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Terrestrial organic matter in surface sediments of the Baltic Sea, Northwest Europe, as determined by CuO oxidation

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Abstract—We studied the distribution and composition of terrestrial organic matter in sediments of the Baltic Sea (Northwest Europe). To this end, surface sediments from all basins of the Baltic Sea were analyzed for their lignin oxidation product yields and compositions after CuO oxidation. Lignin oxidation product yields depend on the concentration of organic carbon and range from 0.4 to 10.2 mg g^{-1} total organic carbon (TOC). On the basis of an average of 13 mg g^{-1} TOC in two river sediments, we estimate that the upper limit of terrestrial organic matter in Baltic Sea sediments is 30% of TOC. The contribution of terrestrial organic matter differed between the individual basins, depending on the distance from runoff discharge areas and on the area occupied by each submarine catchment. Lignin composition showed a relative decrease of angiosperm tissue from the Southwest to the Northeast, reflecting the shift from temperate to boreal vegetation type. The Gotland and the Bornholm Seas, which have no significant river input, were characterized by high relative contributions of nonwoody, strongly altered material. The source may either be a mixture of pollen and peat being eroded from geologically older strata at the seafloor or laterally advected material from the other basins. However, the pronounced compositional differences between the basins indicated that interbasin transport of terrestrial organic matter is less important than direct river input, although river signals can only be traced at a few places in the Baltic Sea. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

Organic matter in marine sediments is usually ascribed to primary production in the overlying water column (Berger et al., 1989). Recent work has, however, shown that considerable portions of marine sedimentary organic matter may originate from terrestrial sources (Hedges, 1992) that are transported over considerable distance to the depositional areas. This allochtonous organic carbon is added to the autochtonous marine organic matter and dilutes it. The added terrestrial contribution has consequences for the interpretation of organic molecular biomarker data aimed to reconstruct marine paleoenvironments, as well as for the veracity of global or regional reconstructions of marine organic carbon burial.

Most of the terrestrial material transported into the sea is deposited in near-shore areas on the shelf (Gough et al., 1993). As a consequence, the proportion of terrestrial organic matter in marine sediments decreases with increasing distance from land (Hedges et al., 1997) and varies from ≈60% close to the coast to 10% on the slopes and outer shelf areas (Hedges and Mann, 1979b). Quantitation of terrestrial organic matter in marine sediments is of particular importance in shelf seas that experienced significant changes in land use and anthropogenic impacts over the last century. One example is the Baltic Sea, which receives runoff from a large (1.67×10^6 km^2) and densely populated (80×10^6 inhabitants) catchment. Its depositional basins have accumulated increased amounts of organic carbon during the last 50 yr (Emeis et al., 2000), attributed commonly to higher marine productivity in the wake of steeply rising nutrient inputs (Jonsson et al., 1990).

The Baltic Sea has a large freshwater surplus of 1800 m^3 s^{-1} (Omstedt, 1990) and is connected to the Ocean via the Kattegat and the Skagerrak (Fig. 1). The surplus of freshwater originates mainly from the Skandinavian rivers in the northern part and results in a salinity gradient from the northeast (mean salinity in the northern part of the Gulf of Bothnia is 2) to the southwest (mean salinity at the Danish Straits is 25). It also causes a stable midwater halocline separating a freshwater cap from saltier deep water that originates in the Kattegat area (Ehlin, 1981). The bottom topography is characterized by a series of basins separated by sills that restrict the bottom water circulation and limit material exchange between the basins. The basins below the halocline are depositional areas for sediments (≈30% of the seafloor), whereas the seafloor above the halocline is nondepositional or erosional. Relevant areas of seafloor erosion are areas above wave base (≈20 m water depth) in the South and Southwest and areas of isostatic uplift in the Northwest.

The varied vegetation of the drainage basins and the division into several basins of different salinity make the Baltic Sea an excellent object for studying the input and transport of terrestrial organic matter to marine sediments. The catchment straddles the transition between the temperate and the boreal vegetational zones (Walter and Breckle, 1986). In addition, the southern part of the drainage basin has a higher percentage of agricultural land than the North where forests dominate (Table 1). Terrestrial organic matter in the northern drainage basin is thus dominated by conifer debris, whereas broad-leafed tree debris and nonwoody material contribute substantially to terrestrial organic matter in the South. Because the Baltic Sea is small and well compartmentalized, it offers a unique opportunity to follow basin-to-basin transport of terrestrial organic

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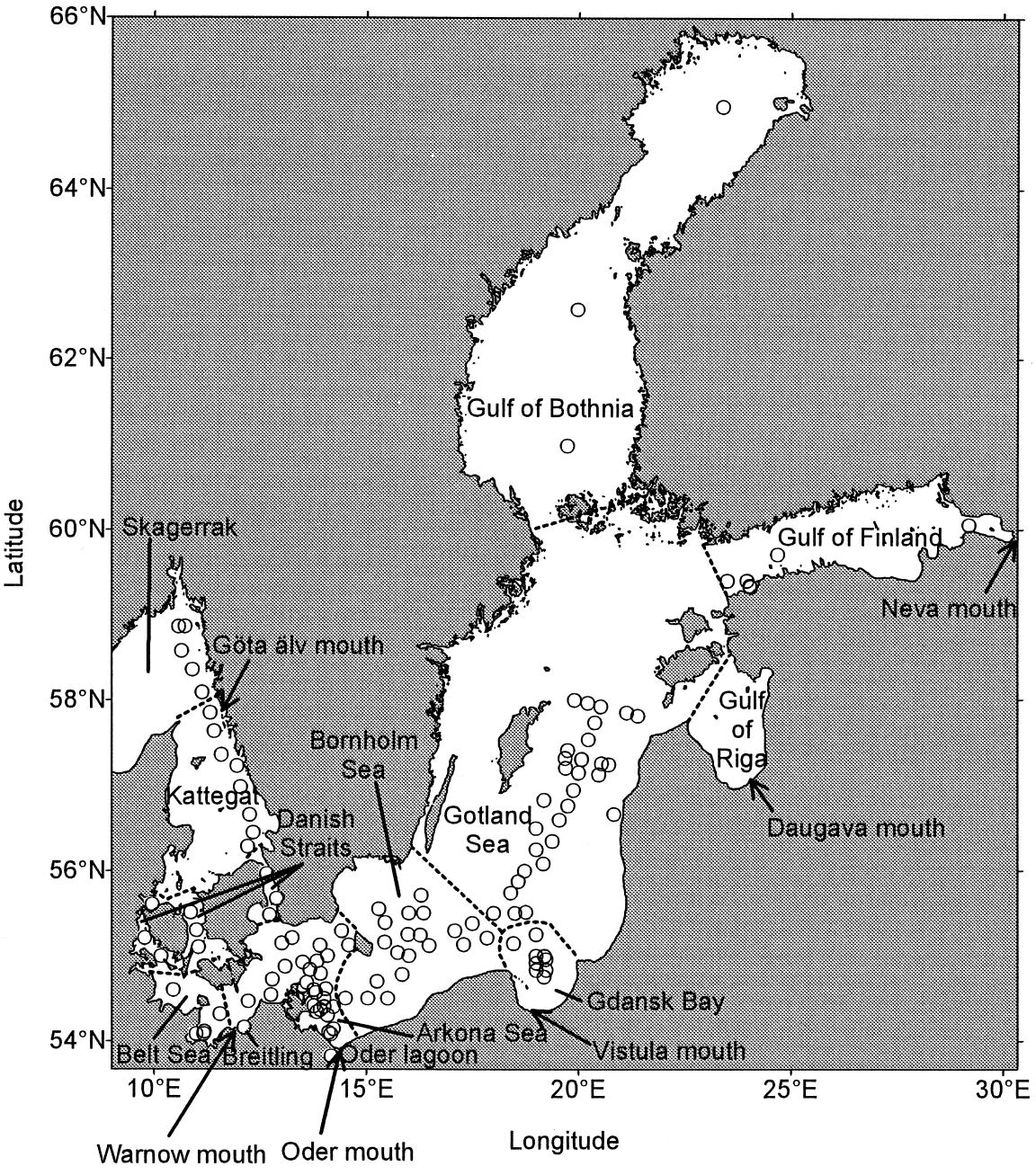

Fig. 1. The individual Baltic Sea basins and the location of the stations.

matter without the risk of substantial biomarker degradation during transport. This is an advantage over earlier studies that traced terrestrial organic matter along a single transect from a river mouth to the sea (Bianchi et al., 1999; 1997a; Goñi et al., 1998; Hedges and Mann, 1979b; Prahl et al., 1994) or in single estuarine systems (Hedges et al., 1988b; Louchouarn et al., 1997; Peresypkin et al., 1990; Reeves and Preston, 1989).

Despite the possibilities the Baltic Sea offers, there are only a few studies on terrestrial organic matter (Bianchi et al., 1997b; Miltner and Emeis, 2000; Pempkowiak and Pocklington, 1983; Voß and Struck, 1997). These studies showed that terrestrial material, i.e., material with the properties of sedimentary or suspended material in the river mouths, accounts for 25% to 50% of the organic matter in sediments or suspended particles in some sectors. However, the cited studies are difficult to compare, because they covered only small areas and were based on different organic matter fractions.

We aimed to produce a consistent data set for terrestrial organic matter in Baltic Sea surface sediments and used the CuO oxidation method (Hedges and Ertel, 1982) to quantify and to characterize the lignin fraction in surface sediments from all parts of the Baltic Sea.

Lignin is a tracer for terrestrial organic matter because it is produced only by vascular plants, which are restricted to ter-

Table 1. Land use in the Baltic Sea drainage basin, given in percent of subdrainage basin area.

	Bothnian Bay	Bothnian Sea	Gulf of Finland	Gulf of Riga	Baltic Proper	Danish Straits	Kattegat	Total Baltic Sea
Forest	72.08	66.48	53.77	37.89	28.63	5.45	53.43	47.90
Arable land	2.64	5.14	8.65	27.93	39.16	55.49	20.37	20.22
Pasture	0.13	0.29	3.59	11.94	11.61	10.94	2.12	5.96
Nonproductive open land	18.29	19.17	16.86	19.59	16.41	19.48	9.27	17.08
Unknown land	2.07	2.96	3.17	0.08	0.83	3.26	2.47	1.93
Urban area	0.21	0.59	0.46	0.65	1.09	3.57	1.15	0.75
Lakes	4.38	5.36	13.51	1.91	2.28	1.80	11.19	6.12
Glacier	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.03

Source: Sweitzer et al., 1996. Wetland data are not included in land cover data because of incompatibility of the data sources.

restrial environments (Moran et al., 1991). Only very shallow water areas may also support some vascular plants. The CuO oxidation method provides an estimate of the lignin contents of the samples, which is indicative of the contribution of terrestrial organic matter, along with the origin (gymnosperm vs. angiosperm tissue, woody vs. nonwoody tissue) and the degree of diagenetic alteration of the terrestrial organic fraction.

Our motivation for the survey was to test if lignin is a suitable indicator for vegetation in the modern environment as a first step to reconstruct vegetation and runoff changes during the late Holocene from sediment cores. We use the data set in this study to address the following questions: How is terrestrial organic matter distributed in surface sediments of the Baltic Sea and do lignin characteristics mirror its origin? What is the contribution of terrestrial to total sedimentary organic carbon in the Baltic Sea? Does lignin composition vary from its riverine sources to the depositional areas and are compositional differences in the original material attenuated by lateral transport from one basin to another?

2. MATERIALS AND METHODS

2.1. Sediment Sampling

We chose a set of samples representative of all Baltic Sea basins including some stations in the eastern Skagerrak (Fig. 1 and Table 2). Although the sample set covers sediments from all over the Baltic, some parts in the North are underrepresented. The conclusion drawn for these regions are thus preliminary.

In addition to sediments from the Baltic Sea, two river mouth stations (Breitling and Oder lagoon) were sampled. In both cases, samples were taken in freshwater lagoons (salinity < 3). Sediments in these lagoons consist of fine-textured material, and we assume that shifts in lignin oxidation product yields and composition with texture will only have minor influence on the comparison between the river and the Baltic Sea samples. Sampling sediments from depositional areas in the river mouths also ensured that the samples will represent a long-term average of particulate matter amount and composition as opposed to suspended matter, which usually varies strongly in time and space.

All samples were taken during several cruises with a box corer or a multicorer (see Table 2). The surface sediments (0–2 cm) were frozen onboard and freeze-dried on arrival in the laboratory.

2.2. Analyses

The samples were analyzed for their contents of total carbon and total inorganic carbon by dry combustion and by treatment with 50% phosphoric acid, respectively. The CO_2 evolved was determined with an ELTRA Metalyt CS 1000 S C/S analyzer by infrared detection. The total organic carbon (TOC) contents were calculated by difference.

The analysis of lignin-derived phenols was performed after CuO oxidation (Hedges and Ertel, 1982). Briefly, 500 to 2000 mg of sediment were oxidized at 170°C for 2 h in the presence of 2 mol/L NaOH, CuO, and $(NH)_4Fe(SO_4)_2$. After centrifugation, the supernatants were acidified to pH 2 with 6 mol/L HCl. The humic acids, which precipitated, were removed by centrifugation. The supernatant was further purified by solid phase extraction. The lignin-derived phenols were sorbed from the acidic solution on C_{18} material and later eluted with ethyl acetate (Kögel and Bochter, 1985). This extraction method differs from the original method but has the advantage of requiring less solvent and being faster. In a previous publication, we have shown that the results obtained by the two methods are identical (Miltner and Emeis, 2000).

The solvent was removed by rotary evaporation, and the phenolic oxidation products were transferred to autosampler vials with methanol that was then removed under a flux of N_2. Before analysis by GC/MS, the samples were dissolved in acetonitrile and derivatized with N,*O*-bis-(trimethylsilyl)trifluoroacetamid (BSTFA) for 1 h at room temperature. Thereafter, they were diluted with acetonitrile according to the expected phenol concentrations. One microliter of each sample was injected in splitless mode, and the phenols were separated in a HP 6890 gas chromatograph equipped with a HP5MS column (30 m $\times$ 250 μm $\times$ 0.25 μm). The temperature program of the gas chromatograph was 100°C isothermal for 4 min, ramp to 220°C at 4°C min^{-1} with a 5-min isothermal period at 120°C, isothermal at 220°C for 3 min, ramp to 300°C at 30°C min^{-1}, and final isothermal for 10 min. The transfer line to the mass spectrometer was kept at 325°C throughout the analysis. The HP 5973 mass spectrometer was operating in the EI mode at 70 eV. The ion source temperature was 230°C, and the quadrupole was kept at 150°C. Compounds were quantitated by integration of the base ions and by comparison of the peak areas with those of synthetic standards. Before oxidation, ethylvanillin was added as an internal standard for the determination of recovery. To rule out possible transformations of the internal standard during the oxidation step, we also processed blanks containing only ethylvanillin and the reagents. GC-FID analysis of these blanks displayed a single peak with the retention time of ethylvanillin, and we found no evidence of any transformation of ethylvanillin during the oxidation step under our experimental conditions. We chose to add the internal standard at the beginning of the analysis to ensure that the internal standard and the lignin oxidation products have the same history during the entire analysis. On average, 75% of the added ethylvanillin was recovered after the complete analytical procedure; the range of recoveries was 50% to 105%.

The yields of phenolic acids and aldehydes were normalized to the TOC contents of the samples and are given in mg phenolic oxidation products g^{-1} TOC. The sum of vanillin, vanillic acid, syringaldehyde, syringic acid, *p*-coumaric acid and ferulic acid, V+S+C, is proportional to the lignin content and thus is an indicator of the contribution of terrestrial organic matter to total sedimentary organic matter (Hedges and Mann, 1979a). The ratio of syringic-to-vanillic moieties, S/V, is indicative of the contribution of angiosperm tissue, whereas the ratio of cinnamic-to-vanillic moieties, C/V, increases with increasing importance of nonwoody tissue. The acid-to-aldehyde ratio of the vanillic moieties, $(Ad/Al)_V$, increases during lignin degradation by white rot fungi, which is the main process of diagenesis. The ratio can therefore be used as an indicator of diagenetic alteration of terrestrial organic matter (Goñi et al., 1993; Hedges et al., 1988a). The values must, however, be interpreted with care, because other degradation pathways,

Table 2. List and short description of stations.

Station	Cruise	Latitude (°N)	Longitude (°E)	Water depth (m)	TOC (%)	Area
220780	40/98/18	58°51.83	10°34.73	128	1.85	Skagerrak
220770	40/98/18	58°52.00	10°43.80	100	2.30	Skagerrak
220730	40/98/18	58°34.76	10°38.82	146	2.07	Skagerrak
220720	40/98/18	58°21.49	10°54.16	117	1.89	Skagerrak
220670	40/98/18	58°05.37	11°07.83	103	1.48	Skagerrak
220660	40/98/18	57°51.04	11°19.16	78	2.01	Kattegatt
220630	40/98/18	57°38.08	11°24.74	68	2.17	Kattegatt
220620	40/98/18	57°21.43	11°34.90	69	2.54	Kattegatt
220590	40/98/18	57°13.71	11°57.06	58	1.05	Kattegatt
220580	40/98/18	56°59.11	12°02.09	50	1.76	Kattegatt
220510	40/98/18	56°39.67	12°15.00	40	3.17	Kattegatt
220520	40/98/18	56°27.03	12°19.97	32	2.63	Kattegatt
220500	40/98/18	56°17.06	12°12.15	30	2.15	Kattegatt
Arhus1[a]	AU	54°59.84	10°09.68	36	4.88	Danish Straits
Arhus2[a]	AU	55°12.63	9°46.77	26	0.59	Danish Straits
Arhus3[a]	AU	55°36.18	9°57.37	18	2.97	Danish Straits
Arhus4[a]	AU	55°30.46	10°51.69	33	3.40	Danish Straits
Arhus5[a]	AU	55°17.97	10°59.80	21	2.35	Danish Straits
Arhus6[a]	AU	55°06.16	11°02.54	31	2.20	Danish Straits
220790	40/98/18	55°57.93	12°38.98	18	2.16	Danish Straits
220800	40/98/18	55°40.28	12°52.84	14	1.66	Danish Straits
220810	40/98/18	55°28.66	12°43.16	14	0.18	Danish Straits
360	40/98/16	54°36.02	10°27.02	17	0.28	Belt Sea
220310	40/98/18	54°05.00	10°59.21	24	6.13	Belt Sea
220300	40/98/18	54°05.02	11°10.05	24	5.54	Belt Sea
220320	40/98/18	54°18.91	11°32.99	21	4.23	Belt Sea
22	40/98/16	54°06.72	11°10.77	21	4.99	Belt Sea
220930	40/98/18	54°09.59	12°07.15	6	1.59	Breitling
46	40/98/16	54°27.96	12°12.92	23	1.43	Arkona Sea
30	40/98/16	54°43.46	12°46.98	22	0.08	Arkona Sea
RB1	40/98/16	55°08.84	13°00.46	33	0.95	Arkona Sea
E2[b]	44/95/05	54°41.23	13°35.46	33	1.26	Arkona Sea
E3[b]	44/95/05	55°07.50	14°34.91	43	0.61	Arkona Sea
E7[b]	44/95/05	55°07.37	13°54.37	46	4.87	Arkona Sea
E9[b]	44/95/05	54°50.34	13°40.03	45	5.52	Arkona Sea
E10[b]	44/95/05	55°17.42	14°24.95	47	0.59	Arkona Sea
E12[b]	44/95/05	55°12.62	13°14.89	40	3.75	Arkona Sea
1[b]	40/95/07	54°32.50	12°45.00	14	0.17	Arkona Sea
10[b]	40/95/07	54°52.50	13°05.00	46	5.82	Arkona Sea
33[b]	40/98/07	54°47.55	13°55.00	42	4.43	Arkona Sea
113	40/98/16	54°55.47	13°29.87	47	5.85	Arkona Sea
ODAS	40/98/14	54°04.85	14°09.52	16	0.47	Arkona Sea
224160	40/99/11	54°06.04	14°06.51	16	0.21	Arkona Sea
224170	40/99/11	54°08.49	14°13.18	16	0.14	Arkona Sea
224180	40/99/11	54°18.02	14°04.93	20	1.02	Arkona Sea
224150	40/99/11	54°20.36	13°49.92	18	0.56	Arkona Sea
Nordperd	40/98/14	54°21.96	13°54.73	22	0.78	Arkona Sea
224140	40/99/11	54°24.64	13°45.60	23	4.13	Arkona Sea
224130	40/99/11	54°24.05	14°00.18	14	0.06	Arkona Sea
224120	40/99/11	54°23.98	14°13.10	11	0.05	Arkona Sea
224190	40/99/11	54°29.92	13°59.96	18	0.11	Arkona Sea
224200	40/99/11	54°34.10	13°48.23	24	0.49	Arkona Sea
Tromper Wiek	40/98/14	54°36.06	13°45.64	27	1.23	Arkona Sea
Arkona Basin	40/98/14	54°56.14	13°49.95	41	5.61	Arkona Sea
109	40/98/16	55°00.00	14°04.95	47	5.37	Arkona Sea
150	40/98/16	54°36.68	14°02.58	20	0.09	Arkona Sea
214280[c]	40/98/05	53°49.20	14°09.96	5	8.20	Oder Lagoon
224110	40/99/24	54°30.00	14°30.23	15	0.02	Bornholm Sea
224100	40/99/24	54°30.00	15°01.82	36	0.07	Bornholm Sea
224090	40/99/24	54°30.03	15°29.98	54	0.52	Bornholm Sea
202	40/98/16	54°42.01	15°14.97	63	5.62	Bornholm Sea
223770	40/99/24	55°09.55	15°25.77	68	0.37	Bornholm Sea
224780	40/99/24	55°23.30	15°26.30	97	5.49	Bornholm Sea
223790	40/99/24	55°32.84	15°17.47	78	4.24	Bornholm Sea
223760	40/99/24	55°02.23	15°44.16	91	5.05	Bornholm Sea
224080	40/99/24	54°46.88	15°50.53	66	2.54	Bornholm Sea
224070	40/99/24	55°00.09	16°00.09	82	6.23	Bornholm Sea
213	40/98/16	55°14.94	15°58.76	88	4.83	Bornholm Sea

(Continued)

Table 2. (Continued)

Station	Cruise	Latitude (°N)	Longitude (°E)	Water depth (m)	TOC (%)	Area
223810	40/99/24	55°29.98	15°59.99	84	3.82	Bornholm Sea
223800	40/99/24	55°42.62	16°17.41	69	4.44	Bornholm Sea
223820	40/99/24	55°30.03	16°20.90	74	5.01	Bornholm Sea
224060	40/99/24	55°14.56	16°16.15	75	1.83	Bornholm Sea
224050	40/99/24	55°07.30	16°28.72	54	0.18	Bornholm Sea
223830	40/99/24	55°17.62	17°04.95	78	3.78	Bornholm Sea
224040	40/99/24	55°08.01	17°17.50	58	0.31	Bornholm Sea
223840	40/99/24	55°22.76	17°29.81	74	3.45	Bornholm Sea
224030	40/99/24	55°12.65	17°50.57	61	1.11	Bornholm Sea
224020	40/99/24	55°08.78	18°28.05	85	0.39	Gdańsk Bay
223940	40/99/24	55°15.00	19°00.03	54	0.59	Gdańsk Bay
223950	40/99/24	55°00.09	18°59.90	104	5.54	Gdańsk Bay
223960	40/99/24	54°59.96	19°11.85	108	5.68	Gdańsk Bay
223970	40/99/24	54°57.54	19°13.94	111	6.69	Gdańsk Bay
224010	40/99/24	54°55.00	19°00.17	105	7.69	Gdańsk Bay
224000	40/99/24	54°49.94	19°00.09	104	7.17	Gdańsk Bay
223980	40/99/24	54°50.04	19°13.99	112	6.57	Gdańsk Bay
223990	40/99/24	54°45.31	19°11.17	106	7.18	Gdańsk Bay
223850	40/99/24	55°30.01	17°59.88	73	3.33	Gotland Sea
223860	40/99/24	55°29.98	18°29.99	92	3.95	Gotland Sea
223930	40/99/24	55°30.70	18°45.36	89	1.97	Gotland Sea
223870	40/99/24	55°44.33	18°24.05	105	5.93	Gotland Sea
223880	40/99/24	55°52.43	18°34.72	116	5.31	Gotland Sea
223890	40/99/24	55°59.96	18°43.74	123	5.47	Gotland Sea
223510	40/99/24	56°05.02	19°09.98	130	4.26	Gotland Sea
223900	40/99/11	56°14.99	19°00.01	127	8.56	Gotland Sea
223520	40/99/11	55°20.82	19°22.86	139	5.93	Gotland Sea
223910	40/99/11	56°29.97	18°59.90	135	7.17	Gotland Sea
223920	40/99/11	56°35.99	19°32.89	148	6.93	Gotland Sea
223540	40/99/11	56°45.95	19°44.94	160	4.09	Gotland Sea
223530	40/99/11	56°49.96	19°11.10	169	5.87	Gotland Sea
223550	40/99/11	56°40.05	20°49.98	35	0.13	Gotland Sea
223560	40/99/11	56°56.87	19°52.89	183	7.07	Gotland Sea
223570	40/99/11	57°08.98	20°00.02	233	9.64	Gotland Sea
223580	40/99/11	57°18.18	20°04.27	252	5.33	Gotland Sea
271	40/98/16	57°18.31	20°04.59	238	3.79	Gotland Sea
220050	99/98/01	57°12.23	19°41.79	148	0.71	Gotland Sea
220020	99/98/01	57°18.99	19°41.05	94	0.40	Gotland Sea
220030	99/98/01	57°24.54	19°44.58	144	10.07	Gotland Sea
220040	99/98/01	57°07.57	20°28.57	101	4.24	Gotland Sea
220010	99/98/01	57°15.28	20°32.37	102	5.89	Gotland Sea
220000	99/98/01	57°14.56	20°42.69	77	1.88	Gotland Sea
223590	40/99/11	57°32.04	20°13.81	180	7.09	Gotland Sea
223600	40/99/11	57°44.09	20°22.92	147	5.50	Gotland Sea
223630	40/99/11	57°55.34	20°31.48	102	1.53	Gotland Sea
223640	40/99/11	57°57.81	20°13.18	132	3.46	Gotland Sea
286	40/98/16	57°59.83	19°54.20	186	8.91	Gotland Sea
223620	40/99/11	57°50.99	21°08.07	81	3.28	Gotland Sea
223610	40/99/11	57°48.70	21°23.77	60	0.37	Gotland Sea
202750[c]	44/97/07	59°24.00	23°58.00		3.98	Gulf of Finland
202820[c]	44/97/07	59°19.60	24°02.90		0.49	Gulf of Finland
202840[c]	44/97/07	59°20.50	24°01.90	22	4.07	Gulf of Finland
202880[c]	44/97/07	59°23.93	23°30.30	102	3.83	Gulf of Finland
GF-1[d]	FIMR	59°42.48	24°41.20	84	3.99	Gulf of Finland
SL-2S[d]	FIMR	60°03.49	29°11.55	29	3.16	Gulf of Finland
EB-1[d]	FIMR	60°59.35	19°43.98	130	3.17	Gulf of Bothnia
US-5B[d]	FIMR	62°35.22	19°58.47	210	3.14	Gulf of Bothnia
F2[d]	FIMR	64°58.47	23°23.33	100	3.89	Gulf of Bothnia

[a] Sample supplied by Dr. Lars Lund-Hansen, Århus University.
[b] Sample supplied by Dr. Hans-Martin Schulz, TU Claustha.
[c] Sample supplied by Dr. Thomas Leipe, Baltic Sea Research Institute.
[d] Sample supplied by Dr. Matti Mälkki, Finnish Institute of Marine Research.

Table 3. Contents of individual lignin oxidation products.

Station	Vanillin	Syringaldehyde	Vanillic acid	Syringic acid	*p*-coumaric acid	Ferulic acid
	mg/g TOC					
220780	1.495	0.675	0.606	0.268	0.234	0.083
220770	1.215	0.475	0.592	0.236	0.245	0.080
220730	1.585	0.769	0.707	0.359	0.318	0.127
220720	1.431	0.700	0.505	0.246	0.187	0.081
220670	1.467	0.763	0.512	0.259	0.274	0.121
220660	2.037	0.976	0.750	0.383	0.195	0.097
220630	1.859	0.940	0.694	0.358	0.205	0.096
220620	1.817	0.803	0.707	0.342	0.330	0.127
220590	1.634	0.742	0.744	0.333	0.343	0.138
220580	1.086	0.477	0.481	0.211	0.246	0.070
220510	1.505	0.628	0.673	0.292	0.415	0.112
220520	1.392	0.673	0.655	0.305	0.427	0.109
220500	1.200	0.602	0.537	0.258	0.499	0.118
Arhus1	1.846	1.238	0.742	0.602	0.410	0.249
Arhus2	2.060	1.515	0.552	0.481	0.227	0.178
Arhus3	2.017	1.413	0.776	0.632	0.311	0.208
Arhus4	1.598	0.990	0.588	0.404	0.347	0.144
Arhus5	2.117	1.419	0.586	0.453	0.362	0.194
Arhus6	1.174	0.795	0.371	0.290	0.153	0.084
220790	2.096	1.216	0.534	0.342	0.373	0.189
220800	1.936	1.342	0.656	0.471	0.408	0.183
220810	0.434	0.323	0.139	0.091	0.084	0.042
360	0.882	0.669	0.332	0.233	0.162	0.068
220310	1.477	1.112	0.641	0.458	0.677	0.226
230300	1.595	1.169	0.611	0.443	0.530	0.230
220320	1.958	1.320	0.727	0.492	0.407	0.170
22	1.666	1.379	0.669	0.476	0.671	0.335
220930	5.545	4.290	1.780	1.489	0.538	0.271
46	2.433	1.603	0.785	0.530	0.348	0.215
30	0.325	0.223	0.167	0.084	0.065	0.055
RB1	1.575	1.243	0.502	0.384	0.395	0.167
E2	2.454	1.608	0.680	0.455	0.378	0.205
E3	1.141	0.661	0.389	0.188	0.314	0.108
E7	1.506	0.992	0.532	0.309	0.474	0.172
E9	2.436	1.779	0.778	0.489	0.601	0.283
E10	0.980	0.576	0.351	0.180	0.288	0.098
E12	2.501	1.588	0.752	0.445	0.420	0.171
1	0.499	0.377	0.206	0.113	0.131	0.096
10	2.095	0.779	0.730	0.518	0.522	0.245
33	2.770	1.786	0.946	0.575	0.704	0.287
113	2.133	1.553	0.869	0.563	0.589	0.245
ODAS	2.437	1.105	0.809	0.380	0.388	0.265
224160	2.415	1.138	0.686	0.315	0.547	0.163
224170	1.465	0.846	0.489	0.244	0.341	0.111
224180	0.831	0.429	0.248	0.127	0.222	0.060
224150	1.113	0.509	0.348	0.147	0.316	0.059
Nordperd	2.403	1.075	0.896	0.380	0.562	0.161
224140	0.955	0.477	0.271	0.154	0.307	0.067
224130	0.557	0.273	0.185	0.084	0.300	0.050
224120	0.132	0.062	0.085	0.039	0.085	0.027
224190	0.341	0.162	0.094	0.039	0.119	0.032
224200	1.269	0.607	0.339	0.167	0.153	0.041
Tromper Wiek	2.049	1.128	0.766	0.398	0.469	0.184
Arkona Basin	2.127	1.461	0.843	0.561	0.537	0.235
109	1.908	1.327	0.715	0.422	0.605	0.225
150	0.527	0.235	0.179	0.076	0.150	0.047
214280	5.461	2.695	1.783	0.949	0.895	0.601
224110	0.272	0.093	0.167	0.036	0.097	0.000
224100	0.654	0.317	0.343	0.122	0.404	0.077
224090	0.617	0.207	0.224	0.075	0.293	0.046
202	0.917	0.434	0.380	0.152	0.507	0.112
223770	0.829	0.343	0.451	0.153	0.391	0.077
223780	0.547	0.276	0.313	0.130	0.570	0.109
223790	0.755	0.272	0.433	0.149	0.620	0.072
223760	0.897	0.421	0.451	0.179	0.657	0.124
224080	1.320	0.472	0.522	0.178	0.478	0.111

(Continued)

Table 3. (Continued)

Station	Vanillin	Syringaldehyde	Vanillic acid	Syringic acid	*p*-coumaric acid	Ferulic acid
	mg/g TOC					
224070	0.853	0.331	0.368	0.149	0.524	0.077
213	0.655	0.309	0.318	0.131	0.614	0.085
223810	0.211	0.071	0.115	0.035	0.140	0.020
223800	0.679	0.224	0.407	0.127	0.798	0.092
223820	0.472	0.190	0.361	0.129	0.651	0.060
224060	1.144	0.405	0.543	0.193	0.647	0.081
224050	1.889	0.566	0.741	0.236	0.360	0.075
223830	0.727	0.217	0.437	0.123	0.805	0.074
224040	0.549	0.169	0.235	0.068	0.218	0.034
223840	0.555	0.140	0.737	0.212	0.901	0.098
224030	0.227	0.067	0.092	0.027	0.111	0.019
224020	2.197	0.612	1.014	0.262	0.417	0.090
223940	0.970	0.259	0.444	0.128	0.298	0.076
223950	1.766	0.575	0.680	0.241	0.694	0.159
223960	2.123	0.788	0.822	0.351	0.551	0.142
223970	1.675	0.678	0.668	0.265	0.458	0.106
224010	1.276	0.474	0.526	0.180	0.639	0.128
224000	1.680	0.606	0.688	0.247	0.701	0.142
223980	1.804	0.618	0.752	0.272	0.488	0.118
223990	1.766	0.754	0.628	0.219	0.454	0.161
223850	0.721	0.150	0.386	0.105	0.887	0.095
223860	0.817	0.203	0.423	0.112	0.771	0.099
223930	1.714	0.442	1.008	0.308	1.156	0.149
223870	0.691	0.182	0.367	0.093	0.928	0.096
223880	0.643	0.156	0.474	0.130	1.243	0.111
223890	0.501	0.135	0.295	0.094	1.092	0.099
223510	1.479	0.280	0.642	0.176	0.485	0.084
223900	0.302	0.087	0.175	0.056	0.563	0.050
223520	0.644	0.134	0.407	0.113	0.914	0.095
223910	1.237	0.172	0.518	0.085	1.187	0.124
223920	0.606	0.164	0.304	0.089	0.873	0.103
223540	0.943	0.173	0.352	0.086	0.596	0.071
223530	0.808	0.075	0.302	0.043	0.487	0.059
223550	0.280	0.040	0.153	0.019	0.013	0.014
223560	1.199	0.139	0.527	0.085	0.493	0.080
223570	1.555	0.153	0.623	0.072	0.517	0.101
223580	2.095	0.151	0.945	0.098	0.493	0.114
271	1.500	0.257	0.674	0.114	0.572	0.106
220050	0.399	0.133	0.199	0.077	0.082	0.028
220020	0.687	0.094	0.256	0.036	0.292	0.049
220030	0.598	0.167	0.312	0.062	0.733	0.014
220040	1.444	0.396	0.698	0.173	0.829	0.143
220010	1.677	0.496	0.760	0.195	0.669	0.138
220000	2.172	0.698	0.747	0.210	0.331	0.125
223590	1.653	0.275	0.644	0.111	0.578	0.104
223600	1.920	0.286	0.496	0.099	0.459	0.082
223630	0.840	0.101	0.354	0.054	0.135	0.020
223640	2.095	0.226	0.853	0.135	0.483	0.083
286	1.338	0.201	0.665	0.091	0.988	0.139
223620	2.345	0.612	0.924	0.272	0.626	0.142
223610	2.655	0.746	1.017	0.308	0.438	0.138
202750	1.642	0.556	0.487	0.177	0.640	0.130
202820	1.383	0.552	0.367	0.166	0.354	0.098
202840	1.758	0.677	0.448	0.209	0.514	0.133
202880	1.420	0.347	0.543	0.145	0.503	0.081
GF-1	2.179	0.325	1.197	0.211	0.468	0.118
SL-2S	5.715	1.047	2.034	0.434	0.756	0.230
EB-1	1.832	0.101	1.173	0.099	0.928	0.106
US-5B	1.529	0.112	0.804	0.077	0.289	0.076
F-2	1.980	0.456	1.275	0.284	0.528	0.117

particularly under submersed conditions, are not reflected in significantly increased acid-to-aldehyde ratios (Opsahl and Benner, 1995).

To check for the analytical precision of the method, we analyzed representative samples of the sample set in duplicate. The coefficient of variance was $<20\%$ for the sum of the phenolic oxidation products and C/V and $<16\%$ for S/V and $(Ad/Al)_V$.

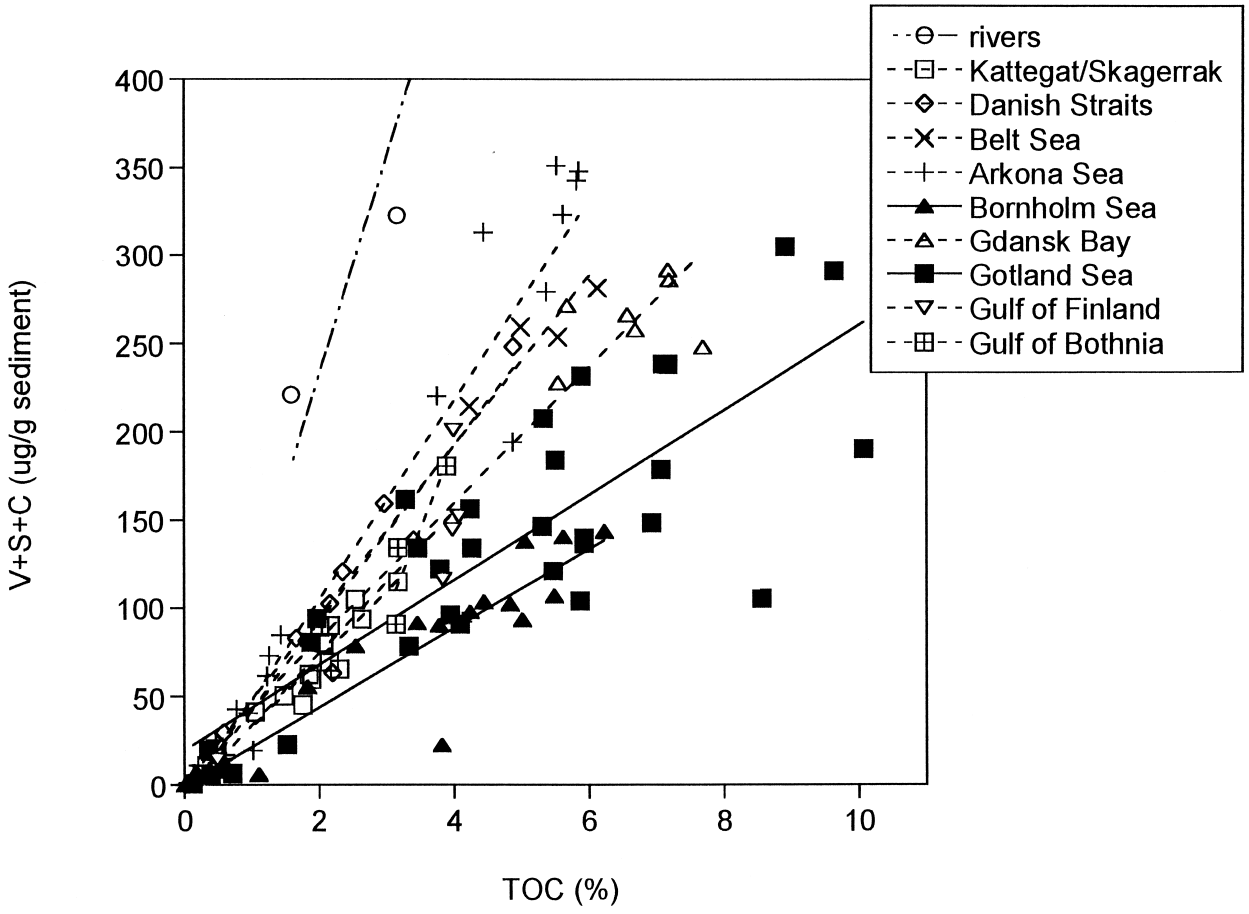

Fig. 2. Relationship between organic carbon content and lignin oxidation product yield in μg g^{-1} sediment.

2.3. Statistics

The data from individual basins were grouped, and all groups were subjected to an analysis of variance to check if lignin oxidation product yield and composition differ significantly between the Baltic Sea basins (Bahrenberg et al., 1992). Differences between the individual basins were considered significant if the confidence limits of the basin means on the 10% level of significance did not overlap (Bahrenberg et al., 1992).

3. RESULTS

3.1. Lignin Oxidation Product Yields

We found lignin oxidation products in considerable amounts in all investigated samples (Table 3). The sum of phenolic oxidation products ranges from 0.13 mg g^{-1} sediment to 1015 mg g^{-1} sediment. Figure 2 shows that the sum of lignin-derived phenols per g sediment correlates significantly with the amount of organic carbon, but that the slopes of the regressions differ between the Bornholm and Gotland Basins and all other areas (Fig. 2). This implies that input of terrestrial relative to marine organic carbon into these two basins differs from all other areas of the Baltic Sea. To reduce the variance attributable to differences in TOC content, which in the western and southern Baltic Sea is closely linked to grain size (Leipe et al., 1995), we normalized the data to TOC content of the samples. These values range from 0.4 to 13.9 mg g^{-1} TOC (average of 3.5 mg g^{-1} TOC) and are highest in sediments in or off the river mouths (Fig. 3). In a basin comparison, we find the lowest lignin oxidation product yields in the Bornholm and the Gotland Seas and the highest yields in the Gulf of Finland (Table 4). A comparison of means (Table 4) reveals that lignin oxidation product yield in the Bornholm Sea is significantly lower than in any other region of the Baltic Sea.

In the individual basins, the lignin oxidation product yields are homogeneous (Table 4, standard deviations) except in the Danish Straits and in the Arkona Sea. In the Arkona Sea, which is a shallow (<50-m water depth) depression collecting fines from a large submarine catchment, low lignin oxidation product yields (<1.5 mg g^{-1} TOC) occur at some peripheral shallow stations with sandy sediments. In the Kattegat/Skagerrak, the yields are enhanced at stations off the mouth of the Göta Älv river. In the Gotland Sea, stations with high yields cluster off the Gulf of Riga, and in the Gulf of Finland, we find a gradient in lignin oxidation product yield from the Neva mouth to the open Baltic Sea.

3.2. Lignin Composition

Lignin phenol composition varies among the different basins. It reflects influences by vegetation patterns on land and diagenetic effects associated with transport. S/V ratios range

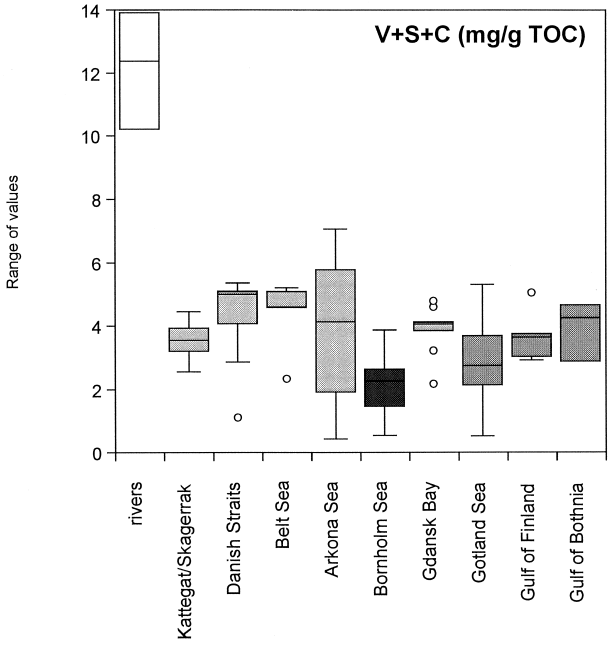

Fig. 3. Box plot of lignin oxidation product yields (mg g^{-1} TOC) of Baltic Sea surface sediments. Each box encloses 50% of the data with the median value of the variable displayed as a line. The top and the bottom of the box mark the limits of ±25% of the variable population (upper quartile, UQ, and lower quartile, LQ). The lines extending from the top and the bottom of each box mark the minimum and maximum values that fall within an acceptable range (<UQ + 1.5 × interquartile distance, IQD, or > LQ − 1.5 × IQD). Outliers are displayed as individual points.

from 0.07 to 0.81, and we see a decrease in S/V from values of ≈0.7 in the Southwest (Danish Straits and Belt Sea) to values between 0.1 and 0.2 in the Northeast (Gulf of Bothnia, Gotland Sea; Fig. 4). The means are significantly different between the southern and northern basins, and S/V ratios in the surface sediments thus appear to faithfully mirror an increasing contribution of gymnosperm tissue to the sediments depending on latitude of the basin catchment.

The total range of C/V, a measure of relative contributions by nonwoody and woody tissue, is found to range from 0.06 to 1.50. It is highest (average 0.5), but also most variable, in the Bornholm and the Gotland Seas, whereas C/V in the other basins ranges from 0.1 to 0.5 (Fig. 5). The significantly higher values in the Bornholm and Gotland Seas (Table 4) point to a greater contribution of lignin from nonwoody sources. C/V ratios in the Arkona Basin, Belt Sea, and the Gdańsk Bay are significantly higher than in the Kattegat and the Danish Straits where C/V is lowest.

The acid-to-aldehyde ratios of vanillic moieties range from 0.26 to 1.33 in the Baltic Sea, and low values suggest that the terrestrial organic matter is only moderately altered by diagenesis (Fig. 6). The average $(Ad/Al)_V$ is lowest in the Danish Straits, the Gulf of Finland, and the Arkona Sea (Table 4). Diagenesis of lignin seems to be more advanced in the Bornholm and Gotland Seas and is most pronounced in the Gulf of Bothnia. The pronounced difference between the Gulfs of Finland and Bothnia is of note, because both are close to major river discharge areas and both have permanently oxic bottom waters.

In some subbasins, we observe regional patterns in lignin composition that are related to proximity of sampling stations to river discharge areas. In the Kattegat/Skagerrak region, the lowest C/V and $(Ad/Al)_V$ ratios are found off the Göta Älv River mouth, at the same stations that have increased lignin oxidation product yields. The lignin composition of Gotland Sea sediments generally resembles the material from the Bornholm Sea. In the northeastern Gotland Sea, however, relatively low C/V and $(Ad/Al)_V$ ratios mark an area bordering the Gulf of Riga and again these samples coincide with high lignin oxidation yields. Finally, we find a gradient in C/V ratios in the Gulf of Finland that matches a gradient in lignin yields away from the Neva River.

3.3. The River Signal

From the stations investigated in our study, it is difficult to assess typical river signals, because only two samples were taken in coastal lagoons of the rivers Warnow and Oder (Breitling and Oder lagoon, respectively). In addition, the easternmost station in the Gulf of Finland is in close proximity to the Neva River mouth and must be close to the river signal. From these limited data, we can estimate that the river input contains a considerable portion of lignin (yield of phenolic oxidation products ≈13 mg g^{-1} TOC). The terrestrial material seems to be characterized by low C/V and low $(Ad/Al)_V$ ratios, i.e., by a low contribution of nonwoody material and by little diagenetic alteration (Figs. 5 and 6). Because the same pattern is found in all three rivers, we assume that it is valid at least for the southern and northeastern part of the Baltic Sea. We do not have any information about Scandinavian rivers, which might carry terrestrial organic matter that is composed differently, because it is derived from other sources.

4. DISCUSSION

4.1. Contribution of Terrestrial Organic Matter to Baltic Sea Sediments

We find terrestrial organic matter in sediments of all Baltic Sea basins, as was expected considering the land-locked nature of the Baltic Sea and the dominance of river discharge in its hydrology. Lignin oxidation products in sediments not directly influenced by rivers range from 0.4 to 7.1 mg g^{-1} TOC in our data set. This is comparable with data reported for humic substances extracted from water and sediments off the Polish coast (Pempkowiak and Pocklington, 1983). Lignin oxidation product yields of sediments from the Gulf of Mexico are also in a similar range (Hedges and van Geen, 1982), whereas sediments from many estuaries yield higher amounts of lignin oxidation products, e.g., the Dabob Bay (Hedges et al., 1988b), the St. Lawrence estuary (Louchouarn et al., 1997), and the estuary of the Northern Dvina (Peresypkin et al., 1990). The latter two estuaries are strongly influenced by pulp and paper industry, resulting in increased input of lignin-bearing material to water and sediments. Sediments from the coast of Cyprus, in contrast, yield lower amounts of lignin oxidation products (Bianchi et al., 1999), as do sediments from the Laptev Sea (Lobbes, 1998) that receive significant input from Siberian

Table 4. Average lignin oxidation product yields and lignin composition of sediments from the individual Baltic Sea basins (averages and standard deviations).

Region	V + S + C (mg/g TOC)	C/V	S/V	$(Ad/Al)_v$
Kattegat/Skagerrak	3.56 ± 0.54^{c}	0.19 ± 0.07^{a}	0.47 ± 0.04^{c}	0.42 ± 0.05^{c}
Danish Straits	4.26 ± 1.41^{c}	0.20 ± 0.03^{a}	0.69 ± 0.05^{e}	0.33 ± 0.05^{a}
Belt Sea	4.36 ± 1.16^{c}	0.32 ± 0.11^{b}	0.74 ± 0.04^{e}	0.39 ± 0.03^{bc}
Arkona Sea	3.84 ± 2.04^{c}	0.27 ± 0.08^{b}	0.58 ± 0.11^{d}	0.35 ± 0.08^{ab}
Bornholm Sea	2.09 ± 0.86^{a}	0.52 ± 0.21^{c}	0.36 ± 0.06^{b}	0.55 ± 0.21^{de}
Gdańsk Bay	3.87 ± 0.77^{c}	0.28 ± 0.08^{b}	0.35 ± 0.05^{b}	0.41 ± 0.03^{c}
Gotland Sea	2.84 ± 1.18^{b}	0.53 ± 0.39^{c}	0.21 ± 0.07^{ab}	0.47 ± 0.10^{d}
Gulf of Finland	4.76 ± 2.78^{bc}	0.25 ± 0.09^{ab}	0.29 ± 0.11^{b}	0.33 ± 0.07^{ab}
Gulf of Bothnia	3.92 ± 0.92^{bc}	0.23 ± 0.10^{ab}	0.12 ± 0.09^{a}	0.60 ± 0.07^{e}

In any column, values followed by different superscripts are significantly different ($\alpha = 0.1$).

rivers. Lignin oxidation product yields of Baltic Sea sediments thus agree with the range reported for coastal zones without direct influence of large rivers despite its relatively high freshwater input.

The interbasin differences in lignin content reflect the basin size, its distance from land, and the influence of rivers. Regions with high yields (the Gulf of Finland, the Gulf of Bothnia, the Gdańsk Bay, and the southwestern Baltic Sea with Danish Straits, Belt Sea, and Arkona Sea) are clearly distinguished from those with low yields (Bornholm and Gotland Seas). The Gulf of Finland receives the discharge of the River Neva, which is the largest tributary to the Baltic Sea and discharges ≈2500 m^3/s (Bergström and Carlsson, 1993). Similarly, the high contribution of terrestrial organic matter in the Gdańsk Bay is explained by discharge of the Vistula River, which is the second largest river with an average runoff of 1065 m^3/s (Bergström and Carlsson, 1993). There is no single large river discharging into the Gulf of Bothnia, but this area is fed by a large number of small and intermediate rivers and receives ≈40% of the total freshwater discharge into the Baltic Sea (Bergström and Carlsson, 1993). High yields in the southwestern Baltic Sea are less readily explained and may be due to relatively small areas and short average distances to the coast. This may result in relatively little dilution of the terrestrial material by marine primary production. In contrast to these areas, the freshwater input to the Bornholm and the Gotland Sea is small compared with their sizes.

The significant correlation between organic carbon content and lignin yield per gram of sediment seen in all basins, and particularly in the surface sediments of the Gotland and Bornholm Seas, begs for an explanation. These two areas of mud deposition are most distant from land, but they collect the bulk of organic material deposited in the Baltic Sea (areas of mud deposition 28,240 km^2 and 11,210 km^2, respectively) and together account for 70% of the depositional area. Both basins (and the Gdańsk Basin) have roughly tripled their sediment and

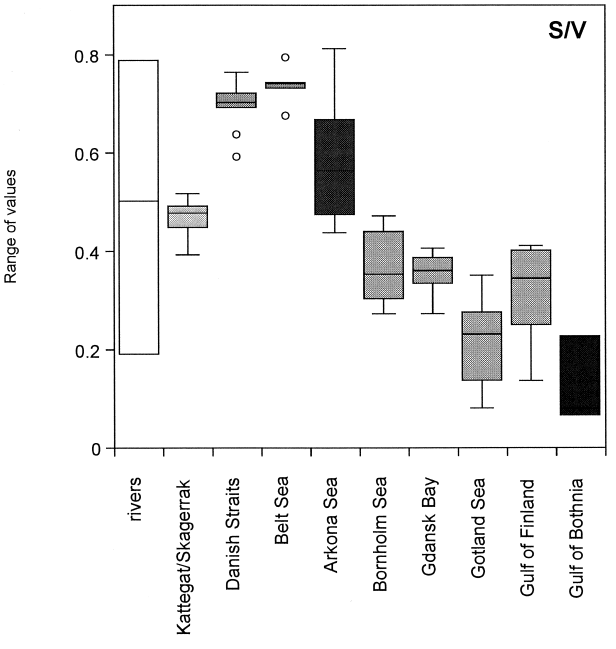

Fig. 4. Box plot of S/V in Baltic Sea surface sediments.

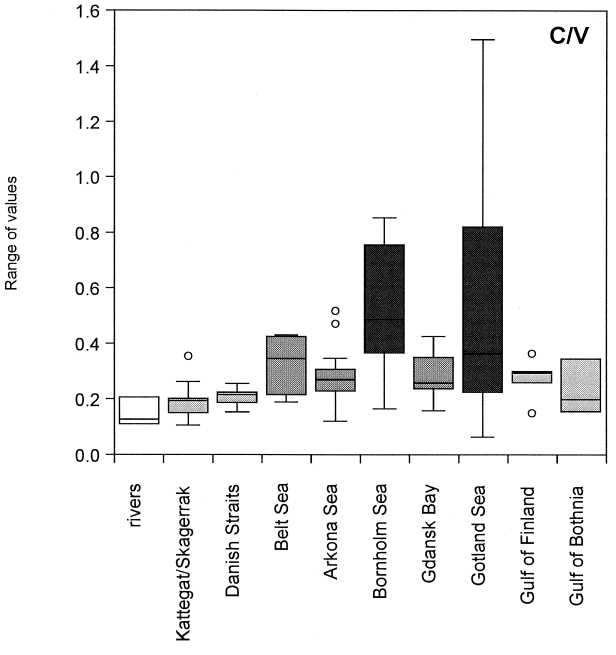

Fig. 5. Box plot of C/V in Baltic Sea surface sediments.

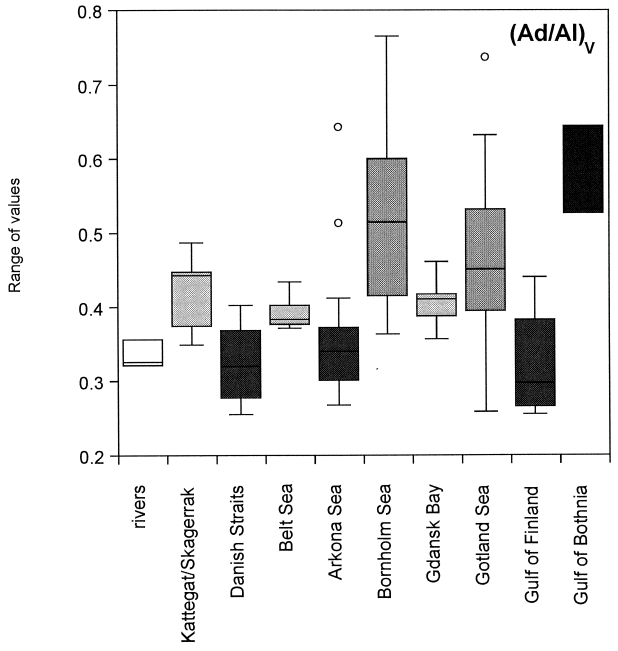

Fig. 6. Box plot of $(Ad/Al)_V$ in Baltic Sea surface sediments.

organic carbon accumulation rates since the 1950s (Emeis et al., 2000), a fact that had previously been attributed to vastly increased nutrient input from land and enhanced burial flux of marine phytoplankton (Jonsson et al., 1990). Even though the relative contribution of terrestrial organic matter is lower here than in the other basins (see Figs. 2 and 3), our data on Gotland and Bornholm surface sediments give no indication for a significant dilution of terrestrial organic matter by a threefold increased marine component. Instead, it seems from our data, that the increase may be fed by both marine and terrestrial sources. Emeis et al. (2000) ruled out enhanced river discharge or intensified seafloor erosion as causes for enhanced sediment burial flux, because neither had increased in a similar magnitude over that period. Before we can solve the seeming enigma, sediment cores need to be studied to check if proportions of marine and terrestrial carbon changed over the last 100 yr. However, a possible explanation offered by Emeis et al. (2000) for the increased carbon burial may hold true for the paired increase of terrestrial and marine carbon burial: In both basins, the increase in carbon burial coincided with prolonged periods of bottom-water anoxia that may have enhanced preservation of both TOC compartments.

The percentage of terrestrial organic matter in Baltic Sea sediments can be estimated by comparing their lignin oxidation product yields to those of appropriate terrestrial end members (Moran et al., 1991), but the result is strongly dependent on the choice of the end member. Considering the limited data available on terrestrial end members in the Baltic Sea area, where sampling in rivers is still hindered by political boundaries, we only can make a rough estimate. The average lignin oxidation product yield of the sediments from two coastal lagoons was 13 mg g^{-1} TOC. This value entails dilution by aquatic organic carbon and is most likely a low estimate, because part of the sedimentary organic matter also derives from autochtonous primary production in the coastal lagoons. However, the value is consistent with the yield of sediment from the Neva River mouth (10.2 mg g^{-1} TOC) and soil data. For example, the uppermost mineral horizons of German and Turkish soils contained from 18 to 31 mg g^{-1} TOC (Kögel, 1987) and 18 to 27 mg g^{-1} TOC (Miltner et al., 1996), respectively. By using 13 mg g^{-1} TOC from the rivers as a minimum terrestrial end member yield in the Baltic Sea (without the Gulf of Bothnia) and the basinwide average sediment yield of 3.3 ± 1.1 mg g^{-1} TOC, we calculate the upper limit of the average contribution of land-derived organic matter to Baltic Sea sediments to be $\approx$30%. The lower limit, using 30 mg g^{-1} TOC from soils as the terrestrial end member, is $\approx$10%. We excluded the Gulf of Bothnia from this estimate, because we do not have any data on Skandinavian rivers, which may possibly differ considerably from those in the South. Our estimate is in line with estimates from subregions of the Baltic Sea, such as the Pomeranian Bight (Miltner and Emeis, 2000; Voß and Struck, 1997), the area off the Polish coast (Pempkowiak and Pocklington, 1983), and the Northern Baltic Sea (Bianchi et al., 1997b). Our maximum estimate is at the high end compared with the world ocean (Hedges and Mann, 1979b).

4.2. Sources of Lignin in Baltic Sea Sediments

The overall lignin composition is indicative of a mixture of all tissue types (gymnosperm and angiosperm tissue, woody, and nonwoody material) in sedimentary organic matter of the Baltic Sea, but interbasin differences reveal variable sources and effects of diagenesis and transport.

The general decrease of S/V ratios toward the North is in line with the shift in vegetation from deciduous forest and agricultural land in Central Europe to boreal forests in Skandinavia. The effect is more pronounced in the Gotland Sea than in the Kattegat, because broad-leafed trees reach further to the North in the West of the Baltic Sea due to the Atlantic influence (Walter, 1979). In addition, the terrestrial organic matter in the Gotland Sea is more strongly altered by diagenesis. This usually results in a decrease of S/V, simulating a higher contribution of gymnosperm tissue than in unaltered material (Hedges et al., 1988a).

The contribution of nonwoody material is highest and most variable in the Bornholm and the Gotland Seas (Fig. 5), and both are also characterized by high $(Ad/Al)_V$ ratios indicative of advanced diagenesis (Fig. 6). Their common properties in lignin composition are consistent with deposition of fine-grained terrestrial material that has experienced transformation during passage from the coast. Sediment distribution maps of the Baltic Sea (Emelyanov et al., 1995; Repecka and Cato, 1998) mark the Bornholm and Gotland Basins as terminal sites for deposition of fine-grained material (proportion of the fraction <63 μm is >50%). They collect resuspended fines from their own submarine catchments situated above the halocline (Emeis et al., 1998) and from advection of material imported by occasional saltwater inflows (Liljebladh and Stigebrandt, 1996). Prevalence of agricultural land in the catchment of the Baltic Proper (of which both are parts) alone may not explain the high C/V ratios found (compare Table 1). More likely, preferential transport of silt- and clay-sized fraction enriches the mud in nonwoody tissue (Gough et al., 1993; Keil et al.,

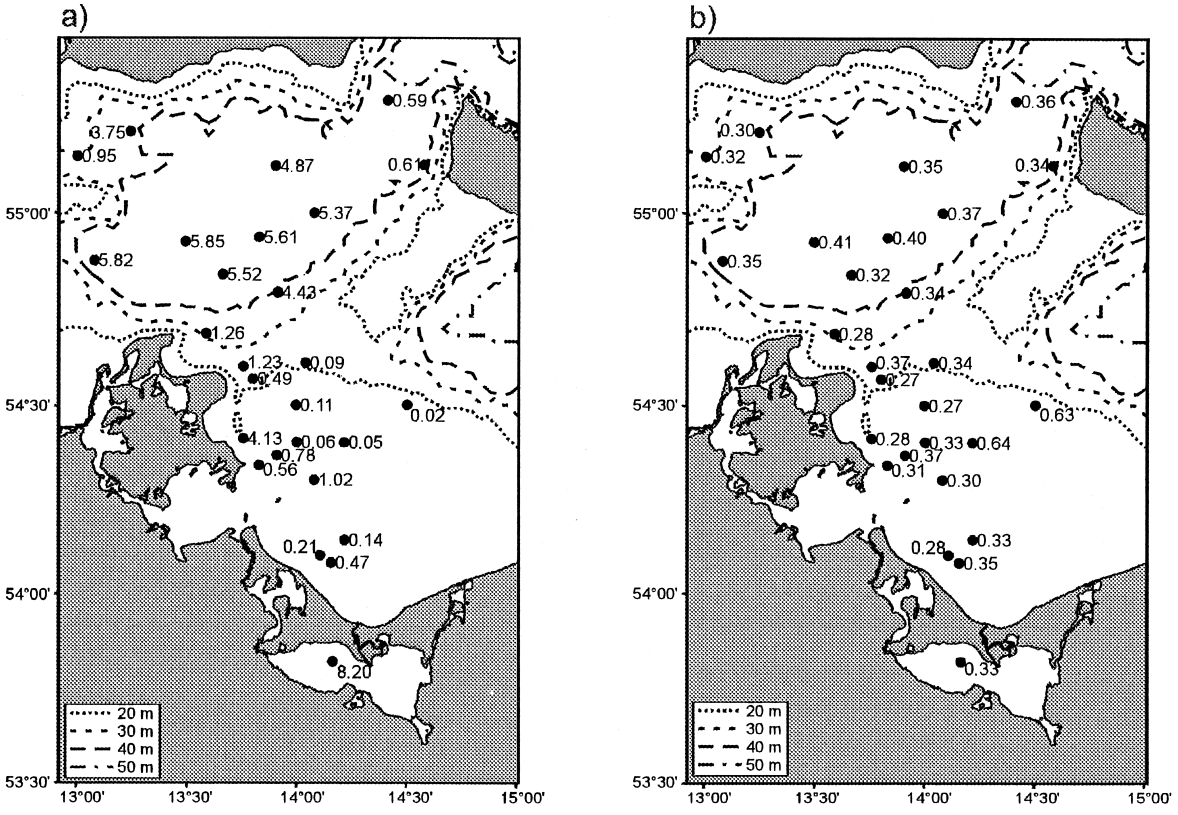

Fig. 7. Map of the Arkona Sea area with location of stations and (a) % TOC and (b) $(Ad/Al)_V$.

1994; Keil et al., 1998) and causes a shift toward higher cinnamyl concentrations in the course of hydrodynamic sorting during lateral transport (Goñi et al., 1998). An argument against this interpretation are significant differences in lignin composition between the adjacent Gdańsk Bay and Bornholm/Gotland Seas (Table 4). Most material imported by the Vistula River is caught in the Gdansk Basin, but a fraction enriched in cinnamyl moieties apparently spills over the separating sill into the adjacent basins. However, relatively short distances should preclude a shift in lignin composition as large as is observed between the sediments. Thus, we have to consider an additional source of lignin to the sediments of the Bornholm and Gotland Seas that must be characterized by both high C/V and high $(Ad/Al)_V$. These are fingerprints of strongly altered nonwoody material. It is unlikely that the highly oxidized material in the sediments of the Gotland and Bornholm Seas is of recent age, because the bottom water in these basins is frequently anoxic.

Highly oxidized terrestrial organic matter may possibly originate from soil organic matter that, after erosion from the land surface, is transported to the sea by rivers. However, there is no reason why the input of this material should be higher to the Bornholm and the Gotland Seas, which receive relatively little freshwater input, than to the other basins of the Baltic Sea. One possible alternative source of material with both high C/V and $(Ad/Al)_V$ ratios are pollen from *Pinaceae*, which are rich in cinnamyl moieties and have intermediate to high vanillic acid-to-aldehyde ratios (Hu et al., 1999; Wehling et al., 1989). *Pinaceae* pollen are easily transported by wind and may be relatively enriched in areas remote from the coast, such as the central parts of the Bornholm and the Gotland Seas. But their contribution would be marked by proportional increases in C/V and $(Ad/Al)_V$ ratios, whereas the C/V increases do not match $(Ad/Al)_V$ increases in Bornholm and Gotland Sea sediments.

Another possible source of highly degraded nonwoody terrestrial organic matter is exhumed peat from strata exposed at the seafloor and progressively eroded because of the ongoing isostatic uplift of the northwestern land. Such a contribution of exhumed terrestrial organic matter explains the advanced oxidation state of the terrestrial fraction in the Gulf of Bothnia sediments. Significant contributions of old organic carbon to surface sediments of the Gotland and Bornholm Seas are indicated by ^{14}C ages of >1000 yr (Erlenkeuser et al., 1974; Kohly, 1998). In contrast, exhumed carbon from the southern Baltic Sea can be excluded as a source. Peat material found at the seafloor of the Pomeranian bight was highly oxidized, but it had S/V and C/V ratios close to zero and thus differed significantly from the presumed source to the sediments from the Northern Baltic Sea (Miltner and Emeis, 2000).

4.3. Small-Scale Spatial Patterns

Small (intrabasin) scale spatial patterns in lignin composition are weak in the Baltic Sea. In the Kattegat/Skagerrak area, we find gradients in lignin oxidation yields, diagenetic alteration and relative importance of nonwoody material at the stations off the Göta Älv River, which is the fifth largest river (by

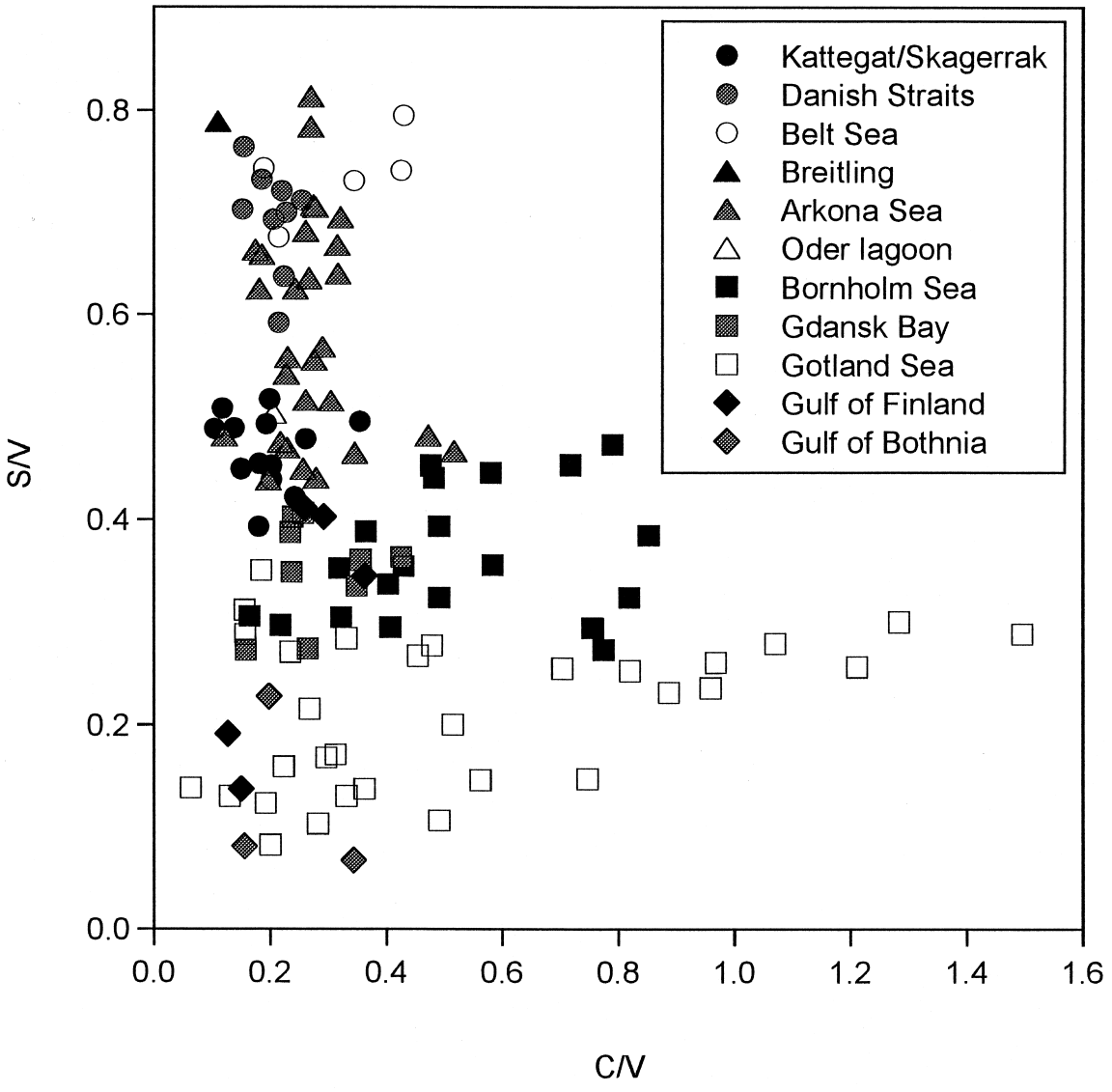

Fig. 8. Scatter plot of S/V vs. C/V in Baltic Sea surface sediments.

runoff) discharging into Baltic Sea (574 m^3/s; Bergström and Carlsson, 1993). The lignin signature at proximal stations thus is closer to the presumed river signal. Similarly, the material imported by the River Neva to the Gulf of Finland results in a pronounced gradient of the lignin oxidation product yields and C/V from the eastern to the western part of the Gulf.

Increased lignin oxidation product yields, less diagenetic alteration, and a lower contribution of nonwoody material are observed in the Northeast of the Gotland Sea and suggest increased terrestrial influence in this area. This most probably reflects the input of terrestrial material from the River Daugava via the Gulf of Riga. The Daugava is the third largest river discharging into the Baltic Sea and delivers ≈659 m^3/s (Bergström and Carlsson, 1993).

Aside from these cases, lignin concentrations and compositions of individual basins are surprisingly homogeneous, despite significant differences in grain size and organic carbon content. Case in point is the Arkona Basin, which is a shallow circular depression (maximum water depth in the center is 55 m), and receives terrestrial input from the Oder River in the South. Only 25% of its seafloor area is depositional and filled with muddy, fine-grained sediment at water depths exceeding 30 m. Figure 7 depicts percent TOC and $(Ad/Al)_V$ ratios of samples from this region. Low TOC percentages are from sandy sediments of the rim; both samples of low and high organic carbon contents do not differ significantly in either $(Ad/Al)_V$ ratios or any other compositional property.

4.4. Implications for Transport of Terrestrial Organic Matter in the Baltic Sea

Although intrabasin differences are muted, lignin concentrations and compositions differ significantly between individual basins. This is illustrated by a S/V vs. C/V plot, where the

individual basins are clearly distinguished (Fig. 8). The characteristic lignin compositions can partly be explained by shifts in the vegetation of the drainage areas. The pronounced differences in lignin composition suggest that the transport of terrestrial organic matter across the basin boundaries is limited. The sills between the basins thus are barriers for particles carrying terrestrial organic matter. Previous studies have shown that clay mineral assemblages in the western Baltic Sea are homogeneous and that their distribution traces the path of inflowing saltwater from the Kattegat (Gingele and Leipe, 1997). Terrestrial organic matter is also transported mainly in form of small particles (Miltner and Emeis, 2000; Pempkowiak and Pocklington, 1983), but compositions in the western basins are quite distinct. We conclude from our results that these small lignin-bearing particles are homogenized during transport in the nepheloid boundary layer of each individual basin, but that they do not pass the sills between the basins in appreciable amounts. Therefore, we conclude that the main mode of transport for terrestrial organic matter is by near-bottom transport and only on the basin scale, rather than by advective transport in the water column and with interbasin currents.

5. CONCLUSIONS

We wanted to test if lignin in marine sediments is a suitable indicator of vegetation in the Baltic Sea region and if interbasin differences are robust enough to record the present-day gradients in river input, vegetation in the river catchment basins, and transport pathways. We find that nonmarine organic matter comprises between 10% and 30% of sedimentary organic matter in the Baltic Sea. The relative contribution of nonmarine organic matter reflects variations in the freshwater input and the size and proximity to land of the individual basins. Sediments from the individual Baltic Sea basins differ significantly in lignin composition, reflecting a variety of sources of terrestrial organic matter to the sediments. Part of the variation, particularly in the relative amount of the syringyl moieties, can be ascribed to shifts in vegetation linked to the climatic conditions in the Baltic Sea drainage area. In the Bornholm and Gotland Basins, high contributions of cinnamyl moieties and an advanced oxidation state of lignin indicate that pollen and peat from eroded strata at the seafloor may be additional sources of terrestrial organic matter.

The pronounced interbasin differences show that the sills between the basins form significant barriers to the transport of terrestrial organic matter. Even small basins such as the Gdańsk Bay efficiently retain terrestrial material and prevent its propagation into areas more remote from land. Therefore, we conclude that most terrestrial organic matter is transported near the sediment–water interface and that transport of terrestrial organic matter between the individual basins is less important than the direct input from the rivers.

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