

Linkages between mineral element composition of soils and sediments with hyporheic zone dissolved organic matter chemistry across the contiguous United States

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Abstract

The hyporheic zone is a hotspot for biogeochemical cycling where interactions with mineral metals preserve the release and biodegradation of organic matter (OM). A small fraction of OM can still be exchanged between localized sediments and the overlying water column, and recent evidence suggest there exists a longitudinal structuring in sediment dissolved OM (DOM) chemistry across the continental United States (CONUS). In this study, we tested a hypothesis that water extractable sediment DOM chemistry could be explained by sediment metal contents and integrative watershed scale features at the CONUS scale. Crowdsourced samples were characterized for high resolution mass spectrometry and coupled with sediment metals determined via x-ray fluorescence as well as with land cover and soil elemental information obtained from national databases. Our results highlight weak relationships between DOM chemistry and elemental composition at the CONUS scale indicating limited transferability of organo-metal linkages into multi-scale hydrobiogeochemical models.

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**Linkages between mineral element composition of soils and sediments with hyporheic zone
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Plain language summary

The hyporheic zone is a vital area for chemical cycling that influences the breakdown of organic matter due to interactions with minerals and metals. Some organic matter moves between sediment and water. Recent findings show a pattern in dissolved organic matter chemistry in sediment across the US. The study tested whether sediment's organic matter chemistry could be explained by its metals and surrounding features. Crowdsourced samples underwent analysis along with sediment metals, land cover, and soil elements. Results revealed weak connections between dissolved organic matter chemistry and elements, indicating limits in applying these connections to continental scale models.

Key Points

1. Sediment dissolved organic matter chemistry is longitudinally structured across the continental United States.
2. Sediment and soil mineral elemental compositions were weakly correlated with sediment dissolved organic matter composition
3. Localized metal-organic matter linkages likely have limited capacity to inform continental-scale hydrobiogeochemical models.

Abstract

The hyporheic zone is a hotspot for biogeochemical cycling where interactions with mineral metals preserve the release and biodegradation of organic matter (OM). A small fraction of OM can still be exchanged between localized sediments and the overlying water column, and recent evidence suggest there exists a longitudinal structuring in sediment dissolved OM (DOM) chemistry across the continental United States (CONUS). In this study, we tested a hypothesis

that water extractable sediment DOM chemistry could be explained by sediment metal contents and integrative watershed scale features at the CONUS scale. Crowdsourced samples were characterized for high resolution mass spectrometry and coupled with sediment metals determined via x-ray fluorescence as well as with land cover and soil elemental information obtained from national databases. Our results highlight weak relationships between DOM chemistry and elemental composition at the CONUS scale indicating limited transferability of organo-metal linkages into multi-scale hydrobiogeochemical models.

Key Words

hyporheic zone; continental; crowdsourced data; organo-mineral interactions; river corridor; hydro-biogeochemistry

1. Introduction

Hyporheic zones within river corridors are considered major hotspots for biogeochemical cycling and are important for nutrient availability, water quality, and ecosystem function (Boano et al., 2014; Findlay, 1995). Within hyporheic zones, organic matter (OM) and nutrients are exchanged between surface sediments and the overlying water column. A fraction of this OM is transported in the dissolved phase (DOM) and is easily metabolized, whereas other fractions are selectively preserved in sediments through interactions with sediment minerals (Lalonde et al., 2012). While a majority of the OM stored in sediments is considered insoluble, a small fraction sorbed onto sediments can be detached and is easily solubilized (Kang & Xing, 2008; Tao & Lin, 2000). This water-soluble OM represents a significant source of sediment contributed DOM to rivers that may be further consumed through microbially mediated processes (Tao, 1998; Zhou et al., 2019), thus, implicating organo-mineral interactions as key contributors to biogeochemical processes in hyporheic zones.

91
92 The relationships between DOM and sediment metals have been well studied (Kleber et al.,
93 2021), and the transferability across scales is crucial to ensure the meaningful adaptation into
94 multi-scale river corridor hydrobiogeochemical models. Broadly, DOM-metal relationships are
95 driven by strong adsorptive processes at the sediment particle surface and are selective for DOM
96 fractions based on the overall sediment metal composition (J.-G. Lin & Chen, 1998). For
97 example, adsorption of DOM onto sediments containing iron oxides and hydroxides involves a
98 combination of both physical and chemical interactions and exhibit considerable adsorption
99 capacity for highly aromatic DOM (Chen et al., 2020; Li et al., 2023; Shields et al., 2016;
100 Wordofa et al., 2019). Similar observations have also been observed involving other metals such
101 as aluminum, manganese, and copper under varying environmental conditions (Coutinho et al.,
102 2021; Lee et al., 2022; Scheel et al., 2007). Our current understanding of such organo-mineral
103 interactions is typically based on laboratory simulations and site level studies, which provide a
104 comprehensive understanding of these interactions at localized scales. However, limitations
105 remain in describing the transferability of such interactions across scales.

106
107 There is some evidence to indicate that sediment DOM chemistry could be linked with sediment
108 metal concentrations at continental scales. Across the continental United States (CONUS),
109 geological formations have largely driven a longitudinal structuring in the elemental composition
110 of soil minerals and sediments (Grossman et al., 2004). Soils in the Western CONUS, for
111 example, are reported to have elevated aluminum and iron concentrations (Shacklette and
112 Boerngen 1984). Similarly, recent evidence suggest that the composition of DOM extracted from
113 hyporheic zone sediments also exhibits longitudinal structuring with clear shifts in
114 thermodynamic favorability along the east-west gradient (Vanessa A. Garayburu-Caruso et al.,
115 2020); however, explanations for this observation have not yet been well constrained.

116
117 In this study, we tested a hypothesis that longitudinal structuring of water extractable DOM from
118 hyporheic zone sediments across the CONUS is linked with sediment metal distributions. More
119 specifically, because iron is known to play a key role in the stabilization of aromatic, carboxylic
120 rich DOM in sediments, we hypothesized that sediment iron would explain more variation in
121 DOM chemistry than other sediment metals. To test these hypotheses, we used crowdsourced

data generated as part of the Worldwide Hydrobiogeochemical Observation Network for Dynamic River Systems (WHONDRS) consortium in summer 2019 (Borton et al., 2022). Data available included sediment elemental composition and ultra-high resolution mass spectrometry for water extracted sediment DOM for samples across the CONUS. In addition, we extended our analysis beyond site level elemental composition to include additional watershed scale features, which would be representative of a more integrative regional scale contributions to the downstream transport and deposition of particulate material to local sediments. As such, we used land cover as an indicator of organic matter source that we hypothesized would be strongly linked with the sediment DOM composition (Liu et al., 2019). Additionally, we included soil elemental data from the US Geological Survey that may serve as an indicator of upstream hyporheic zone sediment sources that interact with DOM during transport within the watershed. For this, we hypothesized that soil elemental composition would not only correlate to hyporheic zone sediment elemental composition (Salomão et al., 2021) but may also account for additional variability in the DOM composition. Our results describe significant though relatively weak linkages between both sediment and soil metals and DOM at the CONUS scale and have significant implications for our conceptualization of organo-mineral interactions and their scalability from localized processes into multi-basin predictive frameworks of hyporheic zone biogeochemical function.

2. Methods

2.1 Sample Collection and Data Availability

The data for this work was obtained from a publicly available database accessed on the Environmental System Science Data Infrastructure for a Virtual Ecosystem (ESS-DIVE) repository (Goldman et al., 2020). The samples were collected as a part of a CONUS scale crowdsourced sampling campaign by the WHONDRS consortium in the Summer 2019 (Stegen & Goldman, 2018). Complete methodological details for sample collections are available at Garayburu-Caruso et al. (2020). Briefly, participants were sent a kit that included basic sampling equipment for sediment collection along with detailed written instructions and a video to ensure standardized sample collections. Within a 6-week period between August and September 2019,

sediments were collected according to NEON protocols (NEON.DOC.001193) at 97 sites, with 3 replicates taken from separate depositional locations within each site. Samples were shipped to the Pacific Northwest National Laboratory within 24 hours of collection. Upon receiving, sediments were sieved to <2mm, flash frozen, and stored at –80 °C until ultra-high resolution mass spectrometry analysis. Sediment samples collected for mineralogy were stored at -20 °C.

2.2 Soil Elemental and Land Use Data

Watershed land cover was extracted for each site from the 2016 National Land Cover Database (Dewitz, 2020) and represents the average relative land cover for the upstream drainage area for each site (Garayburu-Caruso et al., 2022). Primary land cover classes considered include croplands, grasslands, shrubs, urban, and forests. Soil chemical data was obtained from the 2004 National Geochemical Survey provided by the United States Geological Survey (Grossman et al., 2004). The spatial spread of the sample point locations that make up the National Geochemical Survey allowed for a 500m resolution interpolation of the chemical composition across the continental U.S using ordinary Kriging technique (Wackernagel, 1995). Kriging uses the known variance of measured points in area to estimate the continuous composition of a larger region (Pang et al., 2009). Interpolation was completed using point locations of calcium (Ca), copper (Cu), iron (Fe), silicon (Si), and phosphorus (P). Average elemental concentrations within the upstream catchment area from the sampling location were the extracted using the Geospatial Data Puller for Waters in the Contiguous Unites States tool for R (Willi & Ross, 2023).

2.3 X-ray Fluorescence

Sediment elemental analysis was performed using a Bruker M4 plus x-ray florescence (XRF). Sediment samples were prepared by drying at 60 °C for 48 hours and were then ground and homogenized using a ball mill. Ground samples were randomized and packed into the center of custom acrylic disks and sealed with Kapton tape. The XRF samples were run with a XFlash VH50C-LE. Primary analytes measured included silica (Si), phosphorus (P), calcium (Ca), manganese (Mn), iron (Fe), and copper (Cu).

2.4 Sediment Extractions

Extractions were performed on thawed sediments at a 1:2 ratio of sediment to MilliQ water while shaking in the dark at 375 rpm at 21°C for 2 hours. The samples were then centrifuged at 21 °C at 6000 rcf for 5 minutes. The supernatant was filtered through a 0.22µm polyethersulfone (PES) membrane filter. The sediment extracts were then normalized to DOC concentrations of 1.5 mg/L and acidified to pH 2 with 85% phosphoric acid. The DOM was then extracted using PPL (styrene divenyl benzene polymer, Agilent Bond Elut) cartridges using protocols described by Dittmar 2008.

2.5 Fourier Transform ion Cyclotron Resonance Mass Spectrometry

Samples were characterized by Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS) analysis at the Environmental Molecular Sciences Laboratory in Richland, WA. Detailed methodological information is provided in Garayburu-Caruso et al., 2020. Briefly, samples were injected into a 12 T Burker Solarix FTICR mass spectrometer equipped with an electrospray ionization source. Samples were analyzed in negative (-) mode with an ion accumulation of 0.1-0.2s. One-hundred forty-four scans were co-added and internally calibrated with an OM homologous series separated by 14 Da (-CH₂ groups). The mass accuracy was typically within 1 ppm for the collected mass range (100-900 m/z). Bruker Daltonik Data Analysis (version 4.2) was then used to convert spectra into a list of m/z values with a signal to noise threshold set at 7. Peaks were then aligned, and chemical formulae were assigned using Formularity (Tolić et al., 2017) and considering only the presence of C, H, O, N, S, and P. Common molecular indices, such as the aromaticity index (Koch & Dittmar, 2006, 2016) were further calculated with the R package fmsRanalysis (Bramer et al., 2020). We further binned identified peaks based on their presence-absence distributions within a sample into common biomolecular classes (e.g. lignin-like, protein-like) (Kim et al., 2003). We note that placement of a peak within these classes does not constitute a positive identification but is rather a broad acknowledgement of stoichiometric similarity between the molecular formula of the identified peak and the biomolecular class.

2.6 Statistical Analysis

All statistical analyses were performed with the R statistical platform version 4.2.2 (R Core Team, 2015). Prior to analysis, XRF and the relative proportion of binned biomolecular classes for the 3 replicates collected at each site were averaged. General linear relationships among variables were then described with Pearson correlations. Redundancy analysis (RDA) were performed with the vegan package (Okansen et al., 2020) to describe variability among FTICR-MS biomolecular classes (response variables) with sediment elemental composition and other environmental parameters (predictor variables). The final model was built after downselecting important variables using the ‘ordistep’ function, a stepwise model building function for constrained ordination analyses (Okansen et al, 2020).

3. Results and Discussion

3.1 Sediment DOM is significantly but weakly related with sediment elemental composition

At the CONUS scale, we observed that the composition of water extractable DOM released from hyporheic zone sediments was highly variable and exhibited a longitudinal structuring that was weakly correlated with local sediment elemental composition. In the eastern United States, sediment DOM had a proportionally higher diversity of aromatic compounds compared to the west coast, where more saturated and potentially more bioavailable protein and carbohydrate-like molecular formula were detected (Figure 1). This distribution was not explicitly mimicked for the sediment elemental composition as most elements had a poor relationship with longitude (Figure 1). Given such, these elements (Si, P, Ca, Mn & Fe) also exhibited poor or insignificant relationships with the diversity of measured DOM biochemical classes (Figure 2). Alternatively, Cu was the primary element that provided consistent relationships with the observed CONUS scale spatial distribution of DOM. More specifically, there was a significant relationship between Cu and the relative fraction of molecular formula identified as highly aromatic, such as lignin-like ($r^2 = 0.20$, $p < 0.001$) and tannin-like ($r^2 = 0.09$, $p < 0.05$), and an inverse relationship with the relative fraction of molecular formula identified as protein-like ($r^2 = 0.16$, $p < 0.001$) and

carbohydrate-like ($r^2 = 0.27$, $p < 0.001$). This is further highlighted in a redundancy analysis where Cu was the only element to provide significant explanatory power for the diversity of sediment DOM molecules present (Figure 3, Table 1).

While the primary relationships with Cu alone within the RDA were somewhat surprising, it is notable the impact of increased Cu can have on river corridor biogeochemistry that may explain some of these trends. For instance, elevated Cu can have a significant impact on microbial community structure and negatively impact heterotrophic respiration in river sediments (Ahmed et al., 2018), and the availability of DOM for hyporheic exchange may be driven by broad scale heterogeneity in microbial turnover rates and/or diversity of microbial communities (Radke & Maier, 2014; Schaper et al., 2018). Such processes have been directly tied to the release and preferential consumption of protein- and lipid-like DOM within the hyporheic zone (Zhou et al., 2019). Furthermore, organo-metal complexation involving Cu preferentially target aromatic rich DOM fractions (Coutinho et al., 2021; Huang et al., 2021; Skrabal et al., 1997; Xu et al., 2019), and Cu binding ligands involving aromatic humic substances can be easily mobilized out of sediments into overlying surface waters (Lehman & Mills, 1994; Nissenbaum & Swaine, 1976). While we did not directly measure organo-Cu complexation, this potential explanation would be consistent with the linkages between Cu and a higher diversity of aromatic-like molecular formula observed in this study. These relationships highlight Cu as a potential important linkage to our conceptual understanding of DOM exchange within the hyporheic zone.

Organo-metal interactions have been recognized as an important component of local sediment biogeochemical processes. While our results indicate a potential importance of Cu over the chemistry of DOM released from hyporheic zone sediments, we more directly hypothesized that Fe would have stronger explanatory power given its strong affinity for DOM interaction. For example, the adsorption to reactive Fe-oxyhydroxide surfaces is considered as an important mechanism for OM preservation in sediments (Lalonde et al., 2012), and co-precipitation of select aromatic DOM fractions with Fe during aquatic transport can provide a fresh source of terrestrial OM to sediments (Chen et al., 2014; Du et al., 2018). Thus, we found it surprising that there were no clear linkages between the observed DOM chemistry and Fe in this study (Figure 2). As such, this observation suggests a systematic disconnect in the ability to detect predictable

patterns of DOM exchange at the CONUS scale based on known physiochemical associations relevant at local scales. There are several plausible explanations for this observation. First, organic-Fe linkages are strongly driven by the presence of iron(III) (Lalonde et al., 2012). While we assume there is high probability the bulk of iron in these sediments is in the form of iron(III), this was not directly measured. Additionally, the analytical approach taken reflects bulk sediment elemental composition rather than reflecting elements only on the reactive sediment surface where DOM availability would be controlled by surface complexation with iron(III). Organo-Fe linkages are also considered fairly stable, and the dissolution of such complexes generally requires high pH and extreme redox conditions (Grybos et al., 2009). Thus, sediment DOM extracted in MQ may be best described as that which is readily available and easily exchanged at the sediment water interface (Tao & Lin, 2000), which is unlikely to impact stable organo-metal complexes such as those involving iron. On the other hand, Cu-binding organic matter is more easily mobilized from sediments (Skrabal et al., 1997) and is consistent with the observed linkages between Cu and the sediment extracted DOM composition in this study.

Section 3.2: Sediment DOM is significantly but weakly related to land use and soil elemental composition

While the CONUS scale relationships between Cu and DOM composition were significant, we recognize such relationships are statistically weak (e.g., $r^2 < 0.3$ in most cases) indicating significant variability across the dataset that remains unexplained. Like the sediment elemental composition, watershed soil elemental composition provided weak relationships with the individual DOM biochemical classes (Figure 2). Within multivariate space, however, soil Cu again was the only significant addition in terms of explanatory power in the spatial variation in sediment DOM composition and displayed similar linkages to aromatic type molecular formula. However, this added explanatory power was <4% (Table 1) and may not be environmentally relevant on its own.

While soil Cu added a small amount of explanatory power, its relationship with DOM chemistry was significant in both univariate (Figure 2) and multivariate (Figure 3) analyses. This is consistent with the sediment elemental data, and thus indicates Cu as potentially important for

understanding hyporheic zone DOM chemistry across the CONUS. Elements like Cu may play a pivotal role in bioavailability and the residence time of aromatic DOM through a watershed from the upland soils to the hyporheic zone sediments (Liu et al., 2019; Salomão et al., 2021). Such relationships are subject to a myriad of complex interactions, including the impact of human activities (urbanization, mining, agriculture) which can lead to increases in Cu concentrations in streams compared to the surrounding soils (Lin et al., 2022; Wang et al., 2021).

In addition to the soil elemental composition, we included land cover as a source indicator for organic matter traversing the aquatic network that may undergo deposition and exchange at the sediment-water interface. Of the five major land cover classes, shrublands and grasslands provided the only significant relationships with any of the DOM biochemical classes (Figure 2). For instance, each were both inversely related to the relative richness of highly aromatic-like formulae and positively related with higher relative richness of carbohydrate- and protein-like formulae. This result is generally consistent with biomarker research that highlights an enrichment of hemicellulose and protein rich materials in grasslands and a depletion of lignin in comparison to woody forest soils (Bianchi & Canuel, 2011; Dümig et al., 2013). This relationship is further emphasized in multivariate space giving a bidirectional pull along both RDA1 and RDA2, indicating its linkage to more aliphatic type biochemical classes. It is notable however, that land cover provided around 10% of the explanatory power (Table 1) in how sediment DOM is longitudinally structured at the CONUS scale. This observation was surprising given the strong historical support of linkages between landcover and the composition of OM traversing through aquatic realms in both dissolved (S. Chen et al., 2021; Roebuck et al., 2020; Williams et al., 2010; Wilson & Xenopoulos, 2009) and particulate phases (Jung et al., 2015; Longworth et al., 2007; Lu et al., 2014).

4. Conclusions (or Implications)

Our results show a continental scale gradient in the composition of water extractable sediment DOM that displayed significant but weak associations with local sediment elemental composition, as well as soil elemental and land cover composition of the upstream drainage area. Relative to soil elemental or land cover composition, sediment elemental composition had

stronger relationships with relative diversity gradients within compound classes (Fig. 2) and overall DOM chemistry (Fig. 3). This indicates that highly localized processes, within sediment pores, have a stronger influence over hyporheic zone DOM than watershed-scale processes associated with hillslope soils and DOM sources. A conceptually similar inference was found via analyses of DOM biochemical transformations, which were fully decoupled between physically adjacent surface water and sediments (Stegen et al., 2022). Further insights on additional controls over hyporheic zone DOM chemistry remain elusive and further evaluation is needed.

Our results further indicate that highly localized controls on DOM chemistry may be tied to biogeochemical history of sediments in a manner that limit capacity to explain CONUS-scale variation. For example, localized variation in hydrological flow (e.g., sediment transport), sediment residence time (e.g. potential for microbial turnover), and depth of the overlying water column (e.g. potential for photochemical impacts) may all contribute to the underlying biogeochemical controls on DOM chemistry associated with hyporheic zone sediments. We infer that our current understanding of DOM-metal linkages does not necessarily transfer across CONUS streams/rivers, limiting the use of localized studies to inform CONUS-scale models. The minimal explanatory power of both land cover and soil elemental composition further highlights the difficulty in extrapolating site- and regional-scale biogeochemical mechanisms to multi-basin and continental scales. Future studies should continue with efforts to identify broad scale linkages between sediment DOM chemistry and localized biogeochemical process that better enable predictive modeling of river corridors across diverse settings and large spatial scales.

5. Data Availability

All high-resolution mass spectrometry and XRF data used for the curation of this manuscript can be obtained free from the Environmental System Science Data Infrastructure for a Virtual Ecosystem (ESS-DIVE) Data Repository (Goldman et al., 2020). Watershed land cover data is available at ESS-DIVE via V A Garayburu-Caruso et al. (2022). An additional data package containing all scripts relevant to this manuscript in addition to the interpolated National

Geochemical Survey data will be available at the time of revision. For the purposes of review, we have provided a singular data file containing all relevant data and code required to reproduce figures and statistical results.

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8. Tables

Table 1: Redundancy analysis model output showing the proportion of variance in organic matter chemistries explained by the different sediment and soil elements and land cover.

Parameter	Degrees of Freedom	Variance	F	P (>F)
Sediment Copper (wt percent)	1	1.0647	11.3941	0.001
Soil Copper (ppm)	1	0.2909	3.1014	0.031
Percent Shrub	1	0.2360	2.5153	0.075
Percent Grass	1	0.1829	1.1498	0.115
Percent Forest	1	0.4093	4.3636	0.007
Residual	62	5.8162		

Figure 1: Percent of FTICR-MS biomolecular classes as a function of longitude

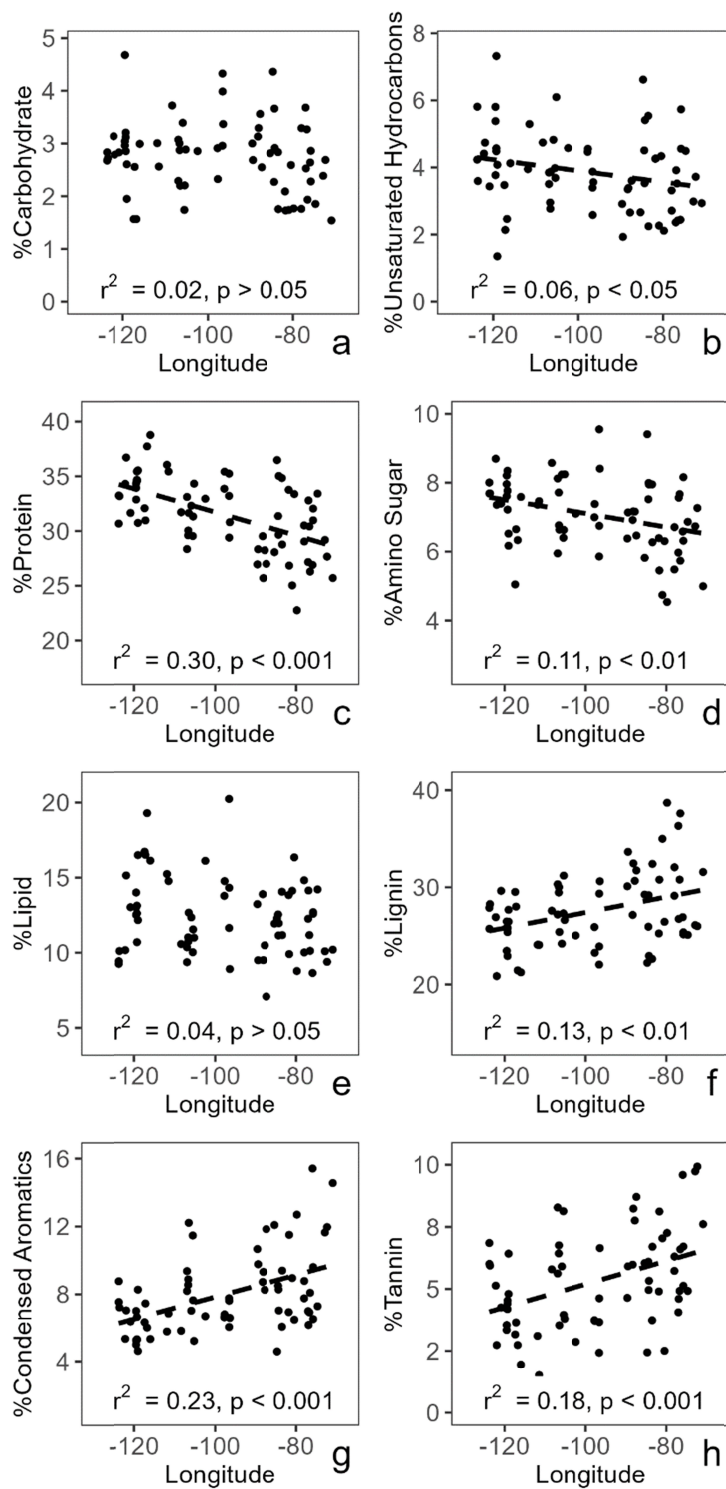


Figure 2: Correlation Matrix to show r^2 values for significant correlations ($p < 0.05$) between FTICRMS biochemical classes with sediment and soil elemental composition as well as land cover.

	%Amino Sugar	%Carbohydrates	%Condensed Aromatics	%Lignin	%Lipid	%Protein	%Tannin	Unsaturated Hydrocarbon	Longitude
Longitude	-0.11		0.22	0.13		-0.29	0.17	-0.06	1.00
%Si (sediment)		-0.10	0.11			-0.06	0.13		
%P (sediment)			0.11				0.07		
%Ca (sediment)		0.14					-0.06		
%Mn (sediment)									
%Fe (sediment)									
%Cu (sediment)	-0.23	-0.29	0.06	0.18		-0.16	0.08		
%Crop									
%Grass		0.12					-0.07		
%Shrub			-0.08			0.11	-0.08		-0.22
%Urban									0.11
%Forest									-0.07
Ca_wt_percent (soil)									
Cu_ppm (soil)	-0.07		0.08			-0.06			0.09
Fe_wt_percent (soil)	0.10		-0.08			0.10			-0.16
Mn_wt_percent (ppm)									
P_wt_percent (soil)	0.06		-0.06	-0.07		0.11			-0.34

Figure 3: Redundancy Analysis generated with results from stepwise model building for constrained ordination. Panel (a) is the RDA while panel (b) displays RDA 1 as a function of longitude.

