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Particulate organic matter export by two contrasting small mountainous rivers from the Pacific Northwest, U.S.A.

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[1] We investigated the export of particulate organic matter (POM) to the ocean by two contrasting small, mountainous rivers, the Umpqua and Eel Rivers, by collecting suspended sediment samples over a range of discharges and analyzing them for a variety of constituents, including organic carbon, nitrogen, biomarkers with distinct biochemical sources, and isotopic compositions (δ^{13}C and Δ^{14}C). Concentrations of all measured constituents in both rivers increased as a function of discharge, resulting in their export being dominated by short-lived, wintertime high-discharge events. In the Umpqua River, marked compositional contrasts between low- and high-discharge conditions were consistent with a shift in the provenance of POM from biogenic sources dominated by non-vascular plant sources at low flows to contributions from vascular plant sources of moderate ^{14}C ages (~300 years before present) dominating at high flows. In contrast, POM from the Eel River, which was highly diluted by mineral sediment at all discharges, had significant contributions from petrogenic sources and displayed lower concentrations of recognizable biomarkers. Both rivers had comparable yields of biogenic POM, which appeared to be moderately degraded and originated primarily from surface soils in erosion prone areas of the watersheds. While tectonic/geologic differences help explain the contrasts in sediment and petrogenic POM yields between the two watersheds, ecological factors such as vegetation coverage, productivity, and soil carbon are more important in influencing the composition of biogenic POM mobilized from these systems.

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1. Introduction

[2] It is now well understood that small mountainous rivers are responsible for a disproportionate fraction of the global delivery of sediment to the ocean [*Milliman and Syvitski*, 1992] and may represent an important source of terrestrial particulate organic carbon [*Lyons et al.*, 2002]. Because most organic matter burial occurs along continental and insular margins with significant sediment supply [e.g., *Berner*, 1982; *Hedges*, 1992], small mountainous rivers are likely to play an important role in this major long-term carbon sink [e.g., *Dunne et al.*, 2007]. However, not much is known about the export of particulate organic matter (POM) by these rivers at global and regional scales [e.g., *Gomez et al.*, 2003; *Hilton et al.*, 2012]. Compared to larger continental rivers, small mountainous rivers are characterized by steep basins with little storage capacity, which minimize the modulation of runoff during periods of elevated precipitation [e.g., *Wheatcroft et al.*, 2010, and references therein]. Hence, although factors such as vegetation, land use, soil characteristics, and geology affect the runoff response of a given watershed [e.g., *Dunne et al.*, 1991; *Dietrich et al.*, 1992; *Beschta et al.*, 2000; *Peel et al.*, 2002], most small mountainous rivers typically display highly variable hydrographs, with short-lived peaks in discharge that can be orders of magnitude greater than base levels [*Milliman and Farnsworth*, 2011, Figure 3.45]. In contrast, large rivers display relatively smooth hydrographs that, although can have high seasonal variability [e.g., *Raymond et al.*, 2007; *Jian et al.*, 2009], lack short-lived peaks in flow because they are buffered by the size and storage capacity of their watersheds [*Milliman and Farnsworth*, 2011, and references therein].

[3] Runoff is a key factor in controlling the supply and transport of sediment to and by streams [e.g., *Dietrich and Dunne*, 1978]. As a result of this first-order control by runoff, most streams exhibit a positive correlation between discharge and sediment load that is often modeled as a power law [e.g., *Cohn*, 1995] and referred to as a sediment

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rating curve. A key consequence of this relationship is that a significant fraction of sediment transport by rivers can occur during episodes of elevated flow [*Benda et al*., 2005]. The balance between the frequency of high-flow events and the transport rate at different flows determines the effective discharge for any given stream and constituent [e.g., *Wolman and Miller*, 1960; *Doyle et al*., 2005; *Wheatcroft et al*., 2010]. Hence, unlike their better studied, larger counterparts, small mountainous rivers export sediment primarily during short-lived, high-discharge events [e.g., *Benda et al*., 2005; *Gonzalez-Hidalgo et al*., 2010] associated with periods of storm-driven precipitation.

[4] Although previous studies have investigated the composition of suspended materials in small mountainous rivers, many questions still remain regarding the magnitude, timing, and character of exported POM. For example, in many small rivers, the organic content of the suspended load decreases with discharge [e.g., *Masiello and Druffel*, 2001; *Coynel et al*., 2005], raising the possibility that carbon fluxes may be diluted at high flows. Investigations of several high sediment-yield small mountainous rivers (e.g., Santa Clara, Eel, and Taiwanese Rivers) highlight the importance of bedrock as a source of fossil organic matter (i.e., petrogenic carbon) that can be mobilized during high-discharge events [e.g., *Masiello and Druffel*, 2001; *Leithold and Blair*, 2001; *Komada et al*., 2004; *Leithold et al*., 2006; *Kao and Liu*, 1996; *Hilton et al*., 2011]. Depending on its fate (mineralization versus burial), this petrogenic carbon may represent an additional source of fossil CO_2 or a zero net gain in terms of carbon burial. Small mountainous rivers also can export significant amounts of biogenic (both aged and modern) organic matter from deep and surface soils as well as from vegetation within their basins [e.g., *Gomez et al*., 2003; *Hilton et al*., 2008; 2012; *Blair et al*., 2010; *Hatten et al*., 2012]. The burial of this land-derived biogenic organic matter in coastal sediments represents a net long-term sink of carbon that supplements burial of marine organic matter [e.g., *Dunne et al*., 2007]. Because these systems have the potential to contribute disproportionally to the transport and burial of POM in the ocean at both global and regional scales [e.g., *Wheatcroft et al*., 2010], it is important to determine the role that different factors such as watershed geology, hydroclimate, tectonic setting, basin productivity, and land use have on the magnitude and composition (i.e., biogenic versus petrogenic) of terrigenous organic matter exported by small mountainous rivers.

[5] In this study, we seek to add to the growing understanding of the role of small mountainous rivers in the global carbon cycle by undertaking a comprehensive characterization of the POM transported by two rivers located along the Pacific Northwest margin of the U.S. We focus specifically on POM because of its key role in carbon burial in marine sediments and the remaining questions regarding its source and composition in different systems. From a regional perspective, numerous small mountainous rivers discharge along this section of the North American margin, contributing significant inputs of freshwater, sediment, and most likely POM [e.g., *Alin et al*., 2012]. Hence, we have chosen to study two contrasting systems from this region, the Eel River in northern California and the Umpqua River in central Oregon. The specific objectives of the study were threefold: (1) to collect large-volume water samples at different discharges, specifically targeting high-flow events, (2) to isolate and measure the concentration of the particulate load under contrasting discharges, and (3) to comprehensively characterize the composition of the organic matter in the particulate load. The results from the two systems are compared directly and used to evaluate the importance of factors such as discharge, hydroclimate, watershed geology, tectonics, vegetation, productivity, and soil carbon in determining the magnitude and composition of the exported POM. Finally, we integrate recent findings in this area of biogeochemistry by discussing our results in the context of other studies of small mountainous rivers around the globe.

2. Background

2.1. Regional Significance of Small Mountainous Rivers Along US Northwest Coast

[6] The Pacific Northwest coast of the U.S. (Figure 1a) has been extensively studied by oceanographers over several decades [e.g., *Hickey and Banas*, 2003; *Checkley and Barth*, 2009]. In terms of land-ocean interactions, a major focus of these investigations has been the Columbia River, a large (~6.7×10^5 km^2 basin) continental river that represents a major point source of freshwater, nutrients, sediment, and organic matter [e.g., *Hickey and Banas*, 2008; *Chawla et al*., 2008; *Prahl et al*., 1994; *Nittrouer and Sternberg*, 1981]. However, the coastline between northern California and Washington State is lined with numerous small mountainous rivers that can contribute significantly to freshwater runoff and sediment supply from land during winter floods [*Ralph et al*., 2006; *Wheatcroft and Sommerfield*, 2005]. To appreciate the regional significance of these systems, it is informative to examine the combined daily freshwater discharge records from US Geological Survey (USGS) gauges of small mountainous rivers along the Pacific Northwest region and compare them to the flows from the Columbia River (Figure 1b).

[7] Compared to the Columbia River, the combined runoff of small coastal rivers from northern California, Oregon, and Washington displays extreme seasonality, with winter flows that are orders of magnitude higher than summer flows (Figure 1c). In contrast, the Columbia discharge is highly modulated, with peaks in flow occurring primarily in the spring and representing ~2 times base flow. During winter, discharges from small mountainous rivers are punctuated by sharp peaks in runoff that are associated with storm systems affecting the US West Coast [e.g., *Ralph et al*., 2006; *Kniskern et al*., 2011]. In contrast, peaks in Columbia River discharge occur during spring, are broad because they integrate inputs from snow melt originating from its vast watershed, and are further modulated by numerous large reservoirs along its main stem and tributaries. Discharge near the mouth of the Columbia displays a secondary winter maxima that are due to inputs from tributaries with drainage basins west of the Cascades. The most significant of these is the Willamette River, which behaves much like a coastal river and responds directly to winter precipitation in the form of short-term seasonal floods (Figure 1b).

[8] A key consequence for the regional hydrography is that during winter, small mountainous river systems (total watershed size of ~98,000 km^2) contribute comparable amounts of freshwater to the coastal ocean than the Columbia River even

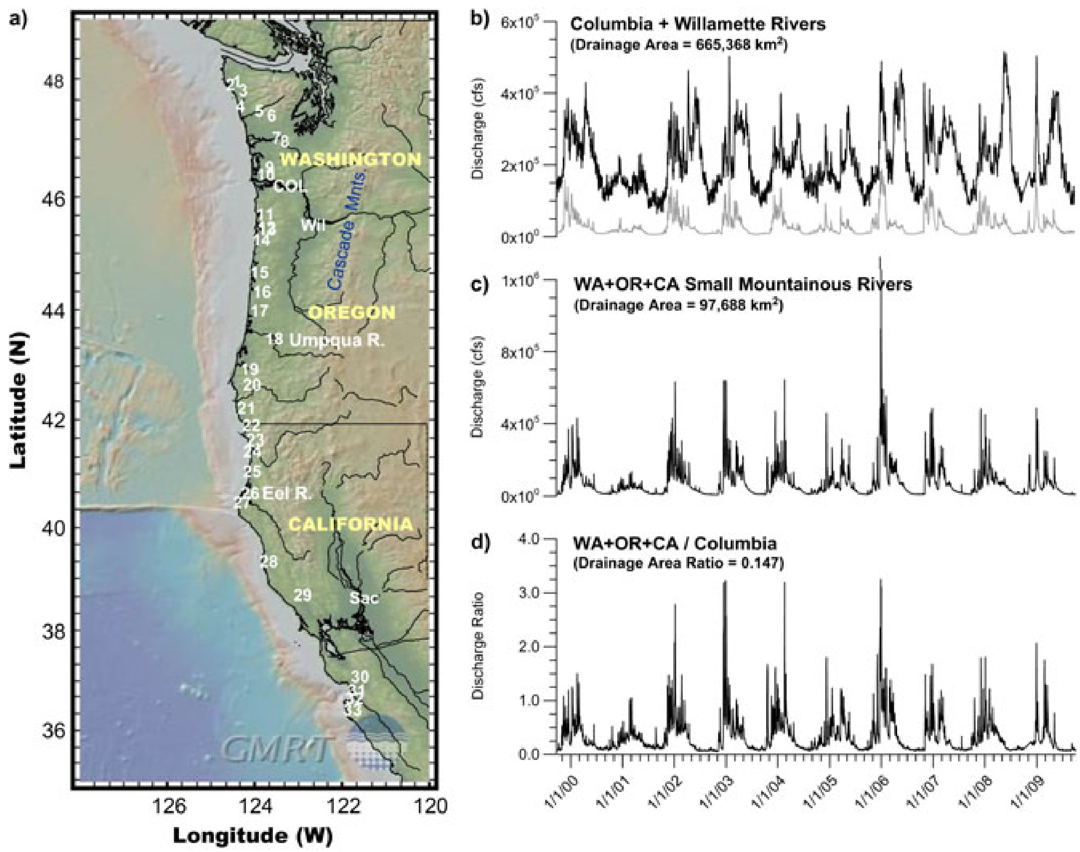


Figure 1. (a) Map of the Pacific Northwest margin of North America with locations of all USGS gauging stations used to compute river discharges; (b) combined discharge of the Columbia River (Willamette River discharge shown in gray); (c) combined discharged of small mountainous rivers (SMRs) in northern California, Oregon, and Washington; (d) ratio of combined SMRs/Columbia River discharge. The numbers and abbreviations represent gauging stations for the following rivers: (1, Calawah; 2, Bogachiel; 3, Hoh; 4, Queets; 5, Quinault; 6, Wynoochee; 7, Satsop; 8, Chehalis; 9, Willapa; 10, Naselle; 11, Nehalem; 12, Wilson; 13, Trask; 14, Nestucca; 15, Siletz; 16, Alsea; 17, Siuslaw; 18, Umpqua; 19, Coquille; 20, Rogue; 21, Chetco; 22, Smith; 23, Klamath; 24, Redwood; 25, Mad; 26, Eel; 27, Matole; 28, Navarro; 29, Russian; 30, Pajaro; 31, Salinas; 32, Carmel; 33, Big Sur; COL, Columbia; Wil, Willamette; Sac, Sacramento). Bathymetry/altitude data from http://gmrt.marine-geo.org.

though they represent less than 15% of its area (Figure 1d). In fact, during week-long periods following major storms, these small rivers dominate the input of freshwater to the Pacific Northwest coast. We infer that these periods of elevated freshwater discharge, which are likely to coincide with high suspended sediment and POM concentrations, have been poorly characterized and dominate material fluxes by these systems.

2.2. Characteristics of Selected Watersheds

[9] Given the regional importance of small mountainous rivers in this section of the North American margin, we chose to investigate in detail two systems, the Umpqua and Eel Rivers (Figure 2), which share several characteristics but display some key differences (Table 1). Both rivers have comparable basin areas, main channel lengths, and maximum elevations. The Umpqua River drains the Coastal Range of Oregon, the Western Cascades, and the Siskiyou Mountains that make up the northern portion of the Klamath Mountains. The Eel River drains the California Coastal Range and a small portion the southern portion of the Klamath Mountains (Figure 2). Both watersheds are characterized by rugged topography with steep slopes and V-shaped valleys and are sparsely populated (<10 inhabitants km^{-2}), with primary land uses that include commercial forestry, cattle grazing, dispersed rural development, and recreation (US Census Bureau). Climate records (Western Regional Climate Center; http://www.wrcc.dri.edu/) indicate that compared to the Eel, the Umpqua watershed is temperate humid, with lower monthly average temperatures and higher annual precipitation rates (Table 1) that range from ~800 mm in the interior valleys to ~1600 mm in the Western Cascades to >2500 mm in the Oregon Coastal Range. In contrast, rainfall in the Eel watershed ranges from ~1000 mm in the interior valleys to ~1700 mm in the high elevations of the California Coastal Range.

[10] The contrasting climates lead to distinct vegetation in the different eco-regions [*Omernik*, 1987]. In the Umpqua watershed, vegetation is dominated by conifer forests, with Douglas-fir being the most abundant species throughout much of the basin. Sitka Spruce and Western Hemlock are found along the Oregon Coastal Range and Grand Fir and

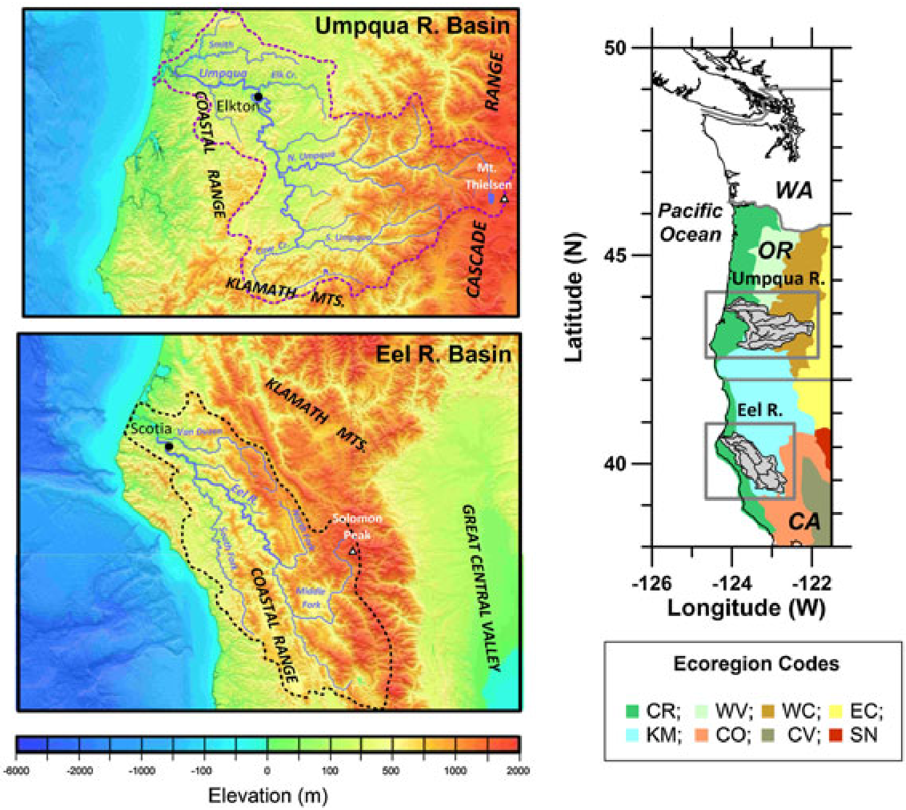


Figure 2. Elevation maps of the Umpqua and Eel River drainage basins with the location of the gauging stations at Elkton and Scotia, major tributaries and mountain ranges identified. The regional map shows the locations of the two watersheds relative to the states of California (CA), Oregon (OR), and Washington (WA). The eco-regions in the western U.S. (*Omernik*, 1987) are also indicated in the regional map and include: CR, coastal range; WV, Willamette Valley; WC, West Cascades; EC, East Cascades; KM, Klamath Mountains; CO, California Chaparral and Oak Woodland; CV, California Central Valley; SN, Sierra Nevada. Note that the areal extent of some eco-regions (e.g., Klamath Mountains) does not coincide directly with geologic regions of the same name.

Table 1. Summary of River and Watershed Characteristics

Variable	Umpqua	Eel
Basin Characteristics		
Total basin size (km^2)	13,000	9537
Length of main channel (km)	179	193
Maximum elevation (m)	2799 (Mt. Thielsen)	2311 (Solomon Peak)
Geologic provinces	Oregon Coastal Range, Western Cascades, Klamath Mountains	California Coastal Range, Klamath Mountains
Basin geology	Cenozoic volcanics, Cenozoic sedimentary rocks	Mesozoic sedimentary rocks
Basin vegetation	Douglas-fir forests, mixed conifer/hardwood forests	Redwood forests, oak woodlands, grasslands
Major land use	Forestry, grazing, recreation	Forestry, grazing, recreation
Climate	Temperate humid	Mediterranean
Annual precipitation (mm)	1200 to >2500	1000 to 2000
Annual temperature averages (°C)	$T_{min} = -1$ to 8; $T_{max} = 13$ to 18	$T_{min} = 3$ to 11; $T_{max} = 17$ to 23
Aboveground biomass (kg C m^{-2})	14 (living), 3 (dead)	14 (living), 2 (dead)
Net primary productivity (kg C m^{-2} yr^{-1})	0.6	0.6
Soil carbon inventories (kg C m^{-2})	12	5
Hydrologic Characteristics		
USGS gauging station	Elkton (USGS ID 14321000. 43.586N, 123.554W)	Scotia (USGS ID 11477000, 40.492N, 124.099W)
Drainage area (km^2)	9539 (73% of basin)	8063 (85% of basin)
Daily discharge (Avg. ± s.d.) (m^3 s^{-1})	208 ± 305	208 ± 517
Annual runoff (Avg. ± s.d.) (km^3)	6.6 ± 9.6	6.6 ± 16
Specific water yield (mm)	692	819
Average annual load (×10^9 kg)	1.4	18
Sediment yield (× tons km^{-2} yr^{-1})	147	2232

Specific data sources discussed in the text.

Western Hemlock along the Western Cascades. Hardwood species, including Big Leaf Maple and Red Alder, are abundant along riparian and disturbed areas. Oak woodlands and savannas are found in the lowland valleys of the Klamath Mountains. Vegetation in the Eel watershed includes Redwood and Douglas-fir forests in the wetter, western regions of the California Coastal Range and Klamath Mountains, whereas White and Black Oak woodlands occupy drier regions. Grasslands and brush are found in the steep and less stable slopes that characterize much of the Eel watershed.

[11] Contrasts in climate and land use also lead to marked differences in aboveground biomass, net primary productivity, and soil carbon stocks among the eco-regions that make up the Umpqua and Eel watersheds [e.g., *Hudiburg et al.*, 2009; *West et al.*, 2010]. Aboveground living biomass ranges from ~20 kg C m^{-2} in the Coastal Range to ~6 kg C m^{-2} in the Klamath Mountains [*Hudiburg et al.*, 2009]. Aboveground, dead biomass ranges from over 5 kg C m^{-2} in the Western Cascades to ~1 kg C m^{-2} in parts of the Klamath Mountains. Estimates of net primary productivity are highest (~0.8 kg C m^{-2} yr^{-1}) in the Coastal Ranges, with lower rates in the Klamath Mountains (~0.6 kg C m^{-2} yr^{-1}) and Western Cascades (~0.4 kg C m^{-2} yr^{-1}). However, given the spatial distribution of each eco-region, we estimate that the overall levels of living biomass and net primary productivity in the two watersheds are comparable (Table 1). Within the Umpqua watershed, carbon inventories in the top meter of soil range from 6 to 16 kg C m^{-2}, whereas in the Eel watershed, they range from 3 to 8 kg C m^{-2} [*West et al.*, 2010]. Based on these data, we estimate that average soil organic carbon stocks are roughly double in the Umpqua relative to the Eel watershed (12 and 5 kg C m^{-2}, respectively; Table 1). Intermediately weathered soils (e.g., Inceptisols and Utisols) characterize both drainage basins [*Soil Survey Staff, N. R. C. S.*, 2011].

[12] The Umpqua and Eel watersheds have highly contrasting geologic and tectonic characteristics (http://www.nationalatlas.gov/). The Coastal Range portion of the Umpqua River drainage basin is underlain by Eocene marine sedimentary rocks (siltstones and sandstones of the Tyee Formation) mixed with volcanic rocks of the same age. Volcanic rocks (andesite and basalt) from late Eocene to late Miocene characterize the Western Cascades and Mesozoic volcanic, and intrusive rocks are found in the Klamath Mountains [e.g., *Molenaar*, 1985; *Wallick et al.*, 2011]. In contrast, most of the Eel watershed is underlain by Late Mesozoic (Cretaceous), marine sedimentary rocks (sandstones and shales) of the Franciscan Formation.

[13] The Eel River drainage basin is located near the Mendocino triple junction and is tectonically active [e.g., *Clarke*, 1992; *Gulick et al.*, 2002], having undergone post-Miocene uplift and exhibiting major faults that have been active in the Late Quaternary [e.g., *Kelsey*, 1980; *Aalto et al.*, 1995]. In contrast, the Umpqua watershed is less tectonically active, with fewer active faults in both the Western Cascades and Coastal Range regions [e.g., *Kelsey et al.*, 1996]. Uplift rates in the Umpqua watershed range from 0 mm yr^{-1} in the Western Cascades to ~2.5 mm yr^{-1} in the Coastal Range, whereas throughout much of the Eel River drainage basin, uplift rates range between 3 to 5 mm yr^{-1} [*Mitchell et al.*, 1994; *Kelsey et al.*, 1996]. Landslide incidence maps reflect these geologic and tectonic differences (http://www.nationalatlas.gov/), with most of the Eel watershed being categorized as a high-incidence region (greater than 15% of the area involved), whereas the Umpqua watershed includes areas of moderate and low landslide incidence [e.g., *Benda and Dunne*, 1997; *Roering et al.*, 2005].

2.3. Hydrologic Characteristics

[14] The contrasting characteristics of the Umpqua and Eel watersheds lead to marked differences in hydrology (Table 1). The USGS has maintained gauging stations in the Umpqua (at Elkton) and in the Eel (at Scotia) since the early 1900's. Daily discharge records yield virtually identical estimates of long-term average discharge (208 m^3 s^{-1}) and annual runoff (~7 km^3) for both systems. This similarity occurs despite the lower precipitation in the Eel watershed. As a result, we estimate higher specific water yields (i.e., annual runoff normalized to watershed area) for the Eel basin (819 mm) than for the Umpqua basin (692 mm). Although beyond the scope of this work, contrasts in rainfall/runoff relationships reflect differences in the routing of water throughout the landscape, which is affected by factors such as vegetation, land use, soil characteristics, geology, and hydroclimate [e.g., *Dunne et al.*, 1991; *Dietrich et al.*, 1992; *Peel et al.*, 2002; *McCabe et al.*, 2007; *Jefferson et al.*, 2010].

[15] Although both rivers have comparable long-term annual freshwater discharges, runoff in the Eel River is much more seasonally variable with larger summer-winter contrasts. For example, frequency analyses [e.g., *Oosterbaan*, 1994] of the long-term daily discharge data (Appendix A) from both rivers reveal that low-flow days (<50 m^3 s^{-1}), which occur predominantly during summer and early fall, are almost twice as common in the Eel River than in the Umpqua River. Monthly averages from both stream gauges (Appendix B) show consistently higher flows during July to October in the Umpqua (30 to 50 m^3 s^{-1}) relatively to the Eel (4 to 20 m^3 s^{-1}). In contrast, the Eel River displays higher discharges (400 to 570 m^3 s^{-1}) during the winter months (December to March) than the Umpqua River (340 to 450 m^3 s^{-1}). High-discharge events in the Eel are more frequent than in the Umpqua. For example, whereas a ~600 m^3 s^{-1} event, which in both rivers represents 3 times the mean discharge (Q:Q_m = 3), has a return period of ~0.045 years in both systems, an event with a flow of ~2000 m^3 s^{-1} (Q:Q_m = 10) has a return period of 0.2 years in the Eel River but 0.7 years in the Umpqua River (Appendix A). Events of larger discharge display the same pattern. An ~4000 m^3 s^{-1} flow (Q:Q_m = 20) in the Eel River has a return period of 1 year, but in the Umpqua River, it has a 6 year return period. A flow of ~6,000 m^3 s^{-1} (Q:Q_m = 30) in the Eel has a return period of ~3.5 years, whereas analyses of long-term records indicate such an event in the Umpqua represents a 100 year flood.

[16] The differences in climate, geology, and hydrology between the two river systems result in marked contrasts in sediment load and yield (Table 1). Using USGS data from 1950s–1990s, *Wheatcroft and Sommerfield* [2005] showed that the average annual sediment load for the Eel River(18×10^9 kg) is over an order of magnitude higher than for the Umpqua River (1.4×10^9 kg). The long-term (1950–1990) sediment yield from Eel basin (2232 tons km^{-2} yr^{-1}) is over 15 times greater than that calculated for the Umpqua (147 tons km^{-2} yr^{-1}).

Notably, on any given year, the total amount of sediment discharged by each river can vary significantly depending on runoff and especially the occurrence of high-discharge events [*Benda et al*., 2005; *Gonzalez-Hidalgo et al*., 2010]. Deviations from the long-term average can also occur due to changes in factors such as climate, land use, and stochastic events such as fire [e.g., *Warrick et al*., 2012]. Determining how these climatic, geologic, and hydrologic contrasts affect the magnitude and composition of the POM load exported by these two rivers is a primary objective of this study.

3. Methods

3.1. Hydrographic Data

[17] Hourly discharge records were obtained from the USGS stream gauges at Elkton, OR (14321000) and at Scotia, CA (11477000). Water sampling was carried out from bridges near the two gauging stations (Figure 3). Because of their proximity and the lack of major tributaries between the gauging and sampling locations, we were able to assign a specific discharge datum from the USGS records to each sample based on the time of collection.

3.2. Large Volume Water Sampling

[18] We used flow predictions from USGS/NOAA to select sampling days that would capture contrasting discharges over a 2 year period from October 2007 to September 2009. Details of particle sampling have been described by *Hatten et al*. [2012]. Briefly, we sampled a total of 60 L of water from ~1 m below the river surface at three cross-channel locations in each system using a Wildco Horizontal Alpha Sampler. This type of sampler allows collection of relatively large volumes of water during the storm conditions that coincide with periods of high discharge, when high winds and large debris being transported downriver make depth-integrated collection of large-volume water samples from bridges meters above the stream impractical and unsafe. We recognize that this approach likely under-samples the coarsest/densest fraction of the sediment load transported near the bed. However, comparison of our suspended load concentrations with depth-integrated data collected by the USGS in these (see below) and other systems [e.g., *Hatten et al*., 2012; *Warrick et al*., 2012] indicates close agreement between both methods, likely as a result of the relatively shallow depths and highly turbulent conditions that characterize these small mountainous rivers. We acknowledge that our data do not capture the transport of the largest-sized suspended and bed loads (e.g., greater than sand-size) but contend they are representative of the finer fractions (e.g., clays, silts, and fine sands), where most of the organic matter resides. Our interpretations reflect these caveats and are limited to these fractions.

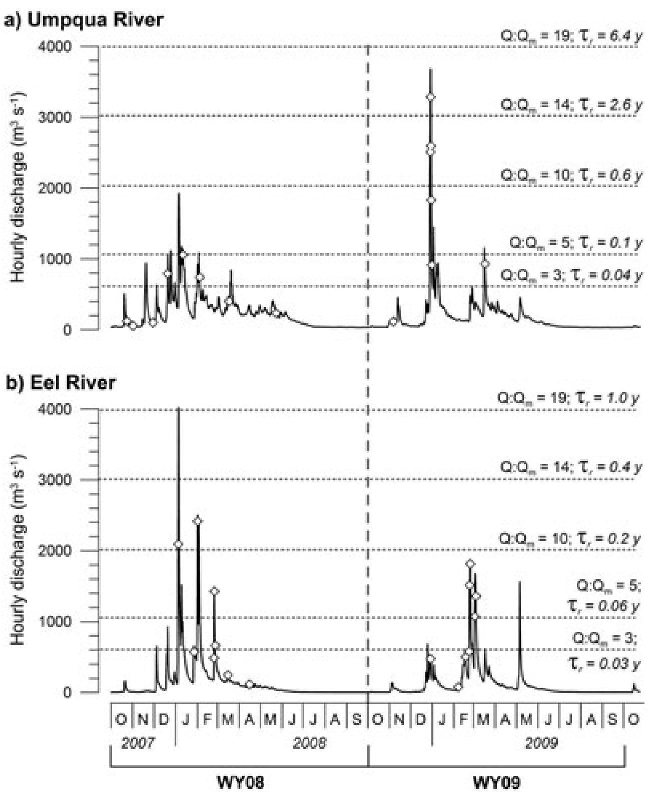


Figure 3. Hourly discharges measured in (a) the Umpqua River at Elkton (USGS ID 1432100) and (b) the Eel River at Scotia (USGS ID 11477000) during WY08 and WY09. The open diamonds indicate large volume samples collected for this study. Levels of discharge relative to mean discharge (Q:Q_m) are indicated in both graphs along with the estimated return period for discharge (τ_r)exceeding each level (Appendix A).

[19] Immediately after collection, samples were transported in dark, cool conditions to the laboratory, where they were passed through a 63 μm stainless steel sieve to recover coarse suspended particles. Fine suspended particles (<63 μm) were isolated by centrifugation. The coarse and fine suspended materials collected in the sieve and centrifugation bottles after processing all the water were oven dried at 60°C until constant weight was achieved and stored for further analyses. Aliquots of water samples that had undergone the centrifugation step were filtered through pre-weighed, 0.45 μm glass-fiber filters to determine the fraction of suspended material not isolated with this approach. Overall, the combined coarse and fine fractions accounted for 93 ± 3 and $98 \pm 1\%$ of the total suspended load in the Umpqua and Eel samples, respectively. The lowest recoveries (<90%) were typically obtained in samples collected during low discharge conditions (Q:$Q_m \leq 1$) when suspended solid concentrations were quite low. For simplicity, in this paper, we focus on trends observed for the combined (coarse plus fine) fractions. Details on the compositions of the individual coarse and fine samples are discussed elsewhere (see Goñi et al., in prep) as they do not alter the main conclusions of this study.

3.3. Chemical Analyses

[20] Samples were subject to a variety of analyses designed to characterize the composition of the suspended load. Details of all analytical techniques used in this study are provided by *Hatten et al*. [2012]. Briefly, weights of suspended solids (SS) were recorded after oven drying. Organic carbon (OC) and nitrogen (N) contents in all suspended samples were determined by high-temperature combustion after homogenization and removal of inorganic carbonates. Based on replicate analyses of selected samples, the precision of these measurements was better than 5% of measured value and analyses of reference materials showed they were accurate to within 2%. The stable isotopic

composition of OC ($\delta^{13}C_{org}$) in POM was determined by isotope ratio mass spectrometry after high-temperature combustion of pre-acidified samples. Precision in the $\delta^{13}C$ measurements was $\pm 0.1‰$, and the analyses of reference materials showed accuracies that were within 5% of measured values. Radiocarbon compositions of organic matter ($\Delta^{14}C_{org}$) in selected samples were determined at the NOSAMS facility at Woods Hole Oceanographic Institution, which reports routine precision of 5‰. Note that at low flows, we only recovered enough material for radiocarbon analyses of the fine fraction. Hence, the ^{14}C data reported here are for this fraction only. We used alkaline CuO oxidation to determine the concentrations of organic compounds derived from different biochemical precursors. In this paper, we report the concentrations of a variety of compounds classes including lignin-derived phenols (LP), which represent the sum of vanillyl, syringyl, and cinnamyl phenols (VP, SP, and CP, respectively); cutin-derived hydroxyfatty acids (CA); amino acid-derived products (AA); p-hydroxybenzenes (PB); and benzoic acids (BA). These organic compounds have distinct biochemical sources, which have been discussed previously [e.g., *Hedges and Mann*, 1979; *Goñi and Hedges*, 1990, 1992, 1995; *Goñi and Thomas*, 2000; *Crow et al*., 2009], and have been used extensively to characterize the composition of natural organic matter in a variety of environments (e.g., *Bianchi et al*., 2007; *Tesi et al*., 2007; *Filley et al*., 2008; *Goñi et al*., 2008, and references therein). We use lignin and cutin CuO products to characterize the sources and diagenetic state of organic matter derived from vascular plant sources and the rest of the compound classes to evaluate contributions from additional non-vascular plant sources. Typical precisions for the measurement of individual biomarkers range from 5 to 10% of the measured value. Comparisons of chemical compositions between the two river systems and between low- and high-flow conditions were performed using ANOVA, and only statistically significant trends ($p < 0.05$) are reported.

4. Results

4.1. River Discharge

[21] Both rivers were sampled during two contrasting water years (WY08 and WY09), which are defined as starting on 1 October and ending on 30 September (Figure 3). Each year, both rivers displayed several high-discharge events, which for the purpose of this manuscript are defined as periods when the discharge (Q) was 3 times higher than the long-term mean (i.e., Q:$Q_m > 3$). These events, which typically lasted several days, occurred during November to April and coincided with periods of high rainfall associated with the passage of storms [e.g., *Ralph et al*., 2006]. Overall, both rivers showed comparable variability in flow, which ranged from 30 to 2800 $m^3 s^{-1}$ in the Umpqua and 1 to 2700 $m^3 s^{-1}$ in the Eel. However, whereas the average annual discharges for the Umpqua River (224 and 173 $m^3 s^{-1}$ in WY08 and WY09, respectively) bracketed the long-term mean (208 $m^3 s^{-1}$), annual averages for the Eel River (143 and 109 $m^3 s^{-1}$) were significantly lower than the long-term mean discharge. Comparison of monthly discharges during WY08 and WY09 (Appendix C) with long-term data (Appendix B) shows that in the case of the Umpqua, almost every month of the study period exhibited flows that were comparable to the long-term mean values. In contrast, there were many months during WY08 and WY09 when the average Eel discharges were significantly lower than long-term means. These lower than normal winter discharges for the Eel River reflect the severe to extreme drought conditions that affected this region of California during the study period (http://www.drought.unl.edu/dm/archive.html).

[22] Our collection effort was designed to recover samples over a range of discharges and specifically targeted high-discharge events. We collected 15 large-volume water samples in the Umpqua and 16 samples in the Eel. The number and frequency of samples was primarily determined by logistical constraints of mobilizing the sampling team at the time of peak flows and by the time and effort it took to process 60 L water samples. As illustrated in Figure 3, our samples span the full range of discharges observed during the 2 year study period (Q:Q_m of 0.2 to over 10).

4.2. Particulate Concentrations

[23] The concentrations of all particulate constituents in both rivers (Table 2) increased exponentially as a function of discharge (Figure 4). The Eel samples consistently displayed higher concentrations at all discharge levels relative to those from the Umpqua River, with this difference being most evident at elevated discharges (Q:$Q_m > 1$). For example, SS concentrations measured in the Eel were ~10 times higher than the concentrations measured in the Umpqua at comparable discharges (Table 2). In contrast, the concentrations of OC, ON, and all biomarker classes were only 2 to 3 times higher in the Eel River than in the Umpqua River at comparable Q:$Q_m > 1$. These trends reflect the elevated particle yields from the Eel basin relative to the Umpqua and indicate mineral-rich sediment is responsible for most of this enhancement.

[24] Our combined (fine + coarse) SS measurements in the Umpqua River displayed a relationship with discharge that was comparable to the historical trend exhibited by total SS concentrations measured by the USGS and Oregon Department of Environmental Quality at Elkton from the late 1970's to the early 2000's (Figure 4a). This agreement indicates that our sampling protocol captured the major trends observed with the depth-integrated sampling carried out by these agencies and suggests that sediment yields have not changed appreciably in the period covered by these studies. In contrast, the concentrations we measured in the Eel River were considerably lower than the historic measurements conducted by the USGS between the late 1950's and the late 1990's (Figure 4b). When we examine our data relative to SS concentrations measured during different decades (Appendix D), it is clear that our 2007–2009 data match the observations made during 1980's and 1990's (gray circles in Figure 4b), yielding rating curves with statistically comparable parameters. The vast majority of the elevated SS concentrations above our measurements originate from the 1950's, 1960's, and 1970's. Historical changes in logging intensity and practices and in the after effects of the 1955 and 1964 floods likely contributed to the elevated sediment yields and distinct rating curves (Appendix D) during this period [e.g., *Kelsey*, 1980; *Syvitski and Morehead*, 1999; *Sloan et al*., 2001; *Sommerfield et al*., 2002]. The agreement between our measurements and those collected in the1980's and 1990's by the USGS indicates

Table 2. Concentrations of Particulate Constituents in the Suspended Load

Q	Q/Q_m	Date	SS	OC	N	VP	SP	CP	CA	BA	PB	AA	FA	DA
(m^3 s^{-1})			(mg L^{-1})			(μg L^{-1})								
Umpqua River														
54	0.3	1 Nov 2007	2.0	0.2	0.02	3.1	1.0	0.3	0.8	0.7	2.1	11.8	1.2	1.0
101	0.5	29 Nov 2007	1.7	0.2	0.02	1.9	0.8	0.2	0.8	0.7	1.9	9.9	1.4	1.3
115	0.5	6 Nov 2008	13.0	0.8	0.10	11.1	6.1	1.8	3.5	2.7	8.1	46.4	7.0	3.2
123	0.6	23 Oct 2007	7.4	0.6	0.07	8.5	3.0	0.9	3.9	2.0	4.0	33.2	2.2	2.5
235	1.1	23 May 2008	7.3	0.5	0.04	11.9	3.8	1.7	4.4	1.2	4.4	25.5	7.1	2.3
404	1.9	17 March 2008	14.7	0.7	0.06	16.5	6.3	1.9	6.1	2.5	5.5	32.0	6.8	2.1
736	3.5	4 Feb 2008	83.3	1.9	0.15	51.7	25.0	6.2	20.1	8.3	10.8	72.1	9.0	4.5
793	3.7	20 Dec 2007	74.9	2.5	0.22	63.7	22.5	6.4	28.5	10.5	15.7	98.6	11.6	8.4
912	4.3	31 Dec 2008	98.0	2.6	0.18	95.3	27.7	7.3	28.1	9.8	15.4	66.5	10.2	7.1
934	4.4	17 March 2009	68.9	2.1	0.16	76.3	23.6	6.6	22.4	10.8	19.4	77.5	14.5	8.4
1058	5.0	11 Jan 2008	48.7	1.2	0.10	36.9	12.9	3.6	11.9	4.8	6.6	51.1	4.3	4.5
1832	8.6	30 Dec 2008	244.5	6.4	0.40	151.1	47.3	15.3	38.3	14.1	22.5	112.2	21.7	14.1
2500	11.8	29 Dec 2008	278.1	10.6	0.77	347.0	121.6	39.7	134.8	45.8	63.4	356.3	48.4	35.9
2574	12.1	30 Dec 2008	330.7	9.1	0.58	343.8	99.8	33.1	94.6	37.7	48.1	244.6	41.0	27.3
3256	15.4	29 Dec 2008	384.7	10.1	0.72	328.7	124.3	37.8	101.3	44.5	62.2	290.9	51.9	35.8
Eel River														
79	0.4	7 Feb 2009	16.8	0.4	0.05	3.5	2.2	0.7	1.7	1.2	2.2	13.6	1.6	1.1
116	0.6	15 April 2008	12.0	0.2	0.02	1.8	1.0	0.3	0.3	0.5	1.4	9.5	1.2	0.5
247	1.2	15 March 2008	81.2	0.8	0.08	9.9	6.0	1.3	4.1	2.3	3.1	25.0	3.7	2.0
476	2.3	29 Dec 2008	174.7	2.0	0.18	21.4	18.0	4.0	19.6	5.2	8.7	48.6	7.4	4.6
480	2.3	24 Feb 2008	378.1	3.1	0.26	25.1	12.7	3.2	8.6	5.7	7.3	59.9	8.1	4.9
503	2.4	17 Feb 2009	112.8	1.0	0.11	15.2	11.3	2.7	7.9	4.4	5.9	31.5	5.3	3.2
568	2.7	22 Feb 2009	607.4	5.2	0.40	83.3	53.5	13.2	47.3	17.9	21.7	118.0	20.3	12.7
583	2.8	27 Jan 2008	327.1	3.1	0.26	26.2	17.5	3.7	11.8	7.6	8.9	72.7	9.3	5.9
665	3.2	26 Feb 2008	248.6	1.8	0.17	21.6	11.6	2.3	10.2	4.4	5.4	44.2	5.2	3.8
1086	5.2	2 Mar 2009	703.3	3.8	0.43	84.7	59.0	13.7	42.3	15.4	19.3	101.3	19.2	10.6
1339	6.4	4 Mar 2009	451.4	2.7	0.26	40.1	27.0	5.9	20.9	7.0	8.9	46.0	12.1	4.6
1424	6.8	25 Feb 2008	1072.2	8.9	0.67	116.3	47.1	9.7	37.4	19.3	30.8	197.3	27.0	19.8
1514	7.3	23 Feb 2009	1136.3	12.9	1.10	177.2	132.2	35.3	158.0	39.0	55.5	299.0	33.3	26.9
1801	8.7	24 Feb 2009	1045.5	9.0	0.77	116.4	82.9	17.7	58.8	25.0	30.9	184.1	26.3	15.9
2166	10.4	4 Jan 2008	3252.8	35.3	2.89	823.3	511.5	83.7	317.1	101.1	151.1	796.8	112.0	89.0
2410	11.6	1 Feb 2008	1909.0	15.4	1.22	222.5	145.8	26.2	94.8	44.6	53.4	385.4	52.8	37.4

Q, hourly discharge; Q:Q_m, ratio of hourly discharge to long-term mean discharge; SS, suspended solids; OC, organic carbon; N, nitrogen. CuO products: VP, vanillyl phenols; SP, syringyl phenols; CP, cinnamyl phenols; CA, cutin acids; BA, benzoic acids; PB, p-hydroxybenzenes; AA, amino acid products; FA, fatty acids; DA, dicarboxylic acids.

that our sampling technique captured the major trends observed by depth-integrated sampling.

[25] To summarize the concentration-discharge relationships of different constituents, we fit the data using the "quasi-maximum likelihood estimator" method described by *Cohn et al.* [1992]:

$$\ln C_i = \beta_0 + \beta_1 \ln Q_t + e \qquad (1)$$

where C_i is the concentration of constituent (i), Q_t the instantaneous discharge, β_0 and β_1 are the least squares regression coefficients, and e is the residual error, which is defined as $s^2/2$ (where s is the standard deviation of the residuals).

[26] Overall, the Eel River displayed higher-rating exponents (β_1) for all constituents relative to their counterparts in the Umpqua River (Table 3), reflecting the steeper increases in loads of all particulate materials at elevated discharges (Figure 4). Among constituents, both rivers displayed similar trends, with elevated rating exponents for SS and vascular-plant derived biomarkers, including lignin phenol (VP, SP, and CP) and cutin acid (CA) products relative to OC, N, and non-vascular plant biomarkers (AA, FA, DA, PB, and BA). These contrasts among rating exponents suggest that different processes are responsible for the introduction and transport of different materials within the two river systems. The reasonably good fits of the power functions for all constituents also suggest a lack of a threshold in their supply from both watersheds over the observed discharge ranges, a feature of other small mountainous river systems [e.g., *Hatten et al.*, 2012; *Hilton et al.*, 2012].

4.3. Compositions of Suspended Particles

[27] To investigate how the compositions of suspended particles differ between the two rivers as a function of discharge, we used the data in Table 2 to calculate the sediment-normalized concentrations of measured constituents (Figure 5). Table 4 summarizes the average compositions for samples collected at high- and low-flow conditions (Q:$Q_m > 3$ and < 3, respectively). Notably, sediment-normalized concentrations of several constituents decreased significantly as discharge increased (e.g., Figure 5). This pattern was most obvious in constituents from the Umpqua River, where particles collected during high-discharge events were significantly depleted in %OC, %N, and non-vascular derived biomarkers such as AA, FA, DA, and PB relative to particles collected at low flows. Thus, for example, whereas particles collected at Q:$Q_m < 3$ had %OC and %N contents that averaged 8 ± 1 and 0.9 ± 0.1 wt.%, respectively, their counterparts collected at Q:$Q_m > 3$ had lower organic %OC and %N contents (3 ± 0.2 and 0.2 ± 0.02 wt.%, respectively) (Table 4). In contrast, sediment-normalized concentrations of vascular plant-derived biomarkers (e.g., VP,

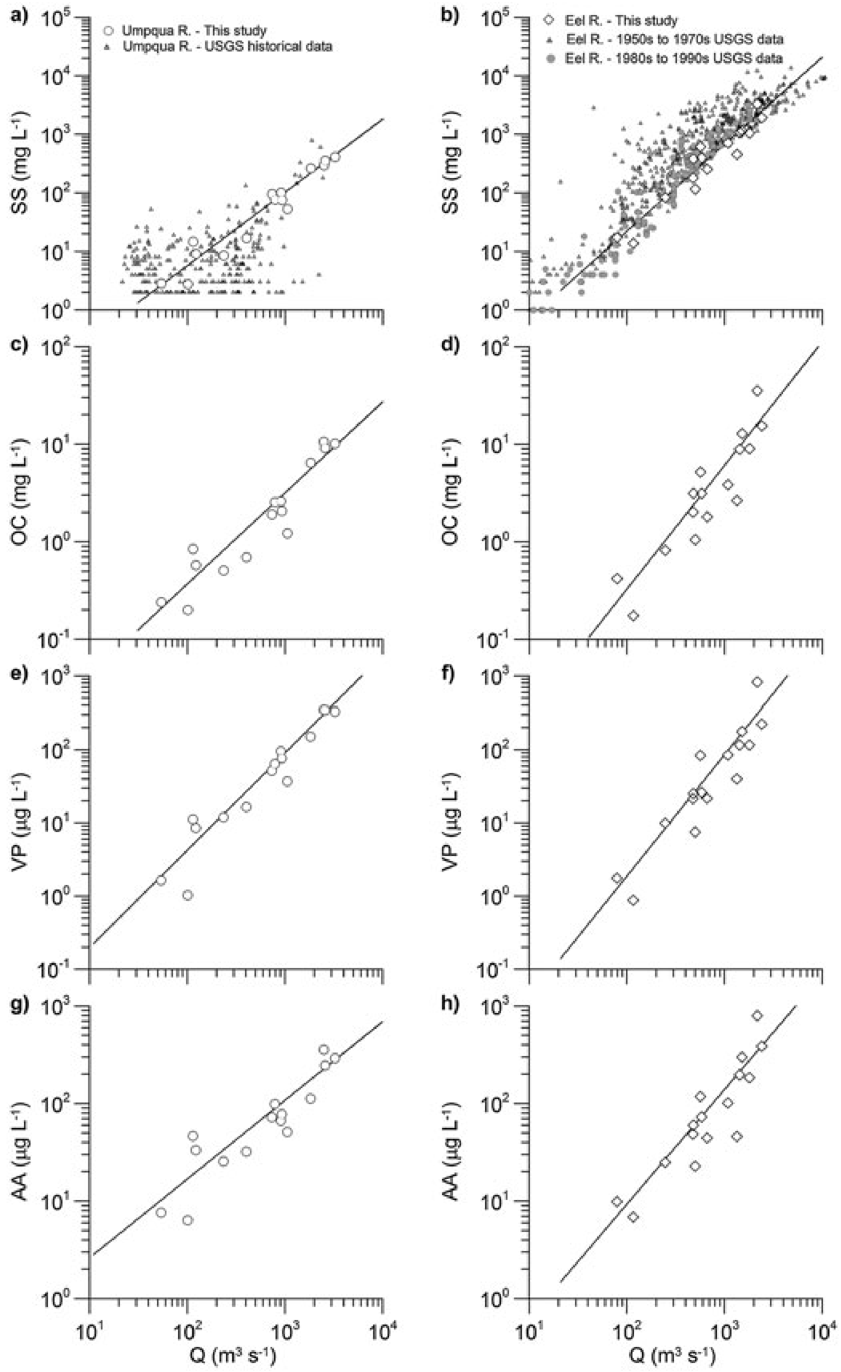


Figure 4. Plots of concentration versus discharge for selected constituents in the Umpqua and Eel Rivers. The particulate concentrations are from Table 2 and include (a, b) suspended solids (SS), (c, d) organic carbon (OC), (e, f) vanillyl phenols (VP), and (g, h) amino acid derived products (AA). The rating curves (equation (1)) for each constituent are included in each graph, and the regression coefficients are shown in Table 3. In the case of SS concentrations, historical data from the Umpqua and Eel Rivers are also plotted. In the case of the Eel River, pre-1980 data are differentiated from data collected in the 1980's and 1990's (see Appendix D for more details).

SP, CP, and CA) did not display marked decreases as flows increased (Figure 5), with values at Q:$Q_m > 3$ that were not statistically different from those at Q:$Q_m < 3$ (Table 4). These trends are consistent with the transport of OM-rich particles characterized by elevated contents of non-vascular plant biomarkers at low flows and the increased entrainment of OM-poor particles enriched in vascular plant-derived biomarkers at high flows.

[28] Particles from the Eel River displayed sediment-normalized concentrations of all organic constituents that were significantly lower than those from the Umpqua River (Figure 5) and the contrasts between high- and low-flow compositions were less pronounced than for the Umpqua. Thus, for example, particles collected at both low and high discharges from the Eel River were characterized by

Table 3. Rating Curve Fit Parameters (ln $C = \beta_0 + \beta_1 \times \ln Q + e$) for Different Constituents[a]

Constituent	Umpqua River				Eel River			
	β_0	β_1	e	r^2	β_0	β_1	e	r^2
SS	−4.71	1.32	0.13	0.93	−4.04	1.51	0.11	0.92
OC	−5.41	0.93	0.11	0.88	−7.13	1.27	0.17	0.83
N	−7.01	0.79	0.13	0.82	−9.02	1.19	0.14	0.84
VP	−4.07	1.22	0.11	0.93	−5.84	1.46	0.20	0.85
SP	−4.83	1.18	0.12	0.91	−6.42	1.48	0.21	0.85
CP	−6.07	1.18	0.12	0.92	−6.90	1.33	0.21	0.82
CA	−4.87	1.18	0.10	0.93	−7.38	1.58	0.31	0.81
AA	−0.51	0.73	0.11	0.82	−2.71	1.08	0.16	0.79
FA	−2.89	0.80	0.14	0.81	−4.97	1.14	0.11	0.86
PB	−2.53	0.78	0.12	0.83	−4.91	1.14	0.18	0.79
BA	−4.62	1.01	0.12	0.88	−6.07	1.26	0.17	0.83
DA	−3.34	0.81	0.11	0.85	−5.88	1.20	0.18	0.81

[a]Constituent codes as in Table 2. Details of calculations are discussed in the text.

generally low %OC (<2 wt.%) and %N (<0.2 wt%) contents as well as low sediment-normalized biomarker concentrations ($< 0.5\,\mathrm{mg\,g^{-1}}$). Overall, Eel samples exhibited sediment-normalized concentrations that were 3 to ~50 times lower than those from their Umpqua counterparts (Table 4). These trends suggest that OM-poor particles comprise a much higher fraction of the suspended load in the Eel River at all discharges, including periods of very low flow.

4.4. POM Compositions

[29] The POM collected during high- and low-flow conditions exhibited marked differences in composition, which were most significant among the Umpqua samples (Table 5 and Appendix E). For example, $[C{:}N]_{org}$ values increased as discharge increased in both rivers (Figure 6a), indicating an enhancement in the contribution of carbon-rich POM in response to increased runoff. The compositional contrasts between high- and low-discharge conditions were clearest among the Umpqua samples, with significantly higher $[C{:}N]_{org}$ values at $Q{:}Q_m > 3$ relative to those measured at $Q{:}Q_m < 3$ (16 and 12, respectively; Table 5). There was a sharp decrease in the $\delta^{13}C_{org}$ of POM of both rivers as discharge increased (Figure 6b). In the Umpqua River, this trend was more pronounced leading to significantly depleted $\delta^{13}C_{org}$ averages during high-discharge events relative to those collected during low-flow conditions (Table 5). The same level of significance did not apply to differences in $\delta^{13}C_{org}$ between low- and high-flow conditions in the Eel River.

[30] At high discharge, POM from the Umpqua River also exhibited consistently elevated OC-normalized concentrations of vascular plant-derived biomarkers (e.g., VP, SP, CP, and CA; Figure 6; and Table 5). In contrast, the OC-normalized concentrations of non-vascular plant products such as AA (as well as FA and DA) were significantly higher in samples collected during low flows. These trends are consistent with a shift in the source of POM [e.g., *Goñi and Hedges*, 1990; 1992; 1995] from materials dominated by non-vascular plant sources (e.g., algae, macrophytes, and microbes) at low flows to enhanced contributions of vegetation-derived materials at high flows. The contrasts in the biogeochemical signatures of POM between low- and high-flow conditions were less clear in the Eel River (Figure 6; Table 5). In fact, there were no statistical differences in most OC-normalized biomarker concentrations of POM collected during high discharges and low-flow conditions (Table 5). The major exceptions were several of the vascular plant biomarkers, specifically VP, SP, and CA, which displayed significantly higher concentrations at high flows than at low flows (p values of 0.02, 0.08, and 0.10, respectively). The consistently lower OC-normalized concentrations of both vascular and non-vascular products in the Eel samples relative to the Umpqua samples suggest that either the former contain more altered biogenic organic matter or that the biogenic contributions are mixed with other sources of organic matter devoid of biomarkers (e.g., petrogenic carbon).

[31] There were significant contrasts in the radiocarbon compositions of organic matter ($\Delta^{14}C_{org}$) and the corresponding ^{14}C ages among Umpqua and Eel samples, reflecting differences in their provenance (Appendix E and Table 5). In the Umpqua River, fine POM samples displayed enriched $\Delta^{14}C_{org}$ signatures (−30 to −59‰) relative to those measured in the Eel River (−444 to −610‰). These radiocarbon compositions are consistent with bulk radiocarbon ages for suspended POM that averaged ~300 years before present (ybp) in the Umpqua River and ~6000 ybp in the Eel River. The highly depleted $\Delta^{14}C_{org}$ signatures measured in all Eel samples indicate that this small mountainous river exports a much higher fraction of aged POM, most likely of petrogenic origin, than the Umpqua River. In both the Umpqua and Eel systems, there were no clear trends in the $\Delta^{14}C_{org}$ signatures collected at high and low flows (Table 5). This was somewhat unexpected, especially in the Umpqua River, given the fact that other compositional parameters such as $[C{:}N]_{org}$, $\delta^{13}C_{org}$, and the OC-normalized concentrations of both vascular and non-vascular plant biomarkers displayed marked contrasts consistent with significant changes in the provenance (i.e., vegetation versus non-vegetation sources) of POM under low- and high-flow conditions. The lack of discharge related trends in $\Delta^{14}C_{org}$ suggests comparable ages for both vegetation- and non-vegetation-derived biogenic POM.

5. Discussion

5.1. Magnitude and Timing of POM Export

[32] Sediment rating curves are based typically on many more observations than what we were able to obtain in this study [e.g., *Syvitski et al*., 2000]; however, the relationships exhibited by different constituents (Figure 4) were statistically robust and showed significant contrasts (Table 3). For these reasons, we suggest that the application of the power functions determined in this study to estimate loads of different constituents provides important insights into the magnitude and mode of particulate export of the two river systems. With this objective in mind, we used the rating exponents and coefficients for each constituent to calculate instantaneous loads based on the hourly water flow records at Elkton and Scotia. Based on those estimates, we calculated daily loads by summing up the 24 hourly estimates and cumulative loads by adding the daily data during the study period.

[33] The daily water fluxes and cumulative loads for SS, OC, and lignin phenols (LP = VP + SP + CP) in the Umpqua and Eel Rivers for WY08 and WY09 are illustrated in Figure 7. The annual load estimates for each river were normalized to their watershed areas to calculate the yields (mass per km^2 of watershed) for all constituents measured (Table 6). Several

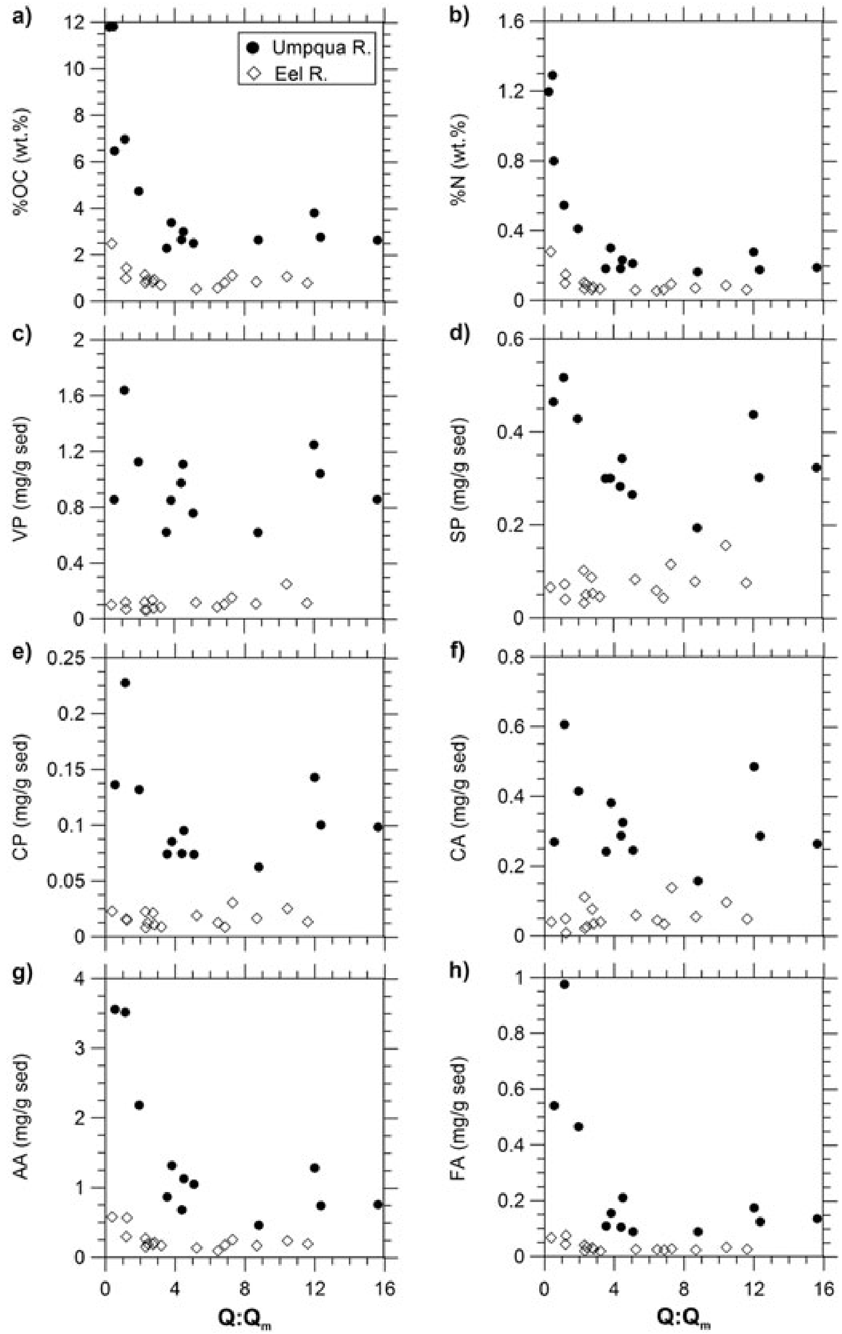


Figure 5. Sediment normalized concentrations of different particulate constituents as a function of mean-normalized discharges in the Umpqua and Eel Rivers. The abbreviations for each constituent are as in Table 2.

trends in these data are worth discussing. For example, cumulative load records highlight the significance of winter floods in the export of water and particulate materials by both rivers (Figure 7). In the Umpqua River, wintertime (November to April) flows accounted for ~80% of the annual water discharge during both years (Appendix F). In the case of the Eel River, the percentage of water flow during the winter was 94% in WY08 and 82% in WY09. These results are consistent with the long-term hydrologic records that indicate highly seasonal flow for these and other small mountainous rivers in the western U.S. (Figure 1). Seasonality is even more pronounced for particulate constituents. For example, in the Umpqua River, winter flows accounted for 89 to 98% of the annual loads of SS, OC, N, and all biomarker classes during both years of the study. In the Eel River, those estimates ranged from 88% in WY09 and ~100% of the annual loads during WY08.

[34] To quantitatively assess the importance of floods, we estimated their contribution to the total annual export of different constituents (Figure 8). We used the Q:$Q_m > 3$ threshold to identify the number of high-discharge days in the 2 year period. During WY08-09, the Umpqua River had 34 high-discharge (i.e., flood) days, whereas the Eel River had 29 days. Despite accounting for only 5% of the study period, the 34 high-discharge days in the Umpqua

Table 4. Average Sediment-normalized Concentrations of Different Particulate Constituents Under Low- (Q:$Q_m < 3$) and High-Flow (Q:$Q_m > 3$) Conditions[a]

Parameter	$Q/Q_m < 3$ Umpqua River Avg. ± s.e.	Eel River Avg.	±	s.e.	$Q/Q_m > 3$ Umpqua River Avg.	±	s.e.	Eel River Avg.	±	s.e.
%OC (wt.%)	8.26 ± 1.19	1.21	±	0.20	2.84	±	0.16	0.82	±	0.07
%N (wt.%)	0.86 ± 0.14	0.12		0.025	0.21		0.016	0.072		0.005
CuO Products (mg/g)										
VP	1.24 ± 0.12	0.13	±	0.016	0.90	±	0.072	0.13	±	0.019
SP	0.46 ± 0.017	0.083	±	0.011	0.31	±	0.022	0.083	±	0.013
CP	0.15 ± 0.016	0.022	±	0.004	0.09	±	0.008	0.017	±	0.003
LP	1.85 ± 0.14	0.23	±	0.03	1.29	±	0.10	0.23	±	0.034
CA	0.46 ± 0.048	0.062	±	0.012	0.30	±	0.031	0.066	±	0.012
BA	0.26 ± 0.039	0.035	±	0.006	0.12	±	0.011	0.023	±	0.002
PB	0.72 ± 0.12	0.059	±	0.015	0.17	±	0.019	0.031	±	0.004
AA	4.24 ± 0.59	0.38	±	0.094	0.92	±	0.10	0.19	±	0.02
FA	0.62 ± 0.10	0.052	±	0.011	0.13	±	0.014	0.027	±	0.001
DA	0.39 ± 0.091	0.030	±	0.006	0.09	±	0.009	0.018	±	0.002

[a]Avg., average; s.e., standard error; all other captions as in previous tables.

Table 5. Chemical and Isotopic Compositions of the POM Under Low-Flow (Q:$Q_m < 3$) and High-Flow (Q:$Q_m > 3$) Conditions[a]

Parameter	$Q/Q_m < 3$ Umpqua River Avg. ± s.e.	Eel River Avg. ± s.e.	$Q/Q_m > 3$ Umpqua River Avg. ± s.e.	Eel River Avg. ± s.e.
$\delta^{13}C_{org}$ (‰)	−24.0 ± 0.7	−25.4 ± 0.2	−26.4 ± 0.3	−25.7 ± 0.1
$\Delta^{14}C_{org}$* (‰)	−48.3 ± 10.2	−510 ± n.a.	−41.2 ± 5.7	−532 ± 48.0
^{14}C age* (ybp)	340 ± 85	5670 ± n.a.	282 ± 48	6127 ± 824
$[C:N]_{org}$ (molar)	11.7 ± 0.9	12.6 ± 0.6	15.9 ± 0.6	13.3 ± 0.6
CuO Products (mg/100 mg OC)				
VP	1.63 ± 0.24	1.10 ± 0.10	3.15 ± 0.18	1.58 ± 0.15
SP	0.62 ± 0.08	0.72 ± 0.09	1.08 ± 0.06	1.01 ± 0.12
CP	0.20 ± 0.04	0.18 ± 0.02	0.31 ± 0.02	0.21 ± 0.03
CA	0.60 ± 0.10	0.55 ± 0.11	1.03 ± 0.06	0.78 ± 0.10
BA	0.32 ± 0.02	0.29 ± 0.03	0.41 ± 0.03	0.29 ± 0.02
PB	0.86 ± 0.04	0.45 ± 0.06	0.60 ± 0.05	0.38 ± 0.02
AA	5.14 ± 0.18	2.96 ± 0.39	3.21 ± 0.27	2.27 ± 0.10
FA	0.81 ± 0.15	0.42 ± 0.05	0.46 ± 0.04	0.34 ± 0.03
DA	0.44 ± 0.05	0.24 ± 0.02	0.32 ± 0.02	0.22 ± 0.01

[a]Captions: as previous tables.

River were responsible for 22% of the total 2 year water flux, contributed >60% of the total SS and vegetation biomarker (VP, SP, CP, and CA) fluxes and ~50% of the OC, N, and non-vascular plant biomarker fluxes (Figure 8). The lower contribution of high-discharge events to the overall transport of bulk OC, N, and non-vascular plant biomarkers reflects the relatively elevated supply of non-vegetation POM sources during non-flood conditions. In the Eel River, the 29 high-discharge days contributed to ~40% of water transport, 88% of the total SS flux, ~90% of the vegetation biomarker fluxes, and 80 to 85% of the OC, N, and non-vascular plant biomarker fluxes. Overall, these results highlight the importance of high-discharge events for the transport of all particulate constituents, especially vascular plant-derived POM and mineral sediments.

[35] Elevated flows are responsible for a significant fraction of the total particulate and dissolved loads of many river systems [e.g., *Gonzalez-Hidalgo et al.*, 2010; *Raymond and Saiers*, 2010]. However, the overwhelming importance of high-discharge events in determining the annual loads and yields of inorganic and organic particulate constituents is a salient characteristic of small mountainous rivers [e.g., *this study*; *Gomez et al.*, 2003; *Benda et al.*, 2005; *Hilton et al.*, 2008; *Wheatcroft et al.*, 2010). Our data show that flood-induced transport of different POM constituents can vary within a single stream system, reflecting the variable role of elevated precipitation and water routing in the mobilization of particulate materials from mountainous watersheds [e.g., *Dunne et al.*, 1991; *Dietrich et al.*, 1992; *Beschta et al.*, 2000; *Peel et al.*, 2002]. The importance of floods for the transport of specific particulate materials also varies among small mountainous rivers, providing additional insight into the inter-basin contrasts. For example, the higher contributions of high-discharge events to overall loads in the Eel River relative to the Umpqua River reflect the extremely event-dominated character of the former, which displays summer and winter base flows that can be quite low (see section 3.1).

[36] Our observations reinforce the idea that average flows are poor predictors of overall load and yield in small mountainous rivers. For example, as it can be seen in Table 6, WY09 was a lower-flow year than WY08 in both systems.

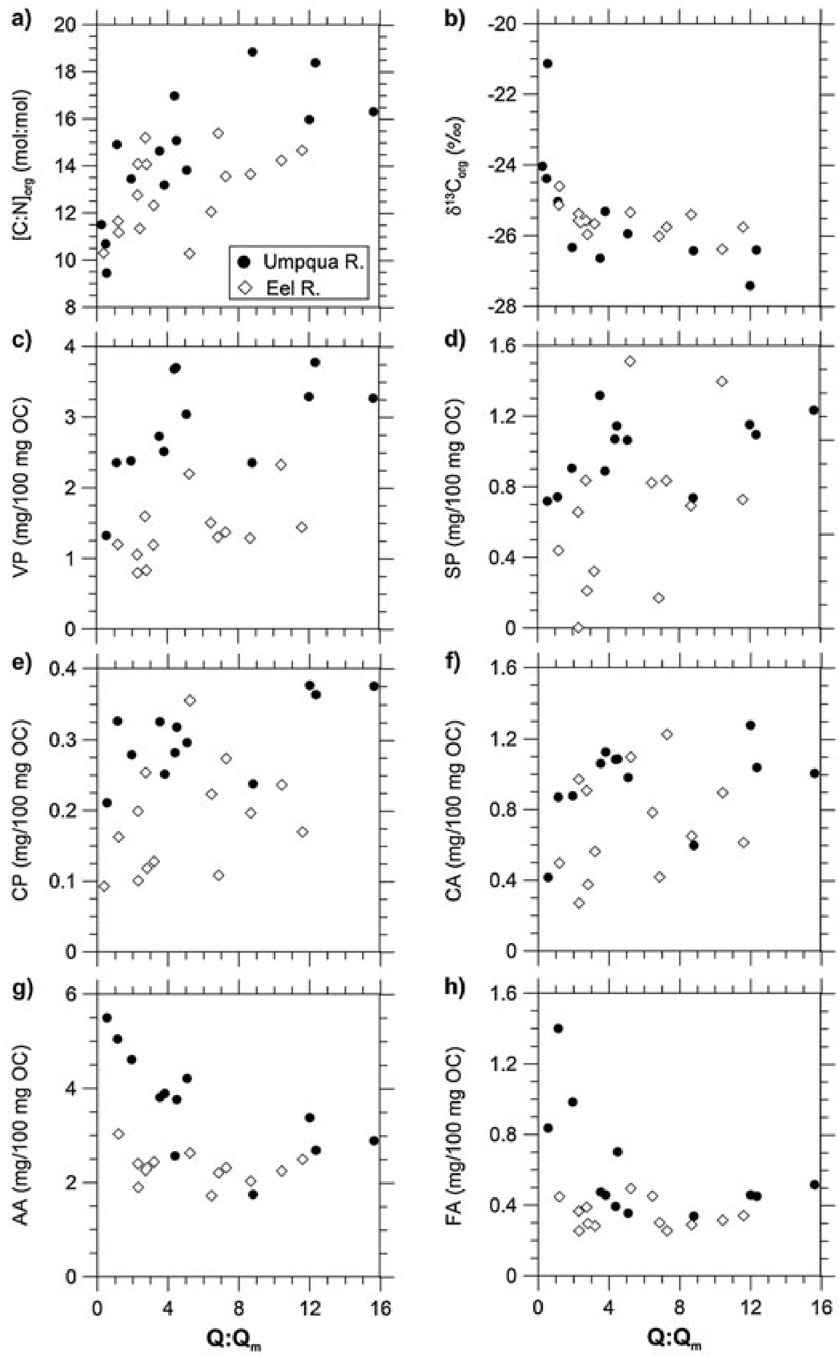


Figure 6. Plots of POM compositions as a function of discharge in the Umpqua and Eel Rivers. The abbreviations for each parameter are as in Tables 2 and 5.

However, in the Umpqua River, the annual yields of all particulate constituents were higher in WY09 than in WY08. The primary reason for this result was the large flood that occurred at the end of December 2008 (Q:$Q_m > 16$), which contributed a disproportionate fraction of the suspended load that year. In the case of the Eel River, whereas the water discharge in WY09 was ~0.7 of the amount in WY08, the yields of all particulate constituents in WY09 were significantly lower (0.3 to 0.5) than those in WY08. The reason for the contrast in water and particulate yields is that WY08 included four moderate floods (Q:$Q_m \geq 6$), whereas WY09 only had two (Figure 7). Again these data illustrate the importance of high-discharge events in the transport of particulate constituents in small mountainous rivers and underscore how utilizing annual averages can lead to incorrect estimates of total export to the ocean.

5.2. Factors Affecting SS and POM Yields

[37] It is useful to compare the magnitude of the estimated annual yields for different constituents between the two systems (Table 6). For example, during our study, the Umpqua and Eel Rivers displayed water yields that ranged between 570 and $750 \times 10^3\ m^3\ km^{-2}$ and between 430 and $550 \times 10^3\ m^3\ km^{-2}$, respectively. Despite the similarities in

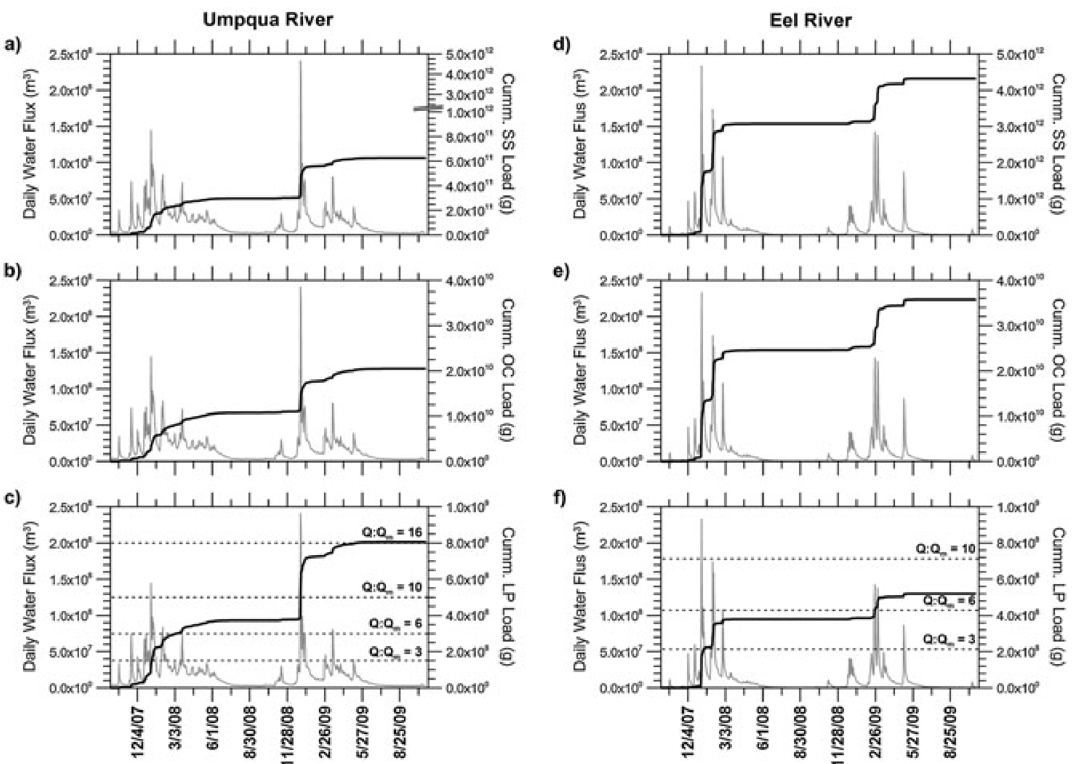


Figure 7. Cumulative loads (thick grey lines) of selected particulate constituents in the Umpqua and Eel Rivers estimated using rating curves in Table 3. The constituents graphed include (a, d) suspended solids, (b, e) organic carbon, and (c, f) lignin products. Also plotted in each graph is the daily water discharge (black lines) for each river during the 2 years of the study. Discharge levels relative to long-term mean are indicated in Figures 7c and 7 f.

Table 6. Annual Yields of Different Particulate Constituents for Each Water Year of the Study

	Umpqua River		Eel River	
Constituent	WY08	WY09	WY08	WY09
Water (10^3 m^3 km^{-2})	754	569	466	364
SS (ton km^{-2})	28	33	319	128
OC (ton km^{-2})	1.1	1.0	2.6	1.2
N (ton km^{-2})	0.10	0.08	0.11	0.05
CuO products				
VP (kg km^{-2})	27	29	20	8
SP (kg km^{-2})	10	10	13	5
CP (kg km^{-2})	2.9	3.1	2.6	1.2
LP (kg km^{-2})	40	43	36	15
CA(kg km^{-2})	9.1	10	11.6	5
AA (kg km^{-2})	43	35	28	14
FA (kg km^{-2})	6.4	5.4	4.0	1.9
DA (kg km^{-2})	4.0	3.4	2.8	1.3
PB (kg km^{-2})	7.7	6.5	4.7	2.3
BA (kg km^{-2})	4.1	3.9	3.6	1.6

Constituent codes as in Table 2. Details regarding the calculations are discussed in the text.

runoff, SS yields in the Eel system were significantly higher (5 to 10 times higher) than in the Umpqua, consistent with previous studies linking the geologic and tectonic characteristic of the Eel watershed to very high erosion rates and elevated SS concentrations [e.g., *Wheatcroft and Sommerfield*, 2005, and references therein]. The contrasts between these two small mountainous rivers are much less clear when one considers the yields of organic constituents (Table 6). For example, if we compare estimates from years of similar runoff (WY09 in the Umpqua and WY08 in the Eel), it is evident that the differences in the yields of most POM constituents between the two systems are much smaller than is the case for lithogenic sediment. Hence, while SS yields in the Eel system (~320 ton km^{-2}) are an order of magnitude higher than those in the Umpqua (~33 ton km^{-2}), the yields of OC (~2.6 ton km^{-2} versus ~1 ton km^{-2}, respectively) and N (~0.11 versus 0.08 ton km^{-2}, respectively) are much more comparable. Moreover, the yields of vegetation and non-vegetation biomarkers are basically the same between the two systems (Table 6), suggesting that although the Eel River exports more inorganic sediment (and bulk POM) per unit area of watershed than the Umpqua, biogenic organic materials are exported with similar efficiencies from both systems.

[38] The trends in yields for the two small mountainous rivers during years with comparable runoff indicate that the contrasts in geological and tectonic characteristics of the two drainage basins directly impact the export of inorganic sediments but appear to affect bulk POM and specific biogenic constituents to a much lesser degree. Elevated supply of sediment from the easily erodible, tectonically active Franciscan Formation in the Eel watershed explains the elevated yields of SS in this system relative to the Umpqua watershed, which has much lower uplift rates and is underlain in part by

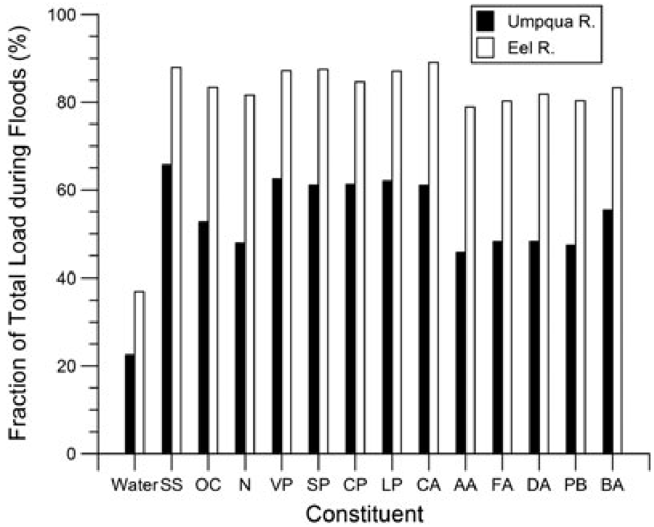


Figure 8. Contribution of flood days (Q:$Q_m > 3$) to the total load of different constituents over the 2 year study period. The abbreviations for each constituent are as in Table 2.

much less erodible volcanic bedrock. Because the Franciscan Formation is composed of sedimentary bedrock with significant amounts of petrogenic carbon [*Leithold and Blair*, 2001], the elevated POM yields in the Eel River are primarily due to contributions of this petrogenic carbon source to the overall suspended load. The depleted $\Delta^{14}C_{org}$ signatures of POM in the Eel samples support this explanation and are consistent with previous studies, which showed significant contributions of kerogen in sediments from the Eel River and related offshore depocenter [*Blair et al*., 2003; *Leithold et al*., 2006]. In contrast, the volcanic rocks that underlie roughly half of the Umpqua basin are much less erodible and contain no petrogenic carbon, thus explaining the lower SS yields and less depleted $\Delta^{14}C_{org}$ signatures in this system.

[39] Unlike SS and bulk POM, the similarity in the yields of vascular and non-vascular plant biomarkers between the Umpqua and Eel systems reflects the fact that bedrock sediments by definition do not contain any biogenic OM and hence do not contribute to the biomarker loads of the two rivers. Among vascular plant-derived biomarkers, some classes such as SP and CA display higher yields in the Eel River relative to the Umpqua River, whereas the opposite is true for compound classes such as VP (Table 6). These differences are consistent with vegetation contrasts between the two watersheds, with the higher abundance of angiosperm and non-woody vegetation (e.g., grass and brush) in the Eel drainage basin explaining the elevated yields of SP and CA and the predominance of conifers in the Umpqua watershed contributing to its elevated VP yields. A priori, despite the similarities in net primary productivity between the two watersheds, we would have predicted higher yields of vegetation-derived biogenic POM components from the Umpqua because of its more temperate conditions (i.e., lower microbial decay rates), thicker soils, and higher soil carbon inventories (Table 1). However, our results do not show such trend, suggesting instead that the elevated erosion rates in the Eel drainage basin may result in greater mobilization of biogenic POM from surface soils, making up for the lower soil carbon stocks in this basin.

[40] Studies of particulate transport by Taiwanese rivers show that biogenic (non-fossil) particulate organic carbon (POC) export scales with discharge and slope gradient in these mountainous subtropical watersheds [*Hilton et al*., 2012, and references therein]. However, in contrast to our findings, suspended sediment yields and biogenic POC yields in Taiwanese rivers were highly correlated. Notably, the annual SS yields (2000 to 100,000 ton km^{-2}) calculated for these rivers [*Hilton et al*., 2012] are much greater than our estimates for the Eel and Umpqua (~130–320 and 28–33 ton km^{-2}, respectively; Table 6). Hence, it is likely that the magnitude and type of erosion processes (e.g., overland flow, bedrock landslides, and mechanical attrition) acting on the landscape of Taiwanese watersheds are quite different than those processes (e.g., shallow landslides) responsible for the mobilization of sediment and biogenic POM from the two Pacific Northwest watersheds under the conditions encountered in this study. Further understanding of the controls that different erosional processes have on material export by rivers requires additional studies comparing watersheds with a broader combination of tectonic, geologic, hydroclimatic, and biogeochemical contrasts over longer periods.

5.3. POM Sources and Provenance

[41] The trends in specific yields discussed above and the compositions of POM in the suspended load from both rivers over a range of discharges provide significant insights into the sources of mobilized particles. In the Umpqua River, all evidence points towards a threshold in discharge (~Q:$Q_m > 3$), at which the load shifts from organic-rich particles likely derived from autochthonous sources, such as algae and macrophytes growing within or near the channel, to mineral-rich particles with a strong vegetation signature. The concentrations of all constituents increase with discharge indicating this threshold coincides with mobilization of materials from the watershed likely through shallow landslides that dominate fine-sediment transport in this region [e.g., *Roering et al*., 2003]. The compositions of lignin phenols and cutin acids (Table 7) in these materials show they originate from conifer-dominated vegetation but with significant inputs of non-woody angiosperm sources (Figures 9a and 9b). These findings are consistent with the observation that unlike the dense conifer forest that characterize stable regions of hillslopes, areas of frequent landslides are often vegetated by a mixture of conifers (e.g., Douglas-fir and Hemlock) and angiosperms (Bigleaf Maple, Red Alder, Vine Maple) [*Roering et al*., 2003], the latter of which are early successional species well adapted to disturbances [e.g., *Kennedy and Spies*, 2004]. POM collected at both low and elevated flows display relatively high lignin-derived acid:aldehyde ratios (0.81 ± 0.04), which are indicative of moderate degradative alteration and consistent with the intermediate weathering that characterizes most of the soils in the Umpqua watershed. The $\delta^{13}C$ and $\Delta^{14}C$ signatures (Figure 9c) suggest that the biogenic POM in this system has an average residence time of a few hundred years, consistent with the transit times of silts and clays mobilized from headwater valleys [e.g., *Lancaster and Casebeer*, 2007]. Based on these compositional trends, we infer that in the Umpqua River, most of the POM transported during the high-discharge events that characterized the 2007–2009 period originated from relatively young, surface soils mobilized during shallow landslides. There is no indication for significant input of materials from deeper soils

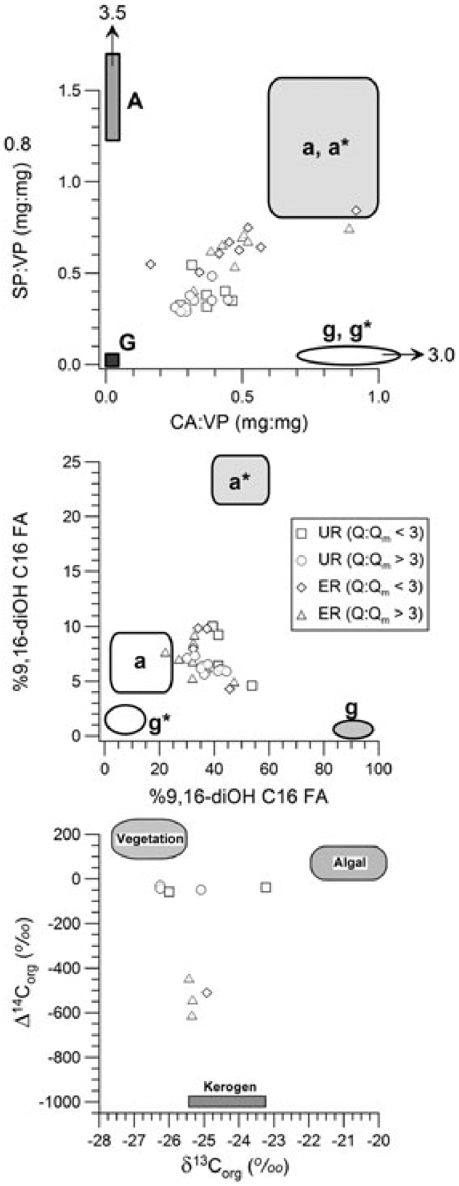


Figure 9. Plots illustrating compositional parameters of vegetation-derived biomarkers including (a) cutin acid:vanillyl phenol ratios (CA:VP) versus syringyl phenol:vanillyl phenol ratios (SP:VP); (b) percent abundances of two of the three isomers of dihydroxyhexadecanoic acids characteristic of cutin: %9,16-dihydroxyhexadecanoic fatty acids versus %8,16-dihydroxyhexadecanoic fatty acid; (c) radiocarbon ($\Delta^{14}C_{org}$) and stable carbon ($\delta^{13}C_{org}$) isotopic compositions of suspended POM in the fine fraction. The biomarker compositional ranges of vegetation sources are plotted in Figures 9a and 9b for reference. These include those of vegetation: (*G*) gymnosperm woods; (*g**) gymnosperm needles from firs/pines; (*g*) gymnosperm needles from redwoods, cedars, and sequoias; (*A*) angiosperm woods (*a*) angiosperm leaves; and (*a**) angiosperm grasses [*Hedges and Mann*, 1979; *Goñi and Hedges*, 1990; 1992; *Goñi and Thomas*, 2000]. The isotopic compositional ranges of organic carbon from non-vascular (i.e., algae), terrestrial (i.e., vegetation), and petrogenic sources (i.e., kerogen) in the Eel Basin [*Blair et al*., 2003; *Leithold and Blair*, 2001] are plotted in Figure 9c for reference.

and/or bedrock (Figure 9), which in this region may only be mobilized by infrequent, deep-seated landslides caused by large hydrologic and/or seismic events [e.g., *Roering et al*., 1999; 2005].

[42] In the case of the Eel River, the $\delta^{13}C$ and $\Delta^{14}C$ compositions are consistent with a significant contribution from bedrock sources (i.e., Franciscan Formation) to the overall POM loads. This petrogenic source, which is responsible for the much older ages of bulk OC (Figure 9c), is mixed with inputs from vascular plant-derived sources [e.g., *Blair et al*., 2003; *Leithold et al*., 2006]. The comparable yields of specific biomarkers from both the Umpqua and Eel watersheds (e.g., Table 6) and the trends in biomarker compositions (Figures 9a and 9b) suggest that the biogenic POM in the Eel River also originates from surface soils. For example, the vascular-plant biomarker signatures (e.g., SP:VP, CA:VP, and % diOH-C_{16}FA) of the Eel samples indicate a greater contribution from angiosperm, non-woody sources [e.g., *Hedges and Mann*, 1979; *Goñi and Hedges*, 1990; 1992] consistent with overall vegetation differences between the Eel and Umpqua drainage basins, and more specifically with the brush and grass vegetation that characterize landslide prone terrains in the Eel watershed. As was the case in the Umpqua, the Eel samples display relatively high lignin-derived acid:aldehyde ratios (0.75 ± 0.09) consistent with moderate degradation expected from the intermediate weathering conditions that characterize the Eel watershed. Thus, biogenic POM exported by the Eel River during our study period likely originates from shallow soils from steep, unstable regions of the watershed and is mixed with bedrock-derived sediment and associated petrogenic OC [e.g., *Blair et al*., 2003; *Leithold et al*., 2006].

[43] If we assume that the average $\Delta^{14}C$ composition of Umpqua samples (-44‰) is representative of the vegetation-derived OC from surface soils in the Eel basin and that the $\Delta^{14}C$ signature of bedrock OC is -1000‰, then we can estimate the relative contributions of biogenic and petrogenic POM in the Eel samples using isotopic mass balance [e.g., *Goñi et al*., 2005]. These calculations reveal that POM in the Eel River suspended load is composed of roughly equal fractions of aged biogenic OM (average age ~300 ybp) and ancient petrogenic OM. These estimates are comparable with the findings of *Blair et al*. [2003], who measured the $\Delta^{14}C$ compositions of clay fractions from selected soils, river particles, and coastal sediments from the Eel system. Our findings are also consistent with the ^{14}C signatures (approximately -50‰) and corresponding ages (~400 ypb) of vascular plant-derived fatty acids measured by *Drenzek et al*. [2009] in recently deposited shelf sediments. As we inferred from the temporal differences in SS loads (e.g., Figure 4 and Appendix D), it is likely that logging practices in the earlier part of the twentieth century and the geomorphic effects of the 1955 and 1964 floods resulted in a different makeup of the mobilized POM during earlier periods relative to present day.

[44] As discussed above, the lower sediment-normalized concentrations of all organic constituents in the Eel River are due to higher lithogenic inputs. However, it is surprising that unlike the Umpqua River, the enhanced contributions of mineral sediment in the Eel occur during both high and low flows (e.g., Figure 6). This behavior suggests that the Eel system contains abundant, mineral-rich materials derived

from bedrock that are readily mobilized at low discharges. A similar trend was observed in rivers draining Taiwan, where %OC of the suspended load was low and relatively invariant as a function of runoff [*Hilton et al.*, 2010]. In contrast, as is the case for other small mountainous rivers with lower sediment yields [e.g., *Coynel et al.*, 2005; *Leithold et al.*, 2006; *Hatten et al.*, 2012], the Umpqua River transports mineral-rich soil materials primarily during elevated flows. Examination of the river channels in the Umpqua and Eel systems reveal that whereas the former is relatively devoid of fine sediments [*Wallick et al.*, 2011], the latter includes many sediment-choked stretches that most likely contribute inorganic particles at all flows. In that respect, the Eel River may be considered a transport limited stream, where the supply of mineral-rich, fine sediment is extremely high due to the geologic and tectonic characteristics of the watershed, overwhelming the transport capacity of the system that is characterized by relatively infrequent high flows. In wetter systems like the Umpqua, river channels are active throughout the year, resulting in little storage of fine-grained sediment. As a result, at low flows, there is little contribution from mineral-rich particle sources, which only become significant once a threshold in discharge is crossed. Because both rivers exhibit concentrations of biogenic components that increase exponentially with discharge once this threshold is achieved, there appears to be no supply limitation when it comes to mobilization of materials derived from surface soils, at least in the discharge ranges observed in this study.

5.4. Summary of Biogeochemical Implications

[45] Our findings allow several inferences regarding the role of small mountainous rivers in global/regional POM transport. For example, basin-wide tectonic/geologic factors appear important in determining the magnitude of the SS and petrogenic POM loads but play a lesser role in controlling the load of biogenic POM. Vegetation and soil processes in erosion-prone regions of drainage basins appear to directly affect the composition of biogenic POM exported by small mountainous rivers. Although only representing a small fraction (0.2 to 0.6 %) of the total net primary productivity in both watersheds, the annual export of biogenic particulate OC and N by the Umpqua and Eel Rivers (~10,000 tons C and ~1000 tons N) is significant if one consider regional coastal carbon budgets [e.g., *Alin et al.*, 2012].

[46] To upscale the measurements from specific watersheds to the whole Pacific Northwest margin (36°N to 48°N) and provide a first-order estimate of terrigenous POM fluvial flux, we can multiply the POC yield of representative systems by the combined watershed area (97,688 km^2) of all the small mountainous rivers along northern California, Oregon, and Washington (Figure 1). Comparison of data from the three systems we have studied to date (Alsea, Umpqua, and Eel Rivers) shows that annual POC yields range from 3.8 tons C km^{-2} yr^{-1} (Alsea River in WY07) [*Hatten et al.*, 2012] to 1.0 to 2.6 tons C km^{-2} y^{r-1} (Table 6) giving an estimate of total POC flux of 0.1 to 0.4 Tg C yr^{-1}. Such simple calculation ignores inter-annual runoff variability and assumes the yields obtained from our 2 year study are representative of other years and rivers. Nevertheless, this type of estimate represents a first for this region of North America, where fluvial inputs of terrigenous carbon from other sources besides major, continental rivers (e.g., Columbia and Fraser) have been poorly constrained [e.g., *Alin et al.*, 2012]. As a contextual comparison, previous estimates of total fluvial POC fluxes along the North Pacific margin (8°N to 45°N) range from 0.3 to 2.4 Tg C yr^{-1} [*Alin et al.*, 2012] and the total flux of CO_2 across air-sea interface from the coastal region is ~2 Tg C yr^{-1} [*Chavez et al.*, 2007]. Although there are huge uncertainties and natural variability in these estimates, they suggest that small mountainous rivers play an important role in the biogeochemistry of this coastal margin that extends beyond sediment inputs [e.g., *Inman and Jenkins*, 1999; *Wheatcroft and Sommerfield*, 2005] and includes allochthonous fluxes of organic matter [*this study*; *Hastings et al.*, 2012], nutrients [*Wetz et al.*, 2006], and trace metals [*Roy et al.*, 2013].

[47] The vast majority of the transport by small mountainous rivers along the Pacific Northwest coast of the US occurs during short-lived, high-discharge events that occur during winter storms (i.e., Figure 1) [*this study*; *Ralph et al.*, 2006]. Consequently, inter-annual variability in the frequency and magnitude of these storms has a disproportionate effect on regulating POM export to the ocean. These rivers display high coherence between flood-producing storms and physical conditions in the coastal ocean [e.g., *Kniskern et al.*, 2011]. Because this coherence facilitates focused deposition of particles in deeper regions of the shelf (i.e., depocenters), high-discharge events also are likely to be key to efficient burial of POM [e.g., *Wheatcroft et al.*, 2010; *Hastings et al.*, 2012]. Therefore, compared to larger rivers, where elevated flows are not coherent with coastal ocean condition [e.g., *Allison et al.*, 2000; *Jian et al.*, 2009], small mountainous rivers may account for a disproportionally high fraction of the global organic carbon burial, both by contributing significant inputs of terrigenous POM and facilitating the preservation of autochthonous POM due to elevated sediment accumulation rates [e.g., *Dunne et al.*, 2007].

Appendix A: Frequency Analysis of Long-Term Discharge (Q) USGS Records

Discharge Range (m^3 s^{-1})	Q/Qm	mi (#events)	Mi (events > mi)	Exceed. Freq F(Mi)	τ_r (years)
Umpqua River Discharge at Elkton (1905–2007)					
0 to 20	0.10	64	37,241	1.00	0.0027
21 to	30 0.14	3566	33,675	0.90	0.0030

(Continues)

Appendix A. (Continued)

31 to 40	0.19	6019	27,656	0.74	0.0037
41 to 50	0.24	2806	24,850	0.67	0.0041
51 to 60	0.29	1474	23,376	0.63	0.0044
61 to 70	0.34	1128	22,248	0.60	0.0046
71 to 80	0.38	954	21,294	0.57	0.0048
81 to 90	0.43	887	20,407	0.55	0.0050
91 to 100	0.48	864	19,543	0.52	0.0052
101 to 200	0.96	7355	12,188	0.33	0.0084
201 to 400	1.9	7145	5043	0.14	0.020
401 to 600	2.9	2615	2428	0.065	0.042
601 to 800	3.8	1023	1405	0.038	0.073
801 to 1000	4.8	514	891 0	024	0.11
1001 to 2000	9.6	731	160	0.0043	0.64
2001 to 3000	14	120	40	0.0011	2.6
3001 to 4000	19	24	16	0.00043	6.4
4001 to 5000	24	12	4	0.00011	26
5001 to 6000	29	3	1	0.00003	102
6001 to 7000	34	0	1	0.00003	102
7001 to 8000	38	1	0	0.00000	n.a.
8001 to 9000	43	0	0	n.a.	n.a.
Eel River Discharge at Scotia (1910–2007)					
0 to 20	0.096	14,789	20,483	0.58	0.0047
21 to 30	0.14	1623	18,860	0.53	0.0051
31 to 40	0.19	1237	17,623	0.50	0.0055
41 to 50	0.24	973	16,650	0.47	0.0058
51 to 60	0.29	866	15,784	0.45	0.0061
61 to 70	0.34	783	15,001	0.43	0.0064
71 to 80	0.38	757	14,244	0.40	0.0068
81 to 90	0.43	706	13,538	0.38	0.0071
91 to 100	0.48	637	12,901	0.37	0.0075
101 to 200	0.96	4429	8472	0.24	0.011
201 to 400	1.9	3895	4577	0.13	0.021
401 to 600	2.9	1566	3011	0.085	0.032
601 to 800	3.8	824	2187	0.062	0.044
801 to 1000	4.8	549	1638	0.046	0.059
1001 to 2000	9.6	1101	537	0.015	0.18
2001 to 3000	14	316	221	0.0063	0.44
3001 to 4000	19	119	102	0.0029	0.95
4001 to 5000	24	45	57	0.0016	1.7
5001 to 6000	29	28	29	0.00082	3.3
6001 to 7000	34	9	20	0.00057	4.8
7001 to 8000	38	10	10	0.00028	9.7
8001 to 9000	43	5	5	0.00014	19
9001 t o 10000	48	1	4	0.00011	24
10001 to 20000	96	3	1	0.00003	97

Q/Q_m, ratio of the maximum discharge in each range bin to the long-term man discharge; mi, number of events within each discharge range; Mi, number of events above each discharge range; Exeed. Freq., frequency of discharge exceeding a given level; τ_r, return period (years) for an event exceeding a given discharge range.

Appendix B: Long-Term* Monthly Mean Discharge (Q) in $m^3 s^{-1}$

Month	Umpqua		Eel	
	Avg	s.d.	Avg	s.d.
Long-Term* Monthly Mean Discharge (Q) in $m^3 s^{-1}$				
Jan	455	242	568	459
Feb	422	192	563	414
Mar	344	149	406	273
Apr	268	109	253	199
May	183	81	107	79
Jun	105	51	36	33
Jul	48	19	10	5
Aug	33	7	4	2
Sep	34	9	4	3
Oct	52	43	18	45
Nov	196	156	137	202
Dec	384	275	410	435
Fraction of annual Q (%)				
Jan	18	8	22	14
Feb	17	7	22	12

(Continues)

Appendix B. (Continued)

Month	Umpqua		Eel	
	Avg	s.d.	Avg	s.d.
Mar	14	5	17	10
Apr	11	4	10	6
May	7	3	4	3
Jun	4	2	2	2
Jul	2	1	0	0
Aug	1	0	0	0
Sep	1	0	0	0
Oct	2	1	1	2
Nov	8	6	6	8
Dec	15	9	16	15

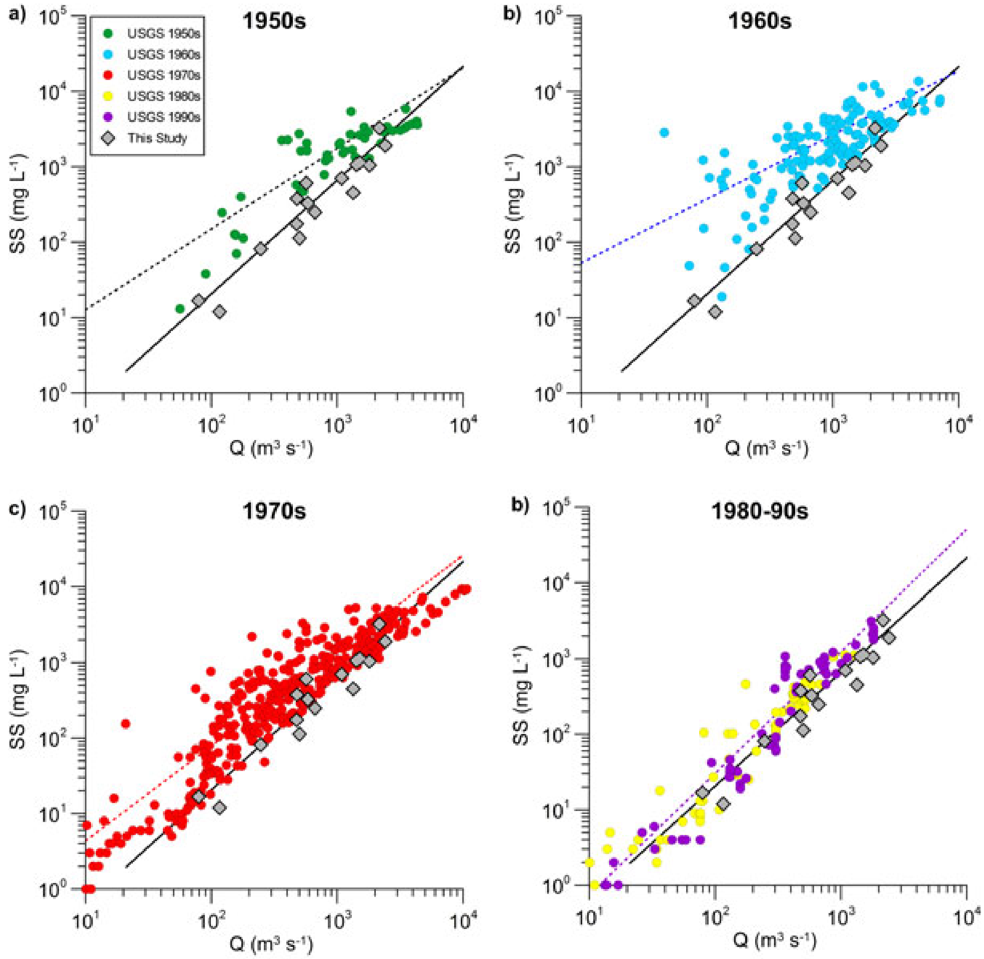
Source: USGS gauging records.
*Umpqua data are from 1905 to 2007; Eel data are from 1910 to 2007.

Appendix C: Monthy Mean Discharges ($m^3\,s^{-1}$) During Study Period

	Umpqua River		Eel River	
WY08	Avg	s.d.	Avg	s.d.
Oct	76	73	20	33
Nov	160	193	12	5
Dec	359	226	183	178
Jan	548	372	596	559
Feb	420	181	553	505
Mar	358	142	170	43
Apr	238	42	98	11
May	258	57	64	17
Jun	148	47	17	9
Jul	55	15	5	1
Aug	37	1	2	0
Sep	35	1	2	0
WY09				
Oct	40	4	5	2
Nov	124	78	26	18
Dec	329	654	112	155
Jan	421	274	116	75
Feb	189	120	362	401
Mar	361	173	397	345
Apr	227	59	75	28
May	182	82	178	226
Jun	77	20	26	10
Jul	39	11	6	2
Aug	33	2	3	1
Sep	33	1	1	1

Source: USGS gauging records.

Appendix D:



Rating Curve Parameters for Eel River Suspended Sediments (lnSS = $\beta_o + \beta_1 \times \ln Q + e$)

Parameter	1950s	1960s	1970s	1980-90s	This Study
β_0	-0.14 ± 0.62	1.73 ± 0.44	-1.72 ± 0.17	-4.22 ± 0.22	-4.04 ± 0.81
β_1	1.07 ± 0.091	0.85 ± 0.065	1.26 ± 0.028	1.61 ± 0.040	1.51 ± 0.12
e	0.23	0.29	0.29	0.20	0.11
r^2	0.76	0.57	0.85	0.92	0.92

Appendix E: Chemical and Isotopic Compositions of POM From Both Rivers

Q	Q:Q_m	$\delta^{13}C_{org}$	$\Delta^{14}C_{org}$*	^{14}C age*	[C:N]$_{org}$	VP	SP	CP	CA	BA	PB	AA	FA	DA
($m^3 s^{-1}$)		(‰)	(‰)	(ybp)	(molar)	(mg 100/mg OC)								
Umpqua River														
54	0.3	−24.0	*n.m.*	*n.m.*	12	1.30	0.42	0.11	0.35	0.28	0.87	4.93	0.51	0.42
101	0.5	−24.4	*n.m.*	*n.m.*	11	0.98	0.39	0.12	0.43	0.34	0.98	4.97	0.71	0.65
115	0.5	−21.1	*n.m.*	*n.m.*	9	1.32	0.72	0.21	0.42	0.32	0.96	5.50	0.84	0.38
123	0.6	−23.1	−38	255	10	1.48	0.52	0.15	0.69	0.36	0.70	5.80	0.39	0.43
235	1.1	−25.0	*n.m.*	*n.m.*	15	2.35	0.74	0.33	0.87	0.24	0.87	5.04	1.40	0.46
404	1.9	−26.3	−59	425	13	2.38	0.90	0.28	0.88	0.36	0.79	4.61	0.98	0.30
736	3.5	−26.6	*n.m.*	*n.m.*	15	2.73	1.32	0.33	1.06	0.44	0.57	3.81	0.47	0.24
793	3.7	−25.3	−49	350	13	2.51	0.89	0.25	1.13	0.41	0.62	3.89	0.46	0.33
912	4.3	−26.5	*n.m.*	*n.m.*	17	3.68	1.07	0.28	1.08	0.38	0.59	2.57	0.39	0.27
934	4.4	−26.5	*n.m.*	*n.m.*	15	3.70	1.14	0.32	1.09	0.52	0.94	3.76	0.70	0.41
1058	5.0	−26.0	*n.m.*	*n.m.*	14	3.04	1.06	0.30	0.98	0.39	0.54	4.21	0.35	0.37
1832	8.6	−26.4	−30	190	19	2.35	0.74	0.24	0.60	0.22	0.35	1.75	0.34	0.22
2500	11.8	−27.4	*n.m.*	*n.m.*	16	3.29	1.15	0.38	1.28	0.43	0.60	3.38	0.46	0.34

(Continues)

Appendix E. (Continued)

Q (m^3 s^{-1})	Q:Q_m	$\delta^{13}C_{org}$ (‰)	$\Delta^{14}C_{org}$* (‰)	^{14}C age* (ybp)	$[C:N]_{org}$ (molar)	VP (mg 100/mg OC)	SP	CP	CA	BA	PB	AA	FA	DA
2574	12.1	−26.4	*n.m.*	*n.m.*	18	3.77	1.10	0.36	1.04	0.41	0.53	2.69	0.45	0.30
3256	15.4	−26.4	−44	305	16	3.26	1.23	0.37	1.01	0.44	0.62	2.89	0.52	0.36
Eel River														
79	0.4	−25.5	*n.m.*	*n.m.*	10	0.85	0.53	0.17	0.41	0.29	0.52	3.26	0.37	0.26
116	0.6	−24.6	*n.m.*	*n.m.*	11	1.01	0.56	0.19	0.17	0.30	0.79	5.44	0.71	0.30
247	1.2	−25.1	−510	5670	12	1.21	0.73	0.16	0.50	0.29	0.38	3.05	0.45	0.24
476	2.3	−25.6	*n.m.*	*n.m.*	13	1.06	0.89	0.20	0.97	0.26	0.43	2.42	0.37	0.23
480	2.3	−25.4	*n.m.*	*n.m.*	14	0.80	0.40	0.10	0.27	0.18	0.23	1.91	0.26	0.16
503	2.4	-25.6	*n.m.*	*n.m.*	11	1.45	1.08	0.26	0.75	0.42	0.56	3.00	0.51	0.30
568	2.7	−25.6	*n.m.*	*n.m.*	15	1.60	1.03	0.25	0.91	0.35	0.42	2.27	0.39	0.24
583	2.8	−26.0	*n.m.*	*n.m.*	14	0.84	0.56	0.12	0.38	0.24	0.28	2.33	0.30	0.19
665	3.2	−25.6	*n.m.*	*n.m.*	12	1.20	0.64	0.13	0.57	0.24	0.30	2.45	0.29	0.21
1086	5.2	−25.3	*n.m.*	*n.m.*	10	2.20	1.54	0.36	1.10	0.40	0.50	2.64	0.50	0.28
1339	6.4	−24.2	*n.m.*	*n.m.*	12	1.51	1.02	0.22	0.79	0.27	0.34	1.74	0.46	0.17
1424	6.8	−26.0	−610	7510	15	1.31	0.53	0.11	0.42	0.22	0.35	2.22	0.30	0.22
1514	7.3	−25.7	*n.m.*	*n.m.*	14	1.38	1.03	0.27	1.23	0.30	0.43	2.33	0.26	0.21
1801	8.7	−25.4	*n.m.*	*n.m.*	14	1.29	0.92	0.20	0.65	0.28	0.34	2.05	0.29	0.18
2166	10.4	−26.4	−444	4660	14	2.33	1.45	0.24	0.90	0.29	0.43	2.26	0.32	0.25
2410	11.6	−25.7	−542	6210	15	1.45	0.95	0.17	0.62	0.29	0.35	2.51	0.34	0.24

$\delta^{13}C_{org}$, stable isotopic composition of OC; $\Delta^{14}C_{org}$, radiocarbon composition of OM in fine fraction*; ^{14}C age, radiocarbon age of fine fraction in years before present; $[C:N]_{org}$, molar C:N ratios of OM; n.m., not measured. All other abbreviations as in previous tables. Shaded rows indicate samples with Q:$Q_m < 3$.

Appendix F: Percentages of Total Annual Fluxes of Different Constituents Contributed During Winter Months (November–April) in Both Rivers

	Winter Months			
	Umpqua		Eel	
Constituent	WY08	WY09	WY08	WY09
Water	78	80	94	82
SS	94	98	100	88
OC	90	95	100	88
N	89	94	100	88
VP	93	97	100	88
SP	92	97	100	88
CP	93	97	100	88
LP	93	97	100	88
CA	92	97	100	88
AA	88	93	100	87
FA	89	94	100	87
DA	89	94	100	88
PB	89	93	100	87
BA	91	96	100	88

All captions as in previous tables.

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