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Terrestrial Organic Matter Inputs to Nearshore Marine Sediment Under Prolonged Drought Followed by Significant Rainfall as Indicated by Lignin

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Abstract

Terrestrial organic matter (TOM) exported to nearshore marine regions may be altered by drought or large amounts of precipitation. We examined how significant precipitation in southern California during the winter seasons of 2015 and 2016, following a prolonged drought from 2011 to 2015, impacted the quantity and quality of TOM transported to nearshore kelp forests of the Santa Barbara Channel. Based on organic matter content, lignin oxidation by-products, and carbon isotopic signatures, biomarkers of TOM were detected in stream, estuarine, and marine sediments. Quantitative measures of lignin differentiated between the three environments. Qualitative lignin signatures revealed temporal patterns that appeared in stream, estuarine, and marine sediment. These patterns indicated that TOM delivered into nearshore coastal regions from mountain watersheds was less degraded over time and its source material changed through time. Our findings suggest lignin oxidation compounds can be used as biomarkers of TOM transported during storm events from coastal watersheds into nearshore marine sediment.

KEY WORDS Lignin · Marine Sediment · Terrestrial Organic Matter · Storm · Degradation · Santa Barbara Channel

Introduction

The land-ocean boundary is a biogeochemically active region where terrestrial organic matter (TOM) is transported from upland areas to nearshore marine environments (Billen et al. 1991). This TOM may be remineralized and provide a nutrient source to primary producers in coastal ecosystems (Opsahl and Benner 1997), such as kelp forests, or be buried in marine sediments (Burdige 2005). TOM transport into nearshore marine areas is a function of landscape and climate (Onstad et al. 2000). Increased agricultural and urban development may alter both the quantities and sources of TOM while storms and extended droughts may alter sources and export of TOM to the ocean (Godin et al. 2017; Masson-Delmotte et al. 2018).

To trace the transport and processing of TOM in coastal environments, lignin can be used as a biomarker to provide a fingerprint of TOM source material. Lignin is composed of structural polymers found in vascular plants and is resistant to degradation relative to other organic compounds (Hedges and Mann 1979a). Degradation of lignin by chemical and physical processes and microbial remineralization depends on environmental conditions such as oxygen and light availability (Opsahl and Benner 1995; Thevenot et al. 2010). Lignin oxidation compounds that result from cupric oxide (CuO) oxidation (Hedges and Mann 1979a; Louchouarn et al. 2000; Moingt et al. 2016) are indicative of source materials and biogeochemical and physical processes (Hedges and Ertel 1982; Hernes et al. 2007; Moingt et al. 2016). Using only stable isotopes, it may be difficult to distinguish between terrestrial materials and marine organic matter (MOM) (Hedges et al. 1997), and one can overestimate the relative amount of MOM (Burdige 2005). Lignin provides a parameter that can be combined with isotopic analyses to improve source identification. However, care should be taken in interpreting results since lignin analyses do not provide a measure of absolute TOM content (Louchouarn et al. 2010; Moingt et al. 2016).

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Lignin has been used as a measure of TOM present in marine environments and as an integrated record of land use change in a downstream water body (Prahl et al. 1994; Opsahl and Benner 1995); both approaches suggest its possible use as a tracer of storm events in a coastal environment. TOM has been identified using lignin in salt marshes (Chen and Torres 2018), mangrove forests (Dittmar and Lara 2001), benthic marine sediments (Hedges and Parker 1976; Hedges and Mann 1979b; Prahl et al. 1994; Tesi et al. 2008), and river systems emptying into marine environments (Goñi et al. 1998; Sun et al. 2017). Lignin is also used as a tracer for land use change, with the downstream water body being a recipient of sediment in runoff and, therefore, a record of human activity such as agriculture (Onstad et al. 2000; Dalzell et al. 2007; Bélanger et al. 2015, 2017), pulp industry (Louchouarn et al. 1999), and logging and mining (Moingt et al. 2014). However, lignin is seldom used in studies with varied ecosystems in the context of multiple storm events, which is our focus in this study.

The purpose of this study was to investigate how storm events influence the quantity and quality, specifically the level of degradation and source material, of TOM transported into coastal regions. We examined how distance from stream mouths and sampling date, following successive winter storms, might impact TOM measured in marine sediments. Our study area in the Santa Ynez Mountain watersheds and nearshore regions of the Santa Barbara Channel in southern California is ideal to address this question due to droughts, episodic rainfall, and wildfires that cause considerable variability in local runoff and solute and particulate export (Aguilera and Melack 2018a). Multiple wildfires occurred in the region during the decade preceding this study, and wildfires can lead to an increased export of suspended sediments (Coombs and Melack 2013; Murphy et al. 2015; Aguilera and Melack 2018b). Fires were spread throughout the sampling region, so our analysis focuses instead on the storms and the preceding drought as controlling factors in organic material condition and transport. In Santa Ynez Mountain watersheds, 50% of annual suspended sediment may be discharged in 0.5–2 days of storm events, suggesting that half of the sediment that reaches the ocean from the land each year may happen in a single storm (Warrick et al. 2015). The short, intermittent streams and episodic storm events produce pulsed inputs of TOM to the Santa Barbara Channel (Blair and Aller 2012).

Due to the large rainfall predicted during the 2015–2016 El Niño Seasonal Oscillation, we hypothesized that sediment collected following the storms would contain greater and fresher lignin content than that collected before the storms. We also hypothesized that following these storms, marine sediments located closest to stream mouths would receive higher TOM loading than sites further from streams. The episodic nature of runoff events makes this region well suited for a study using lignin as a tracer of the effects of meteorological variability on loading of particulate organic matter from the landscape.

Methods

Site Description

Nine stream sites in Santa Ynez Mountain watersheds, two estuarine sites in Santa Barbara County, California, and eight kelp forest sites located offshore in the Santa Barbara Channel (SBC) were sampled (Fig. 1). The watersheds range from 7 to 50 km^2, and maximum watershed elevation is approximately 1000 meters above sea level (Aguilera and Melack 2018a, 2018b). Five marine sites were located immediately downstream of a stream or estuarine site while three others were located near a kelp forest but at least 1 km from the nearest stream mouth. The distance from sampling site to shore ranged from approximately 300 to 2200 m; Goleta Bay (GOLB) and Mission Creek (MICR) were sampled 1.5–2.2 km from shore due to their bathymetric gradient (see sampling locations along the 20 m isobath in Fig. 1). All sites are part of the Santa Barbara Coastal Long Term Ecological Research (SBC LTER) program, which has collected long-term, monthly datasets at these locations for dissolved and particulate constituents (Melack 2019; Washburn et al. 2019).

The region experiences a Mediterranean climate, with cool winters and warm, dry summers (Aguilera and Melack 2018b). Oceanographic conditions consist of three periods: seasonal upwelling of cold, nutrient-rich water in spring (April–June), warm, stratified water in summer and fall (July–November), and episodic runoff from streams during winter storms (December–March) (Brzezinski et al. 2013). A nearshore current (~ 15 m water depth) along the mainland typically flows poleward (westward) with speeds up to 0.1 m s^{-1} with stronger currents in summer (Harms and Winant 1998; Fewings et al. 2015). Average nearshore cross-shelf currents along the benthos typically range from 0.01 to 0.02 m s^{-1} with flow offshore (southward). In water depths of 15 m or less, seawater residence time is approximately 2 days (Fewings et al. 2015). During fair-weather, summer conditions, the wave base, or the water depth to which marine sediment is disturbed due to waves, is up to 20 m. In contrast, marine sediment may be disturbed and resuspended in up to 70 m water depth during stormy, winter conditions (Sommerfield et al. 2009). Along the mainland, sand is transported each winter from beaches and nearshore areas into offshore regions and is returned the next summer (Revell et al. 2011).

Sampling Design

Sampling was designed to encompass the period immediately before and during El Niño Seasonal Oscillation (ENSO) conditions in southern California, from December 2015 to June 2017. Suspended sediment was collected at stream sites and sediment cores were collected at estuarine and marine

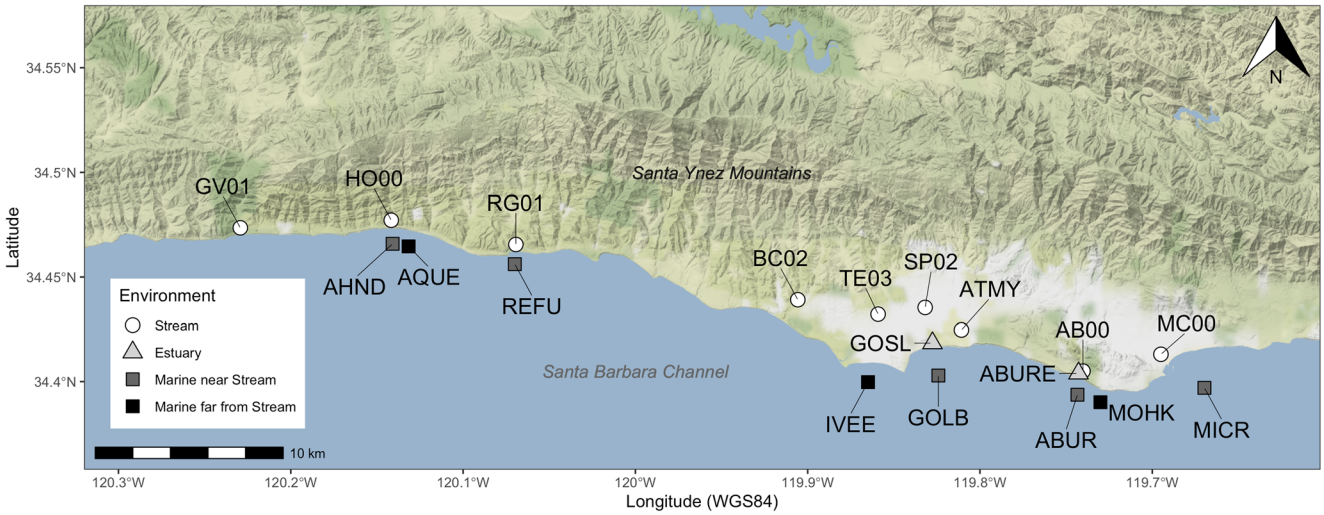

Fig. 1 Locations sampled along the Santa Barbara coast from 2015 to 2017 (See Table A1 for full site names). All locations are regularly monitored sites of the SBC LTER. Marine locations are marked along the 20 m isobath. Image data from the *ggmap* package (Kahle and Wickham 2013)

sites to measure TOM exported during winter storms and deposited via runoff in estuarine and marine environments. Suspended particulate matter was collected at nine streams during winter storms; water samples were transported back to the laboratory and filtered prior to additional analyses. Samples were not collected from streams during dry season periods because they lacked appreciable discharge. At estuarine sites, four replicate sediment cores (5 cm diameter × 20 cm long) were collected using hand corers from the shallow subtidal channels near the inlets. At kelp forest sites, four replicate sediment cores (5 cm diameter × 20 cm long) at two water depths (10 m and 20 m) were collected by SCUBA divers using hand corers. Estuarine and marine cores were split into shallow (0–10 cm) and deep (10–20 cm) subsamples. Sediment core horizons were chosen due to energetic benthic conditions. Samples were transported back to the laboratory and frozen (− 20 °C) prior to analysis.

Sample Processing

All samples were analyzed for OM content, carbon and nitrogen content, carbon and nitrogen stable isotopes, and lignin content. Estuarine and reef samples were also analyzed for grain size; there was insufficient material to do grain size determination on stream samples. OM content was determined by weighing 2 g of thawed sediment, drying at 60 °C for 48 h, combusting at 450 °C for 4 h, and re-weighing the sample. Grain size was determined using 20 g of dried sediment, treating the sample with 5% sodium hexametaphosphate for 24 h (Poppe et al. 2000), and analyzing using a Cilas laser diffraction particle size analyzer. For carbon and nitrogen content as well as isotopic signatures, samples were thawed, and shell and other coarse material removed. Sediment was then dried at 60 °C for 48 h, ground using mortar and pestle, weighed into silver capsules, acidified with 6% sulfurous acid to remove carbonates, and re-dried. Samples were analyzed using a Thermo Finnigan Delta-Plus Advantage isotope mass spectrometer coupled with a Costech EAS elemental analyzer housed at the University of California Santa Barbara (UCSB) Marine Science Institute Analytical Laboratory. Instrument precision for both C and N was ± 0.2‰, determined by replicate analyses of NBS 1572 standard. Isotope values are presented per mil in standard δ notation relative to the Pee Dee Belemnite standard for carbon and atmospheric N_2 for nitrogen. All samples were analyzed for lignin content using a modified version of the alkaline CuO oxidation method described by Goñi and Montgomery (2000) using a Varian 3800/Saturn 2000^{TM} coupled gas chromatograph – mass spectrometer fitted with a fused capillary column (DB-1 from J&W, 60 m, 320 μm) housed at GEOTOP, Université du Québec à Montréal (Moingt et al. 2016).

Lignin analyses were performed to evaluate TOM source material in sediments and the degree to which this material had undergone diagenetic processing. Our results for the standard reference material (SAG 05) were consistent with previously published values (Louchouarn et al. 2000; Moingt et al. 2016; Table A2). Several metrics of lignin amount and provenance were calculated. Sigma 8 is a measure of eight total lignin oxidation products indicating total lignin amount per sample, while Lambda is a measure of the same oxidation products but normalized to organic carbon (OC) content, as an indicator of the proportion of allochthonous to autochthonous OM in aquatic environments (Hedges and Parker 1976). The ratio of cinnamyl to vanillyl phenols (C/V) is used as a measure of the relative contribution of non-woody source materials (Hedges and Mann 1979a) and decreases with biodegradation (Opsahl and Benner 1995; Dittmar and Lara 2001).

The ratio of syringyl to vanillyl phenols (S/V) is used as a measure of the relative contribution of woody angiosperm material (Hedges and Mann 1979a). S/V decreases or remains unchanged due to degradation processes and increases due to physical sorption and leaching processes in aquatic environments (Opsahl and Benner 1995; Hernes et al. 2007). The ratio of *p*-hydroxyl phenols to vanillyl and syringyl phenols (P/(V+S)) is used as a measure of the relative contribution of woody versus non-woody materials (Moingt et al. 2016). P/(V+S) and 3,5-dihydroxybenzoic acid to vanillyl phenols (3,5-Bd/V) are also used as measures of degradation (Hedges and Ertel 1982; Louchouarn et al. 1999; Dittmar and Lara 2001). Lignin has been detected in seagrasses (Klap et al. 2000) and red algae (Martone et al. 2009), but their lignin content is low. We ensured sampling did not occur in areas with these taxa in abundance so as not to confound results.

We examined indicators of overall lignin content (Sigma 8, Lambda) and signatures of source materials and degradation processes (S/V, C/V, P/(V+S), 3,5-Bd/V) to identify spatial and temporal trends. While the extraction efficiency of the cupric oxidation method remains fairly constant, the lignin fraction of a given sample may vary based on the characteristics of the TOM of the sample, so calculating precise loadings of TOM is not advised. However, if lignin content of samples collected from the same location increases through time, one can attribute that to increased TOM input (Louchouarn et al. 1999; Moingt et al. 2016; Bélanger et al. 2017).

Data Analyses

Data organization and analyses were performed using Excel (v 16.24) and R Statistical Software (v 4.0.2). Data formatting and visualization were performed using the *tidyr* and *ggplot2* packages in RStudio (v 1.3.1073) (Wickham 2016, 2018). Linear mixed effects models were used to account for the nested sampling design and to address the lack of independence between certain samples (Millar and Anderson 2004; Chaves 2010). Prior to model construction, seven outliers, from a total of 456 samples, in the lignin dataset were removed; six outliers were removed due to values that were six or greater standard deviations above the dataset mean for a given signature (e.g., S/V), and a seventh value was removed due to contamination concerns. All statistical analyses used an alpha (α) value of 0.05 unless otherwise noted. The lme function within the *nlme* package was used to create and validate each model (Pinheiro et al. 2019). Model creation began with fixed effects and random effects using a random intercept structure. Then, model selection followed the protocol outlined by Zuur et al. (2009, Chapter 5), beginning with a linear model, accounting for variance structure, optimizing the fixed structure, and validating best model fit using distribution of residuals and AIC values. If necessary, data were log-transformed. If fixed effects were found to have a significant effect on lignin values, post hoc tests (Tukey's HSD) were run using the glht function of the *multcomp* package (Hothorn et al. 2017). Data are published on the SBC LTER site (Page et al. 2018). Final results aggregated by environment and sampling date are presented in Table A3. All model results are reported in Table A4.

Results

Precipitation

During a drought from 2011 to 2015, mean annual rainfall measured from Santa Barbara County gauge 234 (34° 25' N, 119° 42' W) was 24.8 cm. From 2015 to 2017, the period of our study, mean annual rainfall approximately doubled to 48.1 cm. The 20-year rainfall average for the two decades preceding our study (1995–2015) was 47.2 cm, with especially large precipitation occurring during the 1997–98 (119 cm) and 2004–05 (94 cm) water years (Fig. 2, Santa Barbara County Flood Control District 2019).

Grain Size

Median grain size of estuarine and marine sediment samples ranged from 6 to 496 μm, and mean and standard deviation values for estuarine and marine sediment were 140 ± 122 μm and 111 ± 62 μm, respectively. Median grain size also decreased slightly with water depth; mean and standard deviation values for marine sediment collected at 10 and 20 m water depths were 127 ± 80 μm and 95 ± 31 μm, respectively. Overall, estuarine sediment consisted of 6.3% ± 5.3% clay, 35.0% ± 25.5% silt, and 58.7% ± 30.3% sand. Marine sediment consisted of 4.5% ± 4.4% clay, 24.3% ± 18.2% silt, and 71.2% ± 22.4% sand.

Lignin Content

Lignin oxidation products (LOPs) were ubiquitous in sediment samples, with at least one of twelve possible LOPs detected in 444 of 456 sediment samples (97%). Mean and standard deviation values of LOPs, organic carbon content, and isotopic signatures presented by environment and date are reported in Table A3. Sigma 8 values of all samples ranged from 0.01 to 15.29 mg/10 g sample, and mean (± 1 SD) values for the stream, estuarine, and marine sediments were 5.85 ± 3.89 mg/10 g sample, 2.75 ± 2.78 mg/10 g sample, and 0.47 ± 0.44 mg/10 g sample, respectively. Due to the lack of homogeneity of variances of values from all environments, Sigma 8 values were log-transformed prior to the construction of a linear mixed effects model. Our final model structure for the full dataset included environment (stream, estuary, or marine) as a fixed effect and sampling site, water depth sampled,

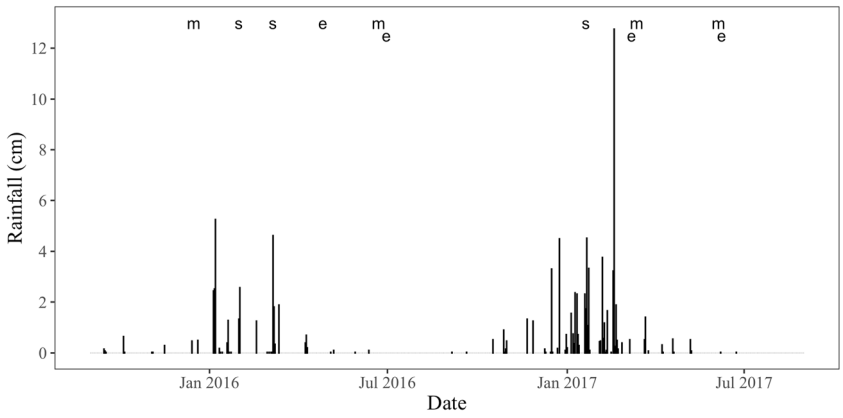

Fig. 2 Daily rainfall for 2015–2017 water years (September 1 through August 31) measured at Santa Barbara County Gauge 234 (Santa Barbara County Flood Control District 2019). Sampling dates are denoted by the letters at the top of the plot with stream, estuarine, and marine sites denoted with "s," "e," and "m" respectively

sample replicate, and sediment depth sampled as nested random effects. Sampling date was not considered as a fixed effect since certain environments were sampled only on certain dates (Table 1), and the same sites were sampled over time resulting in a lack of independence between site type and sampling date. The model results revealed a significant effect of environment on Sigma 8 values (linear mixed effects model (LMEM), $p = 0.0001$). Stream Sigma 8 values were significantly different from the marine values (Tukey's post hoc, $p < 0.001$). Stream Sigma 8 values were consistently greater than other environments sampled.

Lambda values of all samples ranged from 0.04 to 6.01 mg/100 mg OC, and mean values for stream, estuarine, and marine sediments were 2.14 ± 0.99 mg/100 mg OC, 2.17 ± 1.29 mg/100 mg OC, and 1.08 ± 0.76 mg/100 mg OC, respectively (Fig. 3). The final model for the full dataset included environment as a fixed effect and sampling site, water depth, replicate, and sediment depth as nested random effects. Model results suggested a significant effect of environment on Lambda values (LMEM, $p = 0.0009$). Marine Lambda values were significantly different from both stream and estuarine values (Tukey's post hoc, $p < 0.001$ and $p = 0.0062$, respectively). Lambda values for stream and estuarine sediments were greater which indicates they contained greater proportions of TOM than marine sediments.

Contrary to our initial hypothesis, Sigma 8 and Lambda values in marine sediment did not vary significantly between marine sites located near and far from stream mouths. However, sampling date, water depth, and sediment depth were significant predictors of lignin quantity measures. Marine sediment Sigma 8 values ranged from 0.01 to 3.43 mg/10 g sample. Mean values for sites located near and far from stream mouths were 0.51 ± 0.48 mg/10 g sample and 0.38 ± 0.35 mg/10 g sample, respectively. Marine sediment Lambda values ranged from 0.04 to 4.41 mg/100 mg OC, and mean values for sites located near and far from stream mouths were 1.20 ± 0.77 mg/100 mg OC and 0.86 ± 0.70 mg/100 mg OC, respectively. Additional information regarding model structures for marine Sigma 8 and Lambda values can be found in Table A4.

Isotopic Signatures and Lignin Measurements

Higher Sigma 8 values are indicative of greater lignin content in a given sample, and depleted $\delta^{13}C$ signatures (more negative values) also suggest greater input from terrestrial sources (Hedges and Parker 1976). Moingt et al. (2016) found a linear relationship between Sigma 8 and $\delta^{13}C$ signatures, but the samples analyzed were forest soils. Since our samples were collected from varied environments as well as different horizons (suspended and benthic), we present the Sigma 8 and $\delta^{13}C$ signature relationship in a qualitative manner. TOM signatures in the Santa Barbara Channel range from − 25 to − 23‰, kelp forest particulate OM $\delta^{13}C$ signatures range from − 23 to − 17‰, and offshore particulate MOM signatures range from − 22 to − 19‰ (Page et al. 2008). Stream and estuarine

Table 1 Schedule of sampling. Sites were sampled once each time, and from 1 to 6 days within each month were required to sample all sites within an environment category

		2015	2016		2017	
Environment	Sample type	Dry season	Rainy season	Dry season	Rainy season	Dry season
Stream	Suspended sediment		January, March		January	
Estuary	Sediment core			April, June		March, June
Marine	Sediment core	December		June		March, June

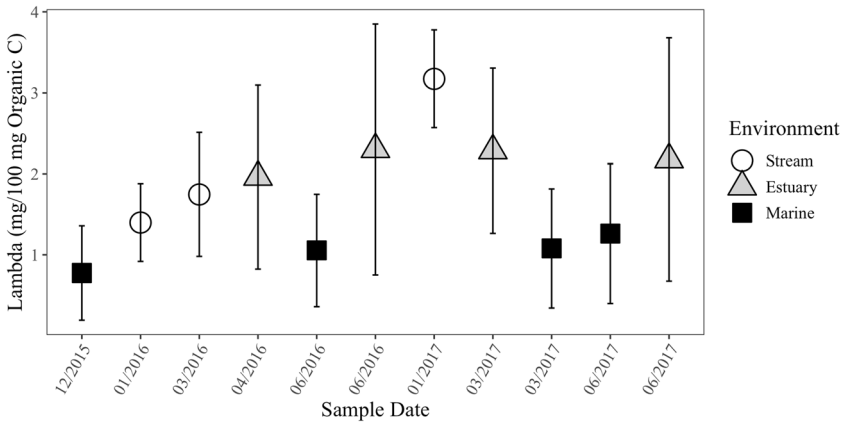

Fig. 3 Mean Lambda values for all environments sampled. Data are aggregated by chronological sampling date. Error bars denote one standard deviation. Note: December 2015 marine samples were collected prior to significant rainfall

sediment had higher Sigma 8 values and more depleted $\delta^{13}C$ signatures, whereas marine sediment had lower Sigma 8 values and more enriched $\delta^{13}C$ signatures (Fig. 4a). Sigma 8 values were most variable at stream and estuarine sites while $\delta^{13}C$ signatures were most variable at marine sites. No distinct grouping emerged in isotopic signatures between marine sites located near or far from streams.

Lignin content and isotopic signatures may be used to indicate material sources and the level of degradation of the OM. Higher values for the 3,5-dihydroxybenzoic acid to vanillyl (3,5-Bd/V) ratio indicate greater levels of TOM degradation (Louchouarn et al. 1999). Fragments of brown macroalgae in sediment samples can also increase 3,5-Bd/V measures due to the presence of tannin and flavonoid compounds in their tissues (Goñi and Hedges 1995). We present the relationship between 3,5-Bd/V and $\delta^{13}C$ signatures to examine the relationship between sampling environment and evidence of degradative processes. Stream and estuarine sediments contained low 3,5-Bd/V values with low variability while marine sediments had greater 3,5-Bd/V values with much greater variability (Fig. 4b). There was no significant difference in 3,5-Bd/V values by marine sites located near and far from streams (Table A4).

Syringyl to vanillyl (S/V) and cinnamyl to vanillyl (C/V) ratios provide information about material sources and degradation processes. S/V values of all samples varied widely, ranging from 0.15 to 11.72. However, mean values of S/V for the stream, estuarine, and marine sediments, 2.45 ± 0.88, 2.73 ± 1.27, and 3.03 ± 1.51, respectively, were not significantly different (LMEM, p = 0.3262). Similarly, C/V values of all samples were highly variable, ranging from 0.01 to 0.75. Mean values of C/V for stream, estuarine, and marine sediments were 0.27 ± 0.13, 0.32 ± 0.0.19, and 0.10 ± 0.08, respectively. There was no significant difference in C/V values between stream and estuarine environments (Tukey's post hoc, p = 0.47). Consequently, we will focus on models created for S/V and C/V values within each environment.

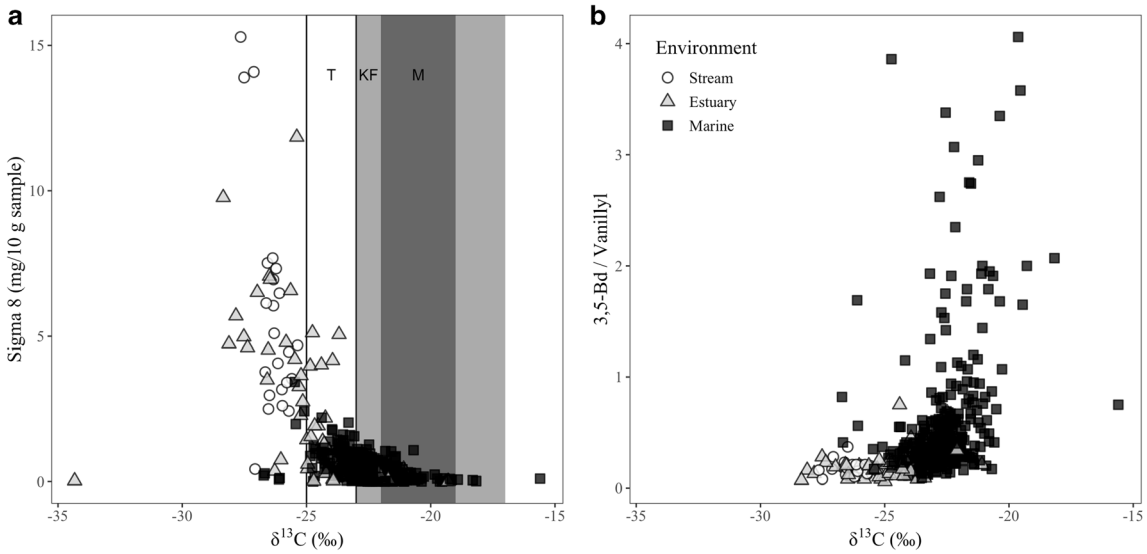

Fig. 4 **a** Sigma 8 and (B) the ratio of 3,5-Bd/V versus $\delta^{13}C$ values for all samples. Boxes in panel **a** are representative of published carbon isotopic signatures of particulate organic matter of various sources sampled from the Santa Barbara Channel nearshore marine environment (Page et al. 2008). "T" refers to terrestrial signatures, "KF" refers to kelp forest signatures, and "M" refers to offshore marine signatures

Stream S/V and C/V values permit an examination of changes in source material quality, prior to significant processing and signature alteration that may occur during transport to the ocean. Stream S/V values ranged from 1.50 to 4.36 while C/V values ranged from 0.09 to 0.54 (Fig. 5a). Linear mixed effects model structure for the stream S/V data only included watershed area and sampling date as fixed effects, sampling site as a random effect, and an additional term allowing different variances by sampling date. The model structure for the C/V data included sampling date as a fixed effect and sampling site as a random effect. Watershed area (km^2) (LMEM, $p = 0.0099$) and sampling date (LMEM, $p = 0.0004$) had a significant effect on S/V values. Sampling date also had a significant effect on C/V values (LMEM, $p = 0.0019$). For S/V values, post hoc results suggested a significant difference between January and March 2016 (Tukey's post hoc, $p = 0.0014$) and January 2016 and January 2017 (Tukey's post hoc, $p < 0.001$). C/V values were significantly different between January 2016 and January 2017 (Tukey's post hoc, $p = 0.0003$) and March 2016 and January 2017 (Tukey's post hoc, $p = 0.0002$). Based on these findings, we conclude that there was a significant change in either the S/V or C/V signatures of stream sediment between each sampling date, and there was an increase in both S/V and C/V values in stream sediment over the course of the full sampling period.

Certain lignin quality measures in estuarine sediments had temporal trends. Estuarine S/V values ranged from 0.69 to 8.74 while C/V values ranged from 0.05 to 0.75. The linear mixed effects model structure for estuarine S/V values included median grain size as a fixed effect, sampling site, replicate, and sediment depth as nested random effects, and a variance term by sampling date. Sediment S/V values increased with increasing median grain size. The final model structure for estuarine C/V values involved sampling date and median grain size as fixed effects, sampling site, replicate, and sediment depth as nested random effects, and a term allowing for different variances by sampling date. Sampling date had a significant effect on C/V values (LMEM, $p < 0.001$), and post hoc testing revealed significant differences between April 2016 and July 2016, April 2017, or June 2017 samples (Tukey's post hoc, $p < 0.003$ for all).

Marine S/V and C/V values were analyzed to determine if patterns in qualitative lignin measures in marine sediment matched those found in stream and estuarine sediment samples. Marine S/V values ranged from 0.15 to 11.72 while C/V values ranged from 0.01 to 0.61 (Fig. 5b). Linear mixed effects model structure for marine S/V values included sampling date, proximity to streams, water depth, sediment depth, and median grain size as fixed effects, sampling site, water depth, replicate, and sediment depth as nested random effects, and a variance term by water depth. Water depth (LMEM, $p = 0.043$) had a significant effect on S/V values; post hoc results suggested a significant difference between cores collected at 10 m and 20 m water depth (Tukey's post hoc, $p = 0.0081$). Sampling date (LMEM, $p = 0.0054$) also had a significant effect on S/V values, with post hoc results suggesting a significant difference between samples collected in December 2015 and March 2017 (Tukey's post hoc, $p < 0.001$). The model structure for C/V values included sampling

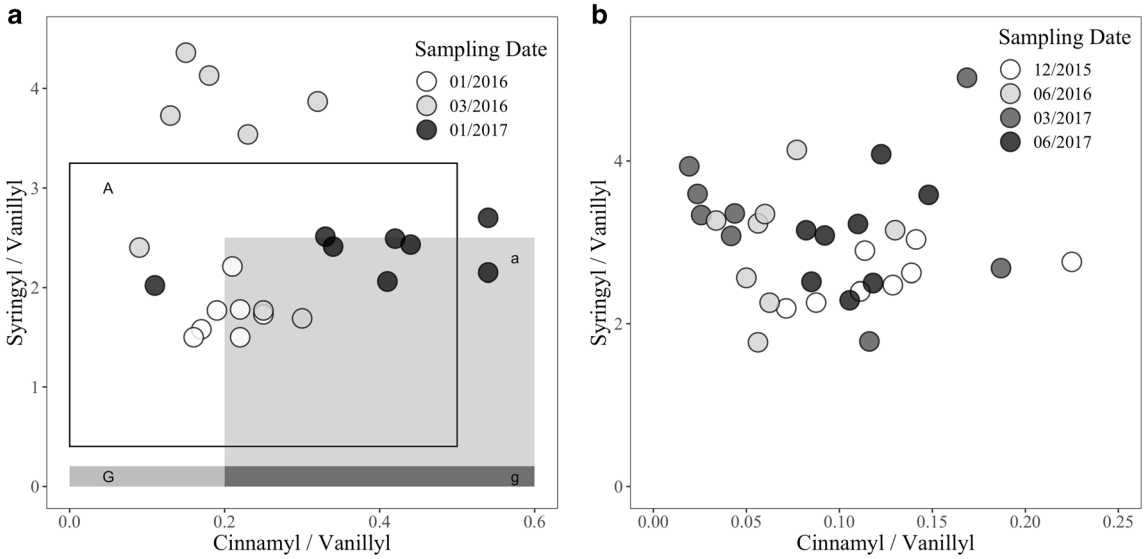

Fig. 5 The ratios of S/V and C/V presented for suspended sediments collected from (**a**) stream and (**b**) marine sites. Boxes in panel **a** are representative of published values of pure terrestrial vegetation tissue sources, both gymnosperm and angiosperm (Hedges and Mann, 1979; Moingt et al. 2016). "A" refers to woody angiosperm tissue, "a" refers to non-woody angiosperm tissue, "G" refers to woody gymnosperm tissue, and "g" refers to non-woody gymnosperm tissue. Marine data in panel **b** is presented as mean values aggregated by site. No distinction between sites near and far from streams has been made since proximity to stream did not have a significant effect on marine sediment S/V or C/V values (Table A4)

date, proximity to streams, and median grain size as fixed effects and sampling site, water depth, replicate, and sediment depth as nested random effects. Sampling date (LMEM, $p < 0.0001$) had a significant effect on C/V values. Post hoc results indicated a significant difference between December 2015 and June 2016 (Tukey's post hoc, $p < 0.001$), December 2015 and March 2017 (Tukey's post hoc, $p < 0.001$), December 2015 and June 2017 (Tukey's post hoc, $p = 0.01$), and June 2016 and June 2017 (Tukey's post hoc, $p = 0.046$). Overall, there was a significant change in S/V and C/V signatures of marine sediment between the initial samples collected prior to significant rainfall (December 2015) and samples collected after two winter storm seasons (March 2017). Similar to stream sediment, there was evidence of increases in S/V and C/V values in marine sediment over the course of the full sampling period.

Lignin degradation indices, such as p-hydroxyl to vanillyl and syringyl (P/(V+S)) and 3,5-Bd/V, are typically used to verify patterns observed in source material signatures, such as S/V and C/V. The ratios of P/(V+S) and 3,5-Bd/V can be used as measures of diagenetic processing, with higher values for both measures indicating greater degradation (Louchouarn et al. 1999; Dittmar and Lara 2001). P/(V+S) values of all samples ranged from 0.03 to 2.17, and mean values for stream, estuarine, and marine sediments were 0.20 ± 0.10, 0.15 ± 0.09, and 0.22 ± 0.25, respectively. 3,5-Bd/V values ranged from 0.06 to 4.06, and mean values for stream, estuarine, and marine sediments were 0.18 ± 0.06, 0.20 ± 0.14, and 0.59 ± 0.63, respectively. There was no significant difference in P/V+S values among environments (LMEM, $p = 0.8299$) and no significant difference in 3,5-Bd/V values between stream and estuarine environments in pairwise comparisons (Tukey's post hoc, $p = 0.9995$). Therefore, we present results of linear mixed effects models run for P/(V+S) and 3,5-Bd/V values for each environment separately.

Stream P/(V+S) and 3,5-Bd/V values were analyzed for patterns in degradation parameters prior to transport to marine regions. P/(V+S) values in stream particulate matter ranged from 0.06 to 0.36, and 3,5-Bd/V values in stream particulate matter ranged from 0.08 to 0.37 (Fig. 6a). The final model structure for P/(V+S) data included sampling date as the singular fixed effect and sampling site as the random effect. P/(V+S) varied significantly by sampling date (LMEM, $p < 0.0001$). Post hoc testing revealed that all dates were significantly different from all others (Tukey's post hoc, $p < 0.001$). The final model for 3,5-Bd/V included land use as a fixed effect, site as a random effect, and an additional variance term by sampling date, but values did not vary significantly by primary land use type (urban, agricultural, or undeveloped). The results of these models indicate that there was a significant change in stream P/(V+S) signatures between each sampling, and there was a decrease in stream P/(V+S) values over the full sampling period.

Estuarine P/(V+S) values ranged from 0.04 to 0.47 while 3,5-Bd/V values ranged from 0.06 to 0.75. The final model structure for P/V+S signatures included sampling date, sediment depth, and median grain size as fixed effects, sampling site, replicate, and sediment depth as nested random effects, and a term allowing for different variances by sampling date. Sampling date also had a significant effect on P/V+S values (LMEM, $p < 0.001$) with post hoc tests revealing significant differences between the 0–10 cm and 10–20 cm sediment horizons (Tukey's post hoc, $p < 0.0001$) and nearly all dates sampled (Tukey's post hoc, $p < 0.04$ for April 2016 and 2017, April 2016 and June 2017, June 2016 and April 2017, and March 2017 and June 2017). The final model structure for estuarine 3,5-Bd/V signatures included median grain size as a fixed effect, sampling site, replicate, and sediment depth as nested random effects, and a term allowing for different variances by sampling date. Sediment 3,5-Bd/V values increased with increasing median grain size.

Marine P/(V+S) and 3,5-Bd/V values were analyzed to determine if trends in upstream samples were mirrored in sediments deposited in nearshore regions. P/(V+S) values in marine sediment ranged from 0.03 to 2.17, and 3,5-Bd/V values ranged from 0.09 to 4.06 (Fig. 6b). The model structure for P/(V+S) data included sampling date, proximity to streams, water depth, sediment depth, and median grain size as fixed effects, sampling site, water depth, replicate, and sediment depth as nested random effects, and a term allowing for different variances by water depth. P/(V+S) values varied significantly by date sampled (LMEM, $p < 0.0001$), proximity to the nearest stream (LMEM, $p = 0.0174$), water depth (LMEM, $p = 0.0124$), sediment depth (LMEM, $p = 0.0006$), and grain size (LMEM, $p = 0.0181$). As P/(V+S) values increased, the median grain size of marine sediments significantly increased. Post hoc results suggested a significant difference between sites near and far from stream mouths (Tukey's post hoc, $p = 0.0087$), between 10 and 20 m water depths ($p = 0.0027$), between the 0–10 and 10–20 cm sediment horizons (Tukey's post hoc, $p = 0.0007$), and nearly all dates sampled (Tukey's post hoc, $p < 0.001$ for December 2015 and March 2017, December 2015 and June 2017, June 2016 and June 2017, and March 2017 and June 2017). The model structure for 3,5-Bd/V data included sampling date, proximity to streams, water depth, sediment depth, and median grain size as fixed effects and sampling site, water depth, replicate, and sediment depth as nested random effects. Sampling date (LMEM, $p < 0.0001$), water depth (LMEM, $p = 0.0154$), sediment depth (LMEM, $p = 0.0025$), and grain size (LMEM, $p = 0.0008$) were all significant fixed effects. 3,5-Bd/V values significantly increased as the median grain size of marine sediments increased. Post hoc testing revealed significant differences between 10 and 20 m water depths (Tukey's post hoc, $p = 0.0025$), between the 0–10 and 10–20 cm sediment horizons (Tukey's post hoc, $p = 0.0033$) as well as December

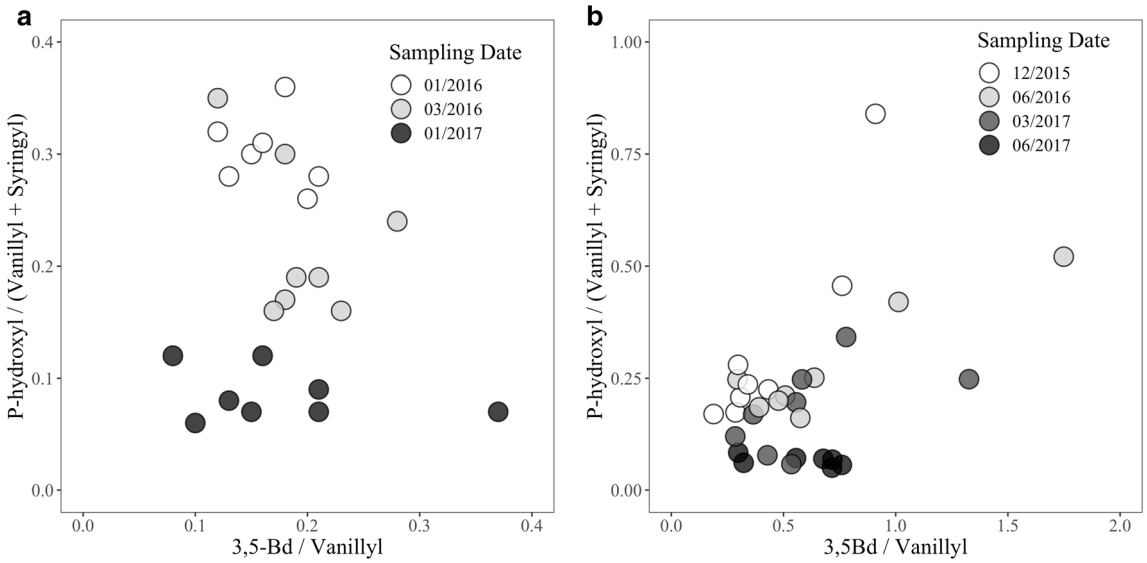

Fig. 6 The ratios of P/(V+S) and 3,5-Bd/V for (**a**) stream and (**b**) marine sites. Marine data in panel **b** is presented as mean values aggregated by site. No distinction between sites near and far from streams has been made since proximity to stream did not have a significant effect on marine sediment 3,5-Bd/V values (Table A4)

2015 compared to June 2016, March 2017, or June 2017 samples (Tukey's post hoc, $p < 0.001$ for all). We conclude that there was a decrease in both marine P/(V+S) and 3,5-Bd/V signatures between the initial samples (December 2015) and samples collected after two winter storm seasons (March/June 2017). Similar to stream sediment, there was a decrease in P/(V+S) values in marine sediment over the course of the full sampling period.

Discussion

Degradation of lignin, as part of the larger pool of bioavailable TOM, depends on the microbial community, physical processes, and light and oxygen availability in a given system (Opsahl and Benner 1995). In terrestrial environments, white-rot fungi are responsible for significant lignin breakdown (Hedges et al. 1988), and although there is currently no evidence of this fungus in marine environments, breakdown of TOM may continue in marine sediments (Burdige 2005). Physical processes, such as dissolution and sorption, can alter lignin phenol values (Hernes et al. 2007), and coarse, lignin-rich materials may be subject to more physical processing than finer, lignin-poor organic materials that provide greater physical protection (Louchouarn et al. 1999). Physical transport, by way of hydrodynamic sorting, may also lead to transport of these finer, lignin-poor particles further offshore in marine regions, with larger, lignin-rich particles deposited in areas closer to shore (Goñi et al. 1997). Our grain size data from marine sediments collected at 10 and 20 m water depth support the likelihood of hydrodynamic sorting occurring at our study sites. Dissolved organic carbon has been demonstrated to flocculate more with increasing salinity; however, this does not occur for lignin compounds transported across the freshwater-marine boundary (Eckes 2020). Flocculation occurring in estuarine and marine environments likely did not alter measured lignin signatures. Furthermore, photo-oxidative, anaerobic, and aerobic lignin degradation processes can lead to a decrease in S/V, C/V, and Sigma 8 values, respectively (Dittmar and Lara 2001; Houel et al. 2006). There is a lack of consensus on whether these various degradation processes dominate in terrestrial ecosystems (Goñi et al. 1998) or if lignin undergoes degradation at comparable rates in the ocean (Opsahl and Benner 1995; Louchouarn et al. 1999). These biologically, chemically, and physically mediated degradation pathways likely occur simultaneously in our system. Therefore, degradation taking place during material transport and following TOM deposition may have amplified degradation signatures in the estuarine and marine environments.

Quantitative lignin measures (Sigma 8, Lambda) differed among the sampled environments (stream, estuarine, marine), reflecting the greater proportional contribution of TOM to streams as compared to marine particulate organic matter. As we hypothesized, sites located close to potential sources of TOM (i.e., streams and estuaries) had the highest mean Sigma 8 and Lambda values. Due to runoff caused by episodic storms, the streams located in the Santa Ynez watersheds contain significant quantities of TOM as suspended particulate matter, with TOM content comparable to larger lotic systems (Table 2). Lignin measures at both estuarine sites were comparable to deltaic sediments collected from larger lotic systems, specifically the Mississippi and Atchafalaya rivers (Table 2). Elevated Lambda values at estuarine sites (Fig. 3)

may be due to input of partially degraded TOM, which contains proportionally more lignin than fresh TOM (Benner et al. 1987). If organic material in estuarine sediment consists of more degraded TOM, it would have higher lignin values relative to the total organic matter content. Greater Lambda values may also be due to input from different TOM sources, as suggested by S/V and C/V values (Fig. 5a), or the low OC content of sandy, estuarine sediments (mean OC of estuarine sediment samples = 0.99 ± 0.88 %). Deposition of TOM in winter coupled with hypoxic periods in summer (Battalio et al. 2015) may lead to extended periods of low oxygen availability which could slow degradation, increase OM sequestration and, as a result, further increase Sigma 8 and Lambda values (Opsahl and Benner 1995; Dittmar and Lara 2001) at estuarine sites.

Runoff during winter storms transported TOM as far as the deepest depth of water where marine sediments were sampled (20 m). However, TOM was not disproportionately retained in marine sediments located closest to stream mouths. Sigma 8 and Lambda measures were unable to distinguish between marine sediment sampled at kelp forest sites located near and far from streams (Table A4). Physical resuspension and transport likely prevent TOM from accumulating in sediments located closer to streams. Indeed, TOM in marine sediments can be transported along shore (Tesi et al. 2008), and storm events that cause strong wave action that may resuspend sediment, exacerbating dilution and dispersion (Airoldi et al. 1996; Cotner et al. 2000). In the energetic system of the Santa Barbara Channel, marine sediment at water depths of 10 to 20 m is routinely resuspended due to waves even during fair weather periods (Sommerfield et al. 2009). There is also an annual pattern of scouring, with sand and sediment transported offshore from beaches and nearshore areas in winter and returned the following summer (Revell et al. 2011). These transport mechanisms may homogenize nearshore marine sediments during and after winter storm events. This connectivity may explain why lignin quantity was indistinguishable between marine sediment sampled near and far from streams.

Water depth was a significant factor, with Sigma 8 and Lambda values greater in marine sediments collected from deeper locations (20 m) (Tukey's post hoc, $p = 0.001$ and $p = 0.03$, respectively). The presence of lignin in most marine sediment samples indicates that TOM reaches these locations and in quantities comparable to other nearshore regions (Table 2). Furthermore, evidence of greater quantities of TOM, due to higher Sigma 8 and Lambda values, and smaller median grain size at deeper marine locations (20 m) suggest the transport of finer particles offshore that, even if relatively lignin-poor (Louchouarn et al. 1999), may accumulate and be sequestered in less energetic benthic environments.

Lignin and isotopic signatures ($\delta^{13}C$) can be used to differentiate the presence of TOM in freshwater versus marine systems. Stream and estuarine sediments contained greater TOM content (Fig. 4a), with greater Sigma 8 values and less enriched (i.e., lighter) $\delta^{13}C$ signatures as compared to isotopic signatures of MOM of the Santa Barbara Channel (Page et al. 2008). Isotopic signatures ($\delta^{13}C$) can also be used as a measure of degradation. Lignin is characterized by $\delta^{13}C$ depleted signatures, and as more degraded TOM contains proportionately more lignin, it has further depleted $\delta^{13}C$ signatures (up to 4‰) (Benner et al. 1987). Tannin and flavonoid compounds found in brown macroalgae can also increase 3,5-Bd content which can inflate 3,5-Bd/V measures (Goñi and Hedges 1995). Overall, more enriched (i.e., heavier) $\delta^{13}C$ signatures and higher 3,5-Bd/V values in marine sediment suggested that TOM in these samples was more degraded than stream or estuarine sediment (Fig. 4b). Marine V values were

Table 2 Lignin oxidation product values from studies examining similar environments alongside our data collected from sites located near Santa Barbara (SB), California, USA. Stream/river locations include data measured from suspended sediment only. Marine locations specify the water depth from which samples were collected

Location	Source	Sigma 8	Lambda	S/V	C/V	3,5-Bd/V
Stream/river						
Santa Ynez Mtns.	This study	5.85	2.14	2.45	0.27	0.18
Central US	Onstad et al. 2000	2.50	1.33	0.82	0.12	–
Indiana, US	Dalzell et al. 2007	1.38	–	1.22	0.61	–
Mississippi R.	Gordon and Goñi 2003	–	2.82	1.22	0.18	0.30
Amazon R.	Hedges et al. 1986	2.56–7.06	2.15–7.31	0.78–0.85	0.07–0.1	–
Estuarine						
SB County	This study	2.75	2.17	2.73	0.32	0.20
Atchafalaya Delta	Gordon and Goñi 2003	–	3.76	0.99	0.22	0.18
Marine						
SB Channel 10 – 20 m	This study	0.47	1.08	3.03	0.10	0.59
Gulf of Mexico 10 – 25 m	Gordon and Goñi 2003	–	1.06	1.13	0.23	0.43
Gulf of Mexico 74 m	Goñi et al. 1998	–	0.36	1.01	0.42	0.16
Adriatic Sea 54 m	Tesi et al. 2008	–	0.94	0.75	0.09	–
Pacific Ocean 55 m	Prahl et al. 1994	–	3.66	0.27	0.05	–

comparable to those measured by Goñi et al. (1998), but 3,5-Bd/V values were an order of magnitude larger, potentially due to macroalgal input. By comparing isotopic signatures with lignin measures, we confirm that stream sediment contained the greatest TOM content and marine sediment contained the most degraded TOM.

Qualitative lignin measures had temporal patterns within stream, estuarine, and marine environments following precipitation events, specifically increases in S/V and C/V signatures and decreases in P/(V+S) signatures (Figs. 5 and 6). These values imply input of varied, but increasingly fresh, terrestrial source material. The relatively high S/V values (> 1.00) in stream suspended particulate matter indicate input from woody and non-woody angiosperm tissues (Hedges and Mann 1979a; Moingt et al. 2016). Higher C/V values (> 0.3) suggest input from non-woody material, while lower values indicate input from woody, structural tissues (Hedges and Mann 1979a). Moingt et al. (2016) reported significant differences in S/V values according to sample type (i.e., woody and non-woody parts of plants and soils in forests dominated by angiosperms). Therefore, January and March 2016 stream samples likely contained more woody angiosperm tissues, whereas January 2017 stream samples contained more soil or non-woody angiosperm tissues. S/V and C/V signatures may also indicate extent of degradation since S and C phenols are preferentially degraded (Opsahl and Benner 1995; Bélanger et al. 2017). When interpreted in this context, higher S/V and C/V signatures in stream, estuarine, and marine sediments may be due to input of less degraded TOM. Lower P/(V+S) values suggest source materials containing woody tissues while higher values suggest input from soil and non-woody tissues (Moingt et al. 2016). Values in January 2016 stream samples suggest greater input of soil and non-woody material, whereas January 2017 samples suggest more woody material. Similar to other lignin signatures, P/(V+S) may also be considered a measure of degradation, with higher values suggesting greater levels of TOM degradation (Dittmar and Lara 2001). In this context, the lower P/(V+S) values measured in stream, estuarine, and marine sediment following storm runoff suggest input of fresh, less degraded TOM over time.

This study highlights our ability to use lignin oxidation products as terrestrial biomarkers in the context of meteorological events in coastal regions. We initially hypothesized that lignin content in all sediments would increase following storms and that marine sediments located closer to streams would receive higher TOM loading than sites further from streams. Quantitative lignin measures — Sigma 8, Lambda — were able to distinguish temporal trends in marine sediments, but they were unable to distinguish between marine sites located near and far from streams. However, as we had hypothesized, samples collected following storms in all three environments did contain fresher lignin content than those collected before the storms. Qualitative lignin measures — S/V, C/V, P/(V+S) — were able to distinguish between sampling dates in stream, estuarine, and marine environments. Increasing S/V and C/V values and decreasing P/(V+S) values in streams and recipient estuarine and marine ecosystems suggest the input of fresh TOM and varied source material from sequential storms.

With the frequency and intensity of droughts and storm events predicted to increase (Masson-Delmotte et al. 2018; Feng et al. 2019), TOM pulses into the coastal ocean may become increasingly variable. Total suspended particulate matter exported from Santa Ynez Mountain watersheds is correlated with significant storm events (Aguilera and Melack 2018a), and storm water runoff has been shown to contain significantly more lignin (Chen and Torres 2018). While lignin is nutritionally poor (Chen and Torres 2018), it can be used as a marker for the simultaneous transport of labile TOM which can be a subsidy for nearshore consumers (Savage et al. 2012; Fong and Fong 2018). This study's purpose was to examine how storm events impact the quantity and quality of TOM transported into coastal regions. Our findings suggest TOM delivered to the nearshore Santa Barbara Channel from Santa Ynez Mountain watersheds was more fresh, and its source material more varied, through time.

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References

Aguilera, R., and J.M. Melack. 2018a. Concentration-discharge responses to storm events in coastal California watersheds: C-Q Storm responses coastal California. *Water Resources Research* 54 (1): 407–424. https://doi.org/10.1002/2017WR021578.

Aguilera, R., and J.M. Melack. 2018b. Relationships among nutrient and sediment fluxes, hydrological variability, fire, and land cover in coastal California catchments. *Journal of Geophysical Research: Biogeosciences* 123 (8): 2568–2589. https://doi.org/10.1029/2017JG004119.

Airoldi, L., M. Fabiano, and F. Cinelli. 1996. Sediment deposition and movement over a turf assemblage in a shallow rocky coastal area of the Ligurian Sea. *Marine Ecology Progress Series* 133: 241–251.

Battalio, B., Behrens, D., Couch, R., Divita, E., Hubbard, D., Lowe, J., Revell, D., Saley, P., 2015. Goleta slough area sea level rise and management plan. *Environmental Science Associates*.

Bélanger, E., M. Lucotte, B. Gregoire, M. Moingt, S. Paquet, R. Davidson, F. Mertens, C.J.S. Passos, and C. Romana. 2015.

Lignin signatures of vegetation and soils in tropical environments. *Advances in Environmental Research* 4: 247–262. https://doi.org/10.12989/aer.2015.4.4.247.

Bélanger, É., M. Lucotte, M. Moingt, S. Paquet, J. Oestreicher, and C. Rozon. 2017. Altered nature of terrestrial organic matter transferred to aquatic systems following deforestation in the Amazon. *Applied Geochemistry* 87: 136–145. https://doi.org/10.1016/j.apgeochem.2017.10.016.

Benner, R., M.L. Fogel, E.K. Sprague, and R.E. Hodson. 1987. Depletion of 13C in lignin and its implications for stable carbon isotope studies. *Nature* 329 (6141): 708–710.

Billen, G.C., C. Lancelot, and M. Meybeck. 1991. N, P, and Si retention along the aquatic continuum from land to ocean. In *Ocean Margin Processes in Global Change*, ed. R.F.C. Mantoura, J.-M. Martin, and R. Wollast, 19–44. Hoboken: Wiley.

Blair, N.E., and R.C. Aller. 2012. The fate of terrestrial organic carbon in the marine environment. *Annual Review of Marine Science* 4 (1): 401–423. https://doi.org/10.1146/annurev-marine-120709-142717.

Brzezinski, M., D. Reed, S. Harrer, A. Rassweiler, J. Melack, B. Goodridge, and J. Dugan. 2013. Multiple sources and forms of nitrogen sustain year-round kelp growth on the inner continental shelf of the Santa Barbara Channel. *Oceanography* 26 (3): 114–123. https://doi.org/10.5670/oceanog.2013.53.

Burdige, D.J. 2005. Burial of terrestrial organic matter in marine sediments: A re-assessment. *Global Biogeochemical Cycles* 19 (4): GB4011. https://doi.org/10.1029/2004GB002368.

Chaves, L.F. 2010. An entomologist guide to demystify pseudoreplication: Data analysis of field studies with design constraints. *Journal of Medical Entomology* 47 (3): 291–298. https://doi.org/10.1093/jmedent/47.1.291.

Chen, S., and R. Torres. 2018. Biogeochemical characteristics and fluxes of suspended particulate organic matter in response to low-tide rainfall: Rainfall-driven POM fluxes and characteristics. *Limnology and Oceanography* 63 (S1): S307–S323. https://doi.org/10.1002/lno.10741.

Coombs, J.S., and J.M. Melack. 2013. Initial impacts of a wildfire on hydrology and suspended sediment and nutrient export in California chaparral watersheds: Wildfire Impacts On Hydrology And Export. *Hydrological Processes* 27 (26): 3842–3851. https://doi.org/10.1002/hyp.9508.

Cotner, J.B., T.H. Johengen, and B.A. Biddanda. 2000. Intense winter heterotrophic production stimulated by benthic resuspension. *Limnology and Oceanography* 45 (7): 1672–1676.

Dalzell, B.J., T.R. Filley, and J.M. Harbor. 2007. The role of hydrology in annual organic carbon loads and terrestrial organic matter export from a midwestern agricultural watershed. *Geochimica et Cosmochimica Acta* 71 (6): 1448–1462. https://doi.org/10.1016/j.gca.2006.12.009.

Dittmar, T., and R.J. Lara. 2001. Molecular evidence for lignin degradation in sulfate-reducing mangrove sediments (Amazônia, Brazil). *Geochimica et Cosmochimica Acta* 65 (9): 1417–1428.

Eckes, D., 2020. Impacts on the flocculation of dissolved organic carbon and lignin with increasing salinity. University of California, Davis. ProQuest Dissertations Publishing 27741984. https://search.proquest.com/docview/2436433439?accountid=14522

Feng, D., E. Beighley, R. Raoufi, J. Melack, Y. Zhao, S. Iacobellis, and D. Cayan. 2019. Propagation of future climate conditions into hydrologic response from coastal southern California watersheds. *Climatic Change.* 153 (1-2): 199–218. https://doi.org/10.1007/s10584-019-02371-3.

Fewings, M.R., L. Washburn, and J.C. Ohlmann. 2015. Coastal water circulation patterns around the Northern Channel Islands and Point Conception, California. *Progress in Oceanography* 138: 283–304. https://doi.org/10.1016/j.pocean.2015.10.001.

Fong, C.R., and P. Fong. 2018. Nutrient fluctuations in marine systems: Press versus pulse nutrient subsidies affect producer competition and diversity in estuaries and coral reefs. *Estuaries and Coasts* 41 (2): 421–429. https://doi.org/10.1007/s12237-017-0291-5.

Godin, P., R.W. Macdonald, Z.Z.A. Kuzyk, M.A. Goñi, and G.A. Stern. 2017. Organic matter compositions of rivers draining into Hudson Bay: Present-day trends and potential as recorders of future climate change: Lignins in Hudson Bay Rivers. *Journal of Geophysical Research: Biogeosciences* 122 (7): 1848–1869. https://doi.org/10.1002/2016JG003569.

Goñi, M.A., and J.I. Hedges. 1995. Sources and reactivities of marine-derived organic matter in coastal sediments as determined by alkaline CuO oxidation. *Geochimica et Cosmochimica Acta* 59 (14): 2965–2981.

Goñi, M.A., and S. Montgomery. 2000. Alkaline CuO oxidation with a microwave digestion system: Lignin analyses of geochemical samples. *Analytical Chemistry* 72 (14): 3116–3121. https://doi.org/10.1021/ac991316w.

Goñi, M.A., K.C. Ruttenberg, and T.I. Eglinton. 1997. Sources and contribution of terrigenous organic carbon to surface sediments in the Gulf of Mexico. *Nature* 389 (6648): 275–278. https://doi.org/10.1038/38477.

Goñi, M.A., K.C. Ruttenberg, and T.I. Eglinton. 1998. A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochimica et Cosmochimica Acta* 62 (18): 3055–3075. https://doi.org/10.1016/S0016-7037(98)00217-8.

Gordon, E.S., and M.A. Goñi. 2003. Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico. *Geochimica et Cosmochimica Acta* 67 (13): 2359–2375. https://doi.org/10.1016/S0016-7037(02)01412-6.

Harms, S., and C.D. Winant. 1998. Characteristic patterns of the circulation in the Santa Barbara Channel. *Journal of Geophysical Research: Oceans* 103 (C2): 3041–3065. https://doi.org/10.1029/97JC02393.

Hedges, J.I., and J.R. Ertel. 1982. Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products. *Analytical Chemistry* 54 (2): 174–178. https://doi.org/10.1021/ac00239a007.

Hedges, J.I., and D.C. Mann. 1979a. The characterization of plant tissues by their lignin oxidation products. *Geochimica et Cosmochimica Acta* 43 (11): 1803–1807. https://doi.org/10.1016/0016-7037(79)90028-0.

Hedges, J.I., and D.C. Mann. 1979b. The lignin geochemistry of marine sediments from the southern Washington coast. *Geochimica et Cosmochimica Acta* 43 (11): 1809–1818. https://doi.org/10.1016/0016-7037(79)90029-2.

Hedges, J.I., and P. Parker. 1976. Land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochimica et Cosmochimica Acta* 40 (9): 1019–1029.

Hedges, J.I., W.A. Clark, P.D. Quay, J.E. Richey, A.H. Devol, and U.M. de Santos. 1986. Compositions and fluxes of particulate organic material in the Amazon River. *Limnology and Oceanography* 31 (4): 717–738.

Hedges, J.I., R.A. Blanchette, K. Weliky, and A.H. Devol. 1988. Effects of fungal degradation on the CuO oxidation products of lignin: A controlled laboratory study. *Geochimica et Cosmochimica Acta* 52 (11): 2717–2726.

Hedges, J.I., R.G. Keil, and R. Benner. 1997. What happens to terrestrial organic matter in the ocean? *Organic Geochemistry* 27 (5-6): 195–212. https://doi.org/10.1016/S0146-6380(97)00066-1.

Hernes, P.J., A.C. Robinson, and A.K. Aufdenkampe. 2007. Fractionation of lignin during leaching and sorption and implications for organic matter "freshness". *Geophysical Research Letters* 34 (17). https://doi.org/10.1029/2007GL031017.

Hothorn, T., Bretz, F., Westfall, P., Heiberger, R.M., Schuetzenmeister, A., Scheibe, S., 2017. multcomp: Simultaneous inference in general parametric models.

Houel, S., P. Louchouarn, M. Lucotte, R. Canuel, and B. Ghaleb. 2006. Translocation of soil organic matter following reservoir impoundment in boreal systems: Implications for in situ productivity. *Limnology and Oceanography* 51 (3): 1497–1513.

Kahle, D., and H. Wickham. 2013. ggmap: Spatial Visualization with ggplot2. *The R Journal* 5: 144–161 http://journal.r-project.org/archive/2013-1/kahle-wickham.pdf.

Klap, V.A., Hemminga, M.A., Boon, J.J., 2000. Retention of lignin in seagrasses: Angiosperms that returned to the sea. *Marine Ecology Progress Series* 1–11.

Louchouarn, P., M. Lucotte, and N. Farella. 1999. Historical and geographical variations of sources and transport of terrigenous organic matter within a large-scale coastal environment. *Organic Geochemistry* 30 (7): 675–699.

Louchouarn, P., S. Opsahl, and R. Benner. 2000. Isolation and quantification of dissolved lignin from natural waters using solid-phase extraction and GC/MS. *Analytical Chemistry* 72 (13): 2780–2787. https://doi.org/10.1021/ac9912552.

Louchouarn, P., R.M.W. Amon, S. Duan, C. Pondell, S.M. Seward, and N. White. 2010. Analysis of lignin-derived phenols in standard reference materials and ocean dissolved organic matter by gas chromatography/tandem mass spectrometry. *Marine Chemistry* 118 (1-2): 85–97. https://doi.org/10.1016/j.marchem.2009.11.003.

Martone, P.T., J.M. Estevez, F. Lu, K. Ruel, M.W. Denny, C. Somerville, and J. Ralph. 2009. Discovery of lignin in seaweed reveals convergent evolution of cell-wall architecture. *Current Biology* 19 (2): 169–175. https://doi.org/10.1016/j.cub.2008.12.031.

Masson-Delmotte, V., Zhai, P., Pörtner, H.O., Roberts, D., Skea, J., Shukla, P.R., Pirani, A., Moufouma-Okia, W., Péan, C., Pidcock, R., Connors, S., Matthews, J.B.R., Chen, Y., Zhou, X., Gomis, M.I., Lonnoy, E., Maycock, T., Tignor, M., Waterfield, T. (ed.), 2018. Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty. Intergovernmental Panel on Climate Change. https://www.ipcc.ch/sr15/.

Melack, J., 2019. SBC LTER: Land: Stream chemistry in the Santa Barbara Coastal drainage area, ongoing since 2000 ver 16. Santa Barbara Coastal Long Term Ecological Research Project. https://doi.org/10.6073/pasta/67a558a24ceed9a0a5bf5e46ab841174.

Millar, R.B., and M.J. Anderson. 2004. Remedies for pseudoreplication. *Fisheries Research* 70 (2-3): 397–407. https://doi.org/10.1016/j.fishres.2004.08.016.

Moingt, M., M. Lucotte, S. Paquet, and B. Ghaleb. 2014. Deciphering the impact of land-uses on terrestrial organic matter and mercury inputs to large boreal lakes of central Québec using lignin biomarkers. *Applied Geochemistry* 41: 34–48. https://doi.org/10.1016/j.apgeochem.2013.11.008.

Moingt, M., M. Lucotte, and S. Paquet. 2016. Lignin biomarkers signatures of common plants and soils of Eastern Canada. *Biogeochemistry* 129 (1-2): 133–148. https://doi.org/10.1007/s10533-016-0223-7.

Murphy, S.F., J.H. Writer, R.B. McCleskey, and D.A. Martin. 2015. The role of precipitation type, intensity, and spatial distribution in source water quality after wildfire. *Environmental Research Letters* 10 (8): 084007. https://doi.org/10.1088/1748-9326/10/8/084007.

Onstad, G.D., D.E. Canfield, P.D. Quay, and J.I. Hedges. 2000. Sources of particulate organic matter in rivers from the continental USA: Lignin phenol and stable carbon isotope compositions. *Geochimica et Cosmochimica Acta* 64 (20): 3539–3546.

Opsahl, S., and R. Benner. 1995. Early diagenesis of vascular plant tissues: Lignin and cutin decomposition and biogeochemical implications. *Geochimica et Cosmochimica Acta* 59 (23): 4889–4904.

Opsahl, S., and R. Benner. 1997. Distribution and cycling of terrigenous dissolved organic matter in the ocean. *Nature* 386 (6624): 480–482.

Page, H., D. Reed, M. Brzezinski, J. Melack, and J. Dugan. 2008. Assessing the importance of land and marine sources of organic matter to kelp forest food webs. *Marine Ecology Progress Series* 360: 47–62. https://doi.org/10.3354/meps07382.

Page, H.M., Lowman, H.E., Melack, J.M., Smith, J.M., Reed, D.C., 2018. SBC LTER: OCEAN: Particulate organic matter content and composition of stream, estuarine, and marine sediments. *Environmental Data Initiative*. https://doi.org/10.6073/pasta/05ca288d7203107bddab618e95524c0a.

Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., Heisterkamp, S., Van Willigen, B., 2019. nlme: Linear and nonlinear mixed effects models.

Poppe, L.J., Eliason, A.H., Fredericks, J.J., Rendigs, R.R., Blackwood, D., Polloni, C.F., 2000. USGS East-Coast sediment analysis: Procedures, database, and georeferenced displays (Open-File No. 00–358). U.S. Geological Survey.

Prahl, F.G., J.R. Ertel, M.A. Goni, M.A. Sparrow, and B. Eversmeyer. 1994. Terrestrial organic carbon contributions to sediments on the Washington margin. *Geochimica et Cosmochimica Acta 58* (14): 3035–3048.

Revell, D.L., J.E. Dugan, and D.M. Hubbard. 2011. Physical and ecological responses of sandy beaches to the 1997-98 El Niño. *Journal of Coastal Research* 27: 718–730.

Santa Barbara County Flood Control District, 2019. Official Daily Rainfall Record. http://www.countyofsb.org/pwd/hydrology.sbc.

Savage, C., S.F. Thrush, A.M. Lohrer, and J.E. Hewitt. 2012. Ecosystem services transcend boundaries: Estuaries provide resource subsidies and influence functional diversity in coastal benthic communities. *PLoS ONE* 7 (8): e42708. https://doi.org/10.1371/journal.pone.0042708.

Sommerfield, C.K., Lee, H.J., Normark, W.R., 2009. Postglacial sedimentary record of the Southern California continental shelf and slope, Point Conception to Dana Point, in: Earth Science in the Urban Ocean: The Southern California Continental Borderland. *Geological Society of America*. https://doi.org/10.1130/2009.2454(2.5)

Sun, S., E. Schefuß, S. Mulitza, C.M. Chiessi, A.O. Sawakuchi, M. Zabel, P.A. Baker, J. Hefter, and G. Mollenhauer. 2017. Origin and processing of terrestrial organic carbon in the Amazon system: Lignin phenols in river, shelf, and fan sediments. *Biogeosciences* 14 (9): 2495–2512. https://doi.org/10.5194/bg-14-2495-2017.

Tesi, T., L. Langone, M.A. Goñi, M. Turchetto, S. Miserocchi, and A. Boldrin. 2008. Source and composition of organic matter in the Bari canyon (Italy): Dense water cascading versus particulate export from the upper ocean. *Deep Sea Research Part I: Oceanographic Research Papers* 55 (7): 813–831. https://doi.org/10.1016/j.dsr.2008.03.007.

Thevenot, M., M.-F. Dignac, and C. Rumpel. 2010. Fate of lignins in soils: A review. *Soil Biology and Biochemistry* 42 (8): 1200–1211. https://doi.org/10.1016/j.soilbio.2010.03.017.

Warrick, J.A., J.M. Melack, and B.M. Goodridge. 2015. Sediment yields from small, steep coastal watersheds of California. *Journal of Hydrology: Regional Studies* 4: 516–534. https://doi.org/10.1016/j.ejrh.2015.08.004.

Washburn, L., Brzezinski, M.A., Carlson, C.A., Siegel, D.A., 2019. SBC LTER: Ocean: Ocean Currents and Biogeochemistry: Nearshore water profiles (monthly CTD and chemistry). Santa Barbara Coastal Long Term Ecological Research Project, *Environmental Data Initiative*. https://doi.org/10.6073/pasta/b73d76d8d1465207be6d7fed19291fda.

Wickham, H. 2016. *ggplot2: Elegant graphics for data analysis*. New York: Springer-Verlag.

Wickham, H., 2018. tidyr: Easily tidy data with "spread()" and "gather()" functions.

Zuur, A.F., Ieno, E.N., Walker, N.J., Saveliev, A.A., Smith, G.M., 2009. *Mixed effects models and extensions in ecology with R, Statistics for biology and health*. New York, NY: Springer.