

RESEARCH ARTICLE

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Key Points:

- Lignin phenols were analyzed in soils and rivers from the Andes to the Amazon basin
- Wet-season POM and dry-season DOM had fresher and more oxidized lignin downstream, respectively
- In stratified, white water rivers, undercurrents may export relatively undegraded lignin

Supporting Information:

- Supporting Information S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Figure S5
- Figure S6
- Table S1

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Source to sink: Evolution of lignin composition in the Madre de Dios River system with connection to the Amazon basin and offshore

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Abstract While lignin geochemistry has been extensively investigated in the Amazon River, little is known about lignin distribution and dynamics within deep, stratified river channels or its transformations within soils prior to delivery to rivers. We characterized lignin phenols in soils, river particulate organic matter (POM), and dissolved organic matter (DOM) across a 4 km elevation gradient in the Madre de Dios River system, Peru, as well as in marine sediments to investigate the source-to-sink evolution of lignin. In soils, we found more oxidized lignin in organic horizons relative to mineral horizons. The oxidized lignin signature was maintained during transfer into rivers, and lignin was a relatively constant fraction of bulk organic carbon in soils and riverine POM. Lignin in DOM became increasingly oxidized downstream, indicating active transformation of dissolved lignin during transport, especially in the dry season. In contrast, POM accumulated undegraded lignin downstream during the wet season, suggesting that terrestrial input exceeded in-river degradation. We discovered high concentrations of relatively undegraded lignin in POM at depth in the lower Madre de Dios River in both seasons, revealing a woody undercurrent for its transfer within these deep rivers. Our study of lignin evolution in the soil-river-ocean continuum highlights important seasonal and depth variations of river carbon components and their connection to soil carbon pools, providing new insights into fluvial carbon dynamics associated with the transfer of lignin biomarkers from source to sink.

1. Introduction

The transport, degradation, and sequestration of terrestrial organic carbon (OC) in river systems are of great interest because of their importance for constraining carbon cycle budgets [Aufdenkampe *et al.*, 2011; Battin *et al.*, 2009]. It is however not easy to disentangle terrestrial OC dynamics given the varied sources of carbon transported within a river. Biomarkers, albeit representing only a small fraction of bulk OC, are excellent tracers of source-specific OC in complex natural systems such as rivers. Lignin, constituting up to 30% of vascular plant biomass, is a classic biomarker of terrestrial OC [Hedges and Mann, 1979; Goñi and Hedges, 1995]. The monomeric composition of lignin phenols upon copper oxide (CuO) oxidation provides useful information on the biological source (woody versus nonwoody and angiosperm versus gymnosperm) as well as oxidation stage of lignin in natural environments [Benner *et al.*, 1984; Hedges *et al.*, 1985; Dittmar and Lara, 2001]. Hydroxy (P) phenols and cutin acids released from CuO oxidation add an additional level of information on the abundance and dynamics of OC components from other sources (such as phytoplankton, tannin, and leaf litter). Lignin phenols and cutin acids have hence been widely used in probing the transformation and transport of land-derived carbon in marine and fluvial systems [Goñi and Hedges, 1990a, 1995; Hernes and Benner, 2002; Ward *et al.*, 2013; Jex *et al.*, 2014].

The Amazon basin is the world's largest fluvial system in terms of drainage area (6.4 million km²) and water discharge (200,000 m³ s⁻¹) [Meybeck and Ragu, 1997]. Carrying an annual flux of ~12 Tg of particulate organic carbon (POC) and 27 Tg of dissolved organic carbon (DOC), it is responsible for ~8% of the global terrestrial OC export to the oceans [Richey *et al.*, 1990; Bouchez *et al.*, 2014; Galy *et al.*, 2015; Raymond and Spencer, 2015]. The geochemistry of bulk terrestrial OC and lignin transported in the Amazon River has been extensively investigated previously [e.g., Hedges *et al.*, 1986, 2000; Quay *et al.*, 1992; Townsend-Small *et al.*, 2005, 2007;

Aufdenkampe et al., 2007; Bouchez et al., 2010, 2014; Clark et al., 2013; Moreira-Turcq et al., 2013]. It has been found that both upstream Andean soils and lowland forests are major sources of OC to the Amazon River [*Richey et al., 1990; Townsend-Small et al., 2005; Clark et al., 2013*] and that dissolved and particulate fractions of organic matter (OM) exhibit varied composition and seasonal dynamics within the Amazon and its tributaries [*Hedges et al., 2000; Aufdenkampe et al., 2007; Townsend-Small et al., 2007*]. For instance, *Hedges et al.* [2000] and *Aufdenkampe et al.* [2007] investigated the composition of coarse particulate organic matter (CPOM), fine particulate organic matter (FPOM), and dissolved organic matter (DOM) in the Bolivian and Peruvian headwaters of the Amazon system, respectively, and observed that degradation increased in the sequence of CPOM < FPOM < DOM. Although no obvious downstream evolution of OM components (i.e., lignin, carbohydrates, and amino acids) was observed for either of the two particulate fractions, lignin seemed more degraded in the DOM downstream in the upper Beni River compared to the Ucayali River [*Hedges et al., 2000; Aufdenkampe et al., 2007*], and, likewise, along the Amazon River mainstem from Óbidos to the river mouth [*Ward et al., 2015*].

These findings seem paradoxical given observations of fast degradation of terrestrial OC and lignin components within the Amazon River [*Mayorga et al., 2005; Ward et al., 2013*]. The apparent paradox may be resolved by considering the continuous (or even stronger) input of fresh terrestrial OC downstream or even through exchange with sediments stored in the floodplains, thereby masking OC degradation within the river. Collectively, these findings imply that lignin input, transport, and transformation are highly dynamic in the Amazon system. Yet it remains unclear to what extent rivers in the Amazon system are primarily conduits for transfer of lignin versus locations of in-river transformation. As terrestrial OC inputs to rivers vary with hydrological conditions (cf., the Pulse-Shunt Concept) [*Wang et al., 2012; Raymond et al., 2016*], monitoring lignin evolution along a river in wet versus dry seasons may provide insights on the dynamics and processing of terrestrial OC within the river. The wet season (October to April) [*Rapp and Silman, 2012*] and high-flow season (May to July) in the downstream Amazon basin are poorly sampled relative to other seasons for lignin studies, in part because it presents more challenging field conditions. However, as erosion is enhanced during the wet season, it is important to compare seasonal variations in the composition and loading of terrestrial OC carried by rivers in order to have a more complete understanding of its sources and transport. Similarly, samples collected along the length of river systems, from headwaters to lowlands, are critical for understanding lignin transport dynamics and transformations including in-river processing.

Previous studies have shown that the Amazon River is stratified with depth, as a result of hydrodynamic differentiation of suspended sediment load [*Bouchez et al., 2011*]. Velocity gradients as well as settling of larger grain sizes toward river bottoms result in characteristic depth profiles of sediment grain size distribution. This hydrodynamic sorting has important implications for suspended load geochemistry, including OC transport, as shown in the Ganges-Brahmaputra [*Galy et al., 2008*] and the Amazon mainstem [*Bouchez et al., 2014*]. However, the influence of depth-dependent sorting on lignin distribution in river particulate organic matter (POM) has not been assessed. While previous studies [e.g., *Hedges et al., 1986*] did collect depth-integrated samples, comparing samples collected from distinct depths may help capture the variability of lignin distribution and its causes in a way not possible from integrated sampling. It also remains to be revealed whether lignin exhibits varied composition and degradation patterns in deep, stratified “white water” river waters (characterized by high suspended sediment load) that experience negligible photooxidation at depth [*Remington et al., 2011*].

Another knowledge gap concerns the connection between plants, soils, and rivers. Lignin transformation in terrestrial ecosystems has rarely been linked to lignin composition in river systems, even though soils and plants are key suppliers of lignin to rivers. Tropical forests in the Amazon basin represent a large stock of terrestrial OC in aboveground biomass (86–247 Mg C ha⁻¹) [*Malhi et al., 2006; Girardin et al., 2014*] with up to 30% by mass being lignin [*Benner et al., 1987*]. Tropical montane forest, while being less productive, contains large stocks of tree biomass with an increasing root component with elevation [*Girardin et al., 2014; Gurdak et al., 2014*]. Tropical montane forest soils are also characterized by thicker organic horizons and greater surface OC stores than lowland soils [*Clark et al., 2015*]. The large flux of lignin from plant biomass to soils in tropical lowland and montane forests is primarily decomposed by fungi, which are more metabolically active in surface litter and organic horizons relative to deeper mineral horizons [*Whitaker et al., 2014a; Nottingham et al., 2015a*]. If we are to fully understand the evolution of lignin from source (plants) to sink (rivers and oceans), it is essential to evaluate soils as a locus of lignin decomposition and storage as we follow lignin transformation through the plant-soil-river-ocean continuum.

Here we examine terrestrial OC transport by a major Andean tributary of the Amazon River (the Kosñipata and Madre de Dios Rivers) and trace particular classes of compounds (lignin phenols and cutin acids) with potential to resolve specific sources and provide insights into transformation processes in the wet versus dry season. We follow these biomarkers in the soils and rivers from high elevations of >3000 m asl (above sea level) to the lowland river system (~ 200 m asl) in the western basin within Peru, before the long transit across the width of Brazil. Once the river reaches >5 m in depth, we test whether or not these compounds have depth-differentiated distributions in the particulate and dissolved phases. Through comparison of our Madre de Dios data with published data elsewhere in the Amazon system, we build a more complete picture of lignin at the Amazon basin scale. We further compare data from rivers to distal deposits of lignin in offshore sediments of the Demerara Abyssal Plain (Atlantic Ocean) in order to understand the ultimate fate of lignin. Our approach allows us to characterize soil sources, and seasonal, elevation, and depth samples from the river sites reveal how lignin composition responds to inputs and modifications along the soil-river-ocean continuum.

2. Sampling and Analytical Methods

2.1. Sampling Scheme

2.1.1. Soil Sampling

Soils were collected in December 2010 from representative locations within the catchment along an elevation gradient from 194 to 3644 m asl on the eastern flank of the Peruvian Andes (see Table 1 for site names and locations), where detailed investigations on plant productivity, soil microbial community, and climate variabilities have been conducted previously [Zimmermann *et al.*, 2010a; Whitaker *et al.*, 2014a; Nottingham *et al.*, 2015a, 2015b]. The catchment has nearly continuous forest cover, which ranges from lowland Amazonian rainforest to tropical montane cloud forest (TMCF) at high elevations. Only the upper site (TC) at 3644 m asl is just above the tree line with grassland (puna). Mean annual temperature (MAT) decreases with increasing elevation (26 to 6°C), and mean annual precipitation (MAP) ranges from 1000 to 5302 mm yr⁻¹, peaking at 1500 m asl in the lower TMCF [Rapp and Silman, 2012; Malhi *et al.*, 2014]. Soils are classified as Umbrisols at sites above 2520 m, Cambisols from 1000 to 2020 m, and Haplic Cambisols and Haplic Allisols at the two lowland sites [Quesada *et al.*, 2010]. Soil pH does not vary significantly along the elevation gradient, with values around 4. The thickness of O horizon varies from 23 cm in the Andes to ~ 1 cm in the lowland.

Samples of O and M horizons were combined from five systematically distributed 40 cm \times 40 cm subplots taken across a 1 ha plot. To keep as much consistency in methodology among these sites with different soil properties, we sampled the top 10 cm where the O-horizon depth was > 10 cm; otherwise, the entire O horizon was collected. Only the top 10 cm of the mineral soil was sampled. All samples were dried and ground before chemical analysis.

2.1.2. River Sampling

Detailed sampling of the Kosñipata and Madre de Dios Rivers was performed during March 2013 (wet season) and August 2013 (dry season) for leaf wax [Ponton *et al.*, 2014] and lignin (this study). River water samples were collected across an elevation gradient from 165 to 2261 m asl, integrating catchments that extend up to >4000 m asl (Table S1 in the supporting information and Figure 1). Sampling locations were selected to span the transition from the Andes to the Amazon lowlands as well as to complement prior investigations in the region of fluvial POM geochemistry [Clark *et al.*, 2013], vegetation [Asner *et al.*, 2014a; Girardin *et al.*, 2014; Feakins *et al.*, 2016], and soils [Nottingham *et al.*, 2015a, 2015b].

At the upper sampling location, San Pedro, samples of the turbulent, well-mixed Kosñipata River were collected in 10 L buckets from the banks. At the lower stations the Madre de Dios River was navigable, and samples were collected from a boat within the channel where the velocity gradients were found to be highest based on Acoustic Doppler Current Profiler (ADCP) transects [after Bouchez *et al.*, 2014] (Figure 1e). By collecting from higher velocity zones, and across as large a range of velocities as possible in each depth profile, we aimed to capture the range of composition of material being transported at the time of sampling. Surface water was sampled by immersing 10 L buckets, and 2–5 depth samples per site were collected by deploying an isokinetic depth sampler consisting of a 10 L vessel, ballast, and a fin for flow orientation. Depth was monitored by a pressure transducer mounted onto the depth sampler. At the desired depth and location, the depth sampler doors were triggered to close by pistons operated by a bicycle pump on board. The depth sampler was brought on board, and the total contents of the depth sampler were carefully

Table 1. Location and Properties of Soil Samples of Peruvian Andes Forests in the Madre de Dios River Catchment

Sample	Location	Latitude (°S)	Longitude (°W)	Elevation (m asl)	MAT (°C) ^a	MAP (mm yr ⁻¹) ^b	Organic Horizon Thickness (cm) ^c	Soil Classification ^c	Organic Carbon (%)	
									Organic Horizon	Surface Mineral Horizon
TC	Tres Cruces	13.123	71.618	3644	6.5	1000	na	na	11.3	6.5
TU1	Trocha Union	13.114	71.607	3400	7.7 ± 1.1	1560	14	Umbrisol	na	na
TU2	Trocha Union	13.111	71.604	3200	8.9 ± 1.0	1560	11.8	Umbrisol	33.1	7.7
WAY	Wayqecha	13.190	71.587	3025	11.1 ± 1.2	1560	22.8	Umbrisol	38.8	13.0
TU3	Trocha Union	13.109	71.600	3020	9.5 ± 1.0	2318	17.2	Umbrisol	21.0	8.0
TU4	Trocha Union	13.107	71.589	2720	11.1 ± 1.0	2318	21.4	Umbrisol	19.3	2.4
TU5	Trocha Union	13.094	71.574	2520	12.1 ± 1.0	2318	13.6	na	na	na
TU7	Trocha Union	13.094	71.574	2020	14.9 ± 1.1	2318	16.8	Cambisol	21.5	na
TU8	Trocha Union	13.074	71.559	1850	16.0 ± 1.3	2318	15.6	Cambisol	19.0	6.4
SP1	San Pedro	13.047	71.543	1751	15.8 ± 1.3	5302	9.6	Cambisol	7.0	5.9
SP2	San Pedro	13.049	71.537	1500	17.4 ± 1.5	5302	16.0	Cambisol	13.3	4.3
VC	Villa Carmen	12.866	71.401	1000	20.7 ± 0.02	2000	3.6	na	na	5.0
TP3	Tambopata	12.830	69.271	210	26.4	1900	2.5	Haplic Cambisol	4.3	1.9
TP4 ^d	Tambopata	12.839	69.296	194	26.4	1900	0.7	Haplic Alisol	9.3	2.0

^aMAT: mean annual temperature; data from Rapp and Silman [2012]. Note that the weather station is in the open field at WAY and in the understory elsewhere.

^bMAP: mean annual precipitation; data from Rapp and Silman [2012].

^cData from Whitaker et al. [2014a] and references therein.

^dSporadically inundated by river.

transferred into 10 L ethylene vinyl alcohol (EVOH) containers (sold as wine bags), sealed free of air, and stored in the dark.

The collected river water samples were filtered within 12 h through 0.2 μm polyether sulfone (PES) filters within pressurized filter units operated by bicycle pump [cf. Galy et al., 2007, 2011]. All filtering for lignin samples was done at night to avoid photodegradation. Filters containing the suspended sediment load were stored in Whirlpak™ bags for recovery and analysis of POM. Filtrate was collected into clean 10 L EVOH bags for DOM extraction within hours. A fraction of the filtered water was filled in 1 L glass bottles and poisoned with concentrated HgCl₂ for DOC analysis.

DOM was concentrated on Mega Bond Elut C₁₈ solid phase extraction cartridges (10 g, 60 mL). Cartridges were first flushed with 100 mL ethanol followed by 50 mL of double deionized water (DDI) acidified to pH2, prior to passing the sample. The 0.2 μm filtrate was acidified to pH2 with hydrochloric acid (HCl), and 50 mL pure ethanol was added to each 10 L bags to improve extraction efficiency [Spencer et al., 2010]. Approximately 20 L filtered river water was pumped through one cartridge with the aid of a peristaltic pump at flow rates of 50–60 mL min⁻¹, followed by 50 mL of acidified DDI water. Up to 90 L of river water was extracted for each location using multiple cartridges. The cartridges were dried and wrapped in aluminum foil to exclude light until their return to the laboratory (3–10 days), where DOM was eluted with 50–80 mL methanol and dried under N₂ (stored at –20°C) until analysis.

2.1.3. Marine Sediment Sampling

Marine samples from the Amazon fan-Demerara Slope and Abyssal Plain (Figure 1) were collected as part of the ANACONDAS cruise aboard the R/V Knorr in May–June 2010. The Amazon fan is the third largest river fan in the world and provides a sedimentary repository for OC burial over geological time-scales. Sediment core top samples (upper 2–4 cm) obtained using a

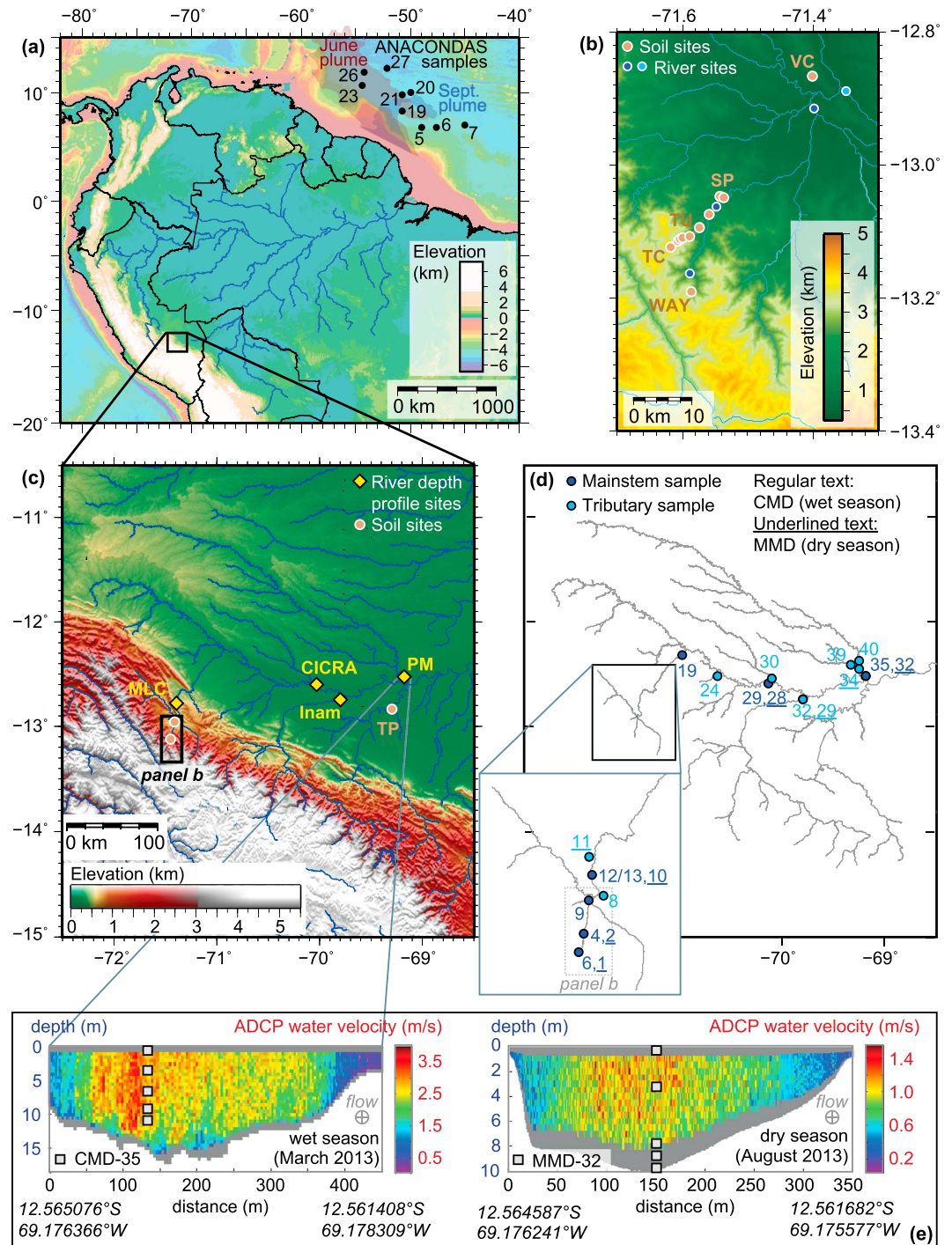


Figure 1. Maps of sampling locations. (a) On land, showing Amazon River system (blue) and country boundaries (black) overlain on topography. Offshore, marine sediment sampling locations relative to the extent of the Amazon River plume by the extent of the 32.5 practical salinity unit boundary [Chong, 2013], contrasting June and September seasons. (b) Soil and river sampling locations, in the Andean sector Kosñipata Rivers in Peru (blue) overlain on elevation. (c) River depth profile locations for the Madre de Dios River and some soil sampling locations. For additional soil sampling locations and Kosñipata River sampling, white box expanded in Figure 1b. (d) River network for the Madre de Dios River and Kosñipata (inset), showing sampling locations in wet season (CMD) and dry season (MMD) and differentiating mainstem and tributary numbers. (e) Transect across the river at PM showing river depth, Acoustic Doppler Current Profiler (ADCP) river flow velocity, and depth sampling locations (boxes). Note that Figures 1c and 1d show the location of Figure 1b. Refer to Tables 1 and S1 for detailed site abbreviations and locations.

Table 2. Location, Bulk, and Biomarker Properties of Amazon Fan Deep Sea Surface Sediment Samples From the Atlantic Ocean^a

Sn #	Location	Water Depth (m)	OC (%)	Σ ($\mu\text{g g}^{-1}$)										Δ (mg g^{-1} OC)			
				Lignin Phenols	P phenols	3,5Bd	Cutin Acids	Lignin Phenols	P phenols	3,5Bd	Cutin Acids	S/N	C/N	P/(V+S)	3,5Bd/V	(Ad/Al) _v	(Ad/Al) _s
5	6.81°N; 49.98°W	3975	0.75	2.0	2.7	0.8	0.08	0.27	0.36	0.11	0.01	0.9	0.2	1.5	0.8	0.9	0.8
6	6.82°N; 47.63°W	4088	0.62	2.0	7.4	0.01	0.08	0.32	1.19	0.001	0.01	0.4	0.01	3.7	0.004	0.04	0.04
7	7.00°N; 45.02°W	4394	0.45	0.3	1.1	0.4	0.03	0.08	0.25	0.10	0.008	0.7	0.2	3.8	2.4	0.6	0.7
19	8.29°N; 50.75°W	4854	0.85	0.8	3.7	0.1	0.02	0.10	0.43	0.01	0.002	0.5	0.0	4.4	0.1	0.1	0.1
20	10.00°N; 49.97°W	4854	0.95	0.7	1.4	0.8	0.04	0.08	0.15	0.09	0.004	0.5	0.2	2.2	1.9	0.4	0.8
21	9.77°N; 50.75°W	4863	0.97	1.1	2.0	0.4	0.10	0.11	0.20	0.04	0.01	1.0	0.3	2.0	0.9	1.0	0.5
23	10.62°N; 54.39°W	4486	0.70	0.4	4.4	0.005	0.06	0.05	0.63	0.001	0.009	0.4	0.01	12.3	0.02	0.1	0.03
26	11.80°N; 54.21°W	4777	0.76	0.7	1.4	0.2	0.08	0.09	0.18	0.02	0.01	0.8	0.3	2.3	0.6	1.3	0.8
27	12.16°N; 52.13°W	5044	0.46	0.8	1.7	0.2	0.09	0.17	0.37	0.05	0.02	0.7	0.2	2.5	0.6	0.8	0.8

^aAbbreviations: OC, organic carbon; Σ , absolute concentration; Δ , OC-normalized concentration; P phenols, *p*-hydroxyl phenols; 3,5Bd, 3,5-dihydroxybenzoic acid; S/V, syringyl/vanillyl phenols; C/N, cinnamyl/vanillyl phenols; P/V + S, *p*-hydroxyl/vanillyl and syringyl phenols; 3,5Bd/V, 3,5-dihydroxybenzoic acid/vanillyl phenols; (Ad/Al)_v, vanillic acid/vanillin; and (Ad/Al)_s, syringic acid/syringaldehyde.

multicorer from water depths of 3975–5044 m were selected to target sites underlying the core and extent of the Amazon River plume in the open Atlantic Ocean in order to assess the reach and burial of river-exported terrestrial OC. Location and sample information for these deep marine samples are provided in Table 2. Detailed sampling procedures are described in *Chong* [2013].

2.2. Analytical Methods

2.2.1. Catchment Characterization

Fluvial samples integrate material from across their catchment areas. In order to assess the mean elevation of the catchment area upstream of a given sample site, catchment boundaries were delineated using a flow-routing algorithm in Geographic Resources Analysis Support System Geographic Information Software using Shuttle Radar Topography Mission (SRTM)-derived digital elevation data with a spatial resolution of 3 arc sec (~90 m). In addition, the distance upstream from Óbidos (the most downstream gauging station on the Amazon River) was determined as above except using a coarser resolution digital elevation data ETOPO1 with a spatial resolution of 1 arc min (~1900 m) in the Amazon lowlands with the finer resolution SRTM to map the catchment above Puerto Maldonado, which is our lowest sampling location on the Madre de Dios River.

2.2.2. Bulk Analysis

POM samples were recovered from the PES filters by washing the sediment off the filters with Milli-Q water and freeze drying the recovered sediment slurry. Sediment load was determined from the dry mass of POM relative to the volume of water filtered in the field. Dry fluvial POM sediment aliquots were homogenized with mortar and pestle and decarbonated by exposure to HCl vapor for 48 h at 70°C followed by drying for 3 days at 70°C. Marine sediment samples were decarbonated by vapor acidification at room temperature, which is sufficient for marine carbonates that do not contain dolomite or other recalcitrant inorganic carbon. Decarbonated sediment samples were analyzed for total organic carbon by high temperature combustion using a Costech Elemental Analyser coupled to a Picarro G2201-i carbon isotope analyzer at the University of Southern California (USC). For samples analyzed in duplicate, reproducibility was better than 5%. DOC was measured for wet-season samples at the National Ocean Sciences Accelerator Mass Spectrometry facility in Woods Hole. Dry-season sample vials were unfortunately damaged during transport; and hence, DOC was not measured for this season.

Specific surface area (SSA) of suspended particulate matter (SPM) was measured on a small aliquot (~0.1–0.3 g) of dry, untreated POM with a Micrometrics Accelerated Surface Area and Porosimetry System 2010 at USC. Prior to analysis, the dry POM samples were degassed

at 70°C and ultralow pressure (>2 mm Hg) until completion (>3 h). The SSA of each sample was measured using a N₂ gas adsorbate in a helium atmosphere, with 10 measurements across a partial pressure of N₂ ranging from 0.066 to 0.32 and at 77 K (following Mayer [1994]). Two external standards (200 m² and 0.5 m²) and an in-house standard (5.0 m², crushed anorthosite) were interspersed between samples and indicate that replicate precision is better than 9% (1 σ) with uncertainties decreasing in measurements of higher SSA.

Grain size distribution was measured on SPM samples using a laser diffraction grain size analyzer (Malvern Mastersizer 2000) coupled to a Hydro 2000G ultrasonic dispersion unit. Pretreatment with HCl to remove carbonates and peroxide to remove organic matter had little effect on patterns of grain size distribution with depth, so all grain size data are reported for samples without these pretreatments. A tuff standard (TS2) with a known grain size distribution between 1 and 16 μ m was measured periodically during each run to assess accuracy and reproducibility. We report the modal grain size in micrometer.

2.2.3. Lignin Phenol Analysis

Dry, ground POM samples were solvent extracted using an Accelerated Solvent Extraction system at USC using 9:1 dichloromethane:methanol (v/v) to remove lipids, with analyses of these compounds reported elsewhere [Ponton *et al.*, 2014]. Lignin-derived phenols were isolated from solvent-extracted POM and dried DOM samples using a CuO oxidation method at the Chinese Academy of Sciences [Feng *et al.*, 2011]. Briefly, POM (0.3–0.8 g) or DOM samples were mixed with 0.5 g CuO, 50 mg ammonium iron (II) sulfate hexahydrate [Fe(NH₄)₂(SO₄)₂·6H₂O], and 20 mL of 2 M N₂-purged NaOH solution in teflon-lined bombs. All bombs were flushed with N₂ in the headsapce for 10 min and heated at 170°C for 2.5 h. The lignin oxidation products (LOPs) were spiked with an internal standard (ethyl vanillin), acidified to pH1 with 6 M HCl, and kept in the dark for 1 h. After centrifugation (2500 rpm for 10 min), LOPs were liquid-liquid extracted from the clear supernatant with ethyl acetate and concentrated under N₂ for further analysis.

LOPs were derivatized with N,O-bis-(trimethylsilyl)trifluoroacetamide and pyridine (70°C, 1 h) to yield trimethylsilyl derivatives. The molecular composition was examined on a Trace 1310 gas chromatograph coupled to an ISQ mass spectrometer (MS; Thermo Fisher Scientific, USA) using a DB-5MS column (30 m \times 0.25 mm i.d., film thickness, 0.25 μ m) for separation. Temperature increased from 65°C (initial hold time is 2 min) to 300°C at a rate of 6°C min⁻¹, and helium was used as carrier gas (1.2 mL min⁻¹). Spectra were obtained by scanning over the range of 50–600 amu, and electron impact ionization (EI) at 70 eV was used for all analyses. Quantification was achieved by comparison with internal standards (ethyl vanillin). Errors associated with phenol concentration data are typically <10% based on replicate analysis of the same sediment sample.

2.3. Lignin Indicators and Data Analysis

Indicators based on LOPs are used to assess the abundance, source, and degradation stage of terrestrial OC in the Madre de Dios River system. The concentration of lignin phenols is summarized as absolute concentrations (\sum_{lignin} ; in the units of mg g⁻¹ soil or sediment, i.e., milligram lignin phenols per gram of soil or sediment or μ g L⁻¹ in DOM) and OC-normalized concentrations (Λ_{lignin} ; in the units of mg g⁻¹ OC, i.e., milligram lignin phenols per gram of OC) of eight “characteristic” lignin-derived monomeric phenols [Hedges and Mann, 1979], including vanillyl (V; vanillin, acetovanillone, and vanillic acid), syringyl (S; syringaldehyde, acetosyringone, and syringic acid), and cinnamyl (C; *p*-coumaric acid and ferulic acid) units. CuO oxidation also releases *p*-hydroxyl (P) phenols (including *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone, and *p*-hydroxybenzoic acid) and 3,5-dihydroxybenzoic acid (3,5 Bd) that may derive from proteins and “tannin-like” compounds or from demethylation of lignin [Prah *et al.*, 1994; Goñi and Hedges, 1995; Goñi *et al.*, 2000]. Furthermore, aliphatic lipids, including ω -hydroxyhexadecanoic acid, α,ω -dihydroxyhexadecanoic acid, 9,10, ω -trihydroxyoctadecanoic acid, are often observed in the LOPs and may be used to trace cutin which forms protective coatings on foliar surfaces [Goñi and Hedges, 1990b]. The abundance of P phenols, 3,5 Bd, and cutin acids is also represented by respective absolute (\sum) and OC-normalized concentrations (Λ).

Ratios of syringyl-to-vanillyl phenols (S/V) and cinnamyl-to-vanillyl phenols (C/V) are used to indicate the relative input of angiosperm and nonwoody tissues versus gymnosperm wood, respectively [Hedges and Mann, 1979; Goñi and Hedges, 1995]. Demethylation of lignin (e.g., by brown-rot decay) leads to selective loss of methoxylated phenols (such as V and S) [Ertel *et al.*, 1986] with nonmethoxylated phenols (such as P phenols) unaffected. The ratio of P/(V + S) may therefore reflect the diagenetic state of lignin when the other sources of P phenols (such as protein) are relatively constant [Dittmar and Lara, 2001; Zaccone *et al.*, 2008]. By

comparison, 3,5 Bd is most enriched in soil/peat OM [Prah et al., 1994b; Goñi et al., 2000; Houel et al., 2006; Otto and Simpson, 2006]. Hence, the ratio of 3,5 Bd/V is considered to reflect OM transformation in soils. The acid-to-aldehyde (Ad/Al) ratios of V and S phenols are used to indicate lignin degradation through propyl side-chain oxidation (e.g., by white-rot decay) [Ertel et al., 1986; Hedges et al., 1988; Goñi and Hedges, 1992; Opsahl and Benner, 1995; Otto and Simpson, 2006].

Relationships between phenol abundance, indicative ratios, and environmental parameters of soils and rivers were assessed using ordinary least squares linear regression analysis. Differences in LOP abundances and indicators between different sampling depths, seasons, DOM, and POM were examined using *t* tests or paired *t* tests where appropriate. Correlations and differences were considered to be significant at a level of $p < 0.05$.

3. Results and Discussion

3.1. Bulk OC and Lignin Characteristics in the Peruvian Andean Forest Soils

Bulk OC content was 4.3–38.8% and 1.9–13.0% in the O and surface mineral (M) horizons of Peruvian Andean forest soils, respectively, both peaking at the Wayqecha site at an elevation of 3025 m asl (Table 1). SP1-O, TP3-O, and TP4-O contained OC < 10% whereas WAY-M contained OC > 10%, suggesting varied soil organic carbon content and qualities among these sites (see Table 1 for site names and locations). We kept the original classification to differentiate the upper (O) and lower layers (M) with varied lignin contents, respectively. The OC content of both O and M horizons appeared to increase with elevation except at the highest site above the tree line (Figure S1a), consistent with the increase of O-horizon depth at higher elevations ($r^2 = 0.61$, $p < 0.05$; Figure S1b). These trends are opposite to the decline of net primary productivity (NPP) with elevation [Girardin et al., 2014; Huaraca Huasco et al., 2014; Malhi et al., 2014], and slower decomposition rates resulting from lower temperatures [Davidson and Janssens, 2006; Nottingham et al., 2015a, 2015b] likely contribute to the greater accumulation of soil OC at high elevations [Zimmermann et al., 2010a; Clark et al., 2015; Nottingham et al., 2015a].

Lignin phenol concentrations were 1.8–14.9 mg g⁻¹ soil (for \sum_{lignin}) or 15.8–92.0 mg g⁻¹ OC (for Λ_{lignin}) in the O horizons and 0.2–2.1 mg g⁻¹ soil or 3.5–32.3 mg g⁻¹ OC in the surface mineral soils (Figure 2a and Table S1). These values are within the range of lignin phenol concentrations reported in forest soils elsewhere [Thevenot et al., 2010]. Consistent with prior studies [Feng et al., 2010; Wu et al., 2015], lignin phenols were much more enriched in the O horizons than in the upper mineral soils ($p < 0.05$), reflecting a decreased input and/or progressive loss of lignin with soil depth [Kögel-Knabner et al., 1988; de Montigny et al., 1993; Thevenot et al., 2010]. Λ_{lignin} was negatively correlated with elevation in the O horizons ($r^2 = 0.58$, $p < 0.05$; Figure 2a), likely resulting from increased input (i.e., NPP) at lower elevations (see discussion in Text S1). The Λ values of P phenols (Figure 2b) and 3,5 Bd were only slightly higher in the O horizons (2.4–13.2 and 1.5–34.4 mg g⁻¹ OC, respectively) than in mineral soils (1.0–7.6 and 0.4–5.3 mg g⁻¹ OC, respectively; $p < 0.05$), likely indicating that diagenetic losses of these compounds are counteracted by an increased contribution of microbial protein-derived sources and/or demethoxylated degradation products of lignin in mineral soils. Similarly, cutin acids exclusively derived from aboveground leaf litter [Kögel-Knabner, 2002] had slightly higher Λ values in the O horizons than in mineral soils (0.05–5.1 mg g⁻¹ soil or 1.2–23.4 mg g⁻¹ OC; $p < 0.05$; Figure 2c), suggesting that they are well preserved in the soil profile relative to lignin, probably due to sorptive preservation of these hydrophobic molecules onto soil minerals [Feng et al., 2005]. Alternatively, cutin acids may be well preserved in cuticle fragments in the Andean sector because leaves are thicker and waxier at the high elevation [Asner et al., 2014b].

The lignin source indicator S/V and C/V ratios were 0.4–1.4 and 0.2–1.8, respectively (Figures 2d and 2e), implying significant inputs of angiosperm-derived OC and nonwoody tissues [Hedges and Mann, 1979; Goñi and Hedges, 1995; Keil et al., 1998]. Both ratios decreased from O horizon to mineral soils ($p < 0.05$), consistent with the preferential loss of S and C phenols during lignin degradation [Hedges et al., 1988; Opsahl and Benner, 1995; Otto and Simpson, 2006]. The ratio of P/(V + S) slightly increased in the mineral soils ($p < 0.05$; Figure 2f), in line with an increasing loss of methoxy phenols (especially S phenols) during lignin degradation [Dittmar and Lara, 2001]. The C/V ratio increased significantly with increasing elevation in both O horizon and mineral soils ($r^2 = 0.58$ and 0.67, respectively; $p < 0.05$; Figure 2e). In this forest-dominated catchment, grassland distribution is very limited even at high elevations. Hence, the C/V increase with elevation is most likely associated with more foliar or nonwoody input at higher elevations, consistent with lower

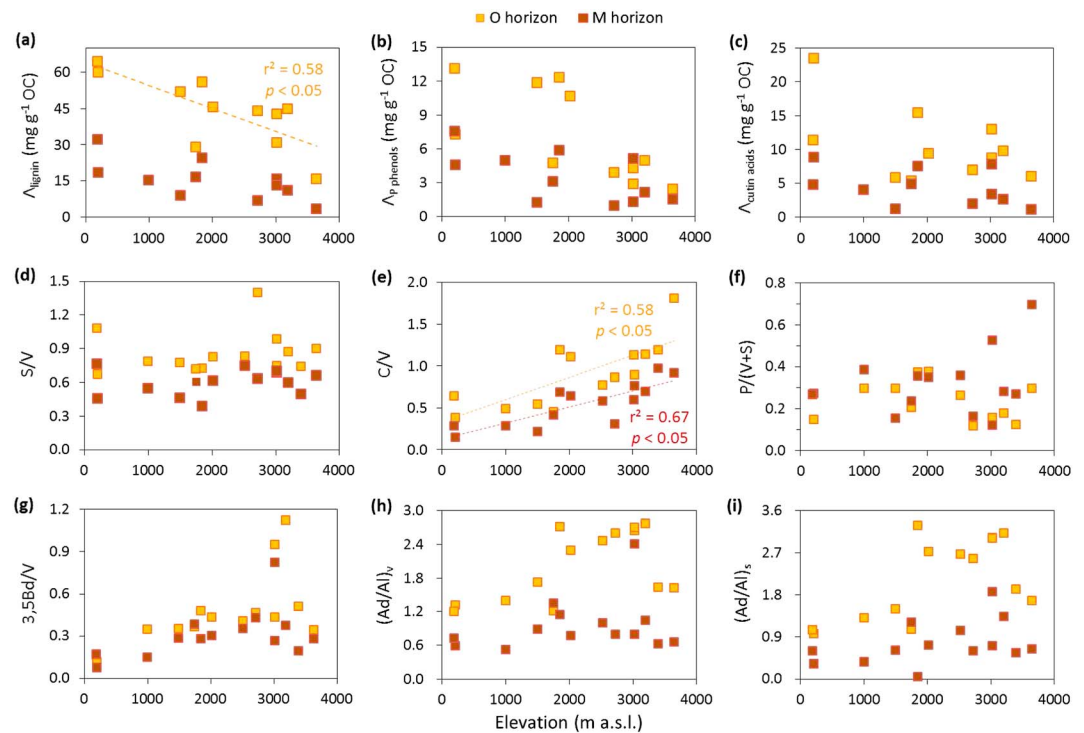


Figure 2. Changes in the organic carbon-normalized concentration (Λ) of (a) lignin phenols, (b) hydroxy (P) phenols, (c) cutin acids and lignin parameters in the organic (O) and surface mineral (M) horizons of Peruvian Andes-Amazon forests with elevation: (d) ratios of syringyl/vanillyl phenols (S/V), (e) cinnamyl/vanillyl phenols (C/V), (f) *p*-hydroxyl/vanillyl and syringyl phenols (P/V + S), (g) 3,5-dihydroxybenzoic acid/vanillyl phenols (3,5 Bd/V), (h) vanillic acid/vanillin (Ad/Al)_v, and (i) syringic acid/syringaldehyde (Ad/Al)_s; asl: above sea level. Orange and red dotted lines represent linear regressions of O and M horizons, respectively ($p < 0.05$).

canopy height (smaller trunk biomass) and thicker leaves [Asner *et al.*, 2014b]. These trends in trunk wood and leaf traits result in an increase in the proportion of leaf biomass-derived NPP despite the overall decline in NPP with elevation [Girardin *et al.*, 2014; Huaraca Huasco *et al.*, 2014; Malhi *et al.*, 2014]. Another possible explanation for increasing C/V with elevation is better preservation of the relatively labile C phenols at lower temperatures [Feng and Simpson, 2008]. Hence, both production and preservation may explain the observed positive trend of C/V ratio with elevation.

The ratio of 3,5 Bd/V showed higher values in the O horizon than in mineral horizons ($p < 0.05$; Figure 2g), suggesting a high degree of soil OM transformation in the surface organic layers of the humid tropical forests at our study sites [Houel *et al.*, 2006]. Similarly, the Ad/Al ratios of V and S phenols were higher in the O horizon (1.2–2.8 and 1.0–3.3) than in the mineral soils (0.5–2.4 and 0.1–1.9; $p < 0.05$; Figures 2h and 2i), indicating enhanced side-chain oxidation of lignin in the surface layers despite a lower lignin degradation stage (evidenced by S/V, C/V, and P/(V + S) ratios). These observations are contradictory to the commonly observed trend of increasing 3,5 Bd/V and Ad/Al ratios with soil depth in grasslands and temperate/boreal forests [Kögel, 1986; Hedges *et al.*, 1988; Opsahl and Benner, 1995; Karroum *et al.*, 2005; Otto and Simpson, 2006]. Little information is available on lignin oxidation state in tropical montane forests. Low Ad/Al ratios (0.18–0.37) were reported from the O horizons of a tropical montane forest in Ecuador [Wilcke *et al.*, 2008]. Enhanced oxidation (high 3,5 Bd/V, (Ad/Al)_v, and (Ad/Al)_s ratios) in the O horizons may be particular to these Peruvian Andean forest soils. The Ad/Al ratios of both V and S phenols showed a positive correlation with soil OC content in all soil samples ($r^2 = 0.75$ and 0.78 , respectively; $p < 0.05$, Figures S2a and S2b) and with layer thickness in the O horizon ($r^2 = 0.59$ and 0.56 , respectively; $p < 0.05$, Figures S2c and S2d), suggesting that lignin is more oxidized in soils with a higher OC content and thicker O horizon. This is similar to the findings of Wilcke *et al.* [2008] that Ad/Al ratios increased with elevation in the O horizons of a tropical montane forest in Ecuador, while soil OC degradation declined (as indicated by higher C:N ratios and thickness of O horizons) at higher elevations.

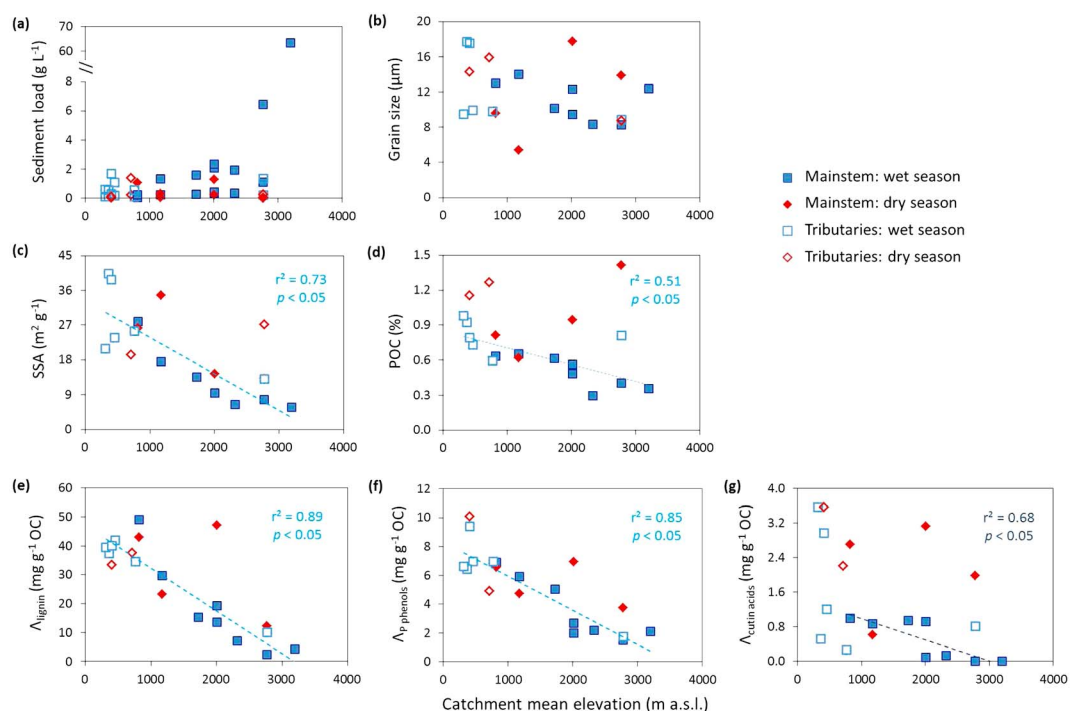


Figure 3. Changes in the (a) sediment load, (b) modal grain size, (c) specific surface area (SSA), (d) particulate organic carbon (POC) content, and POC-normalized concentrations (Λ) of (e) lignin, (f) *p*-hydroxyl (P) phenols, and (g) cutin acids in the mainstem and tributaries of Kosñipata and Madre de Dios Rivers. Blue dotted lines in Figures 3c–3f represent linear correlations of both mainstem and tributary samples in the wet season, while dark blue dotted line in Figure 3g represents linear regression of mainstem samples in the wet season ($p < 0.05$).

We postulate several possible explanations for the unusual pattern of lignin side-chain oxidation decoupled from increased lignin degradation in the mineral soils. First, the Ad/Al ratios exhibited the highest values in the O horizons between 1850 and 3200 m asl (2.3–2.8 and 2.6–3.3, respectively), which corresponds to the zone dominated by montane cloud forest. Montane cloud forests are reported to contain higher concentrations of polyphenols in plant foliar tissues and O horizons than rainforest [Bruijnzeel and Veneklaas, 1998; Zimmermann *et al.*, 2012], possibly contributing to the high 3,5 Bd/V ratios in the O horizons of Peruvian Andes. It remains to be determined whether lignin composition differs in the TMCF (for example, showing higher Ad/Al ratios in plant tissues) [Wysocki *et al.*, 2008], thus leading to an overestimate of lignin oxidation in the O horizons. Second, in this Peruvian Andes transect, surface layers (including O horizon) are characterized by very high activities of phenol oxidase [Nottingham *et al.*, 2016] and a dominance of fungal communities at all elevations [Whitaker *et al.*, 2014a, 2014b], which are key degraders and producers of enzymes associated with lignin oxidation. These communities may contribute to the elevated lignin side-chain oxidation in the O horizons. In particular, the fungal dominance increases with elevation, with fungi comprising 85–95% of microbial biomass above 1000 m asl [Whitaker *et al.*, 2014a]. Increasing fungal communities may explain the increased lignin oxidation at higher elevation sites. Third, root biomass is known to increase as a proportion of NPP with elevation in Andean forests [Girardin *et al.*, 2014; Huaraca Huasco *et al.*, 2014; Malhi *et al.*, 2014], and the direct input of root lignin might provide relatively fresh lignin with low Ad/Al and C/V ratios to the subsurface, while the overlying O horizon receives microbially degraded leaf litter inputs.

In summary, our soil lignin data not only suggest an overall greater degradation in the mineral compared to O horizons (i.e., lower lignin abundances, S/V and C/V ratios, and higher P/(V + S) ratios in mineral soils) but also highlight that some lignin attributes (e.g., lower 3,5 Bd/V and Ad/Al ratios in mineral soils) may be affected by processes that are distinct to TMCFs, leaving apparently more oxidized signatures in the O-horizon material. The production and degradation pathways that generate the unique lignin oxidation patterns observed in TMCF soils here merit further investigation in order to better understand the inputs, transformation

processes, and stability of lignin buried in soils and exported downstream, given that the TMCF soils hold some of the highest OC content of all tropical soils [Zimmermann *et al.*, 2010b; Clark *et al.*, 2015].

3.2. Chemical Properties and Biomarker Composition in Riverine POM and DOM

3.2.1. Downstream Evolution of POM Composition in Surface or Well-Mixed Waters

River waters had distinct hydrological and physiochemical properties during wet versus dry seasons across the study region (Table S1). Sediment load was 0.03–1.39 g L⁻¹ in the surface waters in the dry season and increased to 6.46–63.36 g L⁻¹ in the Andes (CMD-4 and CMD-6) during the wet season (Figure 3a). Modal grain size of SPM from surface waters was relatively invariant across sites in both seasons (5.4–17.7 μm; Figure 3b). The SSA of SPM varied in the both seasons (5.0–40.4 m² g⁻¹) and increased downstream in the wet season ($p < 0.05$; Figure 3c). Surface water POC content in the dry season (0.62–1.42%) was overall higher than in the wet season (0.30–0.65%; $p < 0.05$) likely due to dilution by increased flux of clastic material eroded from the Andes during the wet season [Bouchez *et al.*, 2014]. POC content increased with decreasing catchment mean elevation in the wet season ($r^2 = 0.51$, $p < 0.05$; Figure 3d).

Biomarkers showed similar ranges of Λ values in the surface POM of the mainstem and tributaries of the Kosñipata and Madre de Dios Rivers, of 2.3–49.0, 1.5–10.1, and 0.001–3.6 mg g⁻¹ OC for lignin phenols, P phenols, and cutin acids, respectively (Figures 3e–3g). Λ_{lignin} and $\Lambda_{\text{P phenols}}$ increased with decreasing elevation in the wet season in both the mainstem and tributaries ($p < 0.05$; Figures 3e and 3f), while cutin acids increased in the mainstem ($r^2 = 0.68$, $p < 0.05$; Figure 3g), suggesting a downstream accumulation of land-derived OC. $\Lambda_{\text{cutin acids}}$ was overall higher in the dry season relative to the wet season ($p < 0.05$), indicating that nonplant OC (such as microbial and rock-derived fossil carbon) supply was relatively low in the dry season [Clark *et al.*, 2013].

Lignin S/V and C/V ratios were 0.3–1.2 and < 0.01 –0.3, respectively, in the surface POM in the wet season (Figures S3a and S3b). The C/V ratio was, in general, lower than that of soil samples, implying preferential loss of C phenols (to mineralization or to the dissolved phase) during land-to-river transfer. The P/(V + S) ratio of river POM (0.1–0.7; Figure S3c) showed a similar range of values to that of soils. The 3,5 Bd/V ratio exhibited much lower values in river POM (< 0.01 –0.3; Figure S3d) than in soils (0.1–1.1), suggesting that 3,5 Bd was mainly derived from land sources rather than in situ production in the river such as from macroalgae [Goñi and Hedges, 1995] and was more susceptible to degradation than V phenols. Surface POM in the dry season had similar S/V and C/V ratios except for high values at two Andes sites (MMD-2 and MMD-29). The dry-season POM from MMD-2 also had the highest 3,5 Bd/V ratio, indicative of a stronger influence of OC derived from soil surfaces (O horizon) at this site. The (Ad/Al)_v and (Ad/Al)_s ratios from across the study region showed similar ranges of values in the wet and dry seasons (0.04–0.94 and 0.01–0.74, respectively; Figures S3e and S3f) and were much lower than those of soil samples, potentially related to preferential loss of acidic phenols from POM to DOM via dissolution (section 3.2.2) or direct input of vegetation with low Ad/Al ratios.

Lignin in the Madre de Dios POM showed no consistent compositional changes downstream in the dry season (Figure S3), similar to previous investigations from other Amazon tributaries where lignin composition was invariant in POM of the Bolivian headwaters [Hedges *et al.*, 2000] or along the Vilcanota-Urubamba-Ucayali Rivers [Aufdenkampe *et al.*, 2007] except for a decreasing C/V ratio downstream in both studies. In the wet season, however, lignin seemed to receive more fresh surface inputs downstream in the mainstem POM as indicated by increasing ratios of S/V and C/V and a decreasing ratio of P/(V + S) with decreasing elevation ($p < 0.05$; Figures S3a–S3c). In addition, the (Ad/Al)_s ratio increased downstream ($p < 0.05$; Figure S3f). As the O horizons of the catchment showed higher (Ad/Al)_s ratios, elevated ratios in the downstream POM may also indicate higher lignin inputs from surface soils. These trends are different from the compositional changes of soil biomarkers with elevation (Figure 2) and imply shifting lignin composition from degradation-dominated signals in the erosive Andean terrains to relatively more fresh inputs in the lowland Amazon in the wet season.

Our wet-season results contrast with the Bolivian and Ucayali studies, in which tributaries drain partially glaciated catchments originating at higher elevations and with large areas of grassland and moderate slopes ($< 14\%$) at high elevations [Hedges *et al.*, 2000; Aufdenkampe *et al.*, 2007]. In contrast, the Madre de Dios River catchment is almost entirely forested with steep topography (slope $\sim 26\%$) in the upstream sector [Clark *et al.*, 2015]. Low grassland coverage explains the low C/V ratio in our study, and the high input of degraded lignin may be attributed to mineral soil erosion from steep slopes in the Madre de Dios. In addition, we sampled

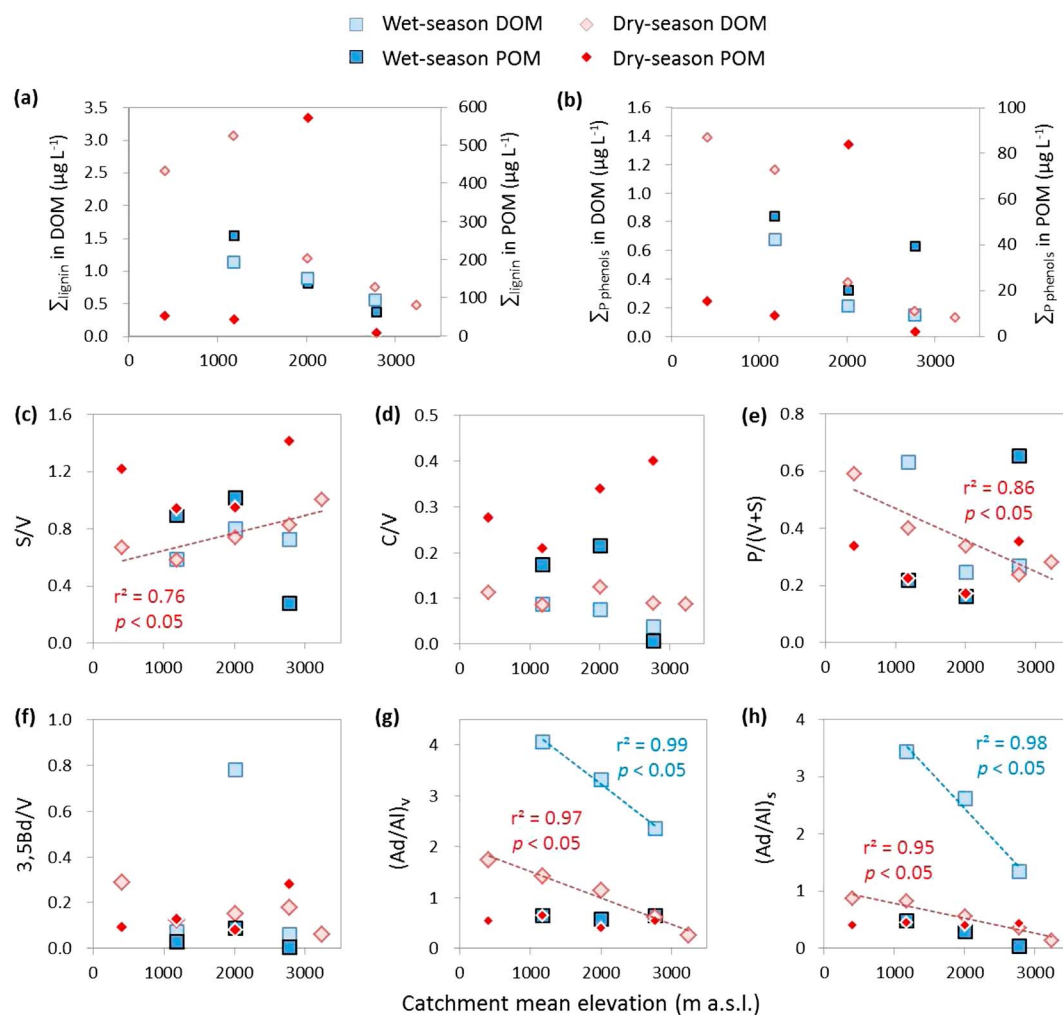


Figure 4. Changes of (a) lignin and (b) *p*-hydroxyl (P) phenol concentrations as well as lignin parameters in the surface dissolved organic matter (DOM) versus particulate organic matter (POM) of the Kosñipata and Madre de Dios Rivers with catchment mean elevation: ratios of (c) S/V, (d) C/V, (e) P/V + S, (f) 3,5 Bd/V, (g) (Ad/Al)_v, and (h) (Ad/Al)_s. Abbreviations are the same as in Figure 3. Blue and red dotted lines represent linear regressions of DOM samples in the wet and dry seasons, respectively ($p < 0.05$).

during the late wet season when we expect lignin input from litter and soil to be elevated due to enhanced overland flow [Feng *et al.*, 2013], whereas both the Bolivian and Ucayali headwaters were sampled at the end of the dry season when fresh lignin input from land may have been limited. The different hydrological conditions most likely affected lignin erosion and contributed to the varied downstream evolution patterns of particulate lignin.

3.2.2. DOM Composition in Surface Waters

Similar to POC, DOC content increased downstream in the surface waters of the Madre de Dios River in the wet season from 33.6 (CMD-4) and 54.4 (CMD-11) to 154.4 $\mu\text{mol L}^{-1}$ (CMD-35). Lignin and P phenols were characterized from eight surface DOM samples and compared with the corresponding POM. Cutin acids were not detected in the DOM due to their low solubility. Σ_{lignin} and $\Sigma_{\text{P phenols}}$ were 0.48–3.06 and 0.13–1.39 $\mu\text{g L}^{-1}$ in the surface DOM, respectively (Figures 4a and 4b), equivalent to 0.4–1.3% of those in the POM at the corresponding sites in the wet season and 5.0–13.9% in the dry season (except 0.2–0.4% at MMD-10). These concentrations are on the low end of values previously reported for dissolved lignin in the Amazon River and its tributaries [Hedges *et al.*, 2000; Aufdenkampe *et al.*, 2007; Ward *et al.*, 2013], indicating that transfer of dissolved lignin is minor in the Madre de Dios River but plays a more important role in the dry season due to less dilution by the reduced water discharge. Both groups of phenols showed

similar Σ values in both seasons in the high-elevation catchment (CMD-4 and MMD-2) but much higher Σ values in the dry versus wet season in the lowland (MMD-32; Figures 4a and 4b). Similar to those in the POM, Σ_{lignin} and $\Sigma_{\text{P phenols}}$ in the DOM increased with decreasing elevation in both seasons, implying a downstream accumulation of land-derived OC.

The S/V and C/V ratios of dissolved lignin showed similar values in both seasons (0.6–1.0 and 0.04–0.1, respectively). Both ratios were lower than those of the corresponding POM at the low elevation and midelevation catchment sites ($p < 0.05$; Figures 4c and 4d). As S and C phenols are reported to have a higher solubility than V phenols [Hernes and Benner, 2002], lower ratios of S/V and C/V in the DOM are not caused by preferential dissolution processes but indicate a higher degradation state of lignin in the dissolved phase, consistent with prior findings in the Amazon system [Hedges et al., 2000; Aufdenkampe et al., 2007]. Dissolved lignin at the high-elevation site (MMD-2) also displayed lower S/V and C/V ratios than particulate lignin in the dry season but showed a similar C/V ratio and a higher S/V ratio in the wet season. DOM at this upstream site may be relatively fresh due to the short transit time in the mountain sections of the river, especially in the wet season, explaining the relatively high S/V ratio. In line with this explanation, we find that the P/(V + S) ratio, which increases with lignin demethylation [Dittmar and Lara, 2001], increases downstream and showed lower values in DOM relative to POM at the high-elevation sites (Figure 4e). The 3,5 Bd/V ratio, ranging from 0.06 to 0.8 in the surface DOM, displayed varied values along the river and across seasons, with much higher values (0.8) than POM (~0.1) in the midelevation catchment in the wet season (CMD-12; Figure 4f). Sources of 3,5 Bd include microbial proteins and tannins from plants [Prahl et al., 1994; Goñi et al., 2000], whose abundance or contribution to 3,5 Bd may be variable as sources shift down river.

Surface DOM showed a decreasing S/V ratio and an increasing P/(V + S) ratio with decreasing catchment mean elevation in the dry season ($p < 0.05$; Figures 4c–4e), suggesting that dissolved lignin was increasingly oxidized downstream. In contrast, S/V and P/(V + S) ratios did not show any systematic downstream trends in the wet season, perhaps because runoff contributes fresh lignin from lowlands and/or because of dissolution of fresh POM delivered from upstream (see discussion in section 3.2.4).

The Ad/Al ratios were 0.3–4.1 and 0.1–3.4 for dissolved V and S phenols, respectively. These values are slightly higher than (or, in the upstream, similar to) those in the POM in the dry season but much higher in the wet season ($p < 0.05$; Figures 4g and 4h). As the O horizons exhibited higher Ad/Al ratios than surface mineral soils in the Madre de Dios catchment (Figure 2), higher Ad/Al ratios in the wet season may be attributed to a higher input of dissolved lignin from O horizons, assuming that dissolved lignin also has higher Ad/Al ratios in the O horizons relative to mineral soils. Furthermore, acidic phenols have a higher solubility, resulting in elevated Ad/Al ratios in DOM relative to POM or sediments due to fractionation during leaching and sorption processes [Hernes and Benner, 2002; Hernes et al., 2007]. High runoff in the wet season may have enhanced lignin dissolution and further elevated the Ad/Al ratio in the aqueous phase. It is very likely that both mechanisms contributed to the observed patterns. Similar to the (Ad/Al)_s ratio of surface POM in the wet season (Figure S3f), both Ad/Al ratios in the DOM increased with decreasing elevation of catchment in both seasons ($p < 0.05$; Figures 4g and 4h). Again, this may indicate an enhanced oxidation of dissolved lignin downstream or more input from O horizons in the lowlands.

3.2.3. POM and DOM Characteristics in River Depth Profiles: A Deep Fresh Woody Current

A total of six depth profiles were sampled for POM characterization during wet and dry seasons (Table S1). Among them, subsurface samples (~5 m) were obtained at two sites sampling relatively high-elevation catchments (CMD-12 for the Madre de Dios mainstem and CMD-32 for the Rio Inambari with total depth of ~4.5 m) during the wet season, and two depth profiles were compared between wet and dry seasons on the mainstem in the lowlands: CMD-29 (10.2 m) and MMD-28 (6.2 m) at CICRA-Los Amigos, and CMD-35 (12.5 m) and MMD-32 (11.5 m) at Puerto Maldonado. For comparison, DOM was also characterized at 0 and ~10 m in both seasons at Puerto Maldonado.

Consistent with Bouchez et al. [2011], as velocity decreased with increasing depths in the river, sediment load and grain size generally increased (Figures 5a and 5b). The exceptions were sites CMD-12 and (to a lesser extent) MMD-32, where sediment characteristics remained relatively constant, most likely associated with the relatively shallow depth (for CMD-12) or fine grain size across the entire water column (for MMD-32) inhibiting hydrodynamic sorting. For the other sites, as grain size increased, both SSA and POC content generally decreased with depth (Figures 5c and 5d). The exception was for the mainstem at Puerto Maldonado, where

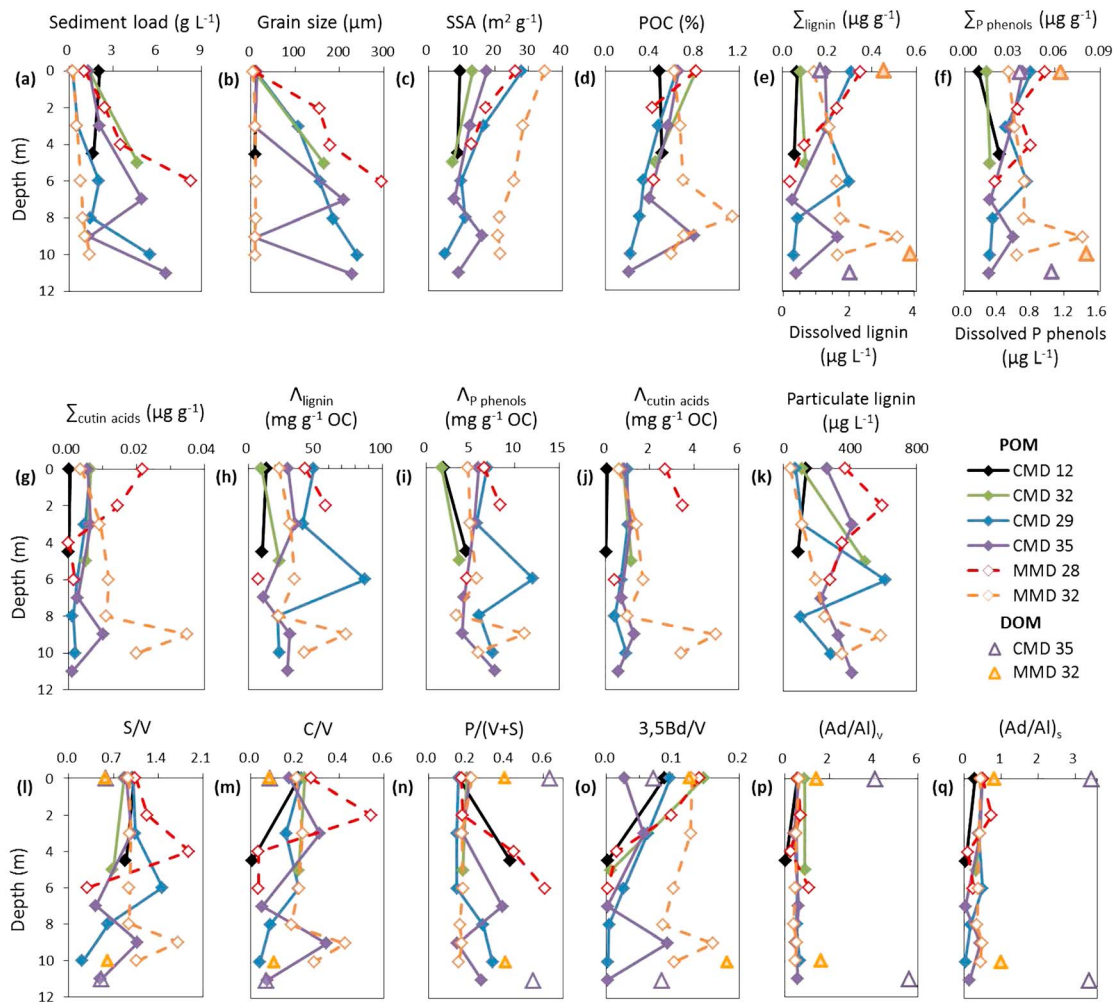


Figure 5. Bulk properties, concentrations, and parameters of biomarkers in the particulate organic matter (POM) and dissolved organic matter (DOM) in the depth profiles of Madre de Dios River: (a) sediment load, (b) modal grain size, (c) specific surface area (SSA), (d) particulate organic carbon (POC) content, concentration (Σ) and POC-normalized concentration (Λ) of (e and h) lignin, (f and i) *p*-hydroxyl (P) phenols, and (g and j) cutin acids, (k) particulate lignin concentration (in $\mu\text{g L}^{-1}$), (l) ratios of S/V, (m) C/V, (n) P/V + S, (o) 3,5 Bd/V, (p) (Ad/Al)_v, and (q) (Ad/Al)_s. Abbreviations are the same as in Figure 3.

the second or third deepest sample showed a lower sediment load, a smaller grain size, and a higher SSA in the wet season (CMD-35-9 m) and a higher POC content in both seasons (CMD-35-9 m and MMD-32-8 m). These data are consistent with observations during sample collection of a greater concentration of visible woody fragments in silty sediments at these penultimate depths, with the very deepest samples carrying more sand-sized sediments not containing visible woody material.

Biomarkers were well mixed with similar Σ values in the high-elevation profiles (Figures 5e–5g), whereas in the mainstem at Puerto Maldonado (CMD-35 and MMD-32) high Σ_{lignin} values was associated with the high POC content. By comparison, Λ values were relatively stable in the depth profile at this site in the wet season but remained elevated at 9 m in the dry season (Figures 5h–5j). The Λ values of lignin and P phenols were also particularly high in the POM at 6 m in CMD 29. Coupled with sediment load data (Figure 5a), it appears that particulate lignin shows a higher concentration (per liter of water; Figure 5k) as a “woody current” at depth in the Madre de Dios River, with buoyancy above that of the coarse mineral grain layer that is transported at greatest depth in the river.

The composition of biomarkers also varied in the POM with depth (Figures 5l–5q). For depths with the highest Σ_{lignin} values in the profiles (6 m in CMD-29; 9 m in CMD-35 and MMD-32), particulate lignin was characterized by elevated (Ad/Al)_v, S/V, and C/V ratios. The 3,5 Bd/V ratio was also highest at 9 m in the CMD-35 and MMD-32 profiles. As these ratios all exhibited higher values in the O horizons than

surface mineral soils in the catchment (section 3.1) and ratios of S/V and C/V decrease with lignin degradation [Hedges et al., 1988; Opsahl and Benner, 1995; Otto and Simpson, 2006], the deep POM woody current seems to carry more fresh input from surface soil layers.

Dissolved lignin and P phenols also had higher Σ values in the deep water (2.02–3.88 and 1.06–1.47 $\mu\text{g L}^{-1}$, respectively) relative to surface water (1.13–3.06 and 0.68–1.16 $\mu\text{g L}^{-1}$, respectively) in the mainstem at Puerto Maldonado in both seasons (Figures 5e and 5f). Ratios of S/V and C/V did not vary much between surface and deep DOM (Figures 5l and 5m). However, the 3,5Bd/V ratio increased at depths in both seasons, while the P/(V+S) ratio decreased and the (Ad/Al)_v ratio increased in the deep DOM in the wet season (Figures 5n–5q). Similar to POM, this may indicate that DOM at depth derives from fresh inputs from surface soils.

Altogether, lignin characteristics in the Madre de Dios River depth profiles suggest that there appear to be “undercurrents” for the delivery of relatively fresh terrestrial OC at depth in deep, white water rivers, potentially forming efficient conveyors for terrestrial OC components such as lignin. We speculate that such currents form because water-logged wood sinks to depths in the river while remaining above the densest layers of coarse-grained sediment at the bottom sampling depths. It remains to be investigated how much such deep currents may contribute to the overall flux of lignin in the entire Amazon River system. For example, such phenomenon may be prevailing in the Amazon mainstem with much deeper (up to 100 m near Óbidos) water, whereas deep transport may be less important in “blackwater” tributaries. Nonetheless, our findings indicate the need to examine lignin transport in the deep water of stratified rivers to determine if such woody undercurrents are a widespread transport mechanism.

3.2.4. Comparison of Phenol Composition in DOM and POM

The connection between dissolved and particulate components in rivers and the oceans has been a long-standing research question [Raymond and Bauer, 2001; Guo et al., 2007]. In the Madre de Dios River, phenol composition was not correlated between DOM and POM in the surface and deep waters (except the C/V ratio; Figure S4), suggesting a decoupling of the two components. Furthermore, phenol composition exhibits varied downstream evolution in POM and DOM, with patterns that appear to be regulated by different processes. While POM is strongly influenced by fresh inputs in the wet season associated with more erosive power [Lowman and Barros, 2014], DOM composition is mainly governed by degradation processes, especially in the dry season when in situ respiration rates are generally higher [Benner et al., 1995; Ward et al., 2013]. This implies that fresh input may not be as important for dissolved lignin as for particulate lignin in the Madre de Dios River, and there may be several causes for this.

First, leaching of fresh dissolved lignin from soils and litter contributes a much smaller flux to rivers relative to particulate lignin as most dissolved lignin has been decomposed, reworked, or sorbed onto minerals in forest litter and mineral soils [Kaiser et al., 2001, 2004; Schwendenmann and Veldkamp, 2005]. Second, the fast turnover of fresh dissolved lignin [Ward et al., 2013] may prevent the detection of “fresh” signature in riverine DOM, leaving most lignin in its oxidized state in the aqueous phase. This explanation agrees with the observation that dissolved lignin exhibits an overall higher oxidation state than particulate lignin in the Madre de Dios and Amazon Rivers (see section 3.2.2). Third, in situ dissolution of fresh particulate lignin probably contributes differentially to the overall budget of dissolved lignin in the Amazon River, given the varied seasonal dynamics of particulate and dissolved lignin phenols. As the ratio of particulate:dissolved lignin is much higher in the wet season (~80–265) than the dry season (<90), dissolution of even a tiny fraction of fresh POM in the wet season may alter the composition of dissolved lignin and obscure the potential trend of downstream oxidation in materials deriving from the headwaters. We postulate that dissolution of POM is a more important source of dissolved phenols in the wet season, whereas leaching from soils and litter constitutes the key source in the dry season. In line with this hypothesis, Σ_{lignin} and $\Sigma_{\text{P phenols}}$ are positively correlated between DOM and POM in the wet season ($r^2 = 0.96$, $p < 0.05$) but not in the dry season (Figure S4a). However, none of the phenol ratios are correlated between DOM and POM in either season. Hence, it seems that POM dissolution affects various monomers differently, likely due to varied solubility and/or sorption capacity [Hernes et al., 2007]. Similarly, Ward et al. [2012] observed different temporal trends in dissolved and particulate lignin compositions during rapid runoff events in temperate rivers, likely as a result of solubility differences.

3.2.5. SSA Controls on OC and Biomarker Distribution in River POM

OC content and biomarker distributions are known to vary with grain size and SSA in riverine and marine particles [Mayer, 1994; Bergamaschi et al., 1997; Gordon and Goñi, 2003; Galy et al., 2008]. In the Madre de Dios River, grain

size is not consistently correlated with POC content or biomarker concentrations from all river depths except for a negative correlation with the POC content along the depth samples of CMD-29 and CMD-35 ($p < 0.05$). SSA is positively correlated with POC content ($r^2 = 0.55$, $p < 0.05$; Figure S5a) and Λ_{lignin} in the wet season ($r^2 = 0.53$, $p < 0.05$; Figure S5b) with one outlier with a particularly high Λ_{lignin} value associated with the “deep woody current” (CMD-29-6 m). These correlations suggest that mineral-associated OC and lignin are important in the wet season, likely mobilized from mineral soils and river banks by increased precipitation, runoff, river discharge, and landslides [Clark *et al.*, 2013, 2015]. By contrast, neither POC content nor Λ_{lignin} correlates with SSA in the dry season (Figures S5a and S5b). This indicates that sources of dry-season POM differ and may consist of more colloidal and/or detrital organics whose distribution is not related to SSA. This explanation is consistent with the higher POC content, Λ values of all biomarkers, and ratios of S/V and C/V in the dry-season POM relative to wet-season samples (especially from high elevation, erosive terrains), indicating higher contribution of O-horizon materials to riverine particles in the dry season.

$\Lambda_{\text{P phenols}}$ is not regulated by SSA in either season when comparing different depths (Figure S5c) but increases with SSA in the wet season in the surface water ($r^2 = 0.75$, $p < 0.05$; Figure S5d), suggesting that mineral-associated soil particles are a dominant source of particulate P phenols in the surface but not in deeper waters. In situ production of P phenols from microbial synthesis and/or lignin demethylation [Dittmar and Lara, 2001] may be a more important source for these compounds at river depth. Unlike lignin and P phenols, $\Lambda_{\text{cutin acids}}$ is not regulated by SSA in either season at any depth (Figures S5e and S5f). As cutin acids exhibit much higher abundances (i.e., Σ values) in the O horizons, it is reasonable to propose that detrital OM from soil surface layers dominates cutin input into the river. Hence, while cutin acids may be sorbed to minerals in the mineral soils (section 3.1), they are dominated by “free” moieties from organic layers that are not associated with mineral surfaces in the riverine POM.

3.3. Lignin Tracers of Terrestrial OC Burial in the Amazon Offshore Sediments

Surface sediments in the Amazon fan and sites further “down plume” had OC contents of 0.45–0.97% and much lower biomarker concentrations compared with soils and river POM (Table 2). P phenols displayed a higher concentration (1.1–7.4 $\mu\text{g g}^{-1}$ or 0.2–1.2 mg g^{-1} OC) compared to lignin phenols (0.3–2.0 $\mu\text{g g}^{-1}$ or 0.1–0.3 mg g^{-1} OC), reflecting planktonic addition in the ocean [Hedges and Mann, 1979; Goñi and Hedges, 1995]. Cutin acids were present at very low concentrations (0.02–0.1 $\mu\text{g g}^{-1}$ or 0.002–0.02 mg g^{-1} OC). In terms of tracing terrestrial OC contributions to ocean sediments, we found that Λ_{lignin} had the highest values at Stations 5 and 6 near the core of the plume (Figure 1a), revealing the potential for lignin to track variations in the plume via sediment core sampling. By comparison, cutin acids showed similar or higher concentrations in the more distal sediments. We hypothesize that the majority of cutin acids (not associated with minerals; section 3.2.5) in the river are labile and degraded during transport to the ocean. By comparison, mineral-associated cutin acids derived from soils, while in lower abundances within the river, persist longer and are transported to more distal sediments in similar concentrations [Keil *et al.*, 1998; Gordon and Goñi, 2003]. The S/V and C/V ratios were 0.4–1.0 and 0.01–0.3, respectively, similar to those of river POM samples. Ratios of P/(V + S) and 3,5 Bd/V (1.5–12.3 and 0.004–2.4, respectively) were higher than those of soils or riverine samples, again reflecting planktonic contribution of P phenols and 3,5 Bd in marine environments. The Ad/Al ratios were 0.04–1.3 and 0.03–0.8 for V and S phenols, respectively. These values were slightly lower than those of mineral soils and similar to those of river POM.

3.4. Source to Sink Comparison of Biomarker Composition in the Madre de Dios and Amazon System

In order to evaluate the Madre de Dios data in a broader context, we compiled published lignin data from the Amazon River system [Ertel *et al.*, 1986; Hedges *et al.*, 1986, 2000; Farella *et al.*, 2001; Kastner and Goñi, 2003; Bernardes *et al.*, 2004; Aufdenkampe *et al.*, 2007; Ward *et al.*, 2013, 2015; Sobrinho *et al.*, 2015]. As noted previously, FPOM (>0.1 or $0.45 \mu\text{m}$ and $< 63 \mu\text{m}$) and CPOM ($>63 \mu\text{m}$) in the Amazon River system have distinct lignin content (Figure 6a), with higher Λ_{lignin} values in the CPOM. It is interesting to note that the OC and lignin phenol contents of Peruvian Andes forest O horizons are close to those of CPOM in lower Amazon and Andean headwaters, whereas the mineral soils resemble FPOM. This result is consistent with previous observations that CPOM chemically resembles sparingly degraded leaf fragments [Hedges *et al.*, 1994], while FPOM appears to be associated with mineral grains [Keil *et al.*, 1997]. It also suggests that CPOM and FPOM may have different sources from land, mainly originating from organic layers and mineral soils, respectively, hence

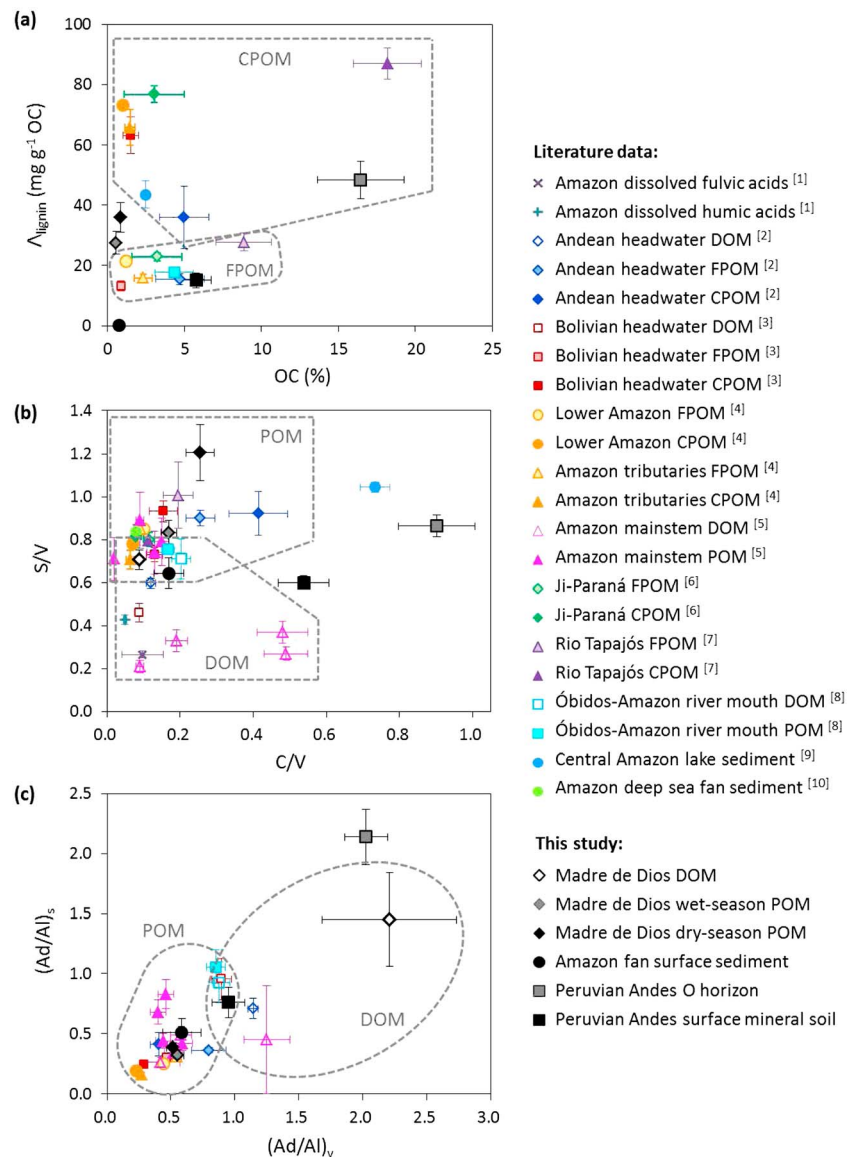


Figure 6. Comparison of organic carbon (OC)-normalized concentration and composition of lignin phenols along the soil-river-ocean continuum in the Amazon River system: (a) lignin concentration versus OC content, (b) S/V versus C/V ratios, and (c) (Ad/Al)_s versus (Ad/Al)_v ratios. Error bars represent standard error of mean values (n = 4 – 20). Refer to the legend of Figure 3 for the abbreviation of parameters. DOM, dissolved organic matter; POM, particulate organic matter; FPOM, fine POM (<63 μm); and CPOM, coarse POM (>63 μm). References are as follows: (1) Ertel et al. [1986]; (2) Aufdenkampe et al. [2007]; (3) Hedges et al. [2000]; (4) Hedges et al. [1986]; (5) Ward et al. [2013]; (6) Bernardes et al. [2004]; (7) Farella et al. [2001]; (8) Ward et al. [2015]; (9) Sobrinho et al. [2015]; and (10) Kastner and Goñi [2003].

exhibiting varied fate and seasonal dynamics with changing hydrological conditions in the Amazon River [Hedges et al., 2000; Aufdenkampe et al., 2007].

The Δ_{lignin} values of bulk POM (>0.2 μm) in the Madre de Dios River lie between those of FPOM and CPOM in the Amazon system and fall within the range reported for CPOM in other Andean headwater rivers, despite lower POC contents (Figure 6a). The OC content decreases in the sequence of O horizon > mineral soil > river POM or marine sediment, while lignin phenols show similar ranges of Δ values in soils (O and mineral horizons) and riverine POM. Δ_{lignin} sharply decreases in the Amazon offshore sediments in our study, suggesting efficient removal and replacement of lignin from sedimentary particles by OC from other sources (such as marine microorganisms), similar to other river-ocean systems [Hedges et al., 1997; Abril et al., 2002; Tesi et al., 2014]. Yet it should also be noted that the Amazon deep sea fan channel-levee deposits show similar Δ_{lignin} values (~30 mg g⁻¹ OC)

when compared to riverine POM [Kastner and Goñi, 2003]. The difference between the deep sea fan sediments measured in this study and the channel-levee deposits emphasizes that the fate of lignin in marine deposits depends on the depositional environment [cf. Blair and Aller, 2012].

Comparison of lignin source and degradation indicators along the soil-river-ocean continuum also reveals several interesting patterns (Figure 6b). The S/V and C/V ratios of POM in the Madre de Dios River fall within the range reported for Amazonian samples previously. DOM from the Madre de Dios shows S/V ratios that are similar to DOM from close to the Amazon River mouth and slightly higher than those in other Amazonian DOM. While the S/V ratio generally exhibits lower values in riverine DOM relative to POM presumably due to degradation or dissolution processes in the dissolved phase [Hernes and Benner, 2002; Hernes et al., 2007], it shows largely overlapping values from soils to riverine and ocean particles. This implies that the S/V ratio in the particulate phase is relatively conservative proxy of lignin source during the land-ocean transfer. By contrast, there is a large offset in the C/V ratios between Peruvian Andes soils and riverine or marine samples in that the C/V ratio decreased significantly in the order of O horizon > mineral soils > riverine POM or DOM, reflecting preferential degradation of C phenols in the soil and during transit from soils to rivers [Hedges et al., 1985; Requejo et al., 1991; Feng et al., 2011; Seki et al., 2014]. Upon entry into the aquatic environment, C phenols seem to be stabilized relative to V phenols as reflected by the relatively narrow range of C/V ratios.

Compared with S/V and C/V ratios, the Ad/Al ratios are grouped into two clusters, with DOM showing higher values than POM in all Amazonian samples (Figure 6c). This DOM-POM distinction is consistent with previous explanations that DOM consists of the most degraded lignin components in the river system. Higher Ad/Al ratios in the DOM may also result from higher solubility of acidic phenols in water [Houel et al., 2006; Hernes et al., 2007]. DOM in the Madre de Dios River displays particularly high Ad/Al ratios compared to those of other headwater DOM, possibly associated with contribution from O horizons of the Peruvian Andean forests which exhibit similarly high Ad/Al ratios. The Madre de Dios catchment also accommodates a number of tropical peatlands in former river meanders [Householder et al., 2012]. Peat is considered to be an important contributor to riverine DOM in other river systems, and peat leachates show elevated Ad/Al values [cf., Amon et al., 2012]. Currently, it is unknown if peats contribute significantly to DOM and dissolved lignin in the Madre de Dios River. By comparison, POM shows relatively similar Ad/Al ratios in all Amazonian tributaries. POM from close to the Amazon River mouth shows the highest Ad/Al values that are similar to those of DOM from the same location, suggesting elevated degradation of particulate lignin in the lower Amazon [Ward et al., 2015]. Overall, there is a progressive decline of Ad/Al ratios in the order of O horizon > mineral soils > riverine POM. This is distinct from increasing or similar ranges of Ad/Al ratios from soils to sediments observed elsewhere [Seki et al., 2014; Tesi et al., 2014; Winterfeld et al., 2015], again highlighting the unique lignin characteristics in the Madre de Dios system, because lignin is highly oxidized in the surface soils in this setting.

It is notable that surface sediments deposited far offshore from the Amazon River mouth exhibit similar Ad/Al ratios to Amazon River POM, indicating that the oxidation stage of lignin is not significantly altered in the particulate phase in the Amazon river-delta system. In other words, lignin has already been transformed within the river before export into the ocean. This result is in line with recent findings that lignin is quickly transformed or degraded in the Amazon River [Ward et al., 2013] and that the majority of bioavailable lignin has been consumed prior to delivery to the plume [Medeiros et al., 2015; Seidel et al., 2015]. Alternatively, hydrodynamic sorting may play a key part in shifting the Ad/Al values of lignin in the ocean [Keil et al., 1998; Wakeham et al., 2009] as lignin associated with fine and heavy particles tends to exhibit a higher degree of oxidation [Hedges et al., 1986, 2000; Aufdenkampe et al., 2007]. Coarse particles containing lignin with low Ad/Al ratios have been observed to deposit preferentially in nearshore or inner shelf sediments emanating from the Columbia [Keil et al., 1998; Coppola et al., 2007], Lena and Kolyma [Tesi et al., 2016], and Mississippi and Atchafalaya Rivers [Gordon and Goñi, 2003; Bianchi et al., 2007], while fine particles with degraded lignin are transported offshore. Similar hydrodynamic processes may concentrate relatively fresh lignin in the Amazon River plume and hence lead to a constant Ad/Al ratio across the river-ocean interface.

4. Conclusions and Perspectives

To investigate lignin evolution along the soil-river-ocean continuum, we examined seasonal, depth, and downstream variation of lignin in the POM and DOM of the Madre de Dios River as related to lignin source characteristics in the watershed soils and final sequestered signals in distal marine sediments. A notable

characteristic of lignin geochemistry in the Peruvian Andes forests is highly oxidized lignin in the O horizons as indicated by Ad/AI ratios that are higher than mineral soils or riverine POM. This novel observation may be related to the high activity of phenol oxidase associated with fungal dominance in these organic layers and/or high concentrations of polyphenols in leaf litter and root litter in TMCF with high Ad/AI signatures. As Andean TMCF covers an extensive area (215,000 km²) [Bruijnzeel *et al.*, 2011], the production and fate of lignin in the TMCF warrant further research. Inputs of highly oxidized lignin from surface O horizons likely influence the Ad/AI ratios of lignin in rivers and should be taken into account for the interpretation of lignin data in the Amazon River system.

The concentration (Λ_{lignin}) of lignin phenols increased downstream in both POM and DOM of Madre de Dios River, suggesting a downstream accumulation of lignin or land-derived OC. In contrast to previous studies, we observed increasing S/V and C/V ratios and a decreasing P/(V + S) ratio in the surface POM of this Amazonian headwater with decreasing elevation in the wet season, implying shifting lignin composition from a degradation-dominated signal in the erosive Andean terrains to fresher inputs in the lowland Amazon. It also appears that mineral-associated POM mobilized from mineral soils and river banks is more important in the wet season, whereas detrital OC from soil surfaces constitutes a higher contribution to POM in the dry season. Unlike particulate lignin that receives more fresh inputs downstream, dissolved lignin is increasingly oxidized as indicated by decreasing S/V and increasing P/(V + S) and Ad/AI ratios downriver in the dry season. This pattern was not observed in the wet season likely because POM constitutes an important source of relatively fresh dissolved lignin in the wet season via dissolution processes.

In river depth profiles, it appears that fresh terrestrial OC is more concentrated in the POM and DOM at depths in the mainstem of Madre de Dios River, with elevated POC and Λ_{lignin} values observed in the deep water (at the lower 60–80% of total depth) in both seasons and lignin composition that exhibits a fresh signal relative to surface waters. For deep rivers, undercurrents may represent important pathways for the delivery of relatively fresh terrestrial OC, specifically the woody fraction, in stratified white water rivers. It remains to be investigated how much such deep current may contribute to the overall flux of lignin in the entire Amazon River, considering the lower velocity and hence smaller water fluxes at depths and that blackwater tributaries within the Amazon River system may behave differently.

Comparison of lignin composition in the Madre de Dios with published data from across the Amazon basin reveals that, as the OC content decreases in the sequence of O horizon > mineral soil > river POM > marine sediment, lignin phenols show similar ranges of OC-normalized concentrations (i.e., Λ values) in soils and riverine POM before they sharply decrease in the Atlantic Ocean offshore sediments. Moreover, the OC content and lignin phenol composition of CPOM in the Amazon mainstem and tributaries are similar to those of Peruvian TMCF O horizons, whereas FPOM resembles mineral soils, suggesting varied terrestrial sources and transport pathways. Given land cover changes associated with road construction, mining, and agriculture in the Amazon basin [Asner *et al.*, 2013], river POM may archive basin-integrated ecological or hydrological changes on longer timescales.

Our study of the source to sink evolution of lignin highlights the importance of seasonal and depth variation of river OC components and their connection to different soil carbon pools in the Madre de Dios. The upper part of the Madre de Dios River may be similar to the steep erosional settings such as the Himalayan headwaters of the Ganges-Brahmaputra River system and other small mountainous rivers globally. In such montane fluvial systems, lignin composition may be dominated by soil sources. In the lower reaches, with flatter relief, lignin of fluvial suspended loads receives new input from floodplain soils and is subject to slowed transit with more time for degradation. The Madre de Dios elevation profile offers insights into fluvial carbon dynamics across headwater to floodplain transitions in one sector of the Amazon basin and helps to constrain the sourcing, fate, and fluxes of lignin components within large fluvial catchments.

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