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Christina R. Pondell
Virginia Institute of Marine Science

Elizabeth A. Canuel
Virginia Institute of Marine Science

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RESEARCH

Multi-Biomarker Analysis for Identifying Organic Matter Sources in Small Mountainous River Watersheds: A Case Study of the Yuba River Watershed

Christina R. Pondell,^{1*} Elizabeth A. Canuel¹

ABSTRACT

Organic matter in soils and sediments derives from a mixture of biological origins, often making it difficult to determine inputs from individual sources. Complicating the determination of source inputs to soil and sedimentary organic matter (OM) is the fact that physical and microbial processes have likely modified the initial composition of these sources. This study focused on identifying the composition of watershed-derived OM to better understand inputs to inland waters and improve our ability to resolve between terrigenous and aquatic sources in downstream systems, such as estuaries and coasts. We surveyed OM sources from the Yuba River watershed in northern California to identify specific biomarkers that represent aquatic and terrigenous OM sources. Multiple classes of organic proxies—including sterols, fatty acids (FA), lignin phenols and stable carbon and nitrogen isotope values ($\delta^{13}\text{C}$,

$\delta^{15}\text{N}$)—were measured in soils, vegetation, charcoal, and freshwater plankton to characterize representative source endmembers. Sterols—including 27-nor-24-cholesta-5,22-dien-3 β -ol, cholesta-5,22-dien-3 β -ol, 24-methylcholesta-5,22-dien-3 β -ol and cholesta-5-en-3 β -ol, and positive $\delta^{15}\text{N}$ values—were associated with aquatic OM (plankton, suspended particulate OM), whereas lignin phenols, long chain FA, and diacids characterized terrigenous sources (soils, charcoal, vegetation). Trends in organic carbon and biomarker signatures in soil samples showed a response to environmental disturbance (i.e., mining, agriculture) through an inverse relationship between OM content and land use. Results from this study demonstrate the utility of multi-biomarker studies for distinguishing between OM from different sources and land uses, offering new insights for biogeochemical studies in aquatic systems.

KEY WORDS

Organic carbon, sterol, fatty acid, lignin, stable carbon and nitrogen isotopes, Yuba River

INTRODUCTION

Human land use—including deforestation, agriculture and urbanization—strongly modifies terrestrial landscapes by changing the amounts

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* Corresponding author: cpondell@vims.edu

¹ Virginia Institute of Marine Science
College of William & Mary
Gloucester Point, VA 23062 USA

and types of vegetation, altering nutrient loadings, and increasing soil erosion and exposure to weathering processes (Regnier et al. 2013; Bauer et al. 2013). In addition to these anthropogenic stressors, climate transforms the terrestrial landscape through drought, flooding, and wildfires, changing the composition and quantity of terrestrial organic matter (OM) (e.g., Harjung et al. 2019; Walker et al. 2019). Many studies focus on describing OM in coastal landscapes such as estuaries and the land–ocean margin, where human activities have contributed to profound ecosystem changes (e.g., Zimmerman and Canuel 2002; Lotze et al. 2006). However, there is considerable uncertainty regarding OM cycling in aquatic inland systems such as lakes and reservoirs, particularly those in mountainous regions (Butman et al. 2018), which limits the understanding of carbon cycling in lakes, rivers, and streams (Butman et al. 2018). As a result, the connectivity between OM composition in the watershed and what is transferred to downstream depositional settings needs to be understood.

The ability to deconvolute OM sources in lake and river systems is augmented by understanding the signatures of OM in the watershed, and how these signatures are modified during long- and short-term storage as material travels downstream. This study focused on identifying the signatures of organic carbon (OC) from a variety of watershed sources to a small, mountainous river and its associated impounded lake. To characterize OC sources, we used a variety of biomarker compounds—molecules whose origin can be linked to a specific organic source—that have been used successfully in many aquatic and marine environments (Bianchi and Canuel 2011). Lipid biomarkers have been identified for different OM sources, including short chain fatty acids and sterols like 24-methylcholesta-5,22-dien-3 β -ol (brassicasterol), which are indicative of microalgae (Volkman 1986; Zimmerman and Canuel 2002), and branched fatty acids and specific amino acids of bacterial origin (Canuel and Martens 1993; Veuger et al. 2007). Similarly, lignin phenols have proven to be effective tools for quantifying terrestrial inputs to marine environments (e.g., Hedges and Mann 1979;

Houel et al. 2006; Blair and Aller 2012), fecal sterols (e.g., coprostanol) have been used to trace wastewater effluent and human contamination (Eganhouse and Sherblom 2001; Carreira et al. 2015; Reichwaldt et al. 2017), and lipid biomarkers have been used to determine the contribution of terrestrial and marine OM sources along the estuarine salinity gradient (Canuel 2001; Waterson and Canuel 2008; Freymond et al. 2018).

Of the studies that have used biomarkers to investigate OM in terrestrial landscapes and inland waters, a common strategy has been to focus on one class of biomarkers to understand the origin and/or response of a particular source of OM to an outside influence, such as human land use or climate change. Ouellet et al. (2009), for example, used lignin to demonstrate the importance of terrigenous OM as a vector for mercury from watersheds to lakes, and Van Metre et al. (1997) used organochlorine compounds to trace historic declines in water quality in reservoirs adjacent to human population centers. Although single biomarker classes have proven useful in ecosystems where few sources of OM dominate, multi-biomarker approaches have been more successful in resolving OM sources in complex systems (e.g., Goñi et al. 1998; Yunker et al. 2005; Canuel and Hardison 2016). For example, using lipid biomarker and stable isotope data, He et al. (2014) were able to identify three different sources of OM (terrestrial plants, estuarine, and marine diatoms) to the Shark River Estuary in south Florida, and quantify the contribution of each OM source to the surface sediments from the estuary. Overall, multi-proxy studies have advanced the understanding of ecosystem responses to various stressors by allowing for the identification of multiple OM sources, and tracing temporal and spatial changes in these sources (e.g., Waterson and Canuel 2008; Canuel et al. 2017).

One limitation of using biomarkers in inland aquatic systems is that OM sources are influenced by a wide range of watershed variables (e.g., land use, vegetation, elevation, and lithology; Glendell et al. 2018), and biomarkers typically used to identify aquatic or terrigenous OM sources in estuaries and coastal ecosystems may

not be transferable to inland aquatic systems (Derrien et al. 2017; Li et al. 2018). This study characterized the biomarker composition of some of the representative OM sources to a lake from its watershed in northern California to identify the source signatures of watershed derived organic matter, and compared these watershed signatures to OM composition from surface sediments in Englebright Lake to describe the relative contribution of the representative OM sources to the lake OM deposition. Sterols, fatty acids, lignin, and stable carbon and nitrogen isotope values of vegetation, soil, charcoal, and freshwater plankton were examined because these biomarker compounds have often been used to identify OM sources in coastal ecosystems. The biomarker composition of these materials was then used to distinguish between aquatic and terrigenous OM sources in surface sediments collected from Englebright Lake CA, contributing to an improved understanding of watershed controls on the sources of OM to this lake.

Study Site

Englebright Lake and the Yuba River watershed, located in the Sierra Nevada mountain range in northern California, were chosen as the study sites because their ecologic setting and history of human impact provide a variety of OM sources across a range of degradation states. The Yuba River drains a 3,470-km² watershed and includes three tributaries: the North Yuba River, Middle Yuba River and South Yuba River. These three tributaries converge at Englebright Lake, the downstream extent of the upper Yuba River watershed (Figure 1). The Yuba River watershed experiences a Mediterranean climate, with hot, dry summers, and precipitation occurring primarily between October and April. River discharge is controlled by winter storms and spring snowmelt. The headwaters of the Yuba River and its tributaries lie at elevations greater than 2,780 m where the soils exhibit minimal horizon development or are of volcanic origin (Staff 2013). At these elevations, the dominant vegetation is mixed conifer forest, dominated by Ponderosa pine and Douglas fir. At lower elevations in the watershed, soils become more developed and fertile, and the vegetation

cover changes to oak woodlands and chaparral communities. The upper Yuba River watershed has a population of approximately 16,000 people, and only 1.6% of the watershed is considered urban (Friedl et al. 2010). Forest and woodland land cover dominate the upper Yuba River watershed, and recent human activities in the watershed include logging (Curtis et al. 2006), dam construction (James 2005), and agriculture, including rangeland, cropland, and vineyards (Federal 2000). Additionally, during the mid 19th century, the upper Yuba River watershed was heavily affected by hydraulic mining for gold (Wright and Schoellhamer 2004; James 2005), which contributed to high sediment yields in the upper Yuba River (Gilbert 1917) and high rates of sediment accumulation (6 to 145 cm year⁻¹) in Englebright Lake (Pondell et al. 2015).

METHODS

Sample Collection

A total of 37 samples were collected throughout the upper Yuba River watershed in July 2011 and July 2012 to characterize representative sources of OM (Table 1; Figure 1). Sampling focused on collecting plants and soils from the ecoregions described above, including conifer, oak woodland, and chaparral. Soil and plant samples were also collected to represent the various human impacts in the watershed, including agriculture (rangeland, cropland, and vineyards), hydraulic mining, and from roadsides in the watershed. A common occurrence in this region—and one that is expected to increase with climate change—is forest fires, so samples were collected at two sites that had experienced fire within the 2 years before samples were collected. The final set of samples was collected from Englebright Lake and its periphery. Samples included fresh vegetation, leaf litter and bark, charcoal samples from recent forest fire sites, soils, plankton, algae, and suspended particulate matter from lake water (Table 1). Because the dominant bedrock material in the Yuba River watershed is of volcanic or granitic origin (Staff 2013), it was assumed that contributions of OM from bedrock sources would be minimal (Raymond and Bauer 2001; Ishikawa et al. 2015). For these reasons, this source was not included in this study.

Table 1 Description and location of samples collected from the upper Yuba River watershed. The IDs are assigned based on the type of OM source represented by each sample collected from the watersheds of the North Yuba River (NYR), Middle Yuba River (MYR), South Yuba River (SYR), and Englebright Lake. In these samples, MS = mining soils, RS = roadside soils, FS = forest soils, SS = subsurface soils, AS = agricultural soils, CC = charcoal, V = vegetation, PL = plankton, POM = particulate matter collected from lake water, and ALG = algal biofilm. The Munsell Soil Color is reported *in parentheses* in the description for all soil samples.

ID	Type	Latitude	Longitude	Description
Soil samples				
MS1	Mining	39° 22' 13"N	120° 59' 50"W	North Columbia Mine (10YR 7/2)
MS2	Mining	39° 22' 00"N	120° 55' 32"W	Malakoff Diggins SHP ^a (2.5Y 7/2)
SS1	Subsurface	39° 14' 36"N	121° 15' 19"W	Roadside outcrop (10YR 5/6)
SS2	Subsurface	39° 23' 50"N	121° 08' 00"W	Lakeside outcrop (10YR 5/6)
RS1	Road-side, Mesic	39° 22' 11"N	121° 06' 17"W	North San Juan (2.5Y 4/4)
RS2	Road-side, Mesic	39° 19' 13"N	120° 33' 54"W	HWY 80 construction Site (2.5Y 3/3)
RS3	Road-side, Frigid	39° 20' 03"N	120° 24' 12"W	Donner Summit PUD ^b (2.5Y 3/3)
RS4	Road-side, Frigid	39° 33' 57"N	120° 38' 09"W	Sierra City (2.5Y 5/3)
RS5	Road-side, Mesic	39° 33' 36"N	120° 49' 43"W	Downieville (2.5Y 6/3)
AS1	Agriculture	39° 14' 53"N	121° 16' 32"W	Rangeland (7.5YR 4/4)
AS2	Agriculture	39° 22' 17"N	121° 04' 22"W	Organic farm (7.5YR 4/3)
AS3	Agriculture	39° 20' 21"N	121° 03' 25"W	Vineyard (10YR 4/4)
AS4	Agriculture	39° 20' 20"N	121° 03' 19"W	Vineyard (10YR 4/3)
FS1	Forest	39° 24' 28"N	120° 58' 11"W	MYR watershed (7.5Y 3/3)
FS2	Forest	39° 22' 24"N	120° 46' 18"W	SYR watershed (2.5Y 6/2)
FS3	Forest	39° 23' 55"N	121° 07' 57"W	NYR watershed (7.5YR 5/6)
Charcoal samples				
CC1	Charcoal	39° 23' 55"N	121° 07' 57"W	Litter, natural forest fire site
CC2	Charcoal	39° 14' 56"N	121° 17' 11"W	Litter, controlled fire site
Vegetation samples				
V1	Gymnosperm	39° 22' 24"N	120° 46' 18"W	<i>Pseudotsuga menziesii</i> (Douglas Fir)
V2	Gymnosperm	39° 22' 24"N	120° 46' 18"W	<i>Pinus lambertiana</i> (Sugar Pine), fresh needles
V3	Gymnosperm	39° 22' 24"N	120° 46' 18"W	<i>Pinus lambertiana</i> (Sugar Pine), needle litter
V4	Angiosperm, Monocot	39° 14' 53"N	121° 16' 32"W	<i>Bromus secalinus</i> (Chess Brome)
V5	Angiosperm, Monocot	39° 14' 28"N	121° 15' 51"W	<i>Juncus effusus</i> (Common Rush)
V6	Angiosperm, Eudicot	39° 14' 53"N	121° 16' 32"W	<i>Trifolium hirtum</i> (Rose Clover)
V7	Angiosperm, Eudicot	39° 14' 53"N	121° 16' 32"W	<i>Linum bienne</i> (Narrow Leaf Flax)
V8	Angiosperm, Eudicot	39° 23' 55"N	121° 07' 57"W	<i>Quercus chrysolepis</i> (Canyon Oak)
V9	Angiosperm, Eudicot	39° 14' 28"N	121° 15' 51"W	<i>Scutellaria galericulata</i> (Marsh Skullcap)
V10	Fern	39° 23' 55"N	121° 07' 57"W	<i>Pteridium aquilinum</i> (Western Bracken Fern)
V11	Moss	39° 14' 28"N	121° 15' 51"W	<i>Leskeella nervosa</i> (Leskeella moss)
V12	Bark	39° 23' 55"N	121° 07' 57"W	Mixed bark samples
Aquatic samples				
PL1	Plankton	39° 14' 28"N	121° 15' 52"W	26 ft vertical tow in Englebright Lake
PL2	Plankton	39° 16' 33"N	121° 13' 20"W	26 ft vertical tow in Englebright Lake
PL3	Plankton	39° 17' 39"N	121° 12' 40"W	30 s tow in 1.9 m ³ s ⁻¹ current
POM1	POM	39° 14' 28"N	121° 15' 52"W	Filtered through 0.7 μm filter
POM2	POM	39° 16' 33"N	121° 15' 40"W	Filtered through 0.7 μm filter
POM3	POM	39° 17' 39"N	121° 12' 40"W	Filtered through 0.7 μm filter
ALG	Algae	39° 14' 26"N	121° 16' 02"W	Algae biofilm scraped from dock

a. State Historic Park.

b. Public Utility District.

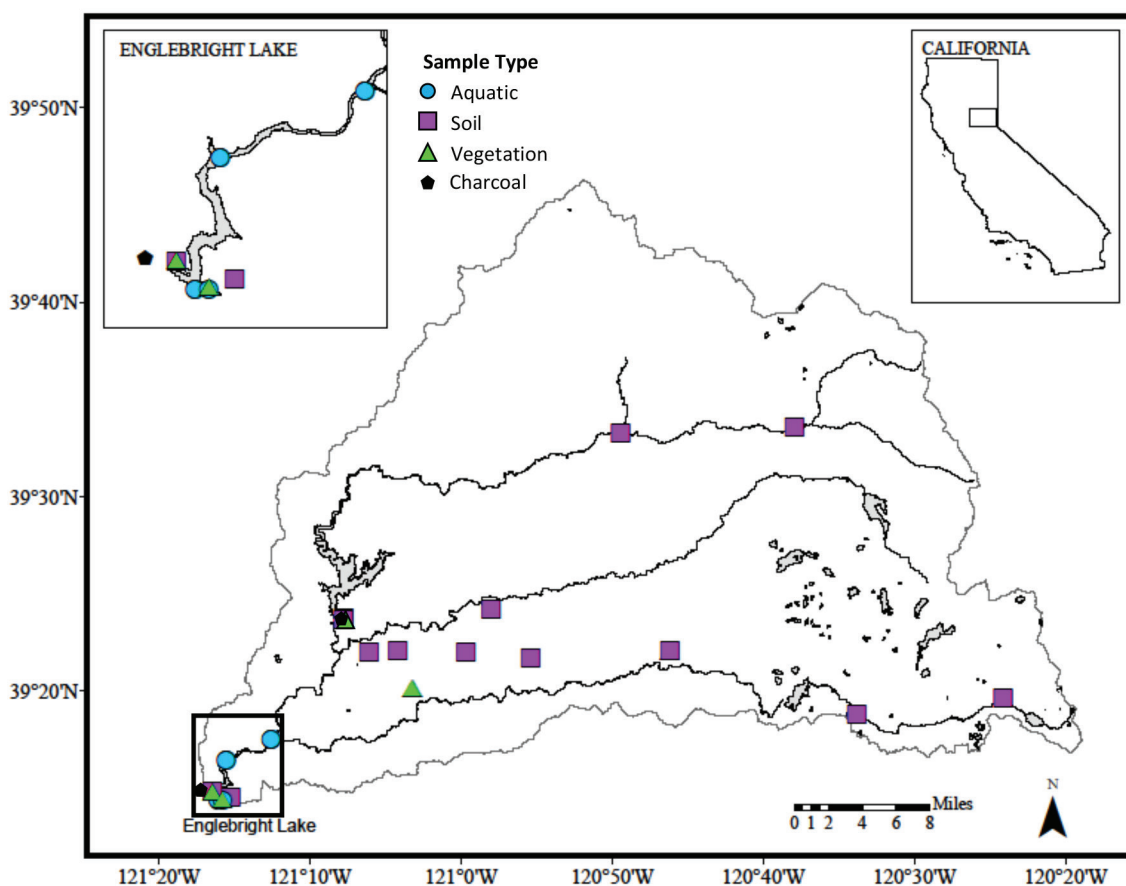


Figure 1 Map showing the location of the sample collections in the upper Yuba River watershed in northern California, including the North, Middle, and South Yuba rivers and Englebright Lake. Aquatic samples (*blue circles*), vegetation (*green triangles*), soils (*purple squares*), and charcoal (*black pentagon*) were collected throughout the watershed to characterize organic matter sources to Englebright Lake. Symbols plotted on top of each other indicate a sampling location where multiple samples were collected. The *inset* shows the locations of samples collected on and near Englebright Lake, and the *blue circles* represent the aquatic samples collected from the lake. Aquatic Site 1 is nearest to the Englebright Dam (*toward the bottom of the inset*), Aquatic Site 2 is in the middle of the lake, and Aquatic Site 3 is upstream near the confluence of the South Yuba River.

Soil and Charcoal

Soil samples were collected from agricultural, mining, forest, and roadside sites in the upper Yuba River watershed. The roadside soils were collected along the side of the main road in each of the more populated areas in the watershed. The top 1 cm of soil, reflecting surface processes that influenced these soils, was collected with a 16-cm² diameter push core. At all sites, three cores were collected from a 1-m² area and combined into a single soil sample (~15 g). Mining samples were collected from mine tailing pits remaining from early 20th century hydraulic mining operations. Two additional samples were collected from subsurface soil horizons exposed

at outcrops near roads (i.e., road cuts); these soils represent deeply buried sediments that have recently been exposed. The subsurface soils were studied to allow soils that have undergone decomposition processes during burial to be compared to recently deposited surface soils that have been exposed to more recent human and climate related disturbances. Charred vegetation from two recent forest fires were collected as charcoal samples. Soil sample colors were recorded using the Munsell Soil Color Index (Table 1) and then stored at -80°C before they were freeze-dried for organic analyses. Freeze-dried samples were sieved through 1.19-mm mesh to remove coarse gravel and plant fragments, and

homogenized with mortar and pestle to a fine powder before analysis.

Vegetation

Vegetation samples represented the dominant plant species in the watershed, and included pine, fir and oak trees, grasses, moss, and ferns (Table 1). The tissues included hard bark, leaves and needles, flowers, and litter samples. Samples were collected from two forested sites, one agricultural site, and from the shoreline of Englebright Lake. All vegetation samples were stored at -80°C , freeze-dried, and homogenized with a mortar and pestle before analysis.

Aquatic Sources

Aquatic samples were collected from Englebright Lake to define autochthonous OM sources. Plankton samples were collected with a 0.5-m-diameter, 63- μm mesh plankton net at three locations in Englebright Lake. At Aquatic Sites 1 and 2, the plankton net was deployed to a depth of 8 m, and a vertical tow was collected through the water column. At Site 3, near the confluence of Englebright Lake and the South Yuba River, a strong current prevented sample collection using a vertical plankton tow. Instead, the plankton net was deployed at the water surface for 30 seconds in a $1.9\text{-m}^3\text{-s}^{-1}$ current (USGS station 11417500). After collection, the plankton samples were transferred to pre-combusted glass jars for storage. At each site, three plankton tows were collected to characterize the $>63\text{-}\mu\text{m}$ plankton assemblage in the lake. The plankton samples were then filtered through 0.7- μm pre-combusted glass fiber filters, stored at -80°C , and freeze-dried before elemental analysis.

Suspended particulate organic matter (POM) samples were collected concurrently at each of the sites where plankton samples were obtained. For biomarker samples, 20 L of lake water were collected with a peristaltic pump from a depth of 10 cm, and filtered through 0.7- μm pre-combusted glass fiber filters. These filters were frozen at -80°C and stored for lipid biomarker analysis. POM samples for total organic carbon (TOC), total nitrogen (TN) and stable isotope analyses were obtained from three replicate water samples

(500 mL each) and filtered through 0.7- μm pre-combusted glass fiber filters. These samples represented the $>0.7\text{ }\mu\text{m}$ plankton assemblage.

Algal biofilm samples from Englebright Lake were collected by scraping algae from the floating dock and buoy on the shoreline. The biofilm was filtered through pre-weighed 0.7- μm pre-combusted glass fiber filters, frozen at -80°C , and freeze-dried. Before being analyzed for lipid biomarkers, the filters were weighed to determine the dry weight of the sample. Together, these three types of samples were expected to represent autochthonous OM in Englebright Lake.

Organic Proxy Analysis

TOC, TN, and Stable Isotope Analyses

Small aliquots (5 to 50 mg) of soils, vegetation, and plankton were acidified with dilute HCl to remove inorganic carbon (Hedges and Stern 1984) and dried overnight at 60°C before being analyzed with a Carlo Erba Elemental Analyzer to measure TOC and TN content. Filters with particulate samples from lake water were placed in a desiccator with 6N HCl and fumed overnight to remove inorganic carbon. Filters were then dried for a minimum of 4 days before being packaged and analyzed for TOC and TN. Replicate analyses ($n=2$ to 4) were run for all samples, and the variation between samples was generally less than 5%, but was $\sim 10\%$ in samples with very low organic contents ($<0.1\%$).

Samples for stable carbon and nitrogen isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) analyses were prepared similarly. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were measured with a Costech ECS 4010 CHNSO Analyzer (Costech Analytical Technologies, Inc.) connected to a Delta V Advantage Isotope Ratio Mass Spectrometer with the Conflo IV interface (Thermo Electron North America, LLC). All $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are reported relative to standard reference materials ($\delta^{13}\text{C}$: PeeDee Belemnite limestone; $\delta^{15}\text{N}$: atmospheric nitrogen).

Lipid Biomarker Analysis

Samples were analyzed for lipid biomarkers following the procedure outlined by Waterson and Canuel (2008). Briefly, aliquots of soils (10 to 50 g),

vegetation (1 to 5 g) and whole water filters were extracted with a mixture of dichloromethane (DCM) and methanol (2:1, v/v) at 80°C and 1200 psi using an accelerated solvent extractor (Dionex ASE 200 Accelerated Solvent Extractor). Extracts were partitioned according to Bligh and Dyer (1959) using a 1:1:0.9 solution of DCM, methanol, and NaCl (20% aqueous solution) to separate organic extracts from the aqueous phase. The organic fraction was saponified, and neutral and acidified fractions were extracted (Canuel and Martens 1993). Neutral lipids were separated into lipid compound classes using silica gel columns, and fractions containing sterols and alcohols were collected. The acidified lipids were methylated and fatty acid methyl ethers (FAMES) were purified using silica gel columns. Sterol and alcohol fractions were derivatized with N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) before analysis with an Agilent 7890A GC (DB-5MS 30-m x 0.32-mm column with 0.25- μ m film) connected to an Agilent 5975C mass spectrometer. FAME fractions were analyzed with an HP5890 series II GC (DB-23 60-m x 0.32-mm, 0.25- μ m film). Compounds were quantified relative to internal standards (C21 FAME for FAME analysis and 5 α -cholestane for sterol analysis) and were blank corrected before data analysis. The average recovery of nonadecanol and 5 α -androstanol (surrogate compounds added before extraction and tracked throughout the entire process) from this analysis was approximately 65%, and replicate samples agreed within $\pm 20\%$.

Lignin Biomarker Analysis

Lignin phenols were measured following the method described by Louchouart et al. (2000). Soil, charcoal, and vegetation samples were subsampled so that approximately 4 mg of organic carbon were analyzed for each sample. Lignin analyses were not conducted on the aquatic samples because the samples were not large enough, and because these samples were not expected to contain lignin (Hedges and Mann 1979). Samples were loaded into stainless steel vessels with 330 mg of CuO, 150 mg Fe(NH₄)Mg, and 2 to 3 mL of 2N NaOH. The CuO oxidation reaction occurred as samples were stirred and heated for 3 hours at 154°C in a modified GC

oven. A standard surrogate solution containing ethyl-vanillin and *trans*-cinnamic acid was then mixed into the vessels, the solution was decanted, and vessels were rinsed twice with 1N NaOH. Lignin oxidation products were separated from this solution with three rinses of ethyl acetate. Samples sat over Na₂SO₄ overnight to remove water, and were dried with a Zymark TurboVap II solvent concentrator before being redissolved in pyridine and derivatized with BSTFA. Lignin oxidation products were measured with an Agilent 7890A GC (DB-5MS 30-m x 0.32-mm column with 0.25- μ m film) connected to an Agilent 5975C mass spectrometer using 1,3,5-triisopropylbenzene as an internal standard to compute the concentrations of 13 lignin phenol compounds. Peak areas were blank-corrected before analysis, and measurements of replicate samples agreed within $\pm 20\%$.

Total lignin concentrations normalized to dry mass of sediment ($\Sigma 8$) were calculated as the sum of vanillyl, syringyl, and cinnamyl lignin phenols (Hedges and Ertel 1982) and were normalized to TOC to calculate total lignin yields ($\Sigma 8$). Ratios of syringyl to vanillyl phenols (S/V) and cinnamyl to vanillyl phenols (C/V) were used to differentiate between vascular plant tissues (Hedges and Mann 1979). Acid to aldehyde ratios of vanillyl phenols [(Ad/Al)v] and 3,5-dihydroxybenzoic acid to vanillyl phenol ratios (3,5-Bd:V) provided information on the degradation state of organic matter derived from vascular plants (Hedges and Mann 1979; Hedges and Ertel 1982).

Data Analysis

Peak areas were integrated using the Chem Station software package (Agilent) and converted to concentrations. These values were analyzed for statistical differences using R-Studio version 0.98.507. Lipid, lignin, TOC, and TN data that did not meet the assumption of normality required for the statistical analyses were log-transformed before regression, correlation, and t-test analysis. Stable carbon and nitrogen values were not transformed for statistical analyses because they met the required assumptions. Data reported here are either presented on a mass-normalized ($\mu\text{g g}^{-1}$) or percent basis.

To identify differences in OM sources in the upper Yuba River watershed, principal components analysis (PCA) was performed on fatty acid, sterol, alcohol and lignin biomarker data. PCA is a data-exploration method that simplifies complex data sets into a small number of principal components to describe factors that control variation within the data. Before the PCA analysis, concentration data for the biomarker compounds were blank-corrected and any undetected values were replaced with the biomarker detection limit, or one-half the minimum detected concentration of each variable (Yunker et al. 2005). Biomarker concentrations were then normalized to the total fatty acid, sterol, or alcohol concentration to reduce artifacts related to large concentration differences (Yunker et al. 2005). Each biomarker value was divided by the geometric mean of that variable across all samples and log transformed. Biomarker compounds were auto-scaled by subtracting the mean and then dividing by standard deviation from each value within a variable class. These normalization steps created a data set for the PCA that was unaffected by negative bias or closure (Yunker et al. 2005). To reduce the number of biomarker variables, biomarker compounds were grouped when appropriate (i.e., when they reflected similar OM sources and grouped together in an exploratory PCA). Three subsequent PCAs were run using this smaller data set, which consisted of 37 observations (samples) and 21 biomarker variables (lipid and lignin biomarkers representative of the OM sources in this study) (Table 2).

RESULTS

TOC, TN, and Stable Isotopes

TOC ranged from 0.27% to 46.96% dry weight in soil, vegetation, and plankton samples (Tables 3 and A1). %TOC was higher in the vegetation ($p < 0.001$) and freshwater plankton ($p < 0.001$) samples than in the soil samples (Table 3). Within the soil samples, %TOC content was higher in forest soils than in agricultural soils ($p = 0.003$) or roadside soils ($p < 0.005$); mining and subsurface soils had lower %TOC ($p < 0.001$) (Figure 2A). TN varied between 0.01% and 6.25%, and was highest

for the plankton samples collected from Sites 1 and 2 in Englebright Lake (Table 3). Mining and subsurface soils had the lowest %TN ($p < 0.001$ for student's t-test among mining and agriculture, forest, and roadside soils and between subsurface and forest soils; $p = 0.005$ between subsurface soils and agriculture and roadside soils) and agricultural and forest soils had the highest %TN (Figure 2B, Table A1).

Carbon to nitrogen ratios ($[C:N]_a$) ranged from 5.6 to 81.5, and were lowest in freshwater plankton samples (8.5 ± 3.4 , $p < 0.02$) and highest in plant samples (55.7 ± 21.2 , $p < 0.005$) (Tables 3 and A1). The range in $[C:N]_a$ ratios from soil samples was high (10.8 – 35.8); agricultural soils had lower $[C:N]_a$ ratios than forest soils (23.1 ± 10.6 and 29.7 ± 3.57 , respectively; $p = 0.004$). No trend was observed between soil $[C:N]_a$ and human land use (Table 3).

$\delta^{13}C$ ranged from -33‰ to -23‰ (Table 3). Freshwater plankton samples had lower $\delta^{13}C$ values (-31.72 ± 2.39 ‰) than terrigenous (vegetation and soil) samples (-28.1 ± 2.1 ‰, $p = 0.012$) (Tables 3 and A1). $\delta^{15}N$ ranged from -11‰ to 3‰, with the lowest values associated with the vegetation samples (-7.62 ± 1.02 ‰, Tables 3 and A1). The freshwater plankton samples had the highest $\delta^{15}N$ values (1.48 ± 2.73 ‰, $p < 0.001$) (Tables 3 and A1). Within Englebright Lake, there was a trend of increasing $\delta^{13}C$ and decreasing $\delta^{15}N$ as distance from the dam increased (Figure 3A).

Lipid Biomarkers

Total fatty acid (FA) concentrations ranged from $6.8 \mu\text{g g}^{-1}$ to $8,422.9 \mu\text{g g}^{-1}$, or $1.2 \mu\text{g mg}_{\text{TOC}}^{-1}$ to $25.2 \mu\text{g mg}_{\text{TOC}}^{-1}$ on a carbon-normalized basis (Tables 4 and A2). TOC-normalized total FA concentrations were higher in the aquatic samples ($23.8 \pm 1.4 \mu\text{g mg}_{\text{TOC}}^{-1}$) than in soil ($3.9 \pm 2.1 \mu\text{g mg}_{\text{TOC}}^{-1}$), char ($3.2 \pm 0.3 \mu\text{g mg}_{\text{TOC}}^{-1}$), and plant ($5.1 \pm 2.1 \mu\text{g mg}_{\text{TOC}}^{-1}$) samples ($p < 0.003$; Table A2). Long chain FA (LCFA = $C_{24:0} + C_{25:0} + C_{26:0} + C_{27:0} + C_{28:0} + C_{29:0} + C_{30:0} + C_{31:0} + C_{32:0}$) varied across sample type, with higher contributions in soils ($17.7 \pm 9.6\%$), charcoal ($19.3 \pm 15.3\%$) and vegetation ($12.5 \pm 10.0\%$) than in the aquatic samples (1.2

Table 2 List of compounds that comprise the biomarker groups described throughout this study. Each group was assigned a source based on information collected from this study. Loadings for factors 1 and 2 of the PCA for analyzing all samples, only plant and charcoal samples, and only soil samples are provided.

Group name	Compounds	Source indicator	PCA- all		PCA- plants		PCA- soils	
			Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2
Aquatic Sterols	cholesta-5,22-dien-3 β -ol, 27-nor-24-methylcholesta-5,22-dien-3 β -ol	Aquatic plankton and algae	0.265	0.023				
Cholesterol	cholest-5-en-3 β -ol	Zooplankton	0.282	0.081	0.929	0.084	0.004	0.092
Brassicasterol	24-methylcholesta-5,22-dien-3 β -ol	Generally microalgae, but also plants from Brassicaceae family	0.294	-0.172	-0.284	-0.244	0.072	-0.037
SCFA	C _{12:0'} C _{14:0'} C _{16:0}	Microbial and aquatic sources	0.090	0.369				
C20+C22 PUFA	C _{20:1'} C _{20:6'} C _{22:2'} C _{22:6}	Aquatic phytoplankton and zooplankton	0.209	-0.082				
C16 PUFA	C _{16:2'} C _{16:3'} C _{16:4}	Aquatic phytoplankton and zooplankton	0.143	-0.151	-0.021	-0.117		
Plant sterols	24-methylcholesta-5-en-3 β -ol, 24-ethylcholesta-5,22-dien-3 β -ol, 24-ethylcholest-5-en-3 β -ol	Higher plants	-0.036	-0.049	0.001	0.004	-0.006	-0.003
LCFA	C _{24:0'} C _{25:0'} C _{26:0'} C _{27:0'} C _{28:0'} C _{29:0'} C _{30:0'} C _{31:0'} C _{32:0}	Higher plants	-0.197	-0.442	-0.064	-0.303	-0.170	0.332
LCOH	C ₂₄ OH, C ₂₅ OH, C ₂₆ OH, C ₂₇ OH, C ₂₈ OH, C ₃₀ OH, C ₃₂ OH	Higher plants	-0.096	-0.201				
Σ 8	Sum of all lignin phenols	Higher plants	-0.292	0.200	0.132	-0.026	-0.413	0.471
S/V	Σ Syringyl / Σ Vanillyl Phenols	Angiosperm tissues	0.055	0.127	0.458	-0.591	0.163	0.130
C/V	Σ Cinnamyl / Σ Vanillyl Phenols	Woody plant tissues	0.059	0.398	0.225	0.442	-0.290	0.356
(Ad/Al)v	Vanillic Acid / Vanillin	Degradation of plant tissue	0.406	0.034	-0.250	-0.062	0.294	-0.142
3,5-Bd:V	3,5-dihydroxybenzoic acid / Σ Vanillyl Phenols	Soil humification	0.374	0.141			0.137	-0.087
Diacids	14 α,ω ; 16 α,ω ; 18 α,ω ; 20 α,ω ; 22 α,ω ; 24 α,ω	Break down products from bacteria; Suberin from higher plant roots and cuticles	-0.098	-0.425	-0.204	-0.478	-0.140	-0.023
Odd MUFA	C _{15:1'} C _{17:1'} C _{19:1}	Soil	0.300	-0.227	-0.433	0.077	0.113	0.371
BrFA	i15, a15, i17, a17, i19, a19	Heterotrophic bacteria	0.306	-0.238	-0.575	0.038	0.102	0.90
C18 PUFA	C _{18:2ω6t'} C _{18:3ω3'} C _{18:3ω6'} C _{18:4}	Vegetation and fungi	-0.160	0.063	0.115	0.206		
C16:1 & C18:1	C _{16:1'} C _{16:1ω9'} C _{16:1ω7'} C _{16:1ω5'} C _{18:1ω5'} C _{18:1ω7'} C _{18:1ω9'} C _{18:1ω9t}	Generally nonspecific (specific isomers indicate plant, fungi, or bacterial input)	0.143	-0.151			0.732	0.378
C22:1	C _{22:1ω9'} C _{22:1ω7}	Nonspecific	0.002	-0.167				
C20:1	C _{20:1ω9'} C _{20:1ω7'} C _{20:1ω5}	Nonspecific	0.070	-0.082				

Table 3 Summary of mean (\pm standard deviation) values for bulk organic proxies for each group of samples analyzed (soils, charcoal, vegetation and aquatic). Cases where data are unavailable either because samples were not analyzed for a specific variable or because the sample group comprised only one data point (i.e., no standard deviation available) are identified as “na.”

	TOC (%)	TN (%)	C:N _a	$\delta^{13}\text{C}_{\text{TOC}}$ (‰)	$\delta^{15}\text{N}_{\text{TN}}$ (‰)
Soils	4.09 (4.12)	0.22 (0.18)	20.9 (8.68)	-27.6 (2.39)	-3.16 (2.40)
Mining	0.41 (0.06)	0.02 (0.18)	22.6 (7.42)	-27.3 (0.64)	-3.89 (0.07)
Subsurface	0.44 (0.24)	0.03 (0.01)	16.8 (4.72)	-30.7 (3.15)	-2.01 (0.80)
Roadside	2.46 (1.56)	0.15 (0.15)	23.1 (10.6)	-25.7 (2.21)	-0.81 (1.83)
Agriculture	5.10 (0.57)	0.41 (0.07)	12.6 (1.34)	-28.6 (1.13)	-4.04 (2.89)
Forest	10.4 (5.22)	0.34 (0.14)	29.7 (3.57)	-27.6 (2.29)	-5.43 (0.60)
Charcoal	30.4 (1.09)	0.98 (0.16)	30.5 (3.59)	-29.4 (3.12)	-4.96 (3.11)
Vegetation	43.7 (2.96)	0.96 (0.46)	55.7 (21.2)	-28.6 (1.21)	-6.69 (4.05)
Gymn.	46.7 (0.33)	0.84 (0.23)	53.7 (18.3)	-27.7 (1.41)	-10.0 (0.52)
Monocot	41.7 (2.67)	0.76 (0.35)	6.82 (24.1)	-29.1 (1.75)	-4.23 (7.06)
Eudicot	42.7 (3.58)	0.93 (0.36)	50.8 (17.6)	-29.3 (0.92)	-5.43 (4.37)
Fern	43.8 (na)	2.16 (na)	20.3 (na)	-28.8 (na)	-5.06 (na)
Moss	41.2 (na)	1.03 (na)	40.0 (na)	-28.6 (na)	-4.64 (na)
Bark	46.1 (na)	0.57 (na)	81.5 (na)	-27.3 (na)	-10.4 (na)
Aquatic	26.9 (14.5)	4.29 (3.05)	8.50 (3.40)	-31.7 (2.39)	0.92 (2.04)
Plankton	26.9 (14.5)	4.29 (3.05)	8.33 (4.38)	-31.6 (3.36)	1.48 (2.72)
POM	0.17 (0.01) ^a	0.02 (0.0) ^a	8.92 (1.36)	-32.0 (0.48)	1.12 (0.09)
Algae	na	na	na	na	-1.29 (na)

a. TOC and TN for POM samples are reported in mg L⁻¹.

$\pm 1.5\%$, $p < 0.01$ for all three one-sided t-tests) (Tables 4 and 5). Differences in the concentration of polyunsaturated FA (PUFA) between the samples were evident only for C₁₈ PUFAs, and not for C₁₆ PUFAs or C₂₀+C₂₂ PUFAs. C₁₈ PUFAs were more abundant in the vegetation samples than in aquatic ($p=0.015$) or soil ($p < 0.001$) samples (Tables 5 and A2). On average, mono-unsaturated fatty acids (MUFA) made up $19.6 \pm 8.4\%$ of the total FA composition among samples; branched fatty acids (BrFA) and α,ω -diacids (C₁₄+C₁₆+C₁₈+C₂₀+C₂₂+C₂₄ dicarboxylic acids) were less than 20% of the total fatty acids in all terrigenous samples. Diacids were not detected in any aquatic samples (Table 4). Among the plant samples, MUFA and BrFA were more abundant in gymnosperm, fern, and moss samples than in the angiosperm samples ($p < 0.05$, Figures 4A, 4B). Diacid abundance was elevated

in roadside samples, whereas BrFA were lower in frigid roadside soils than in other soils ($p < 0.01$; Figures 5A, 5B)

Total sterol concentrations ranged from below detection (BD) to $5416.4 \mu\text{g g}^{-1}$ (Table 4), and carbon normalized total sterol concentrations ranged from BD to $14.4 \mu\text{g mg}_{\text{TOC}}^{-1}$ (Table A3). Carbon normalized sterols were higher ($p < 0.05$) in aquatic ($1.8 \pm 1.6 \mu\text{g mg}_{\text{TOC}}^{-1}$) and plant ($2.4 \pm 3.0 \mu\text{g mg}_{\text{TOC}}^{-1}$) samples than in soil ($1.3 \pm 3.5 \mu\text{g mg}_{\text{TOC}}^{-1}$) and char ($0.3 \pm 0.1 \mu\text{g mg}_{\text{TOC}}^{-1}$) (Table A3). The dominant sterols included 27-nor-24-methylcholesta-5,22-dien-3 β -ol, cholesta-5,22-dien-3 β -ol, cholest-5-en-3 β -ol (cholesterol), 24-methylcholesta-5,22-dien-3 β -ol (brassicasterol), 24-methylcholest-5-en-3 β -ol (campesterol), 24-ethylcholesta-5,22-dien-3 β -ol (stigmasterol), 24-ethylcholest-5-en-3 β -ol (sitosterol) (Tables 4

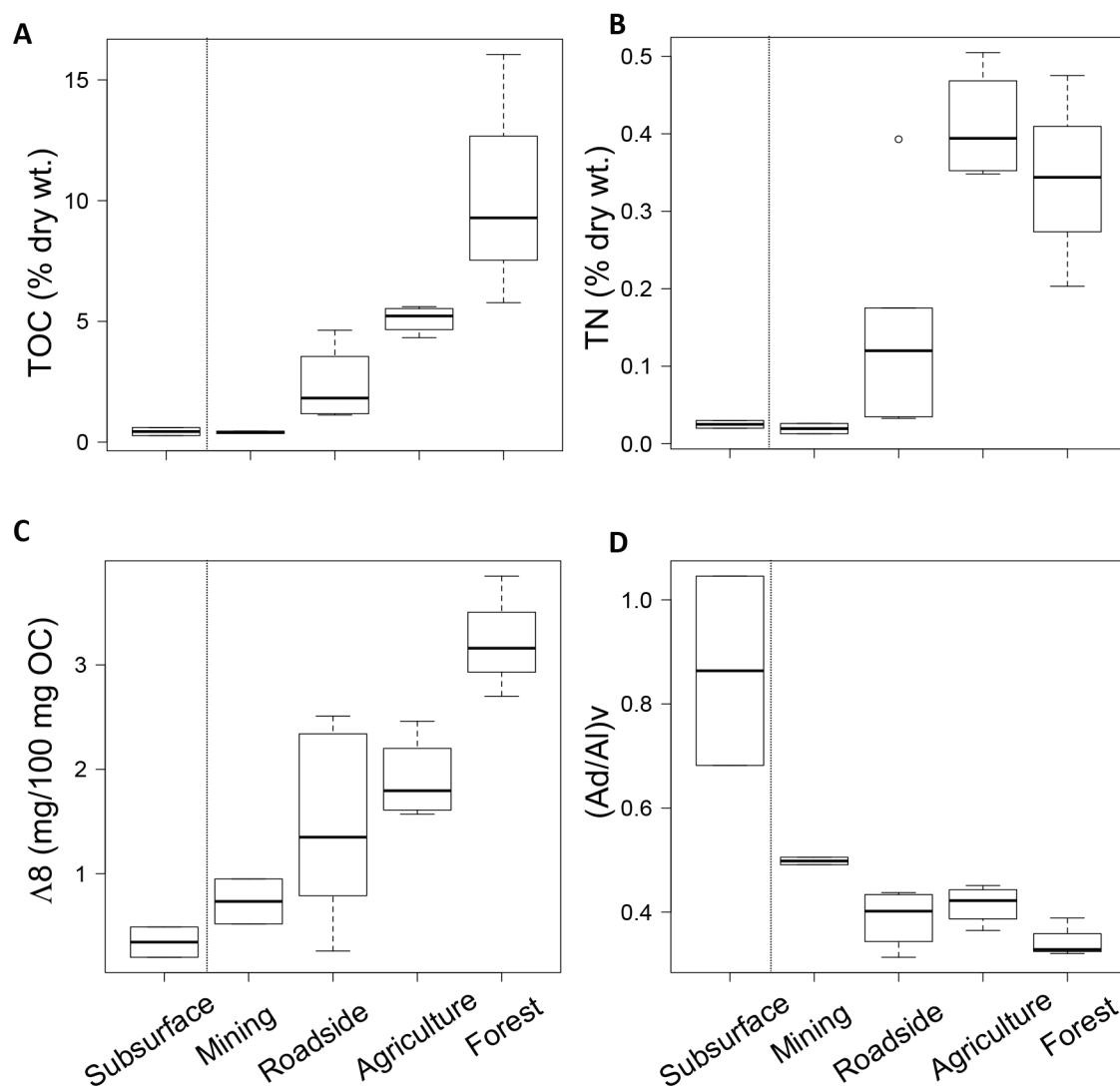


Figure 2 Boxplots showing total organic carbon, total nitrogen and biomarker composition of soils collected from the upper Yuba River watershed. Total organic carbon (A), total nitrogen (B), $\Delta 8$ (C), and (Ad/Al)_v (D) show different trends with level of anthropogenic effect ranging from most affected (mining) to least affected (forest). Subsurface soils are included for comparison but were not part of the analysis of the disturbance gradient described in the text as indicated by the dotted line that separates these samples from the other soils.

and A3). Sterols such as 27-nor-24-methylcholesta-5,22-dien-3 β -ol, cholesta-5,22-dien-3 β -ol and brassicasterol—typically assigned to aquatic sources—were detected in all aquatic samples, as well as the mixed bark (V12) and one agricultural soil (AS2) sample. The proportion of brassicasterol and cholesterol to the total sterol concentration was higher in aquatic samples ($p < 0.04$ and $p < 0.01$, respectively), while the proportion of plant sterols (stigmasterol, campesterol, and sitosterol) was higher in vegetation samples than

in aquatic ($p = 0.01$) and soil samples ($p = 0.002$) (Tables 4 and 5). In the aquatic samples, the proportion of cholesterol and brassicasterol was higher than the proportion of plant sterols at the downstream sites (Sites 1 and 2), but this relationship was reversed (i.e., plant sterols > brassicasterol and cholesterol) at Site 3 near the head of the lake (Figure 3B). Brassicasterol was also detected in all soil samples, and its relative abundance was higher in subsurface and mining

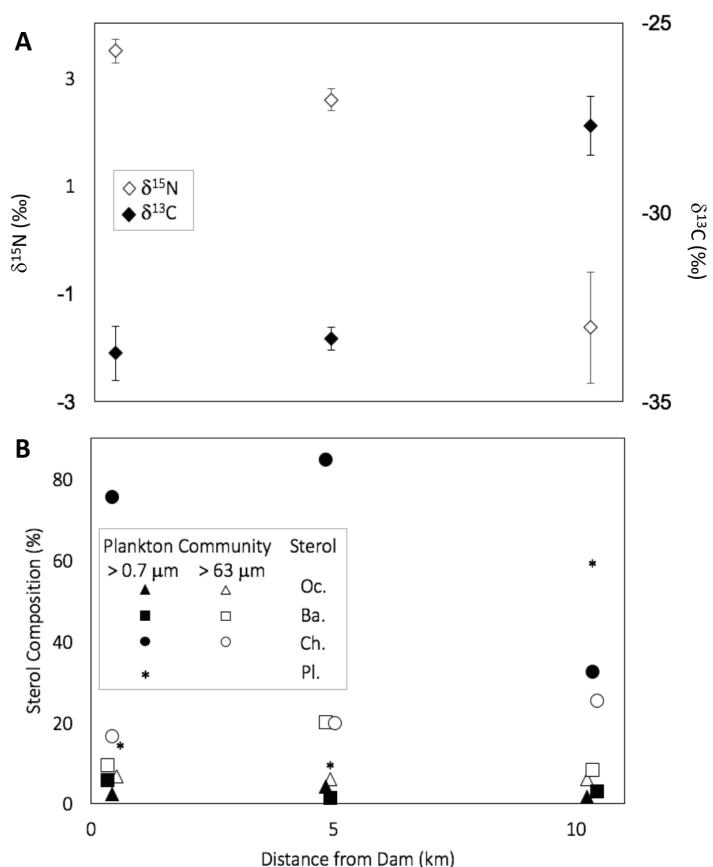


Figure 3 Downstream changes in stable carbon and nitrogen isotope values and (A) sterol composition of the plankton communities with distance from the dam in Englebright Lake (B). Open symbols indicate stable nitrogen ($\delta^{15}\text{N}$) values, closed symbols indicate stable carbon ($\delta^{13}\text{C}$) values and error bars represent standard deviation of the mean. Open symbols in plot B indicate sterols from the larger plankton size (> 63 μm) and closed symbols indicate sterols measured from the small plankton (> 0.7 μm) fraction. Sterols shown here include 27-nor-24-cholesta-5,22-dien-3 β -ol (triangles; Oc.), brassicasterol (squares; Ba.), and cholesterol (large circles; Ch.) for both size fractions, and the small circles represent contributions from higher plant sterols (campesterol, stigmasterol, and sitosterol; Pl) in the small plankton samples. Higher plant sterols remained constant (35% to 50%) in the large plankton samples, and are not included here.

soils than in roadside, agricultural, or forest soils ($p < 0.05$; Figure 5C).

Lignin Biomarkers

Total lignin concentration ($\Sigma 8$) ranged from 0.01 mg g^{-1} to 43.96 mg g^{-1} , and carbon normalized lignin concentration ($\Delta 8$) ranged from 0.18 mg 100 mg TOC^{-1} to 11.39 mg 100 mg TOC^{-1} (Tables 4

and A4). $\Sigma 8$ was higher in the vegetation and charcoal samples compared to the soils ($p < 0.01$); soil samples from the mine sites and from the subsurface horizons had the lowest lignin concentrations (Table 4; Figures 2C and 5D). Ratios of syringyl to vanillyl phenols (S/V) and cinnamyl to vanillyl phenols (C/V), proxies for plant tissue type, had a wide range of values (S/V = 0.002 to 5.61 and C/V = 0.02 to 5.76), with the greatest range observed within the vegetation samples (Figure 4C; Tables 4 and A4). C/V and S/V were similar across vegetation, charcoal, and soil samples ($p > 0.05$). (Ad/Al)v and 3,5-Bd:V, indicators of OM degradation state, ranged from 0.13 to 1.04 and 0.0 to 0.7, respectively, across all soil, vegetation, and charcoal samples (Tables 4 and A4). Overall, (Ad/Al)v and 3,5-Bd:V were higher in soil and charcoal than in vegetation ($p < 0.001$ and $p = 0.02$, respectively; Tables 4 and 5). Both (Ad/Al)v and 3,5-Bd:V were higher in subsurface and mining soils than in any other soil type, although no significant difference was observed for 3,5-Bd:V ($p < 0.05$ for (Ad/Al)v; Figures 2D, 5E, 5F).

Principal Components Analysis (PCA)

PCA was used to determine sources of variability in the lipid and lignin biomarker data. An initial PCA was run on all samples using all the lipid and lignin data (Figure 6A), and Factor 1 and Factor 2 described 35.3% and 17.9% of the variability in the data, respectively. Freshwater plankton samples grouped together with positive scores for Factor 1, soil samples had low but positive scores for Factor 1, and vegetation samples had negative scores for Factor 1. (Ad/Al)v and 3,5Bd:V had the most positive loadings for Factor 1 (0.406 and 0.374, respectively), whereas $\Sigma 8$ and LCFA had negative loadings on Factor 1 (-0.197) (Figure 6A; Table 2). C/V and SCFA had the most positive loading for Factor 2 (0.398 and 0.369, respectively), while LCFA (-0.442) and diacids (-0.425) had the most negative loadings for Factor 2 (Figure 6A; Table 2). Vegetation and freshwater plankton samples had positive scores for Factor 2, while soils and charcoal grouped together with negative scores for Factor 2 (Figure 6A, Table 2)

Table 4 Summary of the average total fatty acid (FA), sterol, and lignin ($\Sigma 8$) concentrations (mg g^{-1}) for each group of samples analyzed, and relative abundances of specific biomarkers within these compound classes. Standard deviations are reported in *parentheses*. Cases where data are unavailable because samples were not analyzed for a specific variable or because the sample group comprised only one data point (i.e., no standard deviation available) are identified as “na.” Concentrations of total fatty acids (FA) and total sterols are reported in mg g^{-1} , unless indicated. Aquatic sterols includes 27-nor-24-methylcholesta-5,22-dien-3 β -ol and cholesta-5,22-dien-3 β -ol, Plant sterols includes 24-methylcholesta-5-en-3 β -ol, 24-ethylcholesta-5,22-dien-3 β -ol, and 24-ethylcholest-5-en-3 β -ol, Brass. indicates brassicasterol, and Chol. indicates cholesterol.

	FA (mg g^{-1})	LCFA (%)	SCFA (%)	BrFA (%)	Diacid (%)	Sterol (mg g^{-1})	Aquatic sterol (%)	Brass. (%)	Chol. (%)	Plant sterol (%)	$\Sigma 8$ (mg g^{-1})	C/V	S/V	(Ad/Al)v	3,5- Bd:v
Soils	0.11 (0.08)	17.6 (9.59)	25.1 (10.5)	1.94 (1.41)	4.16 (5.75)	0.02 (0.03)	0.01 (0.05)	4.37 (3.38)	2.88 (1.99)	83.9 (23.4)	1.00 (1.34)	0.54 (0.36)	0.31 (0.23)	0.49 (0.20)	0.08 (0.05)
Mining	0.02 (0.00)	14.5 (4.10)	36.5 (15.3)	2.20 (2.26)	1.25 (1.06)	1.95 (0.21) ^a	0.00 (0.00)	8.65 (0.49)	2.40 (0.85)	84.1 (6.6)	0.03 (0.01)	0.42 (0.40)	0.23 (0.01)	0.50 (0.01)	0.14 (0.00)
Subsurface	0.04 (0.03)	7.90 (1.98)	25.7 (8.56)	1.35 (0.21)	1.55 (0.64)	0.04 (0.03)	0.00 (0.00)	8.75 (4.17)	3.15 (2.90)	88.1 (1.27)	0.01 (0.00)	0.91 (0.25)	0.23 (0.29)	0.87 (0.26)	0.12 (0.00)
Roadside	0.08 (0.04)	15.2 (11.3)	18.2 (8.08)	1.34 (1.88)	10.1 (7.48)	0.02 (0.04)	0.00 (0.00)	1.64 (1.53)	2.82 (3.00)	74.7 (42.0)	0.44 (0.45)	0.47 (0.39)	0.46 (0.34)	0.47 (0.20)	0.08 (0.00)
Agriculture	0.12 (0.04)	22.3 (9.7)	20.7 (2.97)	2.88 (1.00)	1.38 (1.68)	0.02 (0.04)	0.05 (0.1)	2.43 (1.74)	3.78 (1.33)	87.3 (12.3)	0.98 (0.31)	0.77 (0.22)	0.33 (0.11)	0.41 (0.04)	0.07 (0.00)
Forest	0.24 (0.07)	24.0 (7.64)	34.2 (11.0)	1.93 (0.80)	1.60 (1.20)	0.04 (0.07)	0.00 (0.00)	5.20 (1.77)	1.90 (1.13)	91.7 (2.14)	3.27 (1.57)	0.18 (0.07)	0.16 (0.02)	0.35 (0.04)	0.05 (0.00)
Charcoal	0.97 (0.06)	19.4 (15.3)	26.7 (10.2)	1.60 (0.42)	3.75 (4.88)	0.09 (0.04)	0.00 (0.00)	2.65 (0.78)	0.50 (0.07)	92.5 (6.22)	5.45 (3.56)	0.64 (0.74)	0.27 (0.16)	0.56 (0.19)	0.07 (0.00)
Vegetation	2.27 (1.02)	12.5 (10.0)	29.7 (10.1)	0.99 (1.75)	2.86 (3.22)	1.06 (1.41)	0.02 (0.06)	0.54 (1.04)	0.52 (0.84)	97.1 (4.01)	23.4 (14.9)	1.47 (1.76)	0.83 (1.30)	0.22 (0.12)	0.08 (0.20)
Gymnosperm	3.11 (1.33)	8.60 (3.47)	29.3 (9.35)	2.83 (2.83)	4.97 (4.26)	1.09 (0.36)	0.00 (0.00)	0.93 (1.62)	0.00 (0.00)	99.0 (1.62)	13.7 (6.72)	0.03 (0.03)	0.35 (0.19)	0.23 (0.05)	0.04 (0.00)
Monocot	2.34 (1.11)	9.25 (8.56)	29.0 (1.20)	0.00 (0.00)	0.95 (1.34)	0.54 (0.24)	0.00 (0.00)	0.00 (0.00)	0.40 (0.57)	92.5 (5.52)	43.6 (0.45)	3.62 (2.83)	1.01 (0.60)	0.14 (0.01)	0.01 (0.00)
Eudicot	1.88 (0.56)	13.4 (5.73)	35.8 (4.86)	0.00 (0.00)	1.70 (2.18)	1.62 (2.53)	0.00 (0.00)	0.00 (0.00)	0.65 (1.11)	99.4 (1.11)	276 (13.4)	2.36 (2.21)	0.29 (0.21)	0.16 (0.03)	0.02 (0.00)
Fern	3.06 (na)	8.10 (na)	41.4 (na)	0.40 (na)	0.00 (0.00)	0.68 (na)	0.00 (na)	0.00 (na)	2.20 (na)	97.8 (na)	11.8 (na)	0.00 (na)	0.73 (na)	0.20 (na)	0.06 (na)
Moss	1.82 (na)	4.40 (na)	17.0 (na)	0.09 (na)	2.60 (na)	0.74 (na)	0.00 (na)	1.20 (na)	0.30 (na)	98.5 (na)	0.76 (na)	0.45 (na)	0.74 (na)	0.58 (na)	0.71 (na)
Bark	0.81 (na)	39.80 (na)	9.00 (na)	2.10 (na)	8.10 (na)	0.50 (na)	0.2 (na)	2.50 (na)	0.30 (na)	89.3 (na)	40.4 (na)	4.04 (na)	0.10 (na)	0.23 (na)	0.05 (na)
Aquatic	2.94 (3.78)	10.9 (3.84)	53.2 (11.0)	1.89 (0.71)	0.00 (0.00)	0.25 (0.44)	3.94 (2.22)	8.00 (6.09)	38.9 (28.7)	49.1 (24.9)	na	na	na	na	na
Plankton	6.36 (3.37)	14.0 (2.37)	61.4 (5.84)	2.37 (0.84)	0.00 (0.00)	0.58 (0.56)	2.63 (1.33)	3.30 (2.23)	64.2 (27.9)	29.8 (29.1)	na	na	na	na	na
POM	0.01 (0.00)	8.60 (3.47)	48.1 (12.1)	1.43 (0.40)	0.00 (0.00)	0.83 (0.15) ^a	6.10 (0.44)	12.6 (6.46)	18.2 (1.55)	63.1 (4.80)	na	na	na	na	na
Algae	1.48 (na)	8.10 (na)	43.8 (na)	1.80 (na)	0.00 (0.00)	0.04 (na)	1.40 (na)	8.40 (na)	25.2 (na)	65.1 (na)	na	na	na	na	na

a. Values reported in $\mu\text{g g}^{-1}$.

Table 5 Summary of the major biomarkers explored in this study. *Open circles* indicate the presence of the biomarker in samples that represented each OM source, and *filled circles* indicate the OM source with the highest average concentration of each biomarker.

Biomarker	Aquatic	Higher plant	Soil	Charcoal
Bulk proxies				
C:N _a	< 10	> 20	10 to 36	28 to 35
δ ¹³ C	-33‰ to -27‰	-30‰ to -26‰	-32‰ to -22‰	-31‰ to -27‰
δ ¹⁵ N	-1‰ to 4‰	-11‰ to -4‰	-7‰ to 2‰	-7‰ to -2‰
Sterols				
Aquatic sterols	●	○	○	○
Brassicasterol	●	○	○	○
Cholesterol	●	○	○	○
Plant sterols	○	●	○	○
Fatty acids				
LCFA	○	●	●	●
SCFA	●	○	○	○
C16 PUFA	●	○	○	○
C18 PUFA	○	●	○	○
C20+22 PUFA	○	●	○	○
BrFA	○	○	●	○
Diacids	○	○	●	○
Lignin				
Σ8		●	○	○
Δ8		●	○	○
C/V		●	○	○
S/V		●	○	○
(Ad/Al) _v		○	○	●
3,5-Bd:V ^a		○	●	○

a. Excludes sample V11.

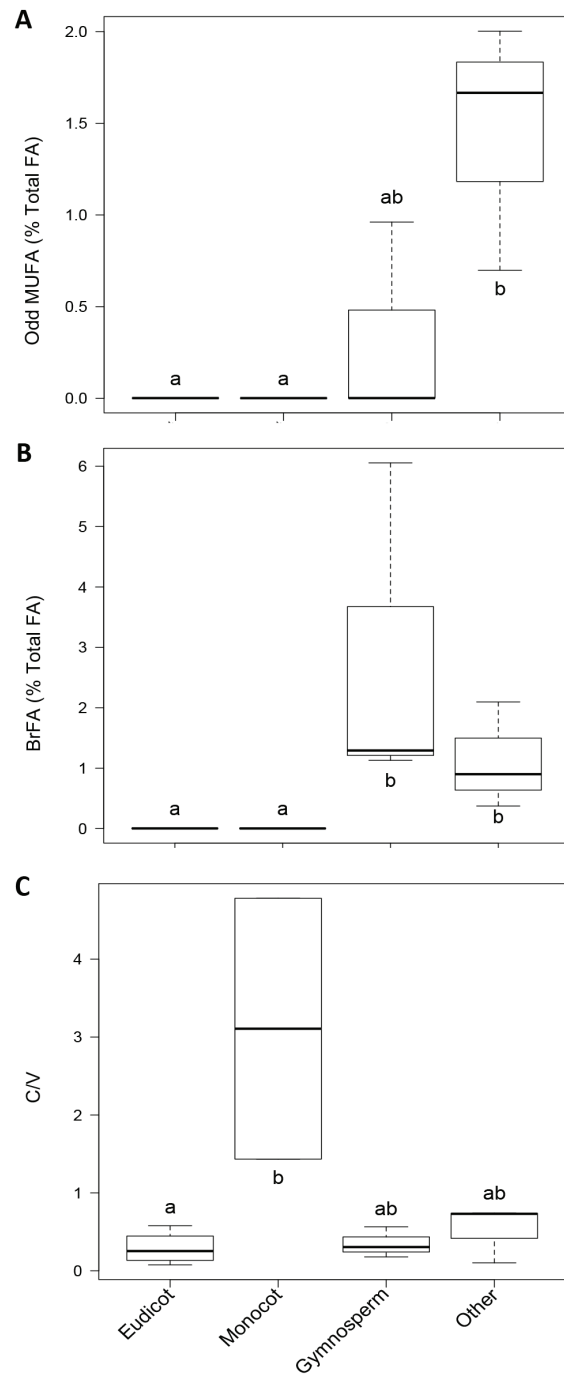


Figure 4 Boxplots showing differences in the abundance of fatty acid and lignin biomarkers for angiosperm clades, including eudicots and monocots, gymnosperms, and other plant types (fern, moss, and bark). Biomarker variables include odd-numbered monounsaturated fatty acids (MUFA) (A), iso- and anteiso-branched fatty acids (BrFA) (B), and the ratio of cinnamyl to vanillyl lignin phenols (C/V) (C). These variables had the highest loadings in the plant PCA and differed significantly as determined with ANOVA. Groups with matching letters indicate no statistical differences, and groups without matching letters indicate statistically significant ($p < 0.05$) differences.

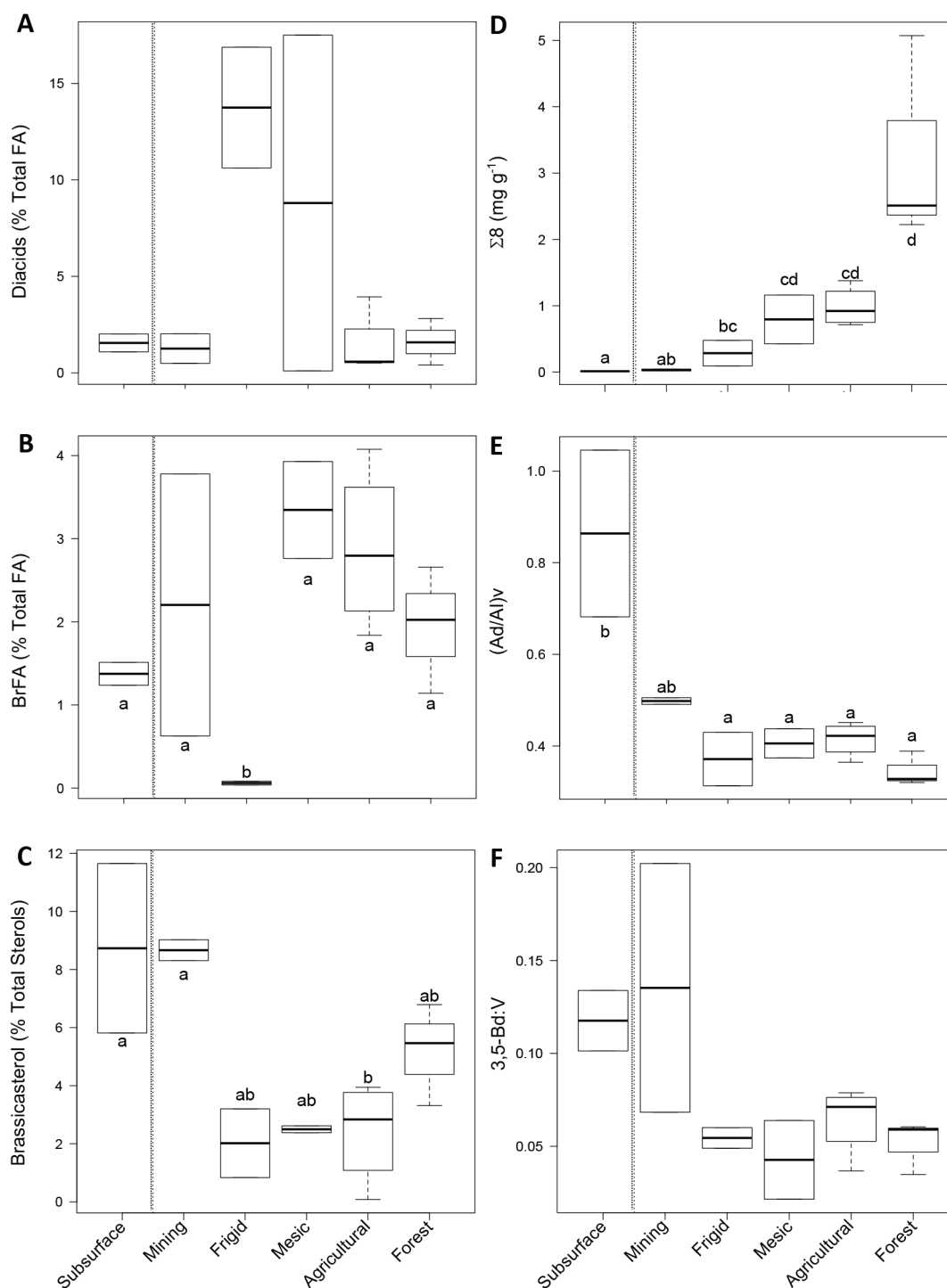


Figure 5 Boxplots showing differences in biomarker composition between soil types, including mining, subsurface, forest, agricultural, and roadside (in the mesic and frigid temperature regimes) soils. Biomarker variables, including α,ω -diacids (**A**), branched fatty acids (BrFA) (**B**), brassicasterol (**C**) (**D**), (Ad/Al)_v (**E**), and 3,5-Bd:V (**F**), represent the variables with the highest loadings in the soil PCA or those variables where significant differences were determined with ANOVA. Subsurface soils are separated by a *dotted line* to indicate that these samples were not part of the analysis of the disturbance gradient described in the text. Groups with matching letters indicate no statistical differences, and groups without matching letters indicate statistically significant ($p < 0.05$) differences. When letters are absent, no significant differences were observed between any soil type.

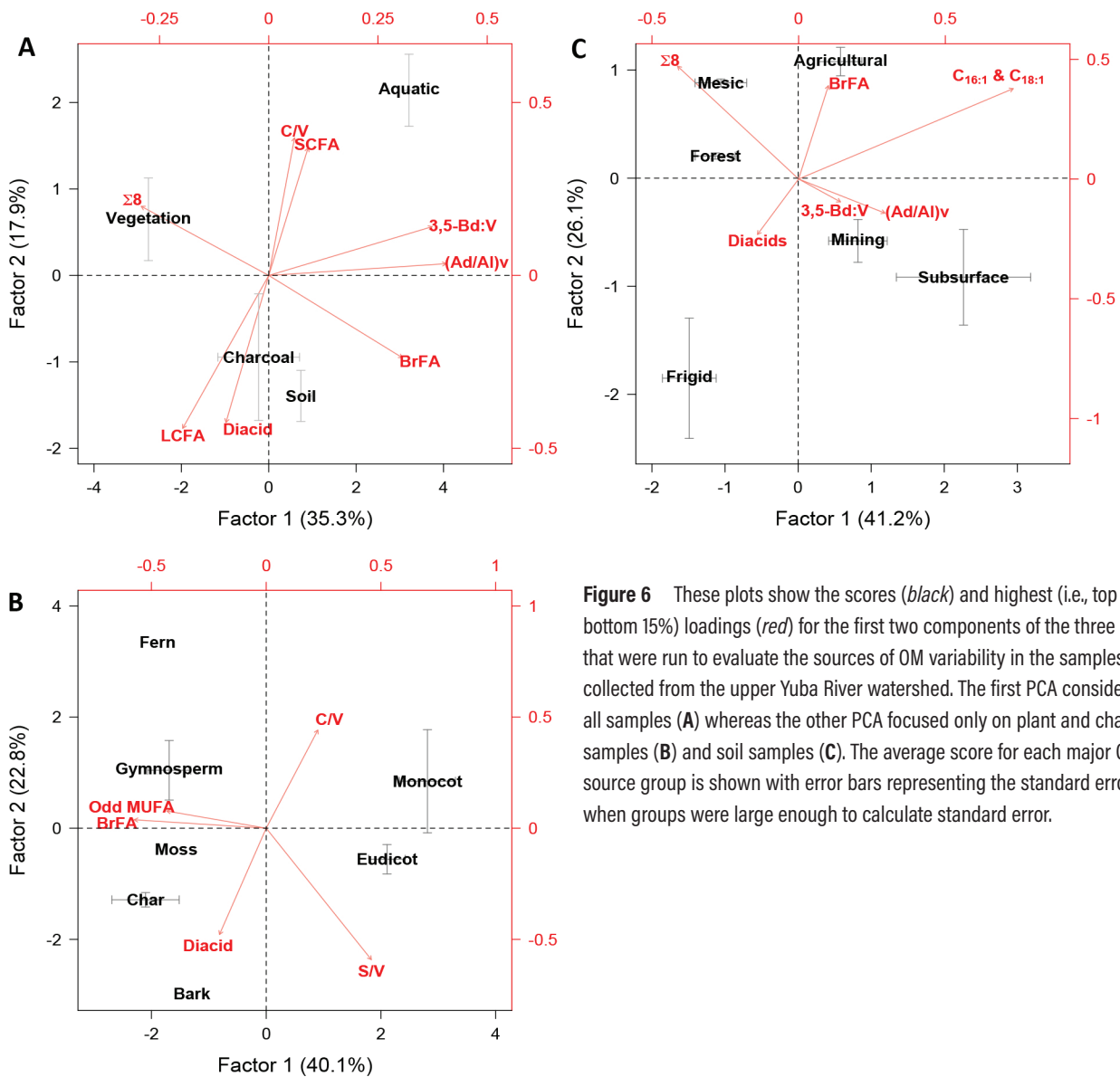


Figure 6 These plots show the scores (*black*) and highest (i.e., top and bottom 15%) loadings (*red*) for the first two components of the three PCAs that were run to evaluate the sources of OM variability in the samples collected from the upper Yuba River watershed. The first PCA considered all samples (A) whereas the other PCA focused only on plant and charcoal samples (B) and soil samples (C). The average score for each major OM source group is shown with error bars representing the standard error, when groups were large enough to calculate standard error.

A second PCA was applied to only the vegetation and charcoal samples using lipid and lignin biomarker data specific to higher plants, bacteria, and fungi (Figure 6B). By excluding aquatic and soil samples, this analysis provided greater resolution between the plant samples. Factors 1 and 2 from this PCA explained a total of 62.9% (40.1% from Factor 1 and 22.8% from Factor 2) of the variability in the biomarker data. Angiosperm samples (monocots and eudicots) grouped together with positive Factor 1 scores, while fir and pine, fern, and moss samples had negative Factor 1 scores. Overall, separation along Factor 1 was driven by positive loadings

for C/V and S/V and negative loadings for odd-numbered monounsaturated FA (Odd MUFA = $C_{15:1} + C_{17:1} + C_{19:1}$), BrFA and diacids (Figure 6B, Table 2). C/V had the highest positive loadings, while S/V and diacids had the most negative loadings for Factor 2. Gymnosperm, ferns, and monocot samples all plotted with positive Factor 2 scores, whereas eudicot, charcoal, bark, and moss samples had negative Factor 2 scores (Figure 6B, Table 2).

PCA was also applied to the soil samples using selected lipid and lignin biomarker data specific to higher plants, bacteria, fungi, and the (Ad/

Al)v degradation index (Figure 6C). Factors 1 and 2 from the soil PCA explained 41.2% and 26.1% of the variability in these biomarker data, respectively. $C_{16:1}$ and $C_{18:1}$ FA had the most positive loading for Factor 1 (0.732), while $\Sigma 8$ (-0.413) had the most negative loadings for Factor 1 (Figure 6C, Table 2). Mining, subsurface, and agricultural soils had positive Factor 1 scores, while the forest and roadside (frigid and mesic) had negative Factor 1 scores (Figure 6C). Agricultural, forest, and roadside mesic soils grouped in the positive region of Factor 2, which had positive loadings for $\Sigma 8$, BrFA, and $C_{16:1}$ and $C_{18:1}$ FA (Table 2, Figure 6C). In contrast, mining, subsurface, and roadside frigid soil samples plotted in the negative region of Factor 2 with (Ad/Al)v, diacids, and 3,5-Bd:V. Results from these PCAs will guide the following discussion, which focuses on trends in the biomarkers that have the highest loadings in these analyses.

DISCUSSION

Evaluating the Application of Bulk Organic Proxies to Discern OM Sources in the Upper Yuba Watershed

The bulk organic proxies (i.e., TOC, TN, $[C:N]_a$, $\delta^{13}C$, and $\delta^{15}N$) varied widely across the OM sources, and were effective in differentiating between aquatic and terrigenous OM sources and between fresh OM (i.e., plankton and higher plants) and the more aged OM (i.e., soils). $[C:N]_a$, $\delta^{13}C$, and $\delta^{15}N$ were most useful in distinguishing aquatic OM from terrigenous OM in the upper Yuba River watershed (Table 3). In general, low $[C:N]_a$ (< 10) and $\delta^{13}C$ values ($< -32\text{‰}$) are characteristic of freshwater aquatic OM sources (Meyers 1994; Kaushal and Binford 1999; Cloern et al. 2002), while high $[C:N]_a$ (> 20) and $\delta^{13}C$ ($-24\text{‰} < \delta^{13}C < -28\text{‰}$) values reflect terrigenous OM sources (Hedges and Oades 1997; Cloern et al. 2002). $[C:N]_a$ and $\delta^{13}C$ from samples collected throughout the upper Yuba River watershed were consistent with these reported values (Table 3), and showed that these proxies can be used to separate freshwater plankton from higher plants in the study region. Additionally, high $\delta^{15}N$ values in freshwater plankton samples reflect greater processing of nitrogen in aquatic samples than in terrigenous OM from the watershed, as has been

shown in other systems (Cifuentes et al. 1988). These $\delta^{15}N$ values are similar to values reported by Cloern et al. (2002) for freshwater seston measured within the San Francisco Bay estuary system ($3.7 \pm 2.8\text{‰}$).

TOC and TN contents were better able to identify differences between fresh OM and older, more processed OM. As expected, TOC and TN were higher in the fresh OM from the plant and plankton samples, and lower in the more aged OM from the soil samples (Table 3). The lower TOC and TN content of soils is consistent with increased OM processing through plant litter decomposition and contributions of microbial and fungal biomass associated with soil OM formation (Wedin et al. 1995).

In this discussion, we refer to aged OM as the OM that undergoes decomposition as it is incorporated into maturing and mature soils, and not to ancient petrogenic sources. Several studies have described radiocarbon throughout California, including the Eel River watershed in the northern Coast Ranges (Blair et al. 2003) and the Sacramento–San Joaquin River Delta (Canuel et al. 2009; Wakeham and Canuel 2016). Although the Blair et al. study (2003) identified kerogen as a source of ancient carbon, the geology of the watershed of the Eel River (shale-dominated Franciscan mélange) differs from the Yuba River, which drains primarily granitic rocks with some older metamorphic rock. Radiocarbon studies in the Delta suggest that aged carbon likely comes from human disturbance (i.e., agriculture and urbanization) and deep soil horizons (Canuel et al. 2009; Wakeham and Canuel 2016) and not from ancient carbon sources, such as kerogen. Therefore, it is unlikely that ancient sedimentary OM contributes a significant amount of OM to soils in the Yuba River watershed.

Using Biomarkers to Describe Differences Between and Within Groups of OM Sources in the Upper Yuba Watershed

Biomarkers in Aquatic Samples

SCFA had one of the highest loadings in the PCA for the full data set, and distinguished between aquatic and terrigenous sources of OM

(Figure 6A). Previous studies have also used SCFA as biomarkers for aquatic OM in lakes (Meyers and Ishiwatari 1993). In addition, odd-numbered MUFA ($C_{15:1} + C_{17:1} + C_{19:1}$) and BrFA were also characteristic of aquatic OM in Englebright Lake, suggesting inputs from microbial and heterotrophic bacteria sources (Volkman et al. 1980; Canuel and Martens 1993). Together, these compounds are consistent with autochthonous sources, including diatoms, protozoa, microbes, and zooplankton (Desvillettes et al. 1997; Jaffé et al. 2001; Lu et al. 2014)

Although the SCFA were able to distinguish broadly between OM from aquatic and terrestrial sources (Table 5, Figure 6A), sterols provided greater insight about the composition of the aquatic community in Englebright Lake. Brassicasterol and cholesta-5,22-dien-3 β -ol, commonly attributed to diatoms (Volkman 2003; Dunn et al. 2008; Nakakuni et al. 2018) and aquatic microalgae (Rampen et al. 2010; Martin-Creuzburg and Merkel 2016), were abundant in aquatic samples from Englebright Lake (Table 4). In addition, cholesterol and 27-nor-24-methylchoesta-5,22-dien-3 β -ol were abundant in the lake samples. Cholesterol has been observed at low levels in many microalgae (Volkman 2003), and is the dominant sterol in crustaceans, insects, and aquatic zooplankton (von Elert et al. 2003; Martin-Creuzburg et al. 2005). 27-nor-24-methylchoesta-5,22-dien-3 β -ol has been observed in marine dinoflagellates (Goad and Withers 1982) and other marine microalgae (Volkman 2003; Ginear et al. 2008; Martin-Creuzburg and Merkel 2016), including diatoms (Ginear et al. 2008; Ginear and Wikfors 2011; Volkman 2016). The absence of dinosterol, a sterol specific to dinoflagellates, in the aquatic samples from Englebright Lake suggests that dinoflagellates were not present, or were present in low abundance at the time of our sampling. Dinosterol has also been observed in eutrophied lakes where dinoflagellate are often abundant (Schwab et al. 2015), and the absence of dinosterol in Englebright Lake is consistent with its non-eutrophied state. The presence of 27-nor-24-methylchoesta-5,22-dien-3 β -ol in this freshwater system was unexpected because it is predominately a

biomarker of marine plankton species, yet it has been suggested that brassicasterol and 27-nor-24-methylchoesta-5,22-dien-3 β -ol are formed through similar pathways (Goad and Withers 1982), which could explain its presence in these freshwater samples. Together, these four sterols suggest that the plankton community in Englebright Lake comprises a mixture of diatoms and microalgae as well as crustaceans and aquatic insects. However, it is important to note that these analyses represent a single sampling of the summer plankton community in Englebright Lake, and that the plankton community's composition likely changes seasonally and interannually.

Aquatic sterols accounted for approximately 80% of the sterols detected in the large plankton fraction of the aquatic samples from Sites 1 and 2 in Englebright Lake, and sterols from higher plants make up the remainder (Table A3). However, at Site 3, higher plant sterols dominate (~60%) the sterol composition for the plankton tow samples (Figure 3B). This is consistent with the $\delta^{13}C$ value for plankton collected at this site, which was more positive (i.e., more similar to the $\delta^{13}C$ measured for the soil and vegetation samples) than the other plankton samples collected from this lake, suggesting there was a combination of aquatic and terrigenous OM at this location (Figure 3A, Table A3). The location of this site, within 200 m of the confluence of the South Yuba River and Englebright Lake, would allow for higher contributions of OM from terrigenous sources than at other locations that were sampled in the lake.

Biomarkers in Vegetation Samples

Additional analysis of the biomarker composition of the vegetation and charcoal samples was used to explore the high variability among these samples (Table 4, Figure 5B), and results from this analysis suggest that the multiple types of plants sampled from the watershed (i.e., gymnosperms, moss, ferns, etc.) contributed to the highly variable biomarker composition of this group of samples. For instance, C/V and S/V ratios and concentrations of BrFA differed between angiosperms samples (e.g., monocots and eudicots) and gymnosperms. BrFA, indicative of

bacterial OM sources (Volkman et al. 1980; Canuel and Martens 1993), were not detected in the monocot and eudicot samples, but were measured in all gymnosperm, moss, and fern samples (Table A2). Concentrations of BrFA likely reflect microbial colonization of these plant samples and not the production of BrFA by plants. Highest concentrations of BrFA were detected in the gymnosperm needle samples at concentrations similar to those reported by Jamieson and Reid (1972) for these gymnosperm clades (i.e., ~3% for *Pseudotsuga* spp. and ~1% for *Pinus* spp., Table A2). S/V followed expected trends and was higher in angiosperm samples than in gymnosperm samples (Table A1; Hedge and Mann 1979), and high C/V ratios were characteristic of monocots but not eudicots (Figure 4). Although a limited number of plants were sampled as part of this study, these data show some differences in the biomarker composition of the plant clades that were sampled, and suggest that more research may help to increase our ability to resolve the dominant vegetation regimes in different terrestrial and aquatic ecosystems.

Biomarkers in Soil

Soils collected from the upper Yuba River watershed were characterized by biomarkers representing contributions from higher plants (i.e., $\Sigma 8$, LCFA, $C_{22:0}$, and α, ω -dicarboxylic acids [C_{14} – C_{24} diacids]), heterotrophic bacteria (i.e., odd-numbered MUFA and BrFA), and fungi (i.e., $C_{18:1\omega 5}$), demonstrating that soil OM composition is a function of higher plant inputs and microbial contribution. For example, biomarkers such as LCFA, $\Sigma 8$, and ratios of S/V and C/V described the amount and type of plant material incorporated into the soils. The microbial biomarkers (i.e., BrFA, Odd MUFA, $C_{18:1\omega 5}$) and other indicators of OM degradation (e.g., (Ad/Al)_v) reflect the incorporation of vascular plant material into soil OM through fungal and bacterial biodegradation of plant OM during soil formation (Zelles 1999).

The soils collected as part of this study were selected to represent different land uses, ranging from relatively pristine forest to highly degraded mine soils, and present an opportunity to examine biomarker composition along a

gradient of land disturbance (forested to mining). For example, soil TOC and TN decreased along the land disturbance gradient (i.e., forested to mining) (Figure 2). Additionally, the abundance of brassicasterol was higher in more disturbed soils, such as the mining soils, and lower in soils such as the agricultural and forested soils (Figure 5C). This suggests that intensive land use such as mining may lead to changes in the dominant vegetation in an area, which affects the overall TOC and TN content in these disturbed soils. Brassicasterol is an indicator of inputs from plants in the Brassicaceae family (Schaeffer et al. 2001; Piironen et al. 2003; González-Pérez et al. 2011). Several species from this family are invasive weeds in North America that are well adapted to thrive in cleared areas such as mine pits or along roadsides (Pyšek 1998; Meekins et al. 2001). The presence of brassicasterol in soil samples from this region suggests a relatively high abundance of *Brassicaceae* in the upper Yuba River watershed, which is consistent with the history of land clearance and disturbance in the Yuba River watershed (i.e., agriculture, logging, mining, and construction). The transition from native plant communities to weedy, opportunistic plants in response to changes in land use has been observed in previous studies (e.g. Groves and Willis 1999; Tilman and Lehman 2001). Therefore, the observed trends in brassicasterol, TOC, and TN from this study likely reflect a transition from the native foothill woodlands or conifer forests characteristic of the Sierra Nevada region to invasive weeds as land was cleared for agriculture, road construction, and mining in the Yuba River watershed.

Along the gradient of land use disturbance, agricultural soils—representing a selection of agricultural practices, including rangeland, vineyards, and cropland—were most like forest soils (Table 2 and Figure 5). Both types of soils were characterized by relatively high inputs from higher plant sources (i.e., $\Sigma 8 > 0.9 \text{ mg g}^{-1}$ and LCFA > 20%, Figures 2C and 5D, Table 4), as compared to the roadside and mining soils. Agricultural soils were also distinguished from other soils by their elevated TN, low [C:N]_a, and concentrations of corprostanol (Figure 2B, Tables 3 and 4).

Corprostanol, combined with the high TN and low $[C:N]_a$, may reflect organic fertilizer addition that contained manure (Peng et al. 2005; Sebilo et al. 2013).

The composition of roadside soils tended to fall between the more plant-rich agricultural and forested soils and the more degraded mining soils. Interestingly, temperature seemed to affect the composition of the roadside samples, especially those characterized as frigid. In this study, roadside frigid soils had mean annual temperature between 0°C and 8°C, and were found at elevations > 1,000 m in the Englebright watershed, whereas roadside mesic soils had mean annual temperatures between 8°C and 15°C (Soil Survey Staff 1999). Concentrations of BrFA were lower in the roadside frigid soils relative to the other soils while $[C:N]_a$ were higher than most other soils collected from the upper Yuba River watershed (Figure 5B, Table 3). This suggests lower contributions of biomass from heterotrophic bacteria, possibly from the lower temperatures (Pietikäinen et al. 2005). In contrast, $[C:N]_a$ were lower and concentrations of BrFA in roadside mesic soils were higher than in the other soils collected for this study (Figure 5B), consistent with warmer temperatures being more favorable for microbial activity (Nicolardot et al 1994; Cleveland and Liptzin 2007; Walker et al 2018; Čapek et al 2019).

The biomarker analyses for the mining and subsurface (road cut) samples showed some interesting similarities. The OM-poor mining soils collected during this study reflect the gold extraction methods used for hydraulic mining during the Gold Rush era, where sediments were pressure washed from mountain-sides and mixed in a slurry of mercury to remove gold before being rinsed again and discarded in mine tailing pits (James 2005). The samples collected from mine tailing pits for this study had unusually low organic carbon content (%TOC < 1) when compared to other soils collected from the watershed. Interestingly, subsurface soil samples were similar in TOC content and biomarker composition to the mining soils (i.e., %TOC < 1, high (Ad/Al)_v, high 3,5-Bd:V, and high

brassicasterol compared to all other soil samples). This similarity likely reflects the degraded nature of the OM in these soils. For example, high 3,5-Bd:V indicate increased soil humification (Prahl et al. 1994; Houel et al. 2006), and high (Ad/Al)_v indicate an increasing degree of oxidative degradation (Hedges et al. 1988; Goñi et al. 1993; Opsahl and Benner 1995). In the mining and subsurface soils, the combination of high (Ad/Al)_v and 3,5-Bd:V are consistent with soil OM degradation either through subsurface microbial processes during soil horizon formation (Quideau et al. 2001) or physical leaching during mining.

Watershed Sources of OM Recorded in Englebright Lake Sediments

This study offers an opportunity to explore the extent to which the signatures of OM from the upper Yuba River watershed are recorded in the material deposited in Englebright Lake. Results from the PCA (Figure 6A) indicate that while multiple biomarker classes (i.e., fatty acids, sterols, and lignin) are needed to explain much of the variability in the composition of OM sources, a few select biomarkers can be used to differentiate between the major OM sources. SCFA, for example, describe aquatic OM, whereas $\Sigma 8$ identifies higher plant OM (Figure 6A). Selecting a biomarker to characterize soil OM presented more of a challenge because a mixture of OM sources (i.e., higher plants and microbes) are incorporated into these soils. Diacids and 3,5-Bd:V biomarkers with the highest values in the soils (Table 5) were selected to characterize soil OM. While diacids are derived from plant OM, they are an indicator of suberin in plant roots. When they are found in soils, they likely represent inputs to the soils from below-ground biomass rather than above-ground biomass (Pisani et al. 2013). Therefore, because concentrations of diacids in soils likely reflect the strong association between soils and root biomass and because 3,5-Bd:V describes the OM degradation common in soils (Prahl et al. 1994), these biomarkers appear to be appropriately specific to soils in the upper Yuba River watershed. BrFA and LCFA, biomarkers indicative of soil OM from the PCA shown in Figure 6A, were not selected for this analysis because they did not distinguish

between plant and soil samples. Additionally, the correlation between $\Sigma 8$ and 3,5-Bd:V—both measurements of lignin phenols—was sufficiently low (-0.19) to allow these biomarkers to be used as independent tracers in the subsequent analysis.

Sediment cores from Englebright Lake were sampled from the deepest channel of the lake in 2002 by the USGS (Snyder et al. 2004), and bulk organic proxies (Pondell and Canuel 2017) and biomarkers (Pondell and Canuel 2020) were analyzed to understand how OM accumulation in the lake responded to changing climate and land use between 1940 and 2000. Results from these studies show that average $\delta^{13}\text{C}$ values ranged from -28 to -22% (Pondell and Canuel 2017) and that concentrations of biomarkers such as LCFA, $\Sigma 8$, brassicasterol, and diacids showed significant responses to events such as floods or dam construction in the watershed (Pondell and Canuel 2020). A comparison of the SCFA, $\Sigma 8$, and (Ad/Al)_v biomarkers in the major OM sources in the upper Yuba River watershed and in the surface sediments deposited in Englebright Lake (Pondell and Canuel 2017, 2020) reveals that terrestrial sources of OM dominate the lake sediments (Figure 7). Since terrestrial OM tends to be more refractory than aquatic OM (Meyers and Ishiwatari 1993), it is expected that the terrestrial OM deposited in Englebright Lake remains relatively unchanged as it gets buried (Meyers 1994). Further, if we assume that the OM composition of the lake surface sediments reflects OM sources from the watershed, sediments deposited in Englebright Lake are most similar to the roadside soil samples collected in the watershed (Figure 7). Roadside soils tended to represent the median values for biomarker concentrations in soils from the watershed, with a few exceptions (Figures 2 and 5). This suggests soils may be a dominant source of OM to Englebright Lake because they may be more susceptible to erosion and mobilization from the watershed to the lake (Lal 2003).

Previous research in Englebright Lake suggests that flooding events affect the delivery and accumulation of sediments in the lake particularly strongly. Sediment accumulation

rates increase significantly during floods (i.e., up to 100 cm yr^{-1} ; Snyder et al. 2006; Pondell et al. 2015, 2017) and OM composition during these events is more characteristic of vegetation and plant detritus (Pondell and Canuel 2020). These observations in Englebright Lake are consistent with storm event deposits in other impounded lakes (e.g., Blair et al. 2018). It is likely that during these flood events—often caused by intense rainfall—heavy precipitation will lead to surface runoff, which transports large amounts of plant detritus from the soil surface into rivers and lakes (Dhillon and Inamdar 2014). Thus, processes such as surface runoff during high-precipitation storm events and soil erosion during periods of normal river discharge likely control the delivery of OM from the Yuba River watershed to Englebright Lake. Results from this study suggest a strong connection between OM sources in the watershed and the deposition of OM in a lake in a small, mountainous river system, and that the mechanisms supporting this connection may change in response to changing watershed conditions, such as discharge, precipitation, and soil erodibility.

Summary

The biomarker composition of materials from Englebright Lake and the upper Yuba River watershed describe OM sources common to small, mountainous river watersheds. The multi-biomarker approach used in this study was able to identify unique signatures for soils, plants, and plankton to characterize OM sources throughout the watershed, and revealed a pattern of increased OM alteration in response to the degree of disturbance (both human- and climate-caused). In this small, mountainous watershed, sediment OM in Englebright Lake closely resembled terrestrial OM sources from the upper Yuba River watershed, including soil OM during average river flow conditions and higher plant OM during flood events. Connectivity between watersheds and lakes and rivers has the potential to significantly affect the global carbon cycle, and information from this study defines the signatures of terrestrial and aquatic (lentic/lotic) OM delivered to aquatic environments, specifically soil, aquatic plankton, and higher plants. This information

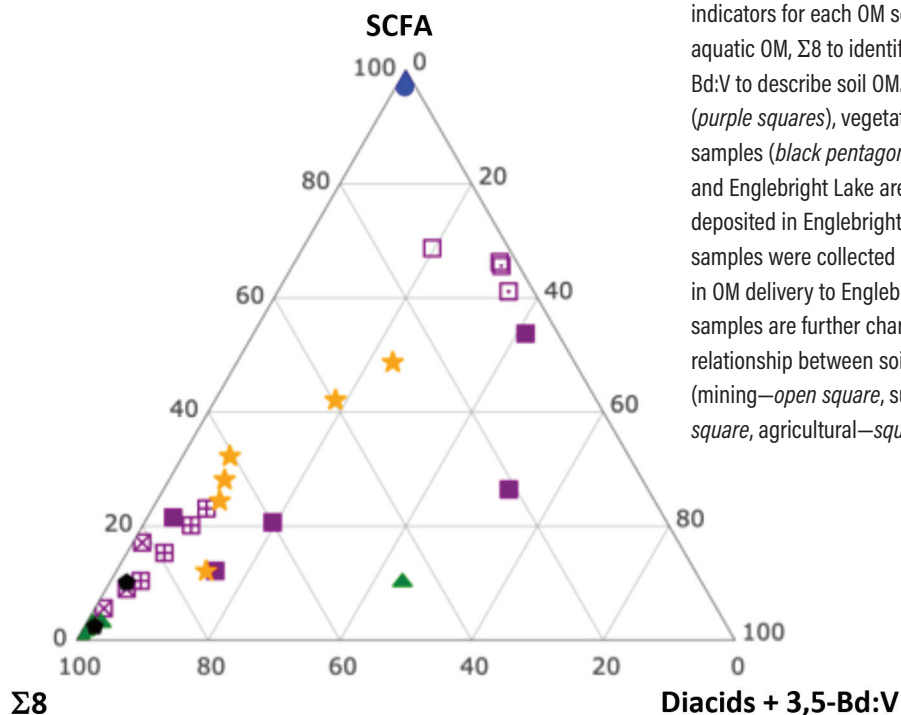


Figure 7 Ternary diagram of biomarkers identified to be the best indicators for each OM source through PCA, including SCFA to identify aquatic OM, $\Sigma 8$ to identify higher plants, and α, ω -diacids and 3,5-Bd:V to describe soil OM. Aquatic samples (*blue circles*), soil samples (*purple squares*), vegetation samples (*green triangles*), and charcoal samples (*black pentagons*) collected from the Yuba River watershed and Englebright Lake are shown along with surface sediment samples deposited in Englebright Lake (*orange stars*). The surface sediment samples were collected as part of a broader study of temporal changes in OM delivery to Englebright Lake (see Pondell and Canuel 2020). Soil samples are further characterized by different symbols to show the relationship between soil sample type and surface sediment composition (mining—*open square*, subsurface—*square with dot*, roadside—*solid square*, agricultural—*square with "+"*, forest—*square with "x"*.)

expands our understanding of processes that influence the source signatures of these materials and enhances our ability to describe organic carbon composition in small mountainous river watersheds.

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