) plume of the Savannah River extending across the shelf, and a low salinity mass resident on the outer shelf at the latitude of Brunswick. Freshwater influence was evident all across the shelf, with no salinity value >35.5‰ (Fig. 5). DOC and humic C concentrations were again negatively correlated with salinity ($r = -0.51$, $P < 0.05$ and $r = -0.52$, $P < 0.05$). Consistent with the presence of significant amounts of freshwater during this cruise, DOC and humic C concentrations were relatively high, ranging from 1.2 to 3.3 mg liter^{-1} DOC and from 0.13 to 0.46 mg liter^{-1} humic C (Table 1). Lignin phenol concentrations varied from 0.9 to 3.3 µg liter^{-1} (Fig. 5) and did not correlate significantly with salinity (Fig. 3), DOC concentration, or humic C concentration. Horizontal patterns of lignin phenol con-

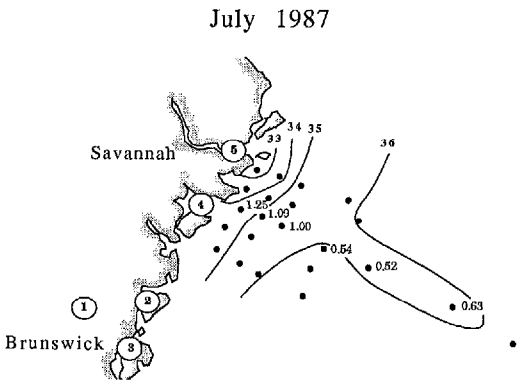

Fig. 4. Lignin phenol concentrations (μg liter^{-1}) and salinity (‰) on the continental shelf in July 1987 (RV *Blue Fin* cruise). Lignin phenol concentrations, measured at only six stations, are indicated by the number to the right of the station location. Salinity, measured at all stations, is indicated by isopleths. Circled numbers show collection sites for river, marsh, and estuary samples: 1—Altamaha River; 2—Duplin River; 3—Hampton River; 4—Ossabaw Sound; 5—Savannah River.

centrations were consistent with the existence of two isolated water masses on the shelf, one with a weak lignin signal (Savannah area, inner shelf) and one with a strong lignin signal (Brunswick area, outer shelf). Lignin phenols accounted for 0.02–0.10% of bulk DOC and 0.20–1.2% of humic C.

During the third cruise in April 1989, three seawater samples were collected from nearshore waters in the vicinity of Savannah. DOC concentrations were 2.5, 2.0, and 1.8 mg liter^{-1} (most shoreward to the most seaward station) and humic C concentrations were 0.44, 0.39, and 0.33 mg liter^{-1} (Table 1). Lignin phenol concentrations (3.8, 3.1, and 2.0 μg liter^{-1}) were negatively correlated with salinity ($r = -1.0$, $P < 0.01$; Fig. 3) and accounted for 0.07–0.10% of DOC and 0.39–0.60% of humic C.

Marsh and riverine samples—Water samples collected from marsh, river, and estuarine sites along the coast of Georgia exhibited a wide range of salinities (0–32‰) and a 10-fold variation in lignin phenol content (14–166 μg liter^{-1}; Table 2). Lignin phenols accounted for 0.14 (salt-marsh creek water) to 1.0% (Altamaha River) of the bulk DOC (Table 1) and 0.6–1.9% of dissolved humic C.

Discussion

Lignin phenol concentrations and distribution—The presence of dissolved lignin derivatives in seawater indicates input of organic matter derived from terrestrial sources. A simple inverse relationship between lignin phenol concentrations and sa-

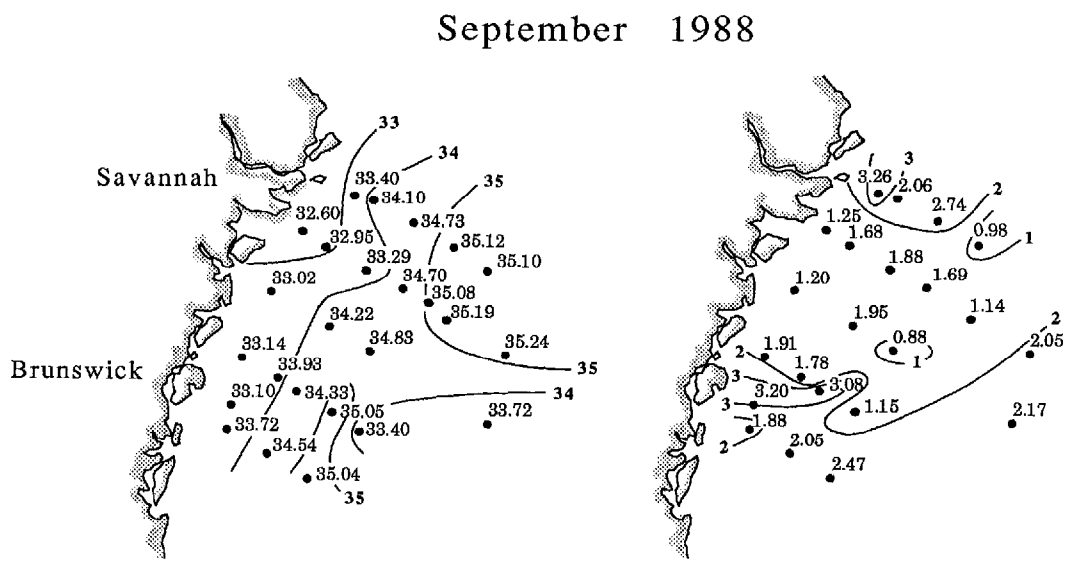

Fig. 5. Salinity (‰; left panel) and lignin phenol concentrations (μg liter^{-1}; right panel) on the continental shelf in September 1988 (RV *Blue Fin* cruise).

Table 2. Composition of dissolved organic matter in water samples from marsh, riverine, and estuarine environments along the coast.

Site and date	DOC (mg liter^{-1})	Humic C (mg liter^{-1})	Lignin		Ad:Al *V*	Salinity (‰)
			(μg liter^{-1})	(% of DOC)		
Altamaha River, 1988	10.0	5.3	166	1.04	0.79	0
Altamaha River, 1988	9.8	5.2	148	0.94	0.75	0
Hampton River, 1988	8.6	5.2	81	0.58	0.85	3.5
Savannah River, 1988	4.1	2.6	29	0.45	1.04	10.9
Ossabaw Sound, 1988	6.8	4.1	51	0.47	1.11	17.8
Duplin River, 1988 (high tide)	6.4	1.7	16	0.15	0.99	28.0
Duplin River, 1988 (high tide)	6.1	1.5	14	0.14	0.99	28.0
Duplin River, 1990 (high tide)	5.3	1.3	17	0.20	0.76	29.5
Duplin River, 1990 (low tide)	5.7	1.5	22	0.24	0.79	32.0

linity is not necessarily expected, however. First, the numerous sources of freshwater to the shelf vary substantially with regard to typical lignin phenol concentrations (Table 2). Second, lignin phenols also enter the shelf in pockets of brackish or seawater that have been resident on the salt marshes for one or more tidal cycles.

For the 40 samples collected during the 1987 *Columbus Iselin* cruise, lignin phenol concentrations were negatively correlated with salinity, as predicted by simple mixing of lignin-rich freshwater and lignin-poor seawater. However, the correlation was not strong for the lower salinity water on the shelf, with a large spread in lignin phenol concentrations measured for a given salinity value within the range of 32–34‰. For example, two seawater collections made close to shore off St. Simons Inlet (Brunswick section) on 27 and 30 October 1987 show especially high lignin content relative to salinity (Fig. 3). These samples may derive from marsh water with lignin concentrations comparable to average river (fresh) water, or they may represent pulses of freshwater with very high lignin content, such as from the Altamaha River. Lignin phenol concentrations and salinity were also inversely correlated for the 1987 ($n = 6$) and 1989 ($n = 3$) *Blue Fin* cruises. Thus although dissolved lignin-derived material cannot be considered biologically inert (Moran and Hodson 1989, 1990), the behavior of lignin phenols appears largely conservative within the time frame of their residence on this part of the shelf (1–2 months).

In contrast, no significant lignin/salinity relationship was found for the 22 samples of the 1988 *Blue Fin* cruise. Calm summer weather conditions and strong density gradients before and during this cruise allowed discrete water masses of varying salinities to persist on the shelf. This lack of correlation between salinity and lignin phenol concentrations may reflect differences in the sources of the entrained freshwater, as two low salinity masses, one with a strong lignin signal and one with a weak signal, were evident on the shelf (Fig. 5). Statistical relationships between lignin concentration and salinity may also be strongly influenced by a high-salt low-lignin oceanic end-member that was not present on the shelf during this cruise.

Lignin phenol concentrations varied temporally during the 15-d *Columbus Iselin* cruise in a pattern which suggests significant influence of wind and weather on concentration and distribution of terrestrially derived material. For four different time intervals, we calculated the average concentration of lignin phenols in a liter of surface water based on the mean of all samples collected along the Brunswick and St. Augustine transects (Fig. 1). Surface water lignin concentrations are likely to be very representative of all depths during this cruise, as depth/salinity profiles indicated a well-mixed water column at these sections (Chandler et al. 1988). Calculations indicate the presence of ~1.1 μg lignin phenols liter^{-1} in the Brunswick-St. Augustine area during the first 3 d of the cruise and an increase to 1.7 μg liter^{-1} by the cruise midpoint, presumably a result of continued inputs of vascular-plant-derived DOC to the shelf. After a westward gale at the midpoint

of the cruise, only 0.7 μg liter^{-1} of lignin phenols remained, more than a twofold decrease in concentrations of lignin-derived material. Higher phenol concentrations were re-established in the area (1.3 μg liter^{-1}) by the final sampling.

Repeated sampling on four different cruises over 2 yr provides information on long-term temporal variability of terrestrially derived DOC in shelf waters. Water samples were collected in the vicinity of the Wassaw Sea Buoy, off Savannah (Skidaway Island) during each of the four cruises. On the basis of the average of the two samples closest to the buoy (all samples were within the area from 31°48.5′ to 31°56.3′N and 80°47.3′ to 80°53.0′W), lignin phenol concentrations were 1.17 (July 1987), 2.41 (October 1987), 1.47 (September 1988), and 3.42 (April 1989) μg liter^{-1}. Lowest concentrations of phenols were measured for the two samples collected during summer weather conditions (July and September) and the highest concentration was measured in spring (April). Although we do not know the possible effects of wind and weather conditions just before these cruises on lignin phenol concentrations, the observed pattern coincides with the expected timing of minimum (summer and early fall) and maximum (spring) terrestrial input from piedmont and coastal plain rivers (Atkinson and Menzel 1985).

Terrestrially derived DOC on the continental shelf—Lignin phenols serve as an indicator of the presence of lignin-derived organic matter in seawater, but they do not represent the total lignin-derived organic matter. This discrepancy between material recoverable as oxidized lignin phenols and actual lignin-derived material is due, in part, to isolation methods. Only organic matter concentrated on the XAD-8 resin (operationally defined as humic substances) is analyzed for the presence of lignin phenols, with the result that any lignin-derived organics associated with the nonhumic fraction of DOC will be missed. Although it is difficult to quantify directly the total lignin-derived material in seawater because salts interfere with evaporative concentration of DOC, our comparisons of freshwater DOC concentrated by evaporation and on XAD-8 resin suggest that the bulk of the lignin-derived organic matter (~90%) is indeed associated with the humic fraction (Moran and Hodson unpubl.).

A more significant discrepancy between measured concentrations of lignin phenols and total lignin-derived DOC results from loss of chemical signal—structural changes during formation or subsequent microbial modification that render lignin-derived DOC unrecognizable by chemical methods. Comparisons of lignin-derived DOC quantified by radiotracer studies, which track lignin-derived C regardless of chemical modifications, with lignin-derived phenols quantified via cupric oxide oxidation and subsequent chromatographic analysis, which track lignin-derived C only if it retains its unique chemical structure, show that recognizable lignin phenols account for only 2–4% of total lignin-derived DOC from degrading *S. alterniflora* lignocellulose (Moran and Hodson 1990). Although similar radiotracer-chemical method comparisons have not been conducted for other vascular plant sources of shelf lignin, discrepancies are likely to be on the same order of magnitude. Finally, even for lignin that has retained its chemical signal, systematic underestimation of lignin phenol content may result from inefficient cupric oxide oxidation of lignin structural units. Oxidation efficiency is thought to be only 30% for *V* phenols (Sarkanen and Ludwig 1971), and values presented here have not been corrected for this possible inefficiency.

Although accounting for a fraction of lignin-derived material, concentrations of vanillyl lignin phenols can nonetheless be used to estimate the quantitative importance of terrestrially derived DOC in marine waters by comparing relative concentrations in seawater with likely terrestrial source waters (Meyers-Schulte and Hedges 1986). Detectable lignin phenols in the nearshore area of the shelf (defined as 0–10-m depth), when data from all cruises are considered, account for 0.03–0.10% of the total DOC (n = 11).

Based on the range of lignin phenol and DOC concentrations measured for a limited number of samples of likely sources of lignin to the shelf (Table 1), we estimated the rel-

ative contribution of terrestrially derived DOC to total DOC in nearshore waters with a simple mixing model:

$$(\%Lig_{shelf} \times 100)/\%Lig_{ter} = \%DOC_{ter}$$

where $\%Lig_{shelf}$ is the lignin phenol concentration in continental shelf samples expressed as a percentage of the total DOC, $\%Lig_{ter}$ is the lignin phenol concentration in terrestrial end-member (marsh and river) samples expressed as a percentage of total DOC, and $\%DOC_{ter}$ is the percentage of bulk DOC in shelf samples that is terrestrially derived. If it is assumed that the terrestrial end-member is a river similar in DOC composition to the Altamaha River (lignin phenols = 1.0% of total DOC; $n = 2$), 6% of the bulk DOC in the shelf nearshore stations is calculated to be terrestrially derived (average of all 0–10-m depth stations). Alternatively, if it is assumed that the lignin source material is a coastal salt marsh similar in DOC and lignin phenol concentrations to the Duplin River (lignin phenols = 0.18% of the total DOC; $n = 4$), 36% of the DOC in an average nearshore sample is calculated to be terrestrially derived (Table 1).

On the inner shelf (11–20-m depth stations), lignin phenols account for 0.01–0.13% of DOC ($n = 37$). If we assume that all lignin phenols are derived from a river similar to the Altamaha, 5% of the bulk DOC is terrestrially derived; if we assume that the source of all lignin phenols is a salt-marsh creek similar to the Duplin River, 26% of the DOC is terrestrially derived. Finally, on the mid- to outer shelf (21–61-m depth stations), lignin phenols account for 0.002–0.10% of the total DOC ($n = 21$), indicating 3% terrestrially derived DOC if lignin phenols are derived from a river similar to the Altamaha and 18% if lignin phenols are derived from a salt-marsh creek similar to the Duplin.

We currently have no information on the relative contributions of marsh- vs. riverine-derived DOM to the shelf with which to refine this simple model. Furthermore, the model is based on at least two very important assumptions. First, it is assumed that the lignin phenol concentrations measured in a limited number of marsh and river samples collected primarily during a 2-month period in 1988 are representative of all sources of terrestrial DOC to the shelf. We have little knowledge, however, of tidal, seasonal, or yearly variations in the concentrations of lignin-derived DOC in the rivers and coastal marshes. Second, lignin phenols are assumed to remain a constant percentage of total terrestrially derived DOC during the transport of organic matter to the shelf and its residence time there. The validity of this second assumption is examined below.

LP : DOC_{ter} ratio—Both biological and physical processes may act to alter the ratio of lignin phenols : total terrestrially derived DOC ($LP : DOC_{ter}$) as organic matter is transported from its sources in salt marshes and rivers to the shelf. For example, lignin-derived material is the least biologically reactive of the various components of vascular plant material, and *V* phenols in particular have a longer half-life than other lignin phenol families or carbohydrate moieties (Hedges and Weliky 1989). Preferential microbial utilization of nonlignin DOC, if occurring within the timespan of 1–2 months (average residence time for water on this portion of the shelf), would lead to an increase in $LP : DOC_{ter}$ and result in overestimation of the importance of terrestrially derived DOC by our simple mixing model. Conversely, other physical and biological processes may bring about a decrease in the $LP : DOC_{ter}$ ratio and result in an underestimation of the quantitative importance of terrestrially derived DOC.

As described above, microbial transformations of lignin-derived DOC may cause chemical changes in the lignin molecule that result in loss of lignin signal without mineralization of the C. Additionally, salt-mediated precipitation (Thurman 1985) of lignin-rich humic acids (Ertel et al. 1986) is known to occur as seawater and freshwater mix in coastal estuaries, a process that would preferentially remove the lignin-derived fraction of terrestrially derived DOC.

We can estimate the potential effect of preferential removal of nonlignin compounds on the $LP : DOC_{ter}$ ratio with information from laboratory studies of bacterial utilization of lignocellulose-derived DOC (Moran and Hodson 1989, unpubl.). After

initially high rates of mineralization during the first few hours of incubation in seawater, DOC derived from *S. alterniflora* lignocellulose was mineralized by natural marine bacteria at an average specific rate of 0.5% d^{-1} up to 30 d after formation of the DOC and regardless of the age (2 weeks to 9 months) of the particulate lignocellulosic detritus from which the DOC was formed. At a utilization rate of 0.5% d^{-1}, only 14% of lignocellulose-derived DOC would be mineralized during a 1-month period of residence on the shelf. Likewise, bacterial utilization of 1.7% of the bulk DOC from a Georgia blackwater river during 3 d of incubation (Meyer et al. 1987) extrapolates to <16% utilization over a 1-month period. Mineralization losses of this magnitude, even if utilization is completely restricted to nonlignin-derived compounds, are not enough to cause significant increases in the LP : DOC_{ter} ratio during transport of organic matter from river and marsh sources to the shelf.

The possibility of decreases in the LP : DOC_{ter} ratio can be investigated from the linear regressions of lignin phenol concentrations against salinity (statistically significant for three of the four cruises; Fig. 3) by predicting the lignin phenol content of marsh (28‰) and river (0‰) end-members. The regression lines predict that the lignin phenol content of marsh water emptying into the shelf is 6.3, 3.8, and 8.1 μg $liter^{-1}$ for the 1987 *Columbus Iselin,* 1987 *Blue Fin,* and 1989 *Blue Fin* cruises, while that of river water feeding into the shelf is 27.1, 14.8, and 31.2 μg $liter^{-1}$. These values are many-fold lower than measured values in the salt marsh and river during 1988 and 1990 (Table 2). Thus although there is good evidence that lignin phenols behave essentially conservatively in higher salinity (>31‰) waters once they are resident on the shelf, the above analysis predicts they may not be conservatively transported from their sources in terrestrial systems to the shelf (i.e. biological or physical lignin sinks may exist). Provided these sinks do not affect all components of the terrestrially derived DOC equally (i.e. provided they work preferentially on the lignin fraction), they would act to decrease the LP : DOC_{ter} ratio.

Two potential mechanisms for preferential losses of lignin phenols are the salt-mediated precipitation of humic material and the degradation-mediated loss of chemical signal from lignin-derived material. In the case of salt-mediated precipitation, freshwater (river) sources of lignin phenols would be more affected than brackish (marsh) sources, as precipitation of the humic acid fraction of DOC has been found to occur primarily at salinities between 5 and 20‰ (Sholkovitz 1976; Thurman 1985). Therefore, our mixing model predictions of the average contribution of terrestrially derived organic matter to the DOC pool of shelf water is more likely to be subject to underestimation when based on river end-members than when based on salt-marsh end-members.

Comparisons with previous models—Spatial and temporal distributions of dissolved lignin phenols can be examined in light of existing physical and biological models of the seaward transport of freshwater (and associated organic matter) across the shelf. Based on the salinity of shelf water and riverine inputs, Atkinson et al. (1978) estimated flushing time for freshwater on the shelf to be 2.7 months. Mechanisms for removal of freshwater from the shelf include entrainment of shelf water into meanders of the Gulf Stream (Atkinson et al. 1978), periodic spilling of freshwater northeastward across the shelf during times of northward wind stress and stratified conditions (primarily during spring and summer; Blanton and Atkinson 1983), and transport of freshwater south along the coast until entrainment in the Gulf Stream near Cape Canaveral during times of southwestward wind stress (primarily during autumn; Blanton 1981).

Lignin phenol distributions on the shelf during the October-November 1987 *Columbus Iselin* cruise are consistent with the suggested autumn pattern of southward transport along the Georgia and north Florida coasts. More importantly, however, they demonstrate the rapidity with which terrestrially derived material can be flushed from the shelf under certain conditions: over half the dissolved lignin phenols appeared to be removed from the shelf in a matter of days

during the gale-force winds of November 1987. This episode of very rapid flushing can be compared to the 2.7-month flushing average calculated from physical data (Atkinson et al. 1978).

Biological models of the importance of terrestrially derived organic matter on the shelf have been strongly influenced by the "outwelling" hypothesis of Odum (1968), which suggests that salt marshes (and rivers) export biologically available dissolved and particulate organic matter into estuaries and nearshore waters, thereby subsidizing secondary production on the shelf. Our lignin phenol data are consistent with this hypothesis to the extent that measurable material derived from vascular plants is being transported to the shelf, and we estimate that 6–36% of nearshore DOC originates in coastal salt marshes and rivers. However, our data cannot address the issue of the trophodynamic role of marsh- and river-derived DOC on the shelf because we lack information regarding the biological quality of exported material; if the exported DOC is biologically unavailable (due to age, origin, or both), its role in subsidizing bacterioplankton production on the shelf is questionable. However, Hopkinson (1985) found evidence that some portion of exported material is indeed biologically available, as community respiration on the shelf is greater than what can be expected from in situ primary production alone, at least for the nearshore region. The timing of the most heterotrophic periods suggested that both riverine inputs (peaking in winter and early spring) and marsh inputs (peaking in summer) are being utilized by the nearshore microbial community (Hopkinson 1985).

The presence of lignin-derived material on the shelf was first demonstrated by Gardner and Menzel (1974) in a survey of bottom sediments. They noted decreases in lignin-derived material as a percentage of total sediment organic matter along seaward transects (e.g. vanillin comprised 1.6% of sediment organic matter 30 km upstream from the mouth of the Ogeechee River but <0.02% 16 km offshore). This pattern parallels our results for lignin-derived DOC in the water column (vanillyl lignin phenols comprised 0.13% of the DOC in the Georgia nearshore but only 0.002% on the outer shelf). Both studies suggest an increasing importance for pelagic (plankton derived) material in organic matter pools of the shelf with distance seaward from coastal rivers and salt marshes.

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