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Sources and concentrations of vascular plant material in sediments of Buzzards Bay, Massachusetts, USA

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Abstract

Samples of surface sediment from Buzzards Bay and creek sediment from Great Sippewissett Marsh were analyzed for lignin and stable carbon isotope composition in 1984. The lack of change in composition of lignins in detritus of *Spartina alterniflora* over two years of decomposition and similar aldehyde/acid ratios of lignin oxidation products of plant and sediment samples indicated minimal diagenesis of lignins in sediments. Remains of non-woody angiosperm tissues made up the bulk of the vascular plant debris in Great Sippewissett Marsh and Buzzards Bay sediments. These plant remains were evenly distributed over the sampling area in Buzzards Bay. Based on model calculations, salt marshes potentially contributed a significant fraction of the total amount of vascular plant debris in coastal marine sediments. The bulk of the organic matter in Buzzards Bay sediments, however, was derived from phytoplankton; vascular plant remains made up only 5 to 7% of the total amount of organic carbon in these sediments.

Introduction

Estuarine and coastal marine environments receive marsh and land-derived organic matter originating from the detritus of vascular plants (Odum and de la Cruz, 1967; Day *et al.*, 1973; Hedges and Parker, 1976; Hedges and Mann, 1979 b). This organic matter, although varying widely in magnitude, may subsidize coastal production (Mann, 1982). In coastal Massachusetts, tidal flushing of salt marshes provides potential sources of vascular plant detritus to coastal waters such as Buzzards Bay. Valiela *et al.* (1982), for example, found that an amount of particulate matter equivalent to 20% of the net annual aboveground production of Great Sippewissett Marsh (one of many salt marshes around Buzzards Bay) was exported into Buzzards Bay. Analysis of fatty acids and sterols in sediments in Buzzards Bay also indicates some input of marsh plant material (Farrington *et al.*, 1977; Lee *et al.*, 1980).

Fluvial transport of terrestrial plant detritus may also add to the input of land-derived organic matter into Buzzards Bay since several small rivers (the Slocum, Weweantic, Acushnet) enter the bay from the northern shore. Such inputs may be significant in magnitude in some areas; Haines (1977) calculated that stream and river flow in Georgia, USA provide potential inputs of organic carbon into coastal waters comparable to that estimated for detrital inputs from salt marshes.

Lignins are complex, aromatic polymers of phenylpropanoid units occurring in cell walls of vascular plants, but are completely absent from marine algae and marine aquatic angiosperms such as *Zostera marina* (Brauns and Brauns, 1960; Swain, 1979). Due to their great abundance, characteristic occurrence in vascular land plants, and resistance to microbial degradation, lignins have been used as indicators of terrestrially-derived organic matter in marine sediments (Leo and Barghoorn, 1970; Gardner and Menzel, 1974; Hedges and Parker, 1976; Hedges and Mann, 1979 b).

We present here a study of the lignin geochemistry and carbon isotope composition of surface sediments within Great Sippewissett Marsh and in Buzzards Bay. Stations were chosen to provide a transition from a clearly marsh-dominated source of organic carbon to marine-dominated sources of organic carbon further away from marsh sources. The concentrations and types of vascular plant remains in sedimentary organic matter are reported and compared to the amounts of organic matter derived from marine sources.

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Materials and methods

Samples

Wood, leaf, and frond samples were collected in spring 1984 from living marine (*Spartina alterniflora, Zostera marina*) and terrestrial plants (*Pinus rigida, Quercus ilicifolia, Ammophila breviligulata*) and an alga (*Ascophyllum nodosum*) growing in Cape Cod, Massachusetts, USA. These species are abundant in coastal environments around Cape Cod and are potential sources of terrestrial organic matter to Buzzards Bay. Tissue samples provide at least one example from each of five categories of plant tissue types: nonvascular tissues and woody and non-woody tissues of gymnosperms and angiosperms. All samples were dried in an oven at 50 °C and ground to pass a 40 mesh (0.425 mm) sieve.

Sediment samples were taken from inside Great Sippewissett Marsh and then along a transect extending from the marsh out to the center of the bay (Fig. 1). Subtidal surface sediments from Buzzards Bay were collected with a Van Veen grab sampler. Samples were taken from the top 10 cm of bay sediments and were collected in duplicate from each location except for a single collection from Site 7. Marsh creek sediments were collected with an open-barreled, 8-cm diameter hand-held corer. The top 30 cm of creek sediment were sampled. Sediment samples were frozen, lyophilized, and ground to pass a 50 mesh (0.300 mm) sieve.

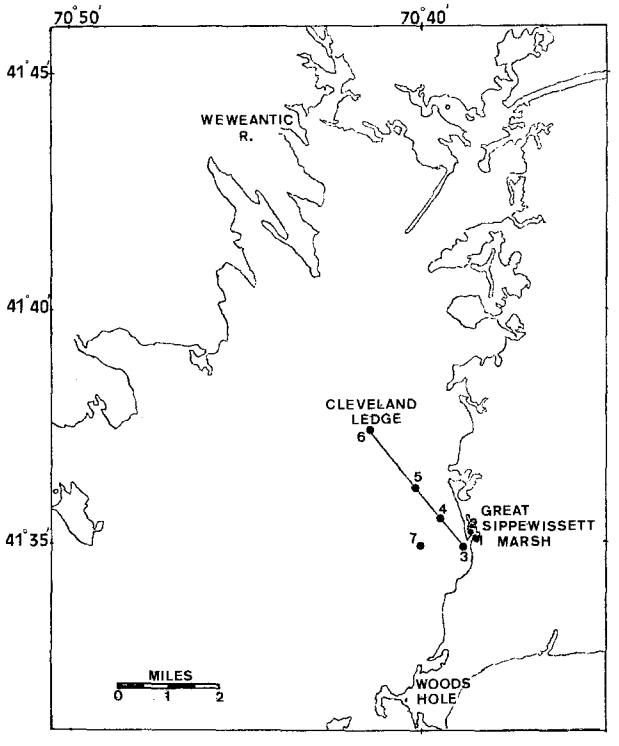

Fig. 1. Study area in Buzzards Bay off the coast of Cape Cod, Massachusetts, USA with location of sampling sites

Isotopic analyses

Samples (80 g) of sediment were acidified with 70 ml of 3N HCl to remove carbonates. Acidified samples were covered with aluminum foil and kept overnight at room temperature (25 °C). The samples were diluted with an equivalent volume of distilled water and dried in a forced air oven at 70° to 80 °C.

Stable carbon isotope compositions ($\delta^{13}C$) were determined for plant and duplicate sediment samples and are reported against the PDB carbon standard. These analyses were performed by Krueger Enterprises, Inc. (Cambridge, MA) and had an average precision ($\pm$ 1 SD) of 0.5‰.

Lignin oxidation product analyses

Cupric oxide oxidations of plant and sediment samples were performed according to Hedges and Ertel (1982). Cupric oxide oxidations were carried out in 10-ml Monel 'minibombs' sealed with Teflon-lined screw caps. The bombs were constructed by Parr Instrument Company (Moline, IL). Minibombs were first loaded with approximately 2.5×10^{-2} μCi of ring-labeled (U-^{14}C)hydroxyacetophenone in 50 μl of toluene and the solvent then completely removed under N_2. The radioactive tracer was used to estimate overall recovery of lignin-derived phenolic oxidation products (see below). Bombs were then charged with 1.00 g of powdered CuO (previously Soxhlet extracted with CH_2Cl_2), 50 mg of $Fe(NH_4)_2 \cdot 6\,H_2O$ (an O_2 scavenger), 7 ml of freshly boiled 2 N NaOH, and a stainless steel ball agitator. Sample loadings ranged between 1.0 and 2.5 g of sediment and 10 to 50 mg plant tissue per bomb.

After loading the solid components into each bomb, the bombs were placed inside an Atmos-bag (Aldrich Chemical Co., Milwaukee, WI), the bag purged with N_2 and sealed. The next day, the NaOH solution (previously boiled and also stored under N_2) was added to each bomb and the bombs sealed under N_2. Bombs were then removed from the bag and loaded into a 200-ml Parr bomb. Four of the minibombs fit snugly within the larger bomb. After sufficient water was added to cover just the top minibomb, the 200-ml bomb was sealed and placed in a heating chamber mounted on a platform shaker. The reaction was carried out at 170 °C $\pm$ 3 C° for 3 h with shaking.

The reaction mixture was then washed with 1N NaOH from each bomb into 50-ml Pyrex centrifuge tubes and centrifuged at 1 500 rpm for 10 min. The supernatant was decanted into 125-ml separatory funnels, and the sediment washed twice with 20 ml of 1N NaOH, treated with ultrasonic vibration to disperse the sediment, and centrifuged once again. The combined reaction mixture was then acidified with 15 ml of 6N HCl to pH 1 and extracted three times in succession with 20 ml of freshly distilled ethyl ether. The ether had been washed with a saturated aqueous solution of ferrous ammonium sulfate to remove

peroxides immediately prior to distillation. The combined ether extract was then passed through an anhydrous column of Na_2SO_4 (previously washed with 2 column volumes of CH_2Cl_2 and 1 column volume of ethyl ether) and the volume of ether reduced in a rotary evaporator to 1 to 5 ml. This volume was treated once more with anhydrous Na_2SO_4 to remove remaining water and then transferred with a Pasteur pipet to a 5-ml Reacti-vial (Pierce Chemical Co., Rockford, IL). The ether was removed under N_2. Solvents used in this procedure were obtained from Burdick and Jackson Chemical Co. (Muskegon, Michigan). Only reagent grade chemicals were used. The water was ultra-pure, Class I grade (Millipore). All glassware was soaked overnight in Count-Off (NEN), washed successively in Na_3PO_4-treated water, distilled water, alkaline methanol, and rinsed successively in distilled water and methanol, and then baked dry.

Gas chromatography of CuO oxidation products

Oxidation products were dissolved in 10 to 50 μl of pyridine containing 0.50 $\mu g\,\mu l^{-1}$ ethylvanillin as an internal standard. From 50 to 150 μl of BSTFA (Pierce Chemical Co.) were then added to form trimethysilyl derivatives of all organic carbons containing acidic hydrogens. Silylation was complete after 30 min at 90 °C. Trimethylsilyl derivatives were analyzed on a 30 m by 0.25 mm i.d. SE-30 fused silica capillary column (J & W Scientific, Inc., Rancho Cordova, CA) installed in a Varian 3 700 gas chromatograph fitted with a flame ionization detector. The column was temperature programmed from 100° to 260 °C at 4 C° min^{-1} with an initial hold of 4 min and a final hold of 3 min. The injection was split at a ratio of approximately 1:50 with a column flow rate (initial) of 1 ml min^{-1} of helium. Nitrogen was used as the make-up gas (40 ml min^{-1}). Injector and detector temperatures were both 300 °C.

Response factors of the Me_3Si derivatives of the major lignin-derived phenols were determined relative to the GC internal standard (ethylvanillin) by injection of aliquots of a standard mixture at the beginning of each series of GC analyses and after approximately every sixth sample. Silylated standard mixtures were prepared from a multicomponent (0.5 mg ml^{-1} of each component, in pyridine) master standard. Yields of the Me_3Si derivatives (W_x) were then determined as

$$W_x = \frac{A_x \times W_i}{A_i \times K_x}$$

where A_x and A_i are the peak areas of the phenolic derivative and internal standard, respectively (area = height × width at 1/2 height), W_i is the amount (mg) of internal standard added, and K_x is the detector response factor for the Me_3Si derivative with respect to that of the internal standard.

Recoveries of lignin-derived phenols were determined using ^{14}C-*p*-hydroxyacetophenone added prior to charging and averaged 60% overall for six pairs of marsh and bay sediment analyses. Following derivatization triplicate 1 to 2.5% aliquots of the reaction mixture were counted in 10 ml of scintillation cocktail (containing 5.0 g of PPO (2,5-diphenyloxazole) and 100 mg POPOP (1,4-bis[5-phenyl-2-oxazolyl]-benzene) per liter of scintillation grade toluene)). Counts of aliquots of the silylated mixture were made with an average accuracy (% SD) of 4.6% (based on triplicate analyses of 2.5% aliquots from 15 samples). The ^{14}C parent spiking material was counted with similar accuracy.

Yields of lignin-derived phenols were determined with an overall reproducibility [% mean deviation; $(100 \Sigma | X - \bar{X} |)/n\bar{X}$] of 23% (based on duplicate analyses of six sets of bay and marsh sediment samples). Procedural blanks containing all reagents yielded less than 0.5 μg $sample^{-1}$ for each of the lignin-derived phenols. The analytical procedure had a detectability limit of approximately 10 μg of lignin in 1 g dry weight of sediment.

Results

Plants

Eleven of the major index phenols from the oxidation product mixtures were selected as indicators of lignin in plant and sediment samples (Table 1). Oxidation of the nonvascular marine brown alga *Ascophyllum nodosum* produced *p*-hydroxyl phenols (i.e. *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone, and *p*-hydroxybenzoic acid) as the major oxidation products. Lignins were absent in this alga, as shown by the very low yields of methoxyl-substituted phenols characteristic of lignin.

The two tissues from pitch pine (*Pinus rigida*) yielded vanillyl phenols (i.e. vanillin, acetovanillone, and vanillic acid) as their major oxidation products (Table 1). Vanillin, an aldehydic phenol, was the predominant reaction product from these gymnosperm tissues and accounted for 50 to 60% of the total amounts of lignin oxidation products (LOP). Small amounts of *p*-hydroxyl and cinnamyl phenols were detected, but syringyl phenols were almost entirely absent. Lignins of pitch pine, as found for other gymnosperms (Sarkanen and Ludwig, 1971), are thus composed largely of vanillyl monomers.

Angiosperm tissues (except *Zostera marina*) produced syringyl phenols (i.e. syringealdehyde, acetosyringone, and syringic acid) as oxidation products in addition to the vanillyl phenols typical of gymnosperms (Table 1). Aldehydic reaction products (i.e. vanillin and syringealdehyde) again predominated. *Z. marina* produced only small amounts of vanillyl phenols and no syringyl phenols as oxidation products, indicating an absence of lignin in its tissues. Tissues of aquatic and submarine vascular plants generally do not contain lignins (Den Hartog, 1970; Swain, 1979).

Table 1. Lignin oxidation products (mean ± 1 SD) from CuO oxidation of tissues from five different vascular plants and one nonvascular marine brown alga

Species	Composition, %										
	p-hydroxyl phenols			Vanillyl phenols			Syringyl phenols			Cinnamyl phenols	
	Ph	Po	Pa	Vh	Vo	Va	Sh	So	Sa	Co	Fa
Nonvascular producer											
Ascophyllum sp.*	83	6	3	0	1	0	0	0	0	0	0
Vascular plants											
Pinus rigida, branch	7 (0.7)	2 (0)	3 (0.7)	56 (4.2)	12 (2.1)	11 (0.7)	1 (0)	0 (0)	0 (0)	1 (0)	9 (0.7)
P. rigida, needles	4 (0)	1 (0)	5 (0.7)	62 (4.9)	9 (1.4)	8 (1.4)	0 (0)	0 (0)	0 (0)	8 (0.7)	5 (0)
Quercus ilicifolia, branch	1 (1.1)	0 (0)	1 (0)	28 (2.8)	6 (1.4)	4 (0.7)	40 (2.1)	11 (1.4)	6 (0.7)	1 (0.5)	3 (0.7)
Q. ilicifolia, leaves	11 (1.4)	1 (0.7)	11 (0.7)	16 (1.4)	3 (0.7)	4 (0.7)	18 (0.7)	5 (0.7)	3 (0)	25 (0.7)	4 (0.7)
Spartina alterniflora, stem	3 (0.7)	2 (0.7)	1 (0)	24 (1.4)	5 (0.7)	3 (0)	14 (0.7)	13 (2.1)	4 (1.4)	16 (1.4)	17 (0)
S. alterniflora, detritus	5	2	1	29	4	3	21	11	5	12	8
Ammophila breviligulata (stem)	4 (2.1)	0 (0)	1 (0)	13 (2.1)	2 (0)	2 (0)	8 (2.1)	10 (0.7)	3 (0)	25 (3.5)	35 (3.5)
Zostera marina *	55	14	8	18	0	1	0	0	0	5	0

Abbreviations: Ph, *p*-hydroxybenzaldehyde; Po, *p*-hydroxyacetophenone; Pa, *p*-hydroxybenzoic acid; Vh, vanillin; Vo, acetovanillone; Va, vanillic acid; Sh, syringealdehyde; So, acetosyringone; Sa, syringic acid; Co, *p*-coumaric acid; Fa, ferulic acid

* Analysis not repeated due to absence of lignin

Table 2. Lignin oxidation product parameters for vascular plant and marine brown algal tissues; V = vanillyl phenols (mg per 100 mg OC); S = syringyl phenols (mg per 100 mg OC); C = cinnamyl phenols (mg per 100 mg OC); Λ = V + S + C. Values of V, S, C, and Λ are means (± SD) based on duplicate analysis of each sample, except for single analyses of tissues of *Zostera marina* and *Ascophyllum nodosum* which contained no lignin

	V	S	C	S/V	C/V	Λ	$\delta^{13}C$*
Alga							
Ascophyllum nodosum	0.07	0	0	0	0	0.07	−15.0
Vascular plants							
gymnosperms:							
Pinus rigida, branch	7.6 (0.4)	0.1 (0.01)	1.0 (0.1)	0 (0)	0.1 (0)	8.8 (0.5)	−29.5
Pinus rigida, needles	5.7 (0.6)	0 (0)	0.9 (0.2)	0 (0)	0.2 (0)	6.6 (0.7)	−30.0
angiosperms:							
Quercus ilicifolia, branch	5.0 (0.5)	7.4 (0.7)	0.5 (0.1)	1.5 (0)	0.1 (0)	12.9 (1.2)	−29.8
Quercus ilicifolia, leaves	1.6 (0.1)	1.7 (0.1)	2.0 (0.1)	1.1 (0.1)	1.3 (0.2)	5.3 (0.1)	−26.3
Spartina alterniflora, stem	6.1 (1.1)	5.9 (0.7)	6.4 (0.8)	1.0 (0.1)	1.1 (0.1)	18.4 (2.6)	−12.5
Ammophila breviligulata, stem	2.4 (0.3)	2.9 (0.6)	8.9 (3.3)	1.2 (0.1)	3.7 (1.0)	14.2 (4.1)	−25.4
Zostera marina, stem	0.2	0	0.1	0	0.5	0.3	−9.0

* $\delta^{13}C$ values are reported against the PDB carbon isotope standard

Table 3. Lignin oxidation products from samples of surface sediments of Buzzards Bay and creek sediments from Great Sippewissett Marsh

Site	Composition, %[a]										
	p-hydroxyl phenols			Vanillyl phenols			Syringyl phenols			Cinnamyl phenols	
	Ph	Po	Pa	Vh	Vo	Va	Sh	So	Sa	Co	Fa
Marsh sites											
1	23 (2.1)	8 (1.4)	6 (2.1)	12 (2.8)	3 (0)	4 (0)	16 (0.7)	5 (0.7)	3 (0.7)	14 (3.5)	10 (2.1)
2	9 (1.4)	7 (4.2)	4 (2.1)	22 (2.8)	4 (0.7)	3 (0.7)	18 (7.1)	6 (1.4)	3 (0)	14 (0)	11 (1.4)
3[b]	30 (2.8)	n.d.	19 (3.5)	36 (0.7)	n.d.	8 (0.7)	n.d.	1 (1.4)	n.d.	7 (2.1)	1 (1.4)
Bay sites											
4	22 (1.4)	11 (2.8)	8 (2.8)	18 (4.9)	2 (0.7)	2 (0.7)	2 (1.4)	2 (0.7)	1 (0)	2 (1.4)	31 (5.7)
5	12 (2.1)	7 (0)	6 (0.7)	24 (0.7)	4 (0)	4 (0)	13 (1.4)	4 (0.7)	2 (0)	13 (2.8)	13 (2.1)
6	34 (1.4)	8 (0.7)	8 (1.4)	17 (2.8)	4 (0)	3 (0)	7 (0)	3 (0.7)	2 (0)	6 (0)	9 (5.7)
7[c]	46 (7.0)	10 (5.5)	7 (1.7)	8 (1.2)	2 (0)	5 (0.6)	7 (1.2)	3 (0.7)	2 (0.6)	8 (1.5)	5 (5.5)

Abbreviations: Ph, *p*-hydroxybenzaldehyde; Po, *p*-hydroxyacetophenone; Pa, *p*-hydroxybenzoic acid; Vh, vanillin; Vo, acetovanillone; Va, vanillic acid; Sh, syringealdehyde; So, acetosyringone; Sa, syringic acid; Co, *p*-coumaric acid; Fa, ferulic acid

[a] Mean (± 1 SD) based on analysis of duplicate samples from each site

[b] Sample taken from a sandbar and contained very low amounts of organic matter

[c] Mean (± 1 SD) based on triplicate analysis of one sample over a range of 0.5, 1.0, and 5.0 g

Non-woody angiosperm tissues produced higher concentrations of cinnamyl phenols (i.e. *p*-coumaric and ferulic acid) than the corresponding woody tissues from the same plant (Table 1). Cinnamyl phenols occurred in highest concentrations in grasses, accounting for 1/3 to 2/3 of the total yield of LOP in these samples. Cinnamyl phenols may thus be used as indicators of non-woody angiosperm tissues, since they were nearly absent from the LOP mixture obtained from woody tissues.

Since different sources vary in the abundance of different lignin oxidation products, selected ratios of these products can more clearly distinguish the nonvascular and major vascular plant types (Table 2). *Ascophyllum nodosum* was easily distinguished from vascular plants by the low yield of vanillyl phenols ($V \sim 0$) and low total yield of lignin-derived phenols ($\Lambda \sim 0$). Angiosperms produced significant amounts of syringyl phenols ($S > 1$ and $S/V > 0$) and could be readily distinguished from gymnosperm tissues. Little difference was found between the yields of cinnamyl phenols from woody and non-woody (needle) tissues of the gymnosperm *Pinus rigida*. The C/V ratio was relatively low in these tissues. Non-woody tissues of angiosperms could be distinguished from the corresponding woody tissues by their lower production of syringyl and vanillyl phenols (cf. leaf and branch tissues of *Quercus ilicifolia*, Table 2) and their production of appreciable amounts of cinnamyl phenols ($C > 1$ and $C/V > 0$).

Carbon isotopic compositions of the vascular plants and alga fell within a range of −9.0 to −30.0‰ (Table 2). *Spartina alterniflora*, a C_4 plant, had $\delta^{13}C$ values of −12.5‰. The $\delta^{13}C$ range (−25.4 to −30.0‰) of the other terrestrial plants in Table 2 lay within the range typical of C_3 plants (Smith and Epstein, 1971). The marine brown alga *Ascophyllum nodosum* had a $\delta^{13}C$ value of −15.0‰, the same as reported for a brown macroalgae *Sargassum* sp. (Hedges and Parker, 1976). Marine phytoplankton range from −18.0 to −22‰ (Degens, 1969; Haines, 1977; Gearing *et al.*, 1984).

Sediments

Measurable amounts of lignin-derived phenols were obtained from the sediments sampled in Great Sippewissett Marsh and Buzzards Bay. The production of all eleven index phenols in the characteristic abundances observed indicated the presence of lignins in the sediments (Table 3).

The concentrations of *p*-hydroxyl phenols were higher in sediments (Table 3) than in vascular plants (Table 1), presumably due to contributions from nonvascular sources. Marine algae such as *Ascophyllum nodosum* yield high amounts of *p*-hydroxyl phenols as oxidation products (Table 1).

Table 4. Lignin oxidation product parameters for samples of surface sediments of Buzzards Bay and creek sediments from Great Sippewissett Marsh; V = vanillyl phenols (mg per 100 mg OC); S = syringyl phenols (mg per 100 mg OC); C = cinnamyl phenols (mg per 100 mg OC); Λ = V + S + C; Σ = lignin-derived phenols (mg of vanillyl, syringyl, and cinnamyl phenols per 10 g sediment). Values of V, S, C, and Λ are means (± 1 SD) based on analysis of duplicate samples from each site

Site	V	S	C	S/V	C/V	Λ	Σ	$\delta^{13}C$[c]
Marsh sites								
1	0.35	0.41	0.42	1.19	1.27	1.17	0.08	− 16.4
	(0.13)	(0.09)	(0.004)	(0.19)	(0.47)	(0.21)		(1.0)
2	1.55	1.49	1.33	0.95	0.87	4.37	0.48	− 15.4
	(0.2)	(0.41)	(0.002)	(0.14)	(0.10)	(0.61)		(0.4)
3[a]	0.22	0.005	0.38	0.03	0.17	0.27	0.005	− 19.3
	(0.03)	(0.007)	(0.011)	(0.03)	(0.07)	(0.01)		(1.2)
Bay sites								
4	0.29	0.07	0.49	0.23	1.64	0.86	0.25	− 20.4
	(0.06)	(0.07)	(0.24)	(0.21)	(0.52)	(0.37)		(0.2)
5	0.35	0.20	0.28	0.57	1.40	0.84	0.28	− 20.3
	(0.01)	(0.01)	(0.06)	(0.04)	(0.35)	(0.06)		(0.1)
6	0.31	0.15	0.20	0.48	0.63	0.66	0.17	− 19.9
	(0.06)	(0.05)	(0.12)	(0.08)	(0.28)	(0.24)		(0)
7[b]	0.25	0.17	0.21	0.70	0.89	0.62	0.23	− 19.9
	(0.04)	(0.04)	(0.09)	(0.23)	(0.44)	(0.07)		

[a] Sample taken from a sandbar – values only approximate due to extremely low yields of lignin-derived phenolics

[b] Mean (± 1 SD) based on triplicate analysis of one sample over a range of sediment dry weights of 0.5, 1.0, and 5.0 g

[c] $\delta^{13}C$ values are reported against the PDB carbon isotope standard

Values of V, S, and C were lower in sediments (Table 4) than in plants (Table 2) due to dilution of vascular plant material by lignin-free marine organic matter. Ratios of S/V and C/V are defined solely in terms of lignin-derived phenols, and are thus unaffected by inputs of nonlignified materials. S/V ratios for Bay sediments indicate that angiosperms contributed a significant fraction of the lignin in these nearshore sediments, while C/V ratios indicate the presence of lignins from non-woody tissues (Table 4). Similar results were obtained for marsh creek sediments, but Site 3, located in a sandbar at the mouth of the marsh, was an exception. Yields of lignin oxidation products were so low at this site that it was difficult to obtain a reliable determination of S/V and C/V for this sample. Relative amounts of lignins in samples of sediments from Buzzards Bay, as indicated by yields of lignin-derived phenols (Λ = 0.62–0.86) were similar to amounts generally present in bay and continental shelf sediments (Λ = 0.1–9, Hedges *et al.*, 1982).

Stable carbon isotope values of sediments from the four sites in the Bay were similar, with a mean of –20.1‰, and fell within the range generally cited for marine sediments (–20.1 to –23.8‰, Gearing *et al.*, 1984). The mean value is also comparable to the value for phytoplankton in Narragansett Bay, Rhode Island, USA ($\delta^{13}C$ = –21.3 ± 1.1‰; Gearing *et al.*, 1984).

Discussion

Stability of lignin

Comparison of the LOP composition of newly senesced tissue of *Spartina alterniflora* with that of 23-month old detritus of *S. alterniflora* indicated that little change occurred over two years of decomposition of litter (Table 2). Both tissues still yielded vanillyl and syringyl phenols in weight ratios of 1 to 1, indicating that the less condensed syringyl moieties in lignins were not attacked selectively. The concentration of cinnamyl phenols in 23-month old detritus, however, was somewhat lower than in the younger detritus (Table 2). These phenols are bound to lignins and other cell wall components by labile ester linkages (Smith, 1955; Higuchi *et al.*, 1967) and thus can be degraded more rapidly than the other structural units of lignins.

Diagenesis of lignins in sedimentary organic matter should further be revealed by decreases in aldehyde/acid ratios of oxidation products, since lignin decomposition is mainly an oxidative process that results in an increased content of carboxylic acids and a concomitant decrease in content of aldehydes (Ishikawa *et al.*, 1963; Grushnikov and Antropova, 1975). Ratios of aldehyde/acid within the vanillyl (V_h/V_a) and syringyl (S_h/S_a) families of phenols

were determined for plant (excluding *Ascophyllum nodosum* and *Zostera marina* which contained no lignin) and sediment samples (values calculated from data in Tables 1 and 3). The overall mean values $[(V_h/V_a+S_h/S_a)/n]$ of 5.9 and 4.9 for aldehyde/acid ratios of plant and sediment samples were not significantly different ($t=1.36$, n.s.), however, and indicate that oxidative degradation of lignins in sediments in Buzzards Bay had not occurred to any great extent.

Distribution of lignins in sediments

Absolute concentrations of lignins, as indicated by Σ values (mg of lignin-derived phenols per 10 g of sediment) and yields of LOP (Λ) did not vary much in sediments in Buzzards Bay (Table 4). Σ values for marsh creek sediments were more variable, with the lowest value occurring in the sediment from a sandbar at the mouth of the marsh.

The range of S/V and C/V values from Bay sediments (Table 4) was narrower than that from plants (Table 2). The uniformity of lignin concentrations in Bay sediments, in conjunction with the similarity of the index phenol composition obtained from these sediments, suggest that vascular plant debris is well mixed and evenly distributed in sediments of Buzzards Bay.

Characterization of lignin sources

A notion of the origin of the remains of vascular plants in marsh and bay sediments can be obtained by plotting S/V and C/V values for the sediment samples, and comparing these to ranges of values for the four major types of vascular plant tissues (Fig. 2). The sediments tend to fall within the region characteristic of non-woody angiosperms. These sediments must be essentially free of woody remains, since additions of even small amounts of woody material significantly reduce C/V ratios (Hedges *et al.*, 1982).

The amount of vascular plant remains in the total sedimentary organic mixture was obtained by comparing a value of Λ calculated for vascular plant remains alone with the measured value of Λ for the sediment. A Λ value of 12.6 (equal to the mean value for all non-woody angiosperms except *Zostera marina*, Table 2) was used as the value for the mixture of vascular plant material in the sediments, based on the assumption that the vascular plant mixture is derived almost entirely from non-woody angiosperms, as indicated above. Since the measured value of Λ for each sediment is determined for total sedimentary organic carbon and is diminished in direct proportion to the amount of lignin-free (i.e. marine) organic carbon present, the ratio of the measured Λ to the value of Λ calculated for vascular plant remains alone corresponds to an estimate of the percentage of vascular plant remains in the sedimentary organic mixture.

Ratios of calculated to measured Λ for Bay sediments show that sediments from Buzzards Bay contain only 5 to 7% of their total organic material as vascular plant remains (Table 5). Higher percentages of vascular plant remains occurred in marsh creek sediments, but these remains still made up at most 1/3 of the total organic matter in these sediments.

A second approach to determining the percentages of vascular plant remains in marsh and bay sediments is by a correlation plot between Λ and $\delta^{13}C$ (Fig. 3). The values of $\delta^{13}C$ and Λ for marine producers and vascular plants differ (see open symbols in Fig. 2). These values are the endmembers of the mixing line for the organic mixtures

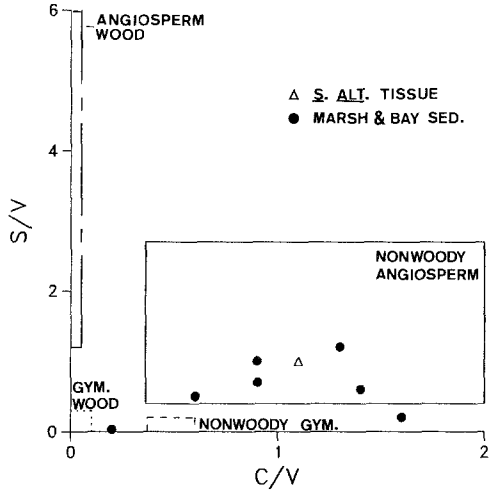

Fig. 2. Plot of lignin oxidation product parameters of the terrestrial component of organic matter in samples of surface sediments from Buzzards Bay and creek sediments from Great Sippewissett Marsh and ranges for gymnosperm woods, non-woody gymnosperm tissues, angiosperm woods, and non-woody angiosperm tissues. The ranges for the four plant groups were adapted from Hedges and Mann (1979a)

Table 5. Percentages of vascular plant debris and marine organic matter in samples of surface sediment from Buzzards Bay and creek sediment from Great Sippewissett Marsh. Percentages were determined from ratios of calculated to measured Λ values and from correlation plots of $\delta^{13}C$ vs Λ and are reported with distance from shore

Site	Distance offshore (km)	% Vascular plant debris		Marine[b] (%)
		Λ ratios	Λ vs $\delta^{13}C$	
Marsh sites				
1	0	9	15	88
2	0	35	29	68
3[a]	0.1	2	5	96
Bay sites				
4	0.6	7	5	94
5	1.4	7	5	94
6	2.8	5	5	95
7	1.5	5	5	95

[a] Sample from sandbar at the mouth of the marsh
[b] Based on the average of the determinations of % vascular plant debris

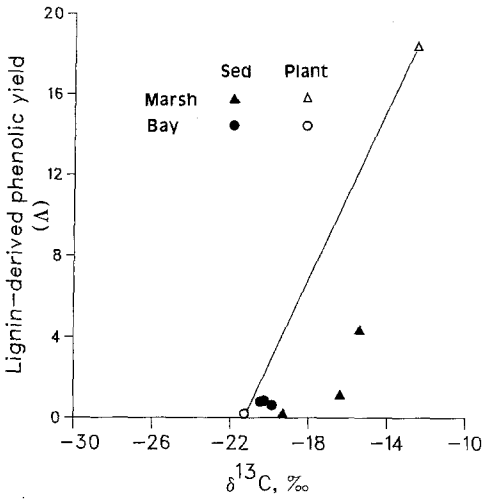

Fig. 3. Plot of Λ (mg of lignin-derived phenolics per 100 mg OC) vs $\delta^{13}C$ for samples of surface sediment from Buzzards Bay and creek sediment from Great Sippewissett Marsh

found in marsh and bay sediments. The Λ and $\delta^{13}C$ values of *Spartina alterniflora* (Table 2) were chosen to represent the vascular plant endmember since *S. alterniflora* is a likely source for the bulk of the non-woody angiosperm remains in marsh and bay sediments (see below) and, due to the high values of Λ for *S. alterniflora,* lead to a conservative estimate of the percentage of vascular plant remains in bay sediments.

Marine phytoplankton have a $\delta^{13}C$ of −21.3‰ (Gearing *et al.,* 1984) and a Λ value of 0 (since they lack lignin). These values were considered to be representative of the purely marine material in the sediments. The mixing line thus represents a range of concentrations of vascular plant material in organic sedimentary mixtures extending from zero at $\Lambda = 0$ to 100% at $\Lambda = 18.4$. The location of each data point along the mixing line then provides an estimate of the percentages of vascular plant remains actually found in the sediment. Since the points did not fall directly on the line, the point on the line closest to the point for each sediment was selected for measurement (Fig. 2). These measurements again indicate that sediments from Buzzards Bay contained low concentrations of vascular plant remains. Slightly higher concentrations of vascular plant debris occurred in marsh creek sediments (Table 5). Approximately 95% of the sedimentary organic carbon in Buzzards Bay sediments was derived from marine sources.

Assuming that the $\delta^{13}C$ of the source organic matter was not altered during diagenesis, the data plotted in Fig. 2 further show that there is organic matter derived from a source other than marine phytoplankton or *Spartina alterniflora* in Bay sediments. Significant changes in $\delta^{13}C$ (i.e. greater than 2‰) have generally not been seen during decomposition of plant material (Eadie and Jeffrey, 1973; Haines, 1977; Fry and Sherr, 1984). Thus, the deflection of the points for all sediment samples to the right, away from the mixing line, most likely indicates that there are significant inputs of organic matter with carbon isotope compositions more positive than *S. alterniflora. Zostera marina* was the only plant measured that had $\delta^{13}C$ values more positive than *S. alterniflora.* The concentrations of *Z. marina* remains in the organic sedimentary mixtures were approximately determined as the distance away from the mixing line towards the point for *Z. marina* ($\delta^{13}C = -9.0$, $\Lambda = 0.3$). Based on these estimations, remains of *Z. marina* made up 7% of the total organic matter in sediments in Buzzards Bay and 30 to 35% of the total organic matter in sediments in creeks in Great Sippewissett Marsh. These calculations, although preliminary, suggest that *Z. marina* is an important source of vascular plant debris in marsh and Bay sediments.

Importance of marsh plant export as a source of vascular plant debris in Buzzards Bay sediments

Salt marshes are plausible sources for inputs of the non-woody angiosperm remains (other than *Zostera marina*) that made up the bulk of the lignin-containing vascular plant debris in marsh and Bay sediments. We estimated that 7.2×10^{12} g of sediment were present in the top 1 cm of sediment in the Bay using a value of 1.2 g/cm^3 for the bulk density of Buzzards Bay sediments (Preiss, 1968; Summerhayes *et al.,* 1977) and the dimensions of the Bay (ca 600 km^2, Hough, 1940). If the sediment has an average organic carbon content of 0.3% (unpublished data) and sedimentary organic carbon consists of 6% vascular plant material, then approximately 1.3×10^6 kg of vascular plant debris are contained in the top 1 cm of Buzzards Bay sediment. Great Sippewissett Marsh exports 1.65×10^4 kg of POC yr^{-1} and makes up 4 to 5% of the total area of marshland around Buzzards Bay (Valiela *et al.,* 1978; Valiela, 1983). The salt marshes around Buzzards Bay are similar to Great Sippewissett in topography, vegetation, and hydrography, so we extrapolated our results to other marshes around the Bay, and calculated an export of 3 to 4×10^5 kg POC annually from marshes into the Bay. This annual export amounts to 25 to 30% of the total amount of vascular plant debris in the top 1 cm of surface sediment in Buzzards Bay. These calculations are based on the assumption that sediments in Buzzards Bay are relatively homogeneous throughout the Bay. While this assumption is not strictly true (Hough, 1940; Sanders, 1958), a large proportion of Buzzards Bay sediments consists of very homogeneous silt deposits in the deeper portions of the Bay or medium to fine-grained sands with fairly constant concentrations of organic matter (Hough, 1940; Moore, 1963). In addition, Hedges *et al.* (1984) showed that variations in sediment texture that can influence the distribution of bulk organic matter apparently have little influence on the concentration of lignin contained in the sedimentary organic mixture. These calculations thus provide an estimate for contributions of vascular plant material from marshes to coastal sediments and point out that these exports may contribute a significant fraction of the total amount of vascular plant debris in coastal marine sediments.

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