

# Terrigenous organic matter sources and reactivity in the North Atlantic Ocean and a comparison to the Arctic and Pacific oceans

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## Abstract

Lignin phenol concentrations and compositions in suspended particulate and dissolved organic matter (POM and DOM) were determined in samples from several locations and depths in the western North Atlantic Ocean. POM lignin phenol concentrations were ~2-fold lower than previous measurements in the Pacific Ocean, but represented up to 28% of the total lignin phenols in the water column. Carbon-normalized yields of lignin phenols and  $\delta^{13}\text{C}$  measurements of POM indicate that up to half of the suspended material in deep water is of terrigenous origin and appears to enter the ocean via atmospheric deposition. This finding emphasizes the need for future research into aerosol compositions and fluxes into the oceans. In contrast to POM, DOM lignin phenol concentrations were ~2-fold higher in the Atlantic, with more than two thirds in the high-molecular weight (HMW; > 1 kDa) fraction. Elevated concentrations of dissolved lignin phenols in North Atlantic Deep Water (NADW) indicated that 10–16% of annual fluxes of terrigenous DOM from Arctic rivers could be entrained during NADW formation. The percentage of lignin phenols in the HMW fraction decreases progressively from the Arctic to Atlantic to Pacific Oceans, reflecting an increasing diagenesis of terrigenous DOM. The average residence time of lignin phenols in the Atlantic is ~35 years. Terrigenous DOC accounts for 1–2% of the DOC in surface and deep waters of the North Atlantic.

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## 1. Introduction

Fluxes of terrigenous organic carbon (OC) to marine systems are 3-fold greater than rates of OC preservation sediments (Hedges et al., 1997), a fact that has led to countless studies of terrigenous organic matter (OM) in continental margin and deep-sea sediments. In contrast, studies of terrigenous OM in suspended particulates and the dissolved phase in marine systems have been much

more limited until recently, perhaps in part because an early study indicated that terrigenous OM was only a minor component of dissolved humics in the Pacific Ocean (Meyers-Schulte and Hedges, 1986). As a consequence, we are only just beginning to understand the importance of water column terrigenous OM relative to global cycling.

As unique components of vascular terrestrial plants, lignin phenols have been invaluable tracers of terrigenous OM in marine sediments, and this has been more recently extended to the dissolved phase. Dissolved lignin phenols have been measured in the Atlantic and Pacific Oceans (Hernes and Benner, 2002; Opsahl and Benner, 1997), and the findings highlight differ-

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ences in terrigenous OM transport and cycling between the two basins. For instance, concentrations of high molecular weight (HMW) dissolved lignin phenols in the Atlantic Ocean were found to be 2.6-fold greater than in the Pacific Ocean due to 3.6-fold greater riverine discharge on a per volume basis into the Atlantic Ocean (Opsahl and Benner, 1997). Average residence times for dissolved lignin phenols for the two basins were found to be ~90 years in the Pacific Ocean (Hernes and Benner, 2002) and 21–93 years in the Atlantic Ocean (Opsahl and Benner, 1997). However, the range of reactivities for dissolved lignin phenols varies from days in river plumes due to photooxidation (Hernes and Benner, 2003; Opsahl and Benner, 1998) to centuries for dissolved lignin phenols in the deep Pacific Ocean. As with the humic acid study (Meyers-Schulte and Hedges, 1986), dissolved lignin phenol carbon-normalized yields indicate that terrigenous DOC in seawater is only a minor component at 1–3% (Hernes and Benner, 2002; Opsahl and Benner, 1997). However, even at these low concentrations, the total pool of terrigenous DOC in the ocean is still two orders of magnitude greater than annual carbon preservation in sediments (Hedges, 1992).

In contrast to the Atlantic and Pacific Oceans, recent work has demonstrated the quantitative importance of terrigenous DOM in the Arctic Ocean, again utilizing tracers such as lignin and stable carbon isotopic signatures (Benner et al., 2005; Opsahl et al., 1999). About 14–24% of total DOC in polar surface waters is terrigenous, and 25–33% of terrigenous DOC discharged into the Arctic Ocean by rivers is exported to the North Atlantic Ocean (Benner et al., 2005; Opsahl et al., 1999). The extent to which this terrigenous DOC could be entrained in North Atlantic Deep Water (NADW) is uncertain, but a preliminary estimate indicates 1.7 Tg of terrigenous DOC is exported annually in Denmark Strait Overflow Water and Classical Labrador Sea Water (Benner et al., 2005). Unlike surface waters where terrigenous DOC can be rapidly degraded by photochemical and microbial processes (Benner and Opsahl, 2001; Hernes and Benner, 2003; Opsahl and Benner, 1998) and thus released to the atmosphere as CO<sub>2</sub>, DOC exported via NADW formation is effectively sequestered for hundreds of years.

In addition to dissolved measurements, lignin phenols have recently been measured in particulate samples at Station Aloha in the North Pacific Ocean (Hernes and Benner, 2002). Carbon-normalized yields were high, indicating that as much as half the particulate material could be terrigenous in origin. This finding could be the first link toward our understanding of how aerosols

deposited in the surface ocean are delivered through the water column into the sediments—a mechanism that has been frequently hypothesized but never confirmed in oligotrophic systems where as much as one third of buried carbon is believed to originate from aerosols (Masiello and Druffel, 1998; Prah and Lyle, 1989; Wakeham et al., 1997).

In this study, we focus on the dynamics of dissolved and particulate lignin phenols by measuring vertical profiles at the Bermuda Atlantic Time Series (BATS) station, at several stations in the western North Atlantic Ocean to characterize North Atlantic Deep Water (NADW), and at a station in the northern Gulf of Mexico. The primary objectives of this study were: (1) to investigate sources of terrigenous DOM in NADW, (2) to conduct an inter-basin comparison of lignin phenol concentrations and compositions, and (3) to better understand sources and cycling of terrigenous POM in the open ocean.

## 2. Sampling and methods

Samples were collected on a cruise track between coastal North Carolina and the Bermuda Atlantic Time Series (BATS) station (31°50'N; 64°10'W) in the North Atlantic Ocean (Fig. 1) in June/July 2000 aboard the *R/V Cape Hatteras*. Water was collected from various depths using Niskin bottles mounted on a rosette with a CTD. Sampling at most stations was focused on four water masses of North Atlantic Deep Water (NADW): Upper Labrador Sea Water (ULSW), Classical Labrador Sea Water (CLSW), Iceland–Scotland Overflow Water (ISOW), and Denmark Strait Overflow Water (DSOW). Water mass identification was based on potential temperature, salinity, and density data as per Smethie et al. (2000) and Smethie and Fine (2001). For the purposes of this study, these include 4.1–6.2 °C and 34.96–35.07 psu for ULSW, 3.1–4.1 °C and 34.95–34.96 psu for CLSW, 2.2–3.1 °C and 34.91–34.95 for ISOW, and <2.2 °C and <34.91 psu for DSOW.

For comparative purposes, a depth profile (2–1000 m) was collected from a northern Gulf of Mexico site (28°04'N, 89°12'W) in May 2000 aboard the *R/V Longhorn*. Sampling included four primary water masses which were identified by published depth, salinity, and temperature characteristics. These include Gulf Water (GW) in the upper 200–250 m, Tropical Atlantic Central Water (TACW) from 250–400 m, Antarctic Intermediate Water (AAIW) from 500 to 1000 m, and a mixture of Caribbean Midwater and upper North Atlantic Deep Water (CMW/NADW) at ~1000 m and below (Morrison et al., 1983, and references therein).

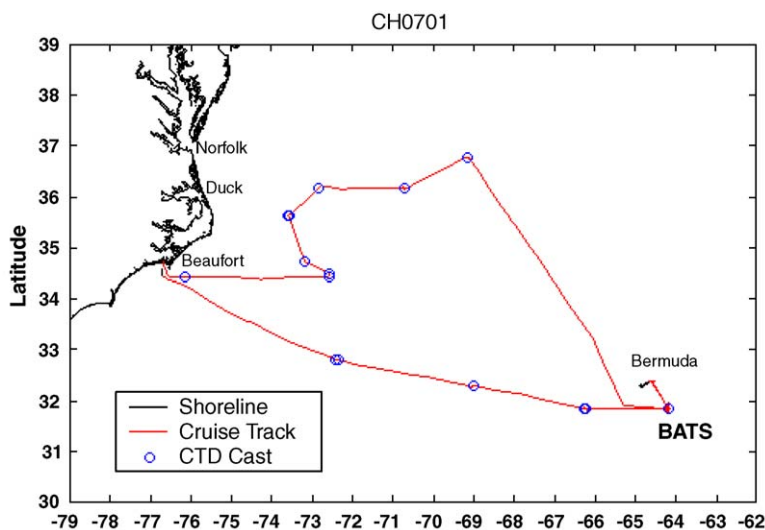


Fig. 1. Cruise track and sampling stations in the north Atlantic.

At most stations, lignin was concentrated by solid phase extraction (SPE) using Varian Mega Bond Elut C18 cartridges according to the protocol of Louchouart *et al.* (2000). Briefly, this involved filtering (0.2- $\mu\text{m}$  pore-size polycarbonate filter cartridges) and acidifying (pH 2.5) seawater samples (15 L) and then pumping them through C18 cartridges at a flow rate of  $\sim 60 \text{ mL min}^{-1}$  using peristaltic pumps. Immediately prior to extracting the sample, the C18 cartridges were first cleaned and primed by rinsing with 50 mL of methanol followed by 50 mL of Milli-Q water acidified to pH 2.5. In five instances, a second cartridge was placed in series with the primary cartridge to evaluate extraction efficiencies.

At BATS, lignin was concentrated both by SPE and ultrafiltration with samples from eight depths. At each depth,  $\sim 700 \text{ L}$  of seawater was collected with four separate casts. SPE was carried out on 15 L of 0.2- $\mu\text{m}$  filtered water from this composite as described above. From 600 L of this composite, the POM (0.1–60  $\mu\text{m}$ ) fraction was isolated aboard ship using an Amicon DC10L ultrafiltration system with a polysulfone hollow fiber filter (H5MP01) as described previously (Benner *et al.*, 1997). The filtrate from the DC10L system was fed directly into an Amicon DC30 ultrafiltration system with polysulfone membranes (S10N1; 1000 Dalton cutoff). After concentration to a volume of  $\sim 10 \text{ L}$  the HMW ( $\sim 1$ –100 nm) sample was transferred to the Amicon DC10L with S10N1 membranes, concentrated to a volume of  $\sim 1 \text{ L}$ , and desalted by diafiltration with 18 L of Milli-Q water (Benner *et al.*, 1997). The LMW filtrate ( $< 1 \text{ nm}$ ) from the last two filtration steps was collected, mixed, and subsampled for lignin SPE (30 L) and DOC (75 mL)

analyses, while the diafiltered HMW concentrate was transferred to a polycarbonate bottle and frozen. The HMW fraction was later dried under vacuum in a Savant SpeedVac concentrator, weighed, and stored for chemical analyses.

In addition to the BATS samples, ultrafiltration was carried out at seven other stations. These include two stations above the slope on the northern track (collected at 1900 and 4300 m) with the full suite of POM, HMW, and LMW samples collected using the identical configuration as outlined above, and five stations (50–2000 m) in which only POM samples were isolated using an Amicon DC10L ultrafiltration system with a cellulose spiral membrane. The latter has a  $\sim 30,000$  Dalton ( $\sim 5 \text{ nm}$ ) cutoff as compared to 0.1  $\mu\text{m}$  for the polysulfone filter described above.

Lignin was analyzed using the CuO oxidation and extraction scheme of Hedges and Ertel (1982) with modifications described by Opsahl and Benner (1997). As per Louchouart *et al.* (2000), sample vessels (i.e. mini-bombs) and solvents were sparged and purged with argon prior to oxidation. Also following Louchouart *et al.* (2000), 10–15 mg of glucose was included in all oxidations in order to eliminate superoxidation effects. HMW samples were weighed into the mini-bombs, while SPE samples were first eluted with 50 mL methanol, dried in the Savant SpeedVac concentrator, redissolved in 8 wt.% NaOH in an argon atmosphere, and transferred to mini-bombs for oxidation, as outlined in Louchouart *et al.* (2000) and Hernes and Benner (2002).

Separation of lignin-derived phenols was achieved using a Hewlett Packard 5890A gas chromatograph fitted with a DB5-MS capillary column (30 m, 0.25-

mm inner diameter, J&W Scientific) and equipped with a Hewlett Packard 5972 mass selective detector. Quantification was achieved using selected ion monitoring with cinnamic acid as an internal standard (Louchouart et al., 2000; Opsahl and Benner, 1998) following the calibration scheme of Hernes and Benner (2002). All samples were blank-corrected due to the presence of trace amounts of contamination in the NaOH reagent. The blank averaged ~30 ng of lignin phenols and was never > 15% of the sample (generally < 10%). Previous determination of SPE procedural blanks indicates no statistical difference from CuO oxidation blanks (Louchouart et al., 2000).

Organic carbon and stable carbon isotope ratios were measured on dried HMW DOM and ultrafiltered POM samples in duplicate using a Finnegan Delta Plus system with in-line combustion. Stable carbon isotopes are presented as  $\delta^{13}\text{C}$  (‰) relative to the Pee Dee Belemnite standard. Dissolved organic carbon (DOC) analyses were carried out by high temperature (680 °C) oxidation with a Shimadzu TOC-5000 carbon analyzer. All samples were collected in TFE-lined bottles and stored frozen until analysis. All reported values were corrected for the instrument blank, which was measured at the time of analysis (Benner and Strom, 1993). Mass balances of DOC [(HMW + measured LMW) \* 100% / Total DOC] during ultrafiltration ranged from 81% to 100% (90% average). As such, LMW DOC concentrations were calculated by difference between total DOC and HMW DOC.

### 3. Results

#### 3.1. OC concentrations

Suspended POC concentrations using the polysulfone membrane (0.1–60  $\mu\text{m}$ ) ranged from 0.07 to 0.31

$\mu\text{M}$  at BATS and two slope stations (Tables 1 and 2). On average, POC represented 0.3% of total OC in the water column. POC concentrations using the cellulose membranes were higher due to the lower size cutoff (0.005–60  $\mu\text{m}$ ), and ranged from 0.14 to 1.82  $\mu\text{M}$ . Data from the cellulose membranes serves primarily as validation of data from the polysulfone membranes, and as such has not been tabulated or plotted.

Concentrations of DOC at BATS and the two slope stations ranged from 32–54  $\mu\text{M}$  in the LMW fraction, 10.4–15.8  $\mu\text{M}$  in the HMW fraction, and 46–70  $\mu\text{M}$  in 0.2- $\mu\text{m}$  filtered water (Tables 2 and 3).

#### 3.2. Stable carbon isotopes

Stable carbon isotopes were measured on ultrafiltered POM and HMW DOM. Values for  $\delta^{13}\text{C}$  in ultrafiltered POM were relatively depleted in  $^{13}\text{C}$ , ranging from –23.4‰ at the surface to –27.0‰ at depth (Tables 1 and 2). In contrast, HMW DOM  $\delta^{13}\text{C}$  values at BATS were relatively enriched in  $^{13}\text{C}$ , ranging from –20.8 to –21.2‰, and indicated a predominant marine source.

#### 3.3. SPE extraction efficiency

An important consideration in the measurement of dissolved lignin phenols using the SPE technique is the extraction efficiency of the C18 cartridges, i.e. the percentage of dissolved lignin phenols that is recovered from seawater. Extraction efficiencies in this study were determined by two means: (1) mass balance comparisons of total dissolved lignin phenol concentrations determined by SPE relative to the sum of HMW and LMW dissolved lignin phenols derived from ultrafiltration samples (representing the total dissolved lignin phenols), and (2) by recovery of lignin phenols that

Table 1  
Concentrations of POC ( $\mu\text{M}$ ), lignin phenols ( $\text{ng L}^{-1}$ ) and carbon-normalized lignin yields ( $\mu\text{g 100 mg OC}^{-1}$ ) in the 0.1–60  $\mu\text{m}$  fraction of water samples from the Bermuda Atlantic Time Series station

Depth	POC	$\delta^{13}\text{C}$ (‰)	VAL	VON	VAD	SAL	SON	SAD	$\Sigma_6$	$\Lambda_6$
BATS										
20	0.31	–23.4	0.89	0.23	0.46	0.12			1.70	45
100	0.22	–23.8	1.54	0.43	0.54	0.30	0.12	0.20	3.13	118
350	0.30	–25.0	4.85	1.17	1.61	1.86	0.34	0.40	10.2	283
500	0.09	–26.8	1.56	0.42	0.67	0.37	0.12		3.14	285
1363 <sup>a</sup>	0.10	–25.4								
2010 <sup>a</sup>	0.07	–27.0								
3253	0.14	–26.7	1.83	0.48	0.89	0.32			3.52	211
4302	0.18	–26.6	2.28	0.64	1.63	0.64	0.19	0.15	5.53	260

POC, particulate organic carbon; VAL, vanillin; VON, acetovanillone; VAD, vanillic acid; SAL, syringaldehyde; SON, acetosyringone; SAD, syringic acid;  $\Sigma_6$ , sum of six phenols;  $\Lambda_6$ , carbon-normalized yields of six phenols.

<sup>a</sup> Lignin phenols not determined due to insufficient sample amount.

Table 2

Concentrations of dissolved (LMW and HMW) and particulate (0.1–60  $\mu\text{m}$ ) lignin phenols ( $\text{ng L}^{-1}$ ), carbon-normalized lignin phenol yields ( $\mu\text{g } 100 \text{ mg OC}^{-1}$ ), and select compositional parameters in water samples from stations along the U.S. Atlantic continental slope

Depth (m)	Size Fract.	Lat.	Long.	$\Phi$ ( $^{\circ}\text{C}$ )	Salinity (PSU)	OC ( $\mu\text{M}$ )	$\Sigma_6$	$A_6$	$\delta^{13}\text{C}$ (‰)	S/V	(Ad/Al) <sub>v</sub>
1904	LMW	36°47'N	69°10'W	3.49	34.94	37	11.3	2.5		0.16	1.19
1904	HMW	36°47'N	69°10'W	3.49	34.94	11	50.0	36.6	−21.1	0.37	1.06
1904	POM	36°47'N	69°10'W	3.49	34.94	0.15	10.1	580	−25.4	0.26	0.36
4210	LMW	36°10'N	70°43'W	1.84	34.89	37	30.4	6.7		0.10	0.61
4210	HMW	36°10'N	70°43'W	1.84	34.89	10	51.6	42.3	−21.2	0.51	0.91
4210	POM	36°10'N	70°43'W	1.84	34.89	0.26	21.9	706	−25.1	0.30	0.28

$\Phi$ , potential temperature;  $\Sigma_6$ , sum of six phenols;  $A_6$ , carbon-normalized yields of six phenols; S/V, ratio of syringyl to vanillyl phenols; (Ad/Al)<sub>v</sub>, ratio of vanillic acid to vanillin; HMW, high-molecular weight dissolved fraction (1–100 nm); LMW, low-molecular weight dissolved fraction (<1 nm); POM, particulate organic matter.

passed through the primary SPE cartridge and are recovered using a second SPE cartridge in series. Average extraction efficiencies based on mass balance were  $88 \pm 25\%$  ( $n=6$ ), while those based on cartridges in series were  $73 \pm 6\%$  ( $n=4$ ). For comparison, previous extraction efficiencies based on ultrafiltration mass balances were 75–80% in the north Pacific Ocean at Station Aloha (Hernes and Benner, 2002), and 80–

85% in the Mississippi River plume in the Gulf of Mexico (Hernes and Benner, 2003).

### 3.4. Lignin phenol concentrations

#### 3.4.1. Ultrafiltration

At BATS, POC lignin phenol concentrations ranged from 1.7 to 10  $\text{ng L}^{-1}$  (Fig. 2b; Table 1), while slope

Table 3

Concentrations of DOC ( $\mu\text{M}$ ) and individual lignin phenols ( $\text{ng L}^{-1}$ ) in water samples from the Bermuda Atlantic Time Series station in the Atlantic Ocean

Depth	$\Phi$ ( $^{\circ}\text{C}$ )	Salinity(PSU)	DOC	VAL	VON	VAD	SAL	SON	SAD
SPE total									
20	23.76	36.57	70	8.24	3.48	14.0	4.07	2.73	11.7
100	19.28	36.65	60	7.99	2.47	12.4	4.50	2.72	10.8
350	18.00	36.56	53	8.04	2.48	9.27	2.99	1.87	6.32
500	17.43	36.49	52	10.3	3.39	11.3	3.24	2.41	10.5
1363	4.63	35.04	46	10.8	5.70	14.4	3.43	3.38	10.6
2010	3.41	34.95	46	14.5	6.26	16.3	3.88	3.18	9.35
3253	2.23	34.92	46	10.6	6.19	9.55	2.57	2.18	2.41
4302	1.84	34.89	46	7.64	6.67	13.4	2.74	3.14	7.62
HMW									
20	23.76	36.57	16	9.26	2.06	8.14	4.35	1.37	2.95
100	19.28	36.65	12	6.28	1.66	7.96	3.26	1.21	1.14
350	18.00	36.56	10	8.43	2.35	8.41	3.32	1.41	2.33
500	17.43	36.49							
1363	4.63	35.04	13	14.4	5.74	15.1	4.48	2.28	4.48
2010	3.41	34.95	12	16.0	5.45	12.5	5.87	2.92	4.86
3253	2.23	34.92	11	12.9	4.47	12.3	5.01	2.56	3.89
4302	1.84	34.89	12	14.2	4.82	13.8	6.14	2.66	4.26
LMW									
20	23.76	36.57	54	2.49	1.75	4.97	1.00	0.96	2.51
100	19.28	36.65	48	2.08	1.62	4.26	0.80	0.65	1.57
350	18.00	36.56	43						
500	17.43	36.49							
1363	4.63	35.04	34	3.13	2.02	3.52	1.15	0.73	1.34
2010	3.41	34.95	34	2.45	1.92	4.53	1.07	0.85	1.76
3253	2.23	34.92	35	6.89	2.90	4.95	1.23	0.88	0.78
4302	1.84	34.89	32	4.48	2.90	4.88	0.90	0.76	1.06

$\Phi$ , potential temperature; DOC, dissolved organic carbon; VAL, vanillin; VON, acetovanillone; VAD, vanillic acid; SAL, syringaldehyde; SON, acetosyringone; SAD, syringic acid; HMW, high-molecular weight dissolved fraction (1–100 nm); LMW, low-molecular weight dissolved fraction (<1 nm).

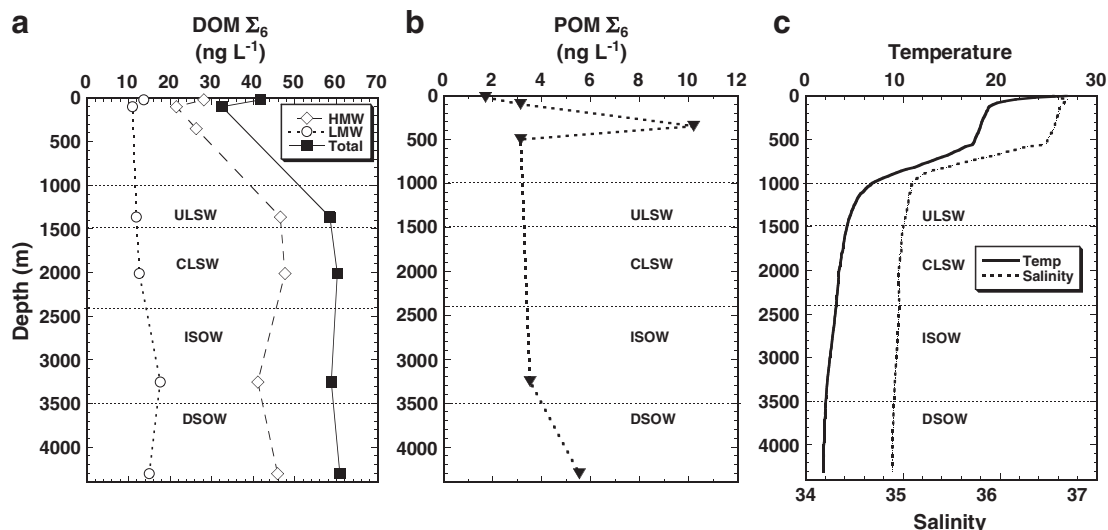


Fig. 2. Concentrations of lignin phenols in (a) LMW, HMW, and total DOM, and (b) suspended POM at BATS; temperature and salinity profile in (c). Abbreviations for water masses in this and all figures: ULSW, Upper Labrador Sea Water; CLSW, Classic Labrador Sea Water; ISOW, Iceland/Scotland Overflow Water; DSOW, Denmark Straits Overflow Water.

samples ranged from 10 to 22  $\text{ng L}^{-1}$  (Table 2). POC lignin phenols constituted 4–28% of the total lignin in the water column, which is considerably higher than the percentage of total OC contained in POC.

Concentrations of lignin phenols at BATS in the HMW fraction were lower in the upper 350 m (22–28  $\text{ng L}^{-1}$ ) than in NADW (41–48  $\text{ng L}^{-1}$ ; Fig. 2; Table 3). In contrast, concentrations in the LMW fraction showed fairly uniform behavior throughout the water column, varying from 11 to 18  $\text{ng L}^{-1}$  with an average of 14  $\text{ng L}^{-1}$  (Fig. 2a; Table 3). In rivers, as much as 90% of dissolved lignin is in the HMW fraction (Opsahl and Benner, 1998). At BATS, the percentage of dissolved lignin in the HMW fraction ranged from

66% to 80%, with higher values in the NADW and lower values near the surface.

#### 3.4.2. NADW SPE

Lignin phenol concentrations as determined by SPE in the four major components of NADW show remarkable uniformity across the stations sampled. Upper Labrador Sea Water (ULSW) and Classical Labrador Sea Water (CLSW) differed by <5% with averages ( $n=6$ ) of 40.9 and 41.8  $\text{ng L}^{-1}$  (Table 4). Similarly, Iceland–Scotland Overflow Water (ISOW) and Denmark Strait Overflow Water (DSOW) were also within 5%, averaging 37.5  $\text{ng L}^{-1}$  ( $n=6$ ) and 36.1  $\text{ng L}^{-1}$  ( $n=5$ ) (Table 4). All values were within one standard

Table 4  
Average lignin-derived phenol data for North Atlantic Deep Water masses

Depth	$n$	$\Phi$ (°C)	Salinity (PSU)		DOC	VAL	VON	VAD	SAL	SON	SAD	$\Sigma_6$	$A_6$	S/V	(Ad/Al) <sub>v</sub>	(Ad/Al) <sub>s</sub>
ULSW	6	4.42–4.76	35.00–35.05	Avg	46.1	13.4	5.5	11.5	4.2	2.6	3.7	40.9	7.4	0.35	0.9	1.0
				(StDev)	(1.2)	(2.7)	(0.5)	(2.3)	(0.4)	(0.4)	(3.4)	(4.9)	(1.0)	(0.11)	(0.3)	(1.0)
CLSW	6	3.30–3.49	34.94–34.98	Avg	45.5	13.4	5.8	11.8	4.4	2.7	3.7	41.8	7.6	0.34	0.9	0.9
				(StDev)	(1.3)	(1.5)	(0.9)	(3.0)	(0.5)	(0.4)	(2.8)	(7.7)	(1.3)	(0.05)	(0.2)	(0.8)
ISOW	6	2.18–2.33	34.91–34.92	Avg	44.1	13.1	5.6	10.2	3.8	2.4	2.4	37.5	7.1	0.30	0.8	0.6
				(StDev)	(1.6)	(2.5)	(0.7)	(2.4)	(0.9)	(0.2)	(0.4)	(6.1)	(1.2)	(0.05)	(0.1)	(0.1)
DSOW	5	1.84–1.87	34.89–34.89	Avg	43.6	10.7	5.1	10.5	3.8	2.5	3.5	36.1	6.9	0.37	1.0	1.1
				(StDev)	(1.6)	(2.7)	(1.1)	(2.1)	(0.8)	(0.4)	(2.3)	(5.5)	(1.1)	(0.07)	(0.4)	(1.0)

As in Tables 1–3, and (Ad/Al)<sub>s</sub>, ratio of syringic acid to syringaldehyde.

deviation of each other. This uniformity also extended to carbon-normalized yields of lignin phenols, ranging from 6.9 to 7.6  $\mu\text{g } 100 \text{ mg OC}^{-1}$ , as well as compositional ratios (Table 4).

### 3.5. Lignin parameters for ultrafiltered samples

#### 3.5.1. Carbon-normalized yields, $A_6$

Carbon-normalized yields of lignin phenols,  $A_6$ , are often used in end-member mixing models to estimate the relative contribution of terrigenous OM in marine systems. POM  $A_6$  ranged from 45  $\mu\text{g } 100 \text{ mg OC}^{-1}$  in surface waters at BATS to 706  $\mu\text{g } 100 \text{ mg OC}^{-1}$  collected in slope waters (0.1–60  $\mu\text{m}$ ; Tables 2 and 3), while  $A_6$  values for the cellulose membranes (0.005–60  $\mu\text{m}$ ) varied from 8 to 112  $\mu\text{g } 100 \text{ mg}$

$\text{OC}^{-1}$ . In contrast, HMW and LMW  $A_6$  values were considerably lower. At BATS, HMW  $A_6$  values varied from 14  $\mu\text{g } 100 \text{ mg OC}^{-1}$  in surface waters to 34  $\mu\text{g } 100 \text{ mg OC}^{-1}$  at 2010 m (Fig. 3a), while the LMW fraction had the lowest  $A_6$  values, ranging from 1.8  $\mu\text{g } 100 \text{ mg OC}^{-1}$  near the surface to 4.0  $\mu\text{g } 100 \text{ mg OC}^{-1}$  at 3253 m (Fig. 3a). For comparison, previous HMW  $A_6$  values measured at BATS averaged 21  $\mu\text{g } 100 \text{ mg OC}^{-1}$  (Opsahl and Benner, 1997). Combined  $A_6$  values of the HMW and LMW fractions were 4.5  $\mu\text{g } 100 \text{ mg OC}^{-1}$  in surface waters increasing to 11  $\mu\text{g } 100 \text{ mg OC}^{-1}$  in NADW (Fig. 3a).

#### 3.5.2. Syringyl/vanillyl ratios

Ratios of syringyl phenols to vanillyl phenols, S/V, can be used to distinguish between gymnosperm and

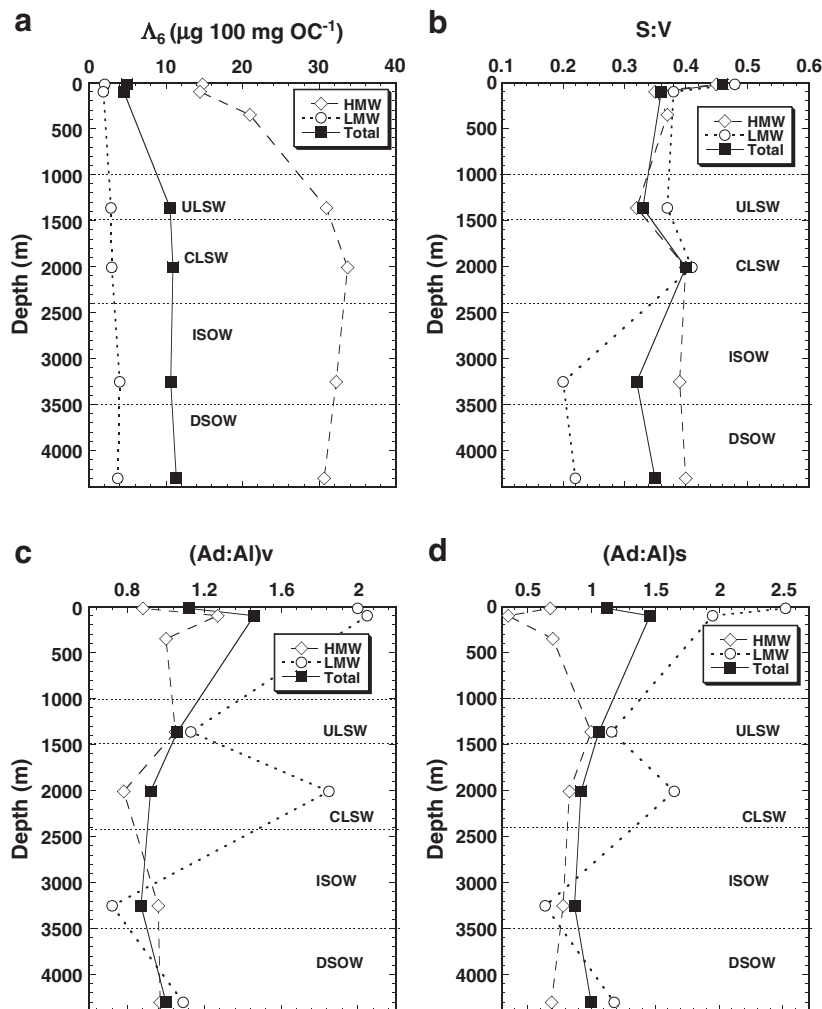


Fig. 3. Depth profiles of (a) carbon-normalized lignin phenol yields, (b) ratio of syringyl to vanillyl phenols, S/V, (c) ratio of vanillic acid to vanillin, (Ad:Al)v, and (d) ratio of syringic acid to syringaldehyde, (Ad:Al)s, in LMW, HMW, and total DOM at BATS.

Table 5

Temperature ( $^{\circ}\text{C}$ ), salinity (PSU), dissolved oxygen ( $\text{O}_2$ :  $\mu\text{M}$ ), DOC ( $\mu\text{M}$ ), total SPE lignin phenol concentrations ( $\Sigma_6$ :  $\text{ng L}^{-1}$  super 1), carbon-normalized lignin phenol yields ( $A_6$ :  $\mu\text{g } 100 \text{ mg OC}^{-1}$ ), and select lignin parameters in the Gulf of Mexico

Depth	Sample	Temp.	Salinity	$\text{O}_2$	DOC	$\Sigma_6$	$A_6$	S/V	(Ad/Al)v
2	LMW	27.5	35.93	127	109	142	12	1.16	2.40
2	HMW	27.5	35.93	127	14	60.6	36	0.68	1.25
2	Total	27.5	35.93	127	123	202	17	0.99	1.88
30	SPE	24.3	36.36	144	136	69.9	4.3	0.75	1.26
80	SPE	21.2	36.45	149	70	59.6	7.1	0.63	1.08
115	SPE	18.8	36.50	105	58	71.8	10.3	0.56	0.79
250	SPE	13.5	35.75	103	55	41.4	6.3	0.49	0.89
500	SPE	8.7	35.05	103	49	44.1	7.5	0.41	0.73
750	SPE	6.0	34.90	131	52	59.0	9.5	0.51	0.93
1000	SPE	4.9	34.94	157	52	59.7	9.6	0.44	0.78

As in Tables 1 and 2.

angiosperm sources, due to the unique occurrence of syringyl phenols in the latter (Hedges and Mann, 1979). S/V ratios have also been shown to decrease during photooxidation due to preferential removal of syringyl phenols (Hernes and Benner, 2003; Opsahl and Benner, 1998). The S/V ratio in POM ranged from 0.1 to 0.3 for samples  $>0.1 \mu\text{m}$  and 0.1 to 0.4 for samples  $>0.005 \mu\text{m}$ . Ratios of S/V in the dissolved phase were somewhat higher, with HMW lignin ranging from 0.32 to 0.45, LMW lignin from 0.20 to 0.48, and total dissolved lignin from 0.32 to 0.46 (Fig. 3b). Ratios of S/V in the dissolved samples were all highest in the 20-m sample. The HMW values in this study were somewhat higher than previous HMW measurements at BATS, which ranged from 0.1 to 0.3 (Opsahl and Benner, 1997).

### 3.5.3. Acid/aldehyde ratios

Ratios of vanillic acid to vanillin, (Ad/Al)v, and syringic acid to syringaldehyde, (Ad/Al)s, are commonly used as diagenetic indicators on a relative scale, with higher values interpreted to indicate greater degradation. In this sample set, POM (Ad/Al)v ranged from 0.3 to 0.7 for both the  $>0.1 \mu\text{m}$  and  $>0.005 \mu\text{m}$  fractions. In the dissolved phase, (Ad/Al)v for the HMW dissolved fraction ranged from 0.8 to 1.3 (1.0 average), LMW values from 0.7 to 2.15 (1.5 average), and total dissolved from 0.9 to 1.5 (1.1 average) (Fig. 3c). Ratios of syringic acid to syringaldehyde, (Ad/Al)s, were highly variable in POM samples and in some cases were not determinable due to the low yields of syringyl phenols in the particulate samples. Ratios of (Ad/Al)s in the dissolved phase were similar to (Ad/Al)v counterparts,

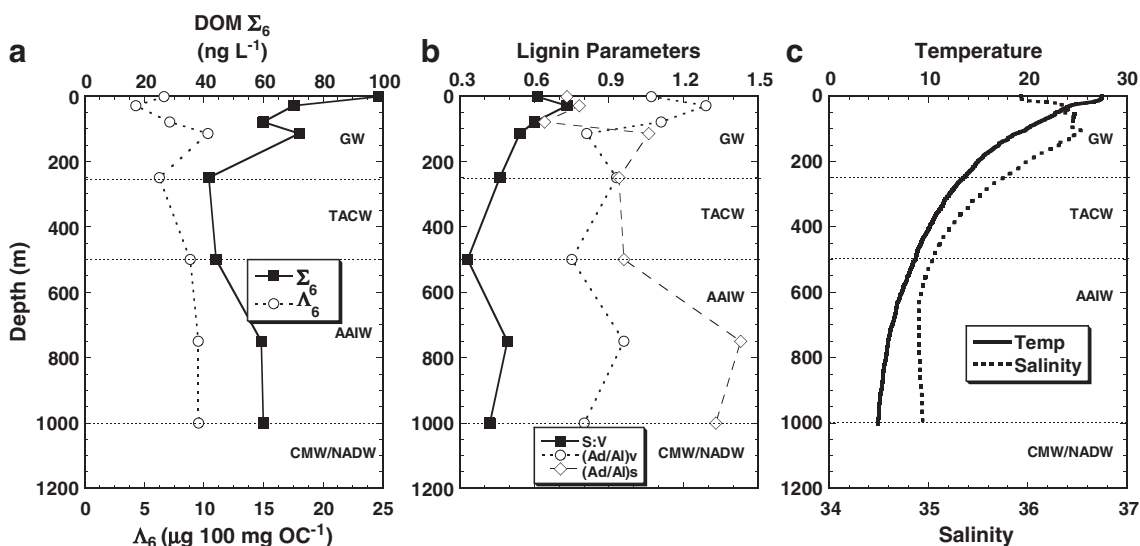


Fig. 4. Concentrations of (a) lignin phenols ( $\text{ng L}^{-1}$ ) and carbon-normalized lignin yields ( $A_6$ ), (b) the lignin parameters S/V, (Ad/Al)v, and (Ad/Al)s, and (c) temperature and salinity vs. depth at a northern Gulf of Mexico site. Abbreviations for water masses: GW, Gulf Water; TACW, Tropical Atlantic Central Water; AAIW, Antarctic Intermediate Water; CMW/NADW, Caribbean Midwater/North Atlantic Deep Water.

varying from 0.6 to 1.0 (0.72 average) in the HMW fraction, 0.6 to 2.5 (1.5 average) in the LMW fraction, and 0.75 to 1.0 (0.9 average) in the combined total (Fig. 3d).

### 3.6. Gulf of Mexico profile

Lignin concentrations in DOM from the Gulf of Mexico (2–1000 m) are presented in Table 5. Lignin concentrations of the six vanillyl and syringyl phenols range from a minimum of 41 ng L<sup>-1</sup> at 250 m to 98 ng L<sup>-1</sup> at the surface with an average of ~60 ng L<sup>-1</sup> (Fig. 4a). Carbon-normalized yields varied from a low of 4.3 to 10.3 µg 100 mg OC<sup>-1</sup> (Fig. 4a). S/V and (Ad/Al)/v ratios were generally higher in the surface and lower at depth, ranging from 0.41 to 0.75 and 0.73 to 1.26, respectively (Fig. 4b,c,d).

## 4. Discussion

### 4.1. North Atlantic deep water signature

The Arctic Ocean receives ~10% of the global riverine input but contains only 1% of the global ocean volume (Opsahl et al., 1999 and references therein). A large fraction of the terrigenous DOC entering the Arctic Ocean is exported to the North Atlantic via surface waters (Benner et al., 2005; Opsahl et al., 1999). The ultimate fate of terrigenous DOC exported from the Arctic Ocean has ramifications for our understanding of ocean circulation as well as the processes responsible for the removal of terrigenous DOC. We now know that some of the terrigenous DOC exported in surface waters is incorporated into components of North Atlantic Deep Water (Benner et al., 2005). Elevated concentrations of HMW lignin phenols (85–107 ng L<sup>-1</sup>) were measured in DSOW and CLSW in the Irminger Sea (Benner et al., 2005).

When compared to surface waters at BATS, deep-water lignin phenol concentrations from the four components of NADW were elevated by ~50% (Fig. 2), while carbon-normalized yields at depth are approximately doubled. Further, this increase appears to be driven entirely by an increase in the HMW fraction of dissolved lignin phenols, consistent with a relatively fresh riverine source (typically >75% HMW) as would be expected from the Arctic Ocean (Benner et al., 2005). The S/V ratios in NADW ranged from 0.3 to 0.4 (Table 4), and are also consistent with Arctic sources (Benner et al., 2005; Opsahl et al., 1999).

The annual HMW lignin phenol discharge from Arctic rivers ( $6.9\text{--}11.5 \times 10^{-2}$  Tg year<sup>-1</sup>) is estimated

based on Arctic riverine concentrations ranging from 20.9 to 34.9 µg L<sup>-1</sup> (Opsahl et al., 1999) and annual riverine discharge of 3,300 km<sup>3</sup> year<sup>-1</sup> (Aagaard and Carmack, 1989). At BATS, HMW lignin phenol concentrations in the four water masses that comprise NADW are ~20 ng L<sup>-1</sup> higher than surface values (Fig. 2), and this “excess” lignin represents the potential loading of Arctic rivers to NADW. Combining this increased loading with an estimated formation rate for NADW of 17.2 Sv (Smethie and Fine, 2001) yields an annual dissolved lignin phenol export flux of  $1.1 \times 10^{-2}$  Tg year<sup>-1</sup>, which represents 10–16% of the annual riverine discharge of dissolved lignin phenols in the Arctic Ocean. Benner et al. (2005) calculated export fluxes of 6.5% for two of the four NADW water masses (CLSW and DSOW) further upstream using excess lignin concentrations of 48 and 68 ng L<sup>-1</sup> and more conservative estimates of deep water formation rates. The lower downstream excess lignin in this study reflect a combination of dilution and potential degradation. Clearly, more measurements are needed to accurately determine how much Arctic river DOM is entrained in NADW, but this study suggests that it could be a significant flux.

Measurements of HMW lignin phenols at BATS measured ~10 year apart reveal one other intriguing dynamic of terrigenous DOM cycling in NADW. While surface samples measured in 1992 (25 ng L<sup>-1</sup>) and in this study (28 ng L<sup>-1</sup>) are quite comparable (Opsahl and Benner, 1997), lignin phenol concentrations in CLSW have increased considerably (28 ng L<sup>-1</sup> at 2400 m in 1992 vs. 48 ng L<sup>-1</sup> at 2000 m in 2001). Formation of CLSW is known to undergo considerable temporal variation on a decadal time scale (Curry et al., 1998; Dickson et al., 1996; Talley and McCartney, 1982), and these differences in lignin concentrations appear to reflect temporal variability in the injection of Arctic river DOM into CLSW.

### 4.2. Sources and cycling of POC

Despite the fact that POC concentrations are much lower than DOC concentrations, POC plays a dominant role in the vertical transport of materials to sediments (Hernes et al., 2001; Seuss, 1980; Wakeham and Lee, 1989). The vertical transport of terrigenous organic matter in the open ocean has been something of an enigma. Several markers of terrigenous organic matter have been measured in marine sediments, including long-chain lipids, cutin, and lignin phenols (Gough et al., 1993; Prahl and Lyle, 1989; Wakeham et al., 1997), in addition to black carbon likely derived from biomass

burning (Goldberg, 1985; Masiello and Druffel, 1998). At the bulk level,  $\delta^{13}\text{C}$  values of  $-26.5\text{‰}$  to  $-26.7\text{‰}$  for aerosols over the Pacific and Atlantic Ocean indicate a predominant terrigenous origin (Chesselet et al., 1981). Molecular analyses have demonstrated the presence of numerous terrigenous biomarkers in aerosols resulting from biomass burning, including lignin-derived constituents (Rogge et al., 1998; Simoneit et al., 1993). This has led to speculation that terrigenous biomarkers in open ocean sediments are derived from an aerosol source. However, very few aerosol compositions have been determined quantitatively, making it difficult to test the feasibility of this mechanism from a mass balance perspective, and none of the terrigenous markers found in sediments have ever been measured in open ocean water column particulates prior to the discovery of significant lignin phenol content in ultrafiltered POM at Station Aloha (Hernes and Benner, 2002).

Similar to Station Aloha samples, carbon-normalized lignin phenol yields ( $260 \mu\text{g } 100 \text{ mg OC}^{-1}$  on average) below 100 m at BATS indicated that POC contained considerable terrigenous content. Increasing lignin phenol yields with depth also indicate that this terrigenous POM is on average much less reactive than marine POM. Recent analysis of a dust sample collected  $\sim 600$  km off the African coast gave carbon-normalized lignin phenol yields of  $7550 \mu\text{g } 100 \text{ mg OC}^{-1}$  (Eglinton et al., 2002). However, aerosol source analysis at BATS indicates that most dust deposited at BATS originates from the North American continent and not Africa (Conte and Weber, 2002). In addition, corresponding  $\delta^{13}\text{C}$  values of ultrafiltered POC at BATS average  $-25.6\text{‰}$ , consistent with a major terrigenous component.

Three mechanisms for delivery of terrigenous POM to the open ocean should be considered: (1) atmospheric transport of aerosols, (2) riverine discharge, and (3) resuspension and horizontal transport of sediments from continental shelves and slopes. In a one-dimensional system, a predominant aerosol source at the surface could lead to a decreasing concentration gradient in lignin phenols with depth, a trend not apparent in these data (Table 3). However, age differences between black carbon vs. sedimentary organic carbon deposited at the same time indicates that black carbon (and hence suspended particulates) may circulate for thousands of years before it reaches the sediments (Masiello and Druffel, 1998). This would indicate that concentrations of suspended particulates derived from aerosols will be much more dependent upon depositional fluxes at the site of water mass formation than the local BATS environment.

If the dominant source is riverine, then it could be expected that particulate lignin phenol concentrations at BATS would be significantly higher than at Station Aloha, given the 3.6-fold greater riverine discharge into the Atlantic Ocean than the Pacific Ocean on a per volume basis (Opsahl and Benner, 1997). However, concentrations at BATS ( $4.5 \text{ ng L}^{-1}$  with polysulfone membranes,  $1.6 \text{ ng L}^{-1}$  with cellulose membranes) were on average 2.9-fold lower than concentrations at Station Aloha (Hernes and Benner, 2002), which would appear to rule out riverine input as a primary source for terrigenous POM in oligotrophic systems.

Resuspension and horizontal transport of sediments is a well-known phenomenon in coastal regimes, leading to increased particle fluxes in sediment traps with increasing depth (e.g. Hedges et al., 1988). Significant concentration gradients of  $^{14}\text{C}$ , DOC, and suspended POC between continental margins and the open ocean are also thought to indicate a net horizontal flux of material toward the open ocean (Bauer and Druffel, 1998). In the Gulf of Mexico, loliolides, which are formed only in sediments, have been measured in the water column at depths that preclude simple diffusion (Bianchi et al., 1997). In this study, the two largest carbon-normalized lignin phenol yields of POC, 580 and  $706 \mu\text{g } 100 \text{ mg OC}^{-1}$ , were derived from deep samples collected over the U.S. Atlantic continental slope (Table 3). Corresponding concentrations of lignin phenols in POM were  $10.1$  and  $21.9 \text{ ng L}^{-1}$ , well above the average concentration at BATS. Concentrations of dissolved lignin phenols were also elevated in these slope samples. The most reasonable explanation for elevated lignin phenol concentrations in POM and DOM slope samples is resuspension of sediments. This could also be partly responsible for elevated lignin phenol concentrations at depth in the Gulf of Mexico profile. If resuspension and horizontal transport is an important mechanism at BATS, then one could expect POM concentrations to increase significantly at depth. In this case, POM concentrations decrease to a minimum at 2010 m before approximately doubling down to  $\sim 4300$  m. Thus, resuspension could be responsible for elevated lignin concentrations in the deep ocean, but does not appear to be a factor above 2500 m.

The presence of high concentrations of lignin phenols in open ocean POM highlights important research directions to pursue in future studies, including (1) extensive temporal and spatial quantification and molecular characterization of aerosol OM fluxes to the ocean, and (2) better spatial coverage of terrigenous markers in POM in marine systems to gain a greater understanding of regions in which riverine and resus-

pension/horizontal transport sources predominate over aerosol sources. Given global averages of 6% for terrestrially derived black carbon in marine sediments (Goldberg, 1985) and regional estimates of terrigenous organic carbon up to 34% (Prahl and Lyle, 1989; Wakeham et al., 1997), it is critical to develop a better understanding of transport and delivery of terrigenous POM to the ocean.

#### 4.3. Dissolved lignin phenol comparisons among ocean basins

Comparisons of lignin phenol concentrations and compositions among the Pacific, Atlantic, Arctic, and Gulf of Mexico highlight important similarities and differences. Station Aloha (Pacific) and BATS (Atlantic) represent two open ocean sites that have minimal direct input of riverine DOM, and as such represent an integration of riverine input from throughout the basin. The Gulf of Mexico exchanges water with the North Atlantic Ocean, including NADW water, but its surface waters are modified by discharge from the Mississippi River. The Arctic Ocean also exchanges water with the North Atlantic Ocean and is heavily influenced by riverine input.

Average residence time comparisons between ocean basins reflect relative environmental reactivities combined with physical export. Actual residence times of dissolved lignin phenols can vary from days in ocean margins due to photooxidation (Hernes and Benner, 2003; Opsahl and Benner, 1998) to centuries in deep waters of the North Pacific Ocean. An estimated average residence time for dissolved lignin phenols in the Atlantic Ocean is determined from the estimated reservoir of dissolved lignin phenols in the Atlantic divided by the annual riverine discharge of dissolved lignin phenols into the Atlantic. This calculation was initially done using only HMW lignin and gave a range of 21–93 years due to the uncertainty of the LMW component (Opsahl and Benner, 1997). Inclusion of the LMW in this study results in a residence time of ~35 years. It appears that dissolved lignin phenols cycle more rapidly in the Atlantic than the Pacific (Hernes and Benner, 2002; Opsahl and Benner, 1997). An average residence time is also estimated for the Gulf of Mexico using existing volume (Bialek, 1966) and riverine discharge data (Guetter and Georgakakos, 1993), an average riverine concentration of lignin phenols ( $21.6 \mu\text{g L}^{-1}$ ), and an average Gulf of Mexico concentration of  $58 \text{ ng L}^{-1}$ . These data yield an average residence time of ~8 years, which is similar to the estimate for the Arctic Ocean (Opsahl et al., 1999). The shorter residence

times in the Gulf of Mexico and Arctic Ocean relative to the Pacific and Atlantic result from greater physical export from the smaller basins.

Collectively, dissolved lignin phenol concentrations from these four basins are consistent with our understanding of global riverine discharge and ocean circulation patterns. Arctic lignin phenol concentrations in surface water (<200 m) are on average ~10-fold greater than those in the Atlantic, which are in turn 40% greater than surface concentrations in the Pacific (Fig. 5a, Benner et al., 2005; Hernes and Benner, 2002; Opsahl et al., 1999). Surface concentrations in the Gulf of Mexico fall between Arctic and Atlantic concentrations. These differences are all readily explained by riverine input. On a per volume basis, riverine input to the Arctic Ocean and Gulf of Mexico is >2-fold higher than to the Atlantic, which in turn is >3-fold higher than to the Pacific. Also a factor contributing to the much higher Arctic concentrations relative to the Atlantic and Pacific Oceans is the significantly shorter residence time as well as lower incident solar radiation and seasonal ice cover, both of which minimize photooxidation.

In contrast to large differences in surface waters, lignin concentrations in deep waters (>1000 m) are very similar between the Arctic Ocean and Atlantic. Deep water lignin concentrations in the Pacific ( $29 \text{ ng L}^{-1}$ ) are ~2-fold lower (Fig. 5a). Higher concentrations in the Arctic and at BATS are due to inclusion of lignin-rich Arctic waters into NADW. Deep water masses in the Pacific Ocean are downstream from those of the Atlantic, and lignin concentrations are expected to be lower due to dilution and degradation. Gulf of Mexico values below 500 m ( $\sim 60 \text{ ng L}^{-1}$ ), compare favorably to deeper waters in the Atlantic ( $\sim 52 \text{ ng L}^{-1}$ ), as would be expected since deep water in the Gulf of Mexico contains a component of NADW water.

Size distribution comparisons of lignin phenols highlight key relationships between size and diagenetic state. LMW lignin phenol concentrations in the Atlantic and Pacific are essentially the same, with averages of 12 and  $14 \text{ ng L}^{-1}$  in the Atlantic surface and deep waters, while corresponding concentrations in the Pacific are 12 and  $15 \text{ ng L}^{-1}$  (Hernes and Benner, 2002). This suggests that LMW lignin is relatively unreactive, which is consistent with  $^{14}\text{C}$  ages of deep water DOC of several thousand years (Druffel et al., 1992). In contrast, average HMW lignin phenol concentrations in the Atlantic are approximately double HMW concentrations in the Pacific <200 m (25 vs.  $13 \text{ ng L}^{-1}$ ) and over 3-fold greater below 1000 m (45 vs.  $13 \text{ ng L}^{-1}$ , this study and Hernes and Benner, 2002). On average,

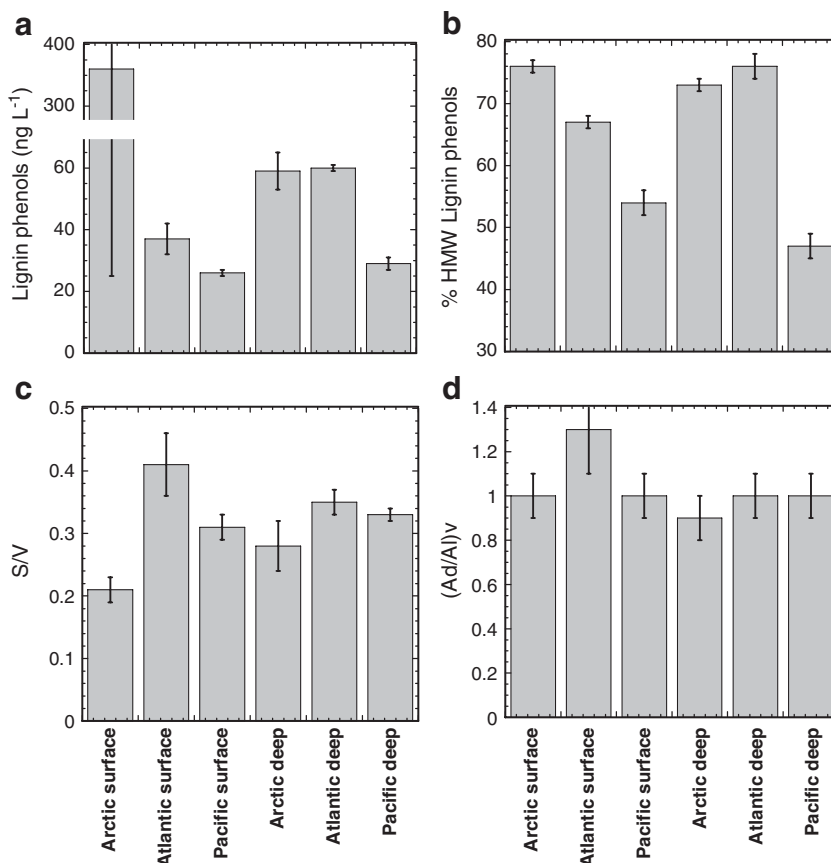


Fig. 5. Comparison of average (a) lignin phenol concentrations, (b) %HMW lignin phenols, (c) S/V ratios, and (d) (Ad/Al)v for surface (0–200 m) and deep (>1000 m) waters for the Arctic, Atlantic, and Pacific Oceans. Station Aloha data from Hernes and Benner (2002), Arctic Ocean data from Opsahl et al. (1999) and Benner et al. (2005).

HMW lignin in surface waters represents 54% of total dissolved lignin in the Pacific, 67% of total dissolved lignin in the Atlantic and 76% of total dissolved lignin in the Arctic Ocean (Fig. 5b). HMW DOC is generally more reactive than LMW DOC (Amon and Benner, 1994; Amon and Benner, 1996; McCarthy et al., 1996). Differences in the size distribution of dissolved lignin among the Arctic, Atlantic, and Pacific oceans are consistent with this trend, indicating terrigenous DOM in surface waters of the Arctic Ocean is less degraded than that of the Atlantic Ocean, which in turn is less degraded than its Pacific counterpart. At depth, the %HMW lignin is similar between the Arctic and Atlantic Oceans due to input of Arctic river DOM into NADW. These values are much greater than the %HMW lignin in deep waters of the Pacific Ocean, which are downstream from those of the Atlantic Ocean.

Lignin phenol compositional parameters reveal subtle differences among sites, but primarily serve to dem-

onstrate the overall consistency of the data. For instance, S/V ratios below 1000 m are similar between the Pacific and Atlantic whereas surface values are 30% lower in the Pacific (Fig. 5c). Photooxidation is an important mechanism for lignin degradation in surface waters and leads to lower S/V ratios (Benner and Opsahl, 2001; Hernes and Benner, 2003; Opsahl and Benner, 1998), while microbial degradation is the primary mechanism at depth and does not appear to substantially alter S/V (Hernes and Benner, 2003). However, S/V ratios are also determined by source, as indicated by the lower S/V ratios in Arctic waters due to the greater abundance of gymnosperms in the boreal forests of large Arctic river drainage basins (Lobbess et al., 2000; Opsahl et al., 1999). Average (Ad/Al)v ratios among ocean basins are fairly uniform (Fig. 5d). Atlantic surface values appear to be slightly elevated, but further studies are needed to determine if this is indicative of greater diagenetic processing. As with S/V ratios, (Ad/Al)v is sensitive to photooxidation, showing

marked increases with increasing exposure to solar radiation (Hernes and Benner, 2003; Opsahl and Benner, 1998).

Previous studies based on stable carbon isotope compositions have indicated that the terrigenous component of DOC in the ocean is minor (Benner, 2004; Druffel et al., 1992). The  $\delta^{13}\text{C}$  values of DOC in this study ranged from  $-20.8\text{‰}$  to  $-21.2\text{‰}$ , which is consistent with a minor terrigenous component. However, studies of sedimentary organic carbon have indicated the potential for a significant “hidden” terrigenous component in marine sediments due to the presence of carbon fixed by C4 plants (e.g. Goni et al., 1998). This has led to speculation that there may be a hidden component in ocean DOC as well. Because lignin is an unambiguous biomarker for terrigenous OM, this hypothesis can be tested by calculating the terrestrial component of DOC in seawater from carbon-normalized lignin phenol yields by the formula ( $A_6$  ocean/ $A_6$  river). This calculation assumes that riverine dissolved lignin is removed from seawater at similar rates as riverine DOC. Based on yields of lignin phenols in HMW DOM, Opsahl and Benner (1997) estimated 2.4% of the DOC in the Atlantic was of terrestrial origin. Incorporating LMW data from this study as well as assumptions about HMW recovery of lignin (90%) and DOC (70%) from rivers, we estimate that 0.7% and 1.6% of the DOC in surface and deep waters at BATS is terrigenous, respectively. Total DOC in the Gulf of Mexico using these same assumptions is 1.3% terrigenous. In comparison, about 0.5% and 1.1% of the DOC in surface and deep water at Station Aloha in the Pacific is terrigenous, respectively (Hernes and Benner, 2002). These values essentially confirm the stable carbon isotope data. We conclude that, with the exception of surface waters in the Arctic and other localized regions directly receiving large amounts of riverine discharge, terrigenous DOC is a minor (<5%) component of the ocean carbon reservoir. Only a small fraction of the terrigenous DOC entering the ocean escapes remineralization by microbial and photochemical processes.

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