

Fractionation of lignin during leaching and sorption and implications for organic matter “freshness”

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[1] Much of what we know about the cycling of terrigenous organic matter (OM) in freshwater and marine systems can be attributed to evidence derived from biomarkers such as lignin. Here we report the fractionation of lignin phenols both during solubilization from plant litters and again during sorption of resulting leachates to soils. Source parameters in both leached and sorbed lignin varied from the parent litters by as much as ten-fold, while elevated lignin oxidation parameters in riverine dissolved OM (DOM) can be completely explained by dissolution and sorption. Carbon-normalized dissolved lignin endmembers indicate a substantial fraction of riverine DOM may not be vascular plant-derived, and thus derived from algal, microbial or non-vascular plant sources such as mosses. These results demonstrate that riverine DOM is less degraded and likely more labile than previously thought, and helps resolve the paradox of diagenetically-altered riverine DOM degrading rapidly in marine systems. **Citation:** Hernes, P. J., A. C. Robinson, and A. K. Aufdenkampe (2007), Fractionation of lignin during leaching and sorption and implications for organic matter “freshness”, *Geophys. Res. Lett.*, 34, L17401, doi:10.1029/2007GL031017.

1. Introduction

[2] Phase transfers of OM between dissolved and particulate fractions are critical to our understanding of processes as diverse as transport and bioavailability of OM in rivers [McKnight *et al.*, 1992] and the marine water column [Hernes and Benner, 2002], carbon sequestration in soils [Kaiser and Guggenberger, 2000], OM dynamics in estuaries [Hedges and Keil, 1999], and preservation of OM in continental margins [Hedges and Parker, 1976]. The use of lignin biomarkers in many of these environments has become widespread due to the fact that they are unique tracers of vascular plant materials in both freshwater and marine systems, are persistent in many environments, and differential reactivities of lignin monomers result in parameters that aid in the reconstruction of diagenetic histories of OM. However, partitioning between dissolved and particulate phases typically is accompanied by fractionation of molecular components of OM due to differing solubilities and surface reactivities [Aufdenkampe *et al.*, 2001; Kaiser and Guggenberger, 2000; McKnight *et al.*, 1992]. If similar

fractionation occurs for lignin phenols, it would have important ramifications for how lignin data is interpreted for most environmental samples.

[3] In the three decades since the first study utilizing molecular-level lignin as a tracer for terrigenous OM in marine sediments [Hedges and Parker, 1976], hundreds of studies have been published in the geosciences literature utilizing measured lignin as either a primary or secondary biomarker for sources, diagenetic processing, or OM “freshness” and degradability in rivers, marine waters, sediments, and soils. Lignin in combination with carbon stable isotopes has proven to be a particularly powerful combination for understanding the fluxes and fates of terrigenous carbon in marine systems [e.g. Hedges and Parker, 1976; Hernes and Benner, 2002], highlighting a paradox of rapid remineralization of riverine OM in marine waters despite its substantial diagenetic alteration or residence in watersheds [Hedges *et al.*, 1997]. While vanillyl lignin phenols (V) are ubiquitous, the unique presence of syringyl phenols (S) in angiosperms and cinnamyl phenols (C) in nonwoody tissues allows distinction between gymnosperm and angiosperm woody and nonwoody tissues in environmental samples [Hedges and Mann, 1979]. Several studies established that degradation of plant tissues results in increased proportions of oxidized (acidic) lignin phenols [e.g. Hedges and Weliky, 1989; Opsahl and Benner, 1995], which has led to the generalization that acid:aldehyde ratios of lignin phenols can be used as relative indicators of diagenetic state.

[4] In lignin studies involving DOM, phase changes have rarely been considered as an important factor when interpreting lignin parameters. Thus, elevated acid:aldehyde ratios in riverine DOM relative to co-existing particulate OM (POM)—either within mineral complexes or as discrete plant detritus—has been cited as evidence that DOM is more highly degraded than POM [Ertel *et al.*, 1986; Hedges *et al.*, 2000]. In soils, comparison of lignin in forest floor leachates with soil DOM at 90 cm suggested a preferential removal of acidic phenols from solution during transport down the soil column, which, although not confirmed by direct measurement, was attributed to sorption to minerals [Kaiser *et al.*, 2004]. Leaching represents another process that can influence lignin compositions [Benner *et al.*, 1990]. The process of leaching DOM from forest floor litters with subsequent transport and sorption to lower mineral phase horizons is increasingly recognized as an important mechanism in soil OM formation and stabilization, and thus has important ramifications for carbon sequestration by soils [Kaiser and Guggenberger, 2000]. If sorption and leaching discriminate between different lignin phenols, then such processes need to be understood.

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[5] In this study, four plant litters (representing the range of lignin compositions observed in the literature) were leached to determine lignin fractionation effects of simple solubilization. Subsequently, the leachates were sorbed to four soils (representing important extremes in mineral surface reactivity found globally in rivers and soils) in order to determine associated lignin fractionation effects. The demonstrated compositional shifts reveal novel insights about sources and the diagenetic state of riverine DOM and the fate of terrigenous OM in coastal margins.

2. Materials and Methods

[6] Litters from a gymnosperm, coastal redwood (*Sequoia sempervirens*), a dicot angiosperm, live oak (*Quercus wislizeni*), and a monocot angiosperm, purple needle-grass (*Nassella pulchra*), were collected from a local arboretum. A second gymnosperm litter, loblolly pine (*Pinus taeda*), was obtained from the Duke Experimental Forest. All litters were oven-dried at 60°C for 24 hours, ground to pass through a 300- μ m sieve, then leached in HDPE bottles using ~5 g of litter in 150 mL carbon-free water for 24 hr at 4°C with constant stirring. Leachates were filtered (0.2 μ m) and 3–5 mL aliquots (800–1450 ppm DOC concentration) immediately frozen for CuO oxidation, while leached residues were freeze-dried and re-ground.

[7] Four soils were chosen from a cross section of the California landscape, including Capay, an Andisol rich in smectites, Fe-oxides and allophane (mixed alluvium parent material); Ione, an Oxisol rich in kaolinite and Fe-oxides (non-marine sediment); Aiken, an Ultisol also rich in kaolinite and Fe-oxides (basalt); and McCarthy, an Andisol rich in amorphous phases, allophane and Fe-oxides (andesitic mudflow). These mineral suites are primary constituents of soils throughout the world [Brady and Weil, 2002]. Prior to sorption experiments, all soils were freeze dried, sieved (<105 μ m), pretreated twice with 6% NaOCl (bleach, adjusted to pH = 8 to minimize mineral alteration as per Mikutta et al. [2005]) for 18-hr to remove lignin phenols, and finally rinsed (six 2-hr rinses with carbon-free water, four 2-hr rinses with a CaCl₂ solution to equilibrate the soil surfaces with calcium, and 4–6 times with carbon-free water until conductivity <20–25 μ S/cm). Measured lignin on treated soils was similar to procedural (reagent) blanks, substantially increasing our sensitivity to quantify compositional changes during sorption.

[8] Each sorption experiment consisted of ~1 g of bleach-treated soil weighed into 50-mL polycarbonate centrifuge tubes, addition of 40 mL leachate diluted to a target DOC concentration of 50–100 mg C L⁻¹, then equilibrated for 2 hr on a shaker table maintained at 25°C for all experiments. Solution:soil ratios and equilibration times were chosen based on common conditions from the literature. Tubes were subsequently centrifuged for 20 min at 1100 \times G, then 35 mL of supernatant drawn off the top for lignin and DOC analyses. The soil pellet was rinsed with carbon-free water, then freeze-dried and ground for elemental and lignin analyses.

[9] Lignin phenols were determined by alkaline CuO oxidation followed by acidification and ethyl acetate extraction, then quantification by GC-MS using cinnamic acid as an internal standard with a five-point calibration scheme

[Hernes and Benner, 2002]. Eight lignin phenols were quantified, including three vanillyl phenols (vanillin, acetovanillone, vanillic acid), three syringyl phenols (syringaldehyde, acetosyringone, syringic acid), and two cinnamyl phenols (*p*-coumaric acid, ferulic acid). Litters, leachates, and leached residues were all analyzed in duplicate, while supernatants and pellets from the sorption experiments were each analyzed once. Blank-corrected carbon concentrations for lignin normalization purposes were determined by high temperature combustion on all litters using a Carlo Erba NA 1500 elemental analyzer, and all liquids using a Shimadzu TOC-V analyzer.

3. Results and Discussion

[10] Early studies of the Amazon River system found that DOM was consistently more diagenetically altered in lignin, carbohydrate and amino acid composition than fine and coarse POM [Ertel et al., 1986; Hedges et al., 1986, 1994]. These and many similar results led to the widely held paradigm that DOM is more degraded than POM. However, the amino acid interpretation was later called into question based on experiments that demonstrated that amino acid degradation products preferentially stay in solution [Aufdenkampe et al., 2001]. In our present study, elevated (Ad:Al)_v in the leachates indicate a similar “hazard” in comparing particulate to dissolved lignin phenols without taking into account phase history. We observed a ~2-fold increase in (Ad:Al)_v from the litters (0.27 \pm 0.01, mean \pm sample mean deviation) to the leachates (0.50 \pm 0.15) simply due to solubilization (Figure 1)—similar to the (Ad:Al)_v increase observed in nonwoody tissues during a four-year litterbag study [Opsahl and Benner, 1995]. Following sorption to soil minerals, (Ad:Al)_v of the supernatants increased even more (0.81 \pm 0.35; Table 1), nearly matching DOM (Ad:Al)_v values from the Amazon River (0.89 \pm 0.22) [Hedges et al., 2000] and Mississippi River (0.93 \pm 0.10) [Benner and Opsahl, 2001; Hernes and Benner, 2003], while (Ad:Al)_v in Russian rivers draining to the Arctic were slightly higher but with much greater variability (0.99 \pm 0.53) [Lobbis et al., 2000].

[11] In addition to the paradigm that riverine DOM is more degraded than POM, a second widely held paradigm in organic geochemistry suggests that riverine OM represents highly degraded remnants of vascular plant sources aged in soils. However, a growing body of ¹⁴C literature suggests that riverine DOM in most systems is modern, much younger than riverine POM, and therefore not likely re-mobilized from aged soil OM pools [e.g., Mayorga et al., 2005]. This study, along with Aufdenkampe et al. [2001], demonstrates a mechanism by which fresh, young DOM with a degraded diagenetic signature can be generated from litters solely through the processes of leaching and sorption, and that these processes may be more important than microbial or photochemical degradation in determining DOM composition in flowing freshwaters.

[12] Carbon-normalized yields of lignin, Λ (mg/100 mg OC), are frequently used to indicate relative contributions of vascular plant sources to POM, or terrigenous OM in marine systems [Hedges et al., 1997; Hedges and Parker, 1976]. However, this analysis has not been extended to riverine DOM. In the Amazon River system, Λ values for

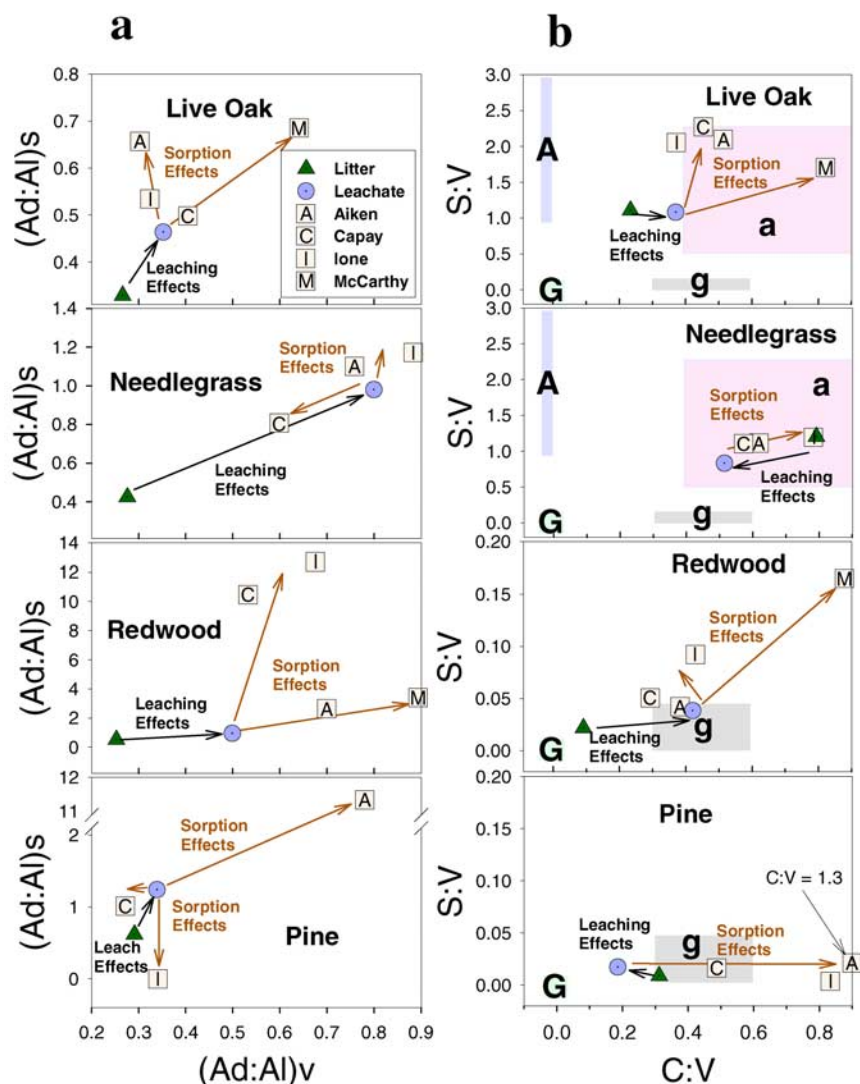


Figure 1. Effects of leaching and sorption on the most prevalent lignin parameters, (a) ratios of vanillic acid:vanillin, (Ad:Al)_v, and syringic acid:syringaldehyde, (Ad:Al)_s, and (b) ratios of syringyl:vanillyl phenols (S:V) vs. cinnamyl:vanillyl phenols (C:V). Sorbed OM on soils (squares) represents two phase transfers from the parent litter (triangle) via the dissolved leachate phase (circle). Shaded areas in the S:V vs. C:V plots represent ranges of source tissues from the original source study of *Hedges and Mann* [1979]: A = woody angiosperms, G = woody gymnosperms, a = nonwoody angiosperms, g = nonwoody gymnosperms.

coarse POM (>63 μm , mostly discrete plant detritus) and fine POM (0.7–63 μm , primarily associated with minerals) were respectively 4–6-fold and 1–1.5-fold higher than Λ for ultrafiltered DOM (~ 1 –200 nm) [*Hedges et al.*, 2000]. This trend is similar to that observed for amino acids and carbohydrates [e.g. *Hedges et al.*, 1994] and interpreted as further evidence that DOM is the most degraded. In our present study, however, the vanillyl component of Λ in leachates (V) were on average 43% lower than “parent” litters (range 17–66%; Table 1), indicating that lignin solubility could be an important factor in decreased V yields in riverine DOM. Thus, if DOM is younger and less degraded than previously thought, and decreased Λ in DOM is largely due to solubility effects and not degradation, then accounting for those solubility effects could lead to important estimations of the source contributions to DOM.

[13] Unambiguous determination of the proportion of autochthonous vs. allochthonous OM in rivers remains a challenge, resulting in a critical gap in our understanding of river biogeochemistry. POM sources have been determined

Table 1. Carbon-Normalized Yields of Vanillyl Phenols (V) for Litters, Leachates, and Supernatants After Sorption, Along With Supernatant Vanillyl Acid:Aldehyde Ratios (Ad:Al)_v^a

	V, mg/100 mg OC			Supernatant (Ad:Al) _v
	Litter	Leachate	Supernatant	
Oak	3.42 (0.09)	1.17 (0.00)	0.78 (0.14)	0.68 (0.24)
Needlegrass	2.67 (0.00)	2.22 (0.24)	2.66 (0.13)	1.21 (0.38)
Redwood	2.71 (0.01)	1.47 (0.04)	1.05 (0.12)	0.97 (0.31)
Pine	2.52 (0.07)	1.45 (0.03)	2.03 (0.14)	0.35 (0.07)
Mean	2.83 (0.21)	1.58 (0.32)	1.53 (0.48)	0.81 (0.35)

^aAll number in parentheses are Sample Mean Deviation.

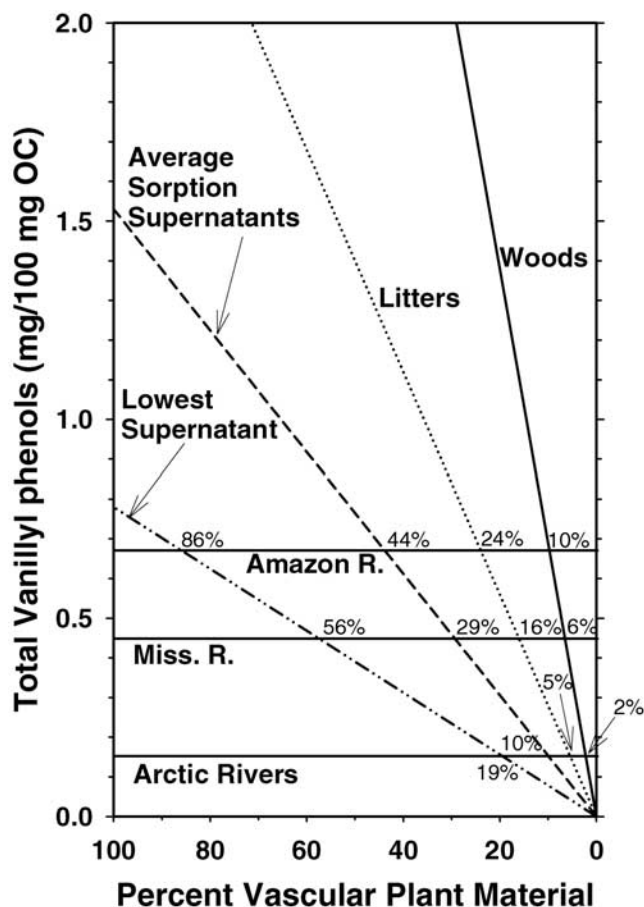


Figure 2. Total vanillyl phenol endmember mixing model demonstrating the significant differences between calculated percent vascular plant material in riverine DOM as determined by source endmember.

using ^{13}C and C:N ratios [Kendall *et al.*, 2001], but defining endmembers is difficult due to the spatial and temporal variability in $\delta^{13}\text{C}$ values of heterogeneous sources (C3 vs. C4 plants and algae) [Finlay *et al.*, 2002], analytical difficulties in determining accurate $\delta^{13}\text{C}$ values for algae and C:N values for DOM, and preferential sorption of organic nitrogen to particles with subsequent decrease in C:N of leaf-derived DOM to values similar to algae [Aufdenkampe *et al.*, 2001]. However, we suggest that the data presented here allow for the first time a reasonable calculation of the proportion of riverine DOM that is derived from vascular plant tissues by using V yields determined on leachates and supernatants as endmembers for vascular plant inputs, rather than utilizing the lignin yields of litters themselves.

[14] For the purposes of this analysis, we only considered the vanillyl phenols due to significant differences in sources and reactivity of the syringyl and cinnamyl phenols. For woody tissues, V yields (all in mg/100 mg OC) have been reported ranging from 2.7–13, while nonwoody tissues ranged from 0.7–3.0 [Hedges and Mann, 1979]. In this study, the average V for the four litters was 2.8 ± 0.2 , the average V for the four leachates was 1.6 ± 0.3 , and the average V for the 14 supernatants as modified by sorption was 1.5 ± 0.5 (Table 1). Using a V value of 1.5 ± 0.5 to represent a 100% vascular plant DOM endmember and

average V values for high molecular weight DOC in the Amazon River (0.67) [Hedges *et al.*, 2000], Mississippi River (0.44) [Benner and Opsahl, 2001; Hernes and Benner, 2003], and Russian rivers draining to the Arctic (0.15) [Lobbess *et al.*, 2000] we can estimate that vascular plant tissue represents $44 \pm 15\%$, $29 \pm 10\%$, and $10 \pm 3\%$, respectively, of the DOM in these three systems.

[15] The relative ranking of these three river systems is supported by independent evidence. The Amazon mainstem has very low rates of algal production [Wissmar *et al.*, 1981] whereas $>50\%$ of POM in the rivers of the upper Mississippi appears algal-derived [Kendall *et al.*, 2001]. In the case of Arctic rivers, the low percentage could reflect the relative importance of non-vascular plants, such as peat mosses (i.e. sphagnum), to DOM sources. In a fourth system local to our chosen plant tissues and soils, the San Joaquin River, V averaged 0.11 (R. S. Eckard, Landscape-scale controls on the vascular plant component of dissolved organic carbon across a freshwater delta, submitted to *Geochimica et Cosmochimica Acta*, 2007), suggesting a vascular plant component of only $7.4 \pm 2.5\%$ and consistent with very high algal biomass throughout the lower San Joaquin River [Leland *et al.*, 2001].

[16] The importance of choosing an appropriate endmember for riverine DOM calculations is demonstrated in Figure 2, where the difference between using plant tissue endmembers versus sorption supernatants alters the calculated percent vascular plant carbon nearly five-fold. The implication of using the appropriate endmember is that more than half of DOM could be algal or microbial in origin, providing molecular-level evidence to go along with the ^{14}C evidence of Mayorga *et al.* [2005] that a majority of riverine DOM may be recently photosynthesized and thus “fresher” than originally thought.

[17] In addition to (Ad:Al)v and V yields, source ratios for lignin also undergo significant fractionation during leaching and sorption, with the primary leaching effect on C:V ratios (Figure 1). Elevated C:V ratios indicate a predominance of nonwoody tissues and can separate monocots from other plants [Hedges and Mann, 1979]. In this study, the C:V ratio in the coastal redwood nearly quadrupled in the leachate, while leachate C:V from the other tissues changed from -40% to $+58\%$ (Figure 1). Such changes could reflect the fact that a significant portion of cinnamyl phenols in plant tissues can be weakly bound to the lignin matrix by ester linkages instead of the typical ether linkages and carbon-carbon bonding [Opsahl and Benner, 1995]. For these four plant sources, leaching had the effect of dampening significant differences: average C:V values for the litters was 0.36, but ranged from 0.09 to 0.79. In the leachates, average C:V was similar to the litters at 0.37, but only ranged from 0.19 to 0.51. C:V values in the leachates were significantly higher than those reported for the Amazon River (0.09) [Hedges *et al.*, 2000], while similar to Mississippi River (0.13–0.53) [Benner and Opsahl, 2001; Hernes and Benner, 2003] and Arctic river values (0.06–0.86) [Lobbess *et al.*, 2000]. Increases in C:V due to leaching, such as occurs with live oak and redwood, highlight potential pitfalls of source attribution when phase changes are not considered. For example, both of these tissues would be significantly underestimated as contributors to DOM with a measured C:V of 0.4 if only litter values for

C:V were considered, whereas leachate C:V values indicate that such DOM could be completely attributed to either plant tissue.

[18] Lignin in sediments and soils holds the greatest potential for capturing and preserving long term records of OM sources and vegetation patterns by indicating succession between angiosperms and gymnosperms or woody and nonwoody tissues [Hedges and Parker, 1976; Kastner and Goni, 2003]. However, most solid-phase OM is complexed to minerals and exhibits much slower turnover than coexisting discrete plant detrital particles. Our findings indicate that preserved lignin signatures must reflect substantial compositional alterations by leaching and sorption. Indeed, two studies that compare lignin composition between density fractions (i.e. mineral complexes vs. plant detritus) demonstrate trends consistent with our experimental results [Dickens et al., 2006; Grunewald et al., 2006]. These coastal margin sediment and soil studies showed (Ad:Al)_v ratios that were >50% higher in the mineral-dominated fraction than the light organic fraction (0.48 vs. 0.30 and 0.33 vs. 0.21, respectively). In the coastal study, this trend was attributed to greater degradation of OM in the mineral fraction [Dickens et al., 2006], yet elevated S:V in the mineral fraction (0.58 vs. 0.21) did not support this interpretation since S:V is known to decrease or remain unchanged with degradation [Opsahl and Benner, 1995]. Similar elevation in S:V between the mineral (1.21) and OM fraction (0.68) was also observed in the soil study [Grunewald et al., 2006]. In our study, S:V of sorbed OM derived from live oak increased two-fold during the combined effects of leaching and sorption, while (Ad:Al)_v was elevated relative to litters in several of the plant/soil combinations (Figure 1). Thus, lignin compositional differences between particle types in soils and coastal sediments could be entirely due to phase changes and not degradation.

[19] Fractionation of OM during leaching and sorption is not unique to lignin. Several studies have demonstrated differential sorptive behavior of amino acids [McKnight et al., 1992] and natural DOM peptides [Aufdenkampe et al., 2001], while a mangrove leaf leaching experiment showed fractionation of condensed tannin along with differential behavior between bulk cyclitols, amino acids, and cutin [Hernes et al., 2001]. However, due to its value and history as a tracer for vascular plant tissues and terrigenous OM, fractionation of lignin may arguably have the most important ramifications. In general, interpretations based on lignin parameters can be relatively robust with particulate to particulate or dissolved to dissolved comparisons. This is particularly true when a physical linkage exists between the sample types such as litterbag decomposition studies [Opsahl and Benner, 1995], discrete down-core tissues [Hedges and Weliky, 1989], or riverine and plume waters that can reasonably be assumed to have the same source of lignin [Hernes and Benner, 2003]. However, phase history can no longer be ignored when interpreting lignin and other biomarkers derived from mineral-associated OM in soils and sediments, while lignin and other endmember signatures for DOM will need to be recalibrated to take into account leaching effects. Finally, the nature of OM that sorbs to minerals at depth during carbon sequestration [Kaiser and Guggenberger, 2000] is likely largely determined by leaching and sorption. Composition will play a

large role in the subsequent reactivity of that OM, and hence could determine the length of time for which it will be sequestered.

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