ORGANIC MATTER SOURCES, COMPOSITION, AND QUALITY

IN RIVERS AND EXPERIMENTAL STREAMS

by

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ABSTRACT

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Organic matter (OM) regulates important ecosystem functions such as nutrient and pollutant retention, ecosystem respiration, and primary production. Through these processes, rivers remove or slow transport of inorganic nutrients and OM that cause eutrophication, and transform pollutants that otherwise are be transported to downstream receiving waters. My study was motivated by research questions such as: How does OM source and composition differ in reference versus urban watersheds with wastewater inputs? How does OM source and quality (*i.e.* lability) differ across watersheds that vary in land cover associated with human development? How much faster does labile OM decay than semi-labile OM in rivers? What is the effect on decay rates when labile and semi-labile OM pools of varying lability are mixed? To address these questions, I

collected particulate OM (POM) and dissolved OM (DOM) in four watersheds of Northeastern Utah. I also measured decay rates of DOM from various experimentally derived OM sources in experimental streams. I identified and quantified the proportion of autochthonous, terrestrial, and anthropogenic sources of OM within an entirely urban watershed, and found significant contribution from anthropogenic sources such as a eutrophic lake and wastewater treatment plant (WWTP) effluent. I evaluated the effects of different land covers including urban and suburban development, crops, and other agriculture on OM composition, and found that OM from WWTPs was distinct from terrestrial and autochthonous OM in the same watersheds. Lastly, I measured microbial rates of OM consumption that varied in source and quality, including high quality OM such as algal leachates and lower quality OM such as soil and plant leachates. These experiments revealed extremely fast DOM decay rates in experimental streams (1.7/day). Forty percent of impaired rivers and streams in the U.S. are impaired due to sedimentation and OM enrichment. My study identified OM sources, characterized lability, and quantified microbial consumption of common OM sources to rivers. This information will inform management decisions aimed at reducing organic matter loads in rivers, such as whether to focus on reducing primary production of autochthonous sources, or regulating terrestrial and anthropogenic OM inputs.

(212 pages)

PUBLIC ABSTRACT

Organic Matter Sources, Composition and Quality in Rivers and Experimental Streams

Julia E. Kelso

Organic matter (OM) is often considered the "currency" for ecosystem processes, such as respiration and primary production. OM in aquatic ecosystems is derived from multiple sources, and is a complex mixture of thousands of different chemical constituents. Therefore, it is difficult to identify all the sources of OM that enter and exit aquatic ecosystems. As humans develop undisturbed land, the rate at which terrestrial OM (*e.g.* soil and plants) and associated nutrients (*e.g.* nitrogen) enters rivers has increased. Increased nutrients may lead to increased primary production from aquatic plants and algae, potentially causing eutrophication and harmful algal blooms. In this study, I identified and characterized different sources of OM in four watersheds of Northeastern Utah with multiple land covers such as cities, forests, and crops. I expected OM in watersheds with human-altered land cover would have more OM produced instream by algae and other primary producers, than OM in less disturbed watersheds, which typically have OM from terrestrial sources. I found that OM at river sites with high human impact had high amounts of OM from instream primary production, but there was also OM produced in-steam at sites with low human impact. The greatest differences in OM across watersheds was due to wastewater treatment effluent. I also measured microbial consumption rates of algal derived and terrestrially derived DOM in experimental streams to quantify how much faster algal derived OM was consumed than

terrestrial OM. I found algal derived OM was consumed extremely fast, so fast that realistic measurements of its consumption in some river ecosystems may not be possible. It is important to identify and characterize sources of OM to rivers, so watershed managers can devise effective OM reduction plans appropriate for the constituent of concern unique to that watershed or region. Constituents of concern associated with OM include pathogens affiliated with manure, toxins in harmful algal blooms, metals, and pharmaceuticals from wastewater treatment effluent. Each pollutant requires a unique mitigation strategy and therefore the first step to pollution mitigation is source identification.

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INTRODUCTION

Rivers are bioreactors of organic matter (OM) that can efficiently utilize energy from terrestrial OM inputs that would otherwise be lost to the atmosphere, or transported to downstream waters (Fisher and Likens 1972). OM processing mediates important ecosystem functions, such as nutrient retention and transformation, which influences water quality in rivers and downstream lakes and estuaries. Constituents of concern that are transformed or retained due to OM processing include trace metals (Mulholland et al. 1981, Kikuchi et al. 2017) such as mercury (Creed et al. 2018), phosphorus (Guillemette

et al. 2013, Larsen et al. 2015), nitrate (Taylor and Townsend 2010), and surfactants (Sickman et al. 2007, DeBruyn and Rasmussen 2012). The balance of OM supply and demand within a watershed regulates the net export of these constituents of concern to downstream waters (Wollheim et al. 2018). Therefore, it is important to identify potential sources of OM, so managers can plan to reduce and effectively limit OM supply or possibly manipulate OM retention or transformation to increase OM demand.

The majority of particulate OM (POM) and dissolved (DOM) is presumed to originate from terrestrial sources, and the remainder is attributed to autochthonous sources, which are produced instream (Findlay and Sinsabaugh 2003, Findlay and Parr 2017). However, depending on OM size-class, stream order, reservoir and lake inputs, and watershed land cover, the proportion of terrestrial versus autochthonous sources of OM in rivers and streams (hereafter rivers) varies greatly (Wilkinson et al. 2013). Coarse POM (CPOM is POM >1 mm) from terrestrial ecosystems is an important energy source for consumers and higher trophic levels. CPOM is also major source of fine POM (FPOM, POM > 0.45 μm and < 1mm) and DOM, but sources of autochthonous CPOM in rivers is rarely reported (Wallace et al. 1982, Tank et al. 2010). FPOM has a large surface area compared to DOM and therefore affects sorption, and nutrient and metal transport in watersheds (Yoshimura et al. 2010, Larsen et al. 2015). While FPOM is assumed to be primarily terrestrial, estimates of autochthonous sources of FPOM in rivers range from less than 1% to as much as 50% (Kendall et al. 2007, Ostapenia et al. 2009, Larsen et al. 2015). Likewise, the majority of DOM is assumed to be resistant to microbial consumption, but portions of humic-like DOM may support a significant portion of microbial OM demand (Volk et al. 1997, Fellman et al. 2008) and the proportion of

humic-like OM may better predict the magnitude of microbial OM processing than more labile OM (Amon and Benner 1996). It is hard to identify and separate autochthonous versus terrestrial sources in the ambient DOM pool. Therefore, estimates of the proportional contributions of each source remain unconstrained (Wilkinson et al. 2013).

As the urban footprint of metropolitan areas expands (Ng 2016), OM loads to rivers have increased (Kaushal and Belt 2012), and the diversity of OM sources has also increased (Stanley et al. 2012). Anthropogenic sources of POM include plastics (McCormick et al. 2016) and wastewater treatment plant (WWTP) effluent (Sickman et al. 2007, Gücker et al. 2011). Human land use has also altered DOM composition as a result of impervious surfaces and agricultural landscapes which transport pollutants such as pesticides, surfactants, and other petroleum products (Griffith et al. 2009, Sickman et al. 2010, McElmurry et al. 2013). WWTP effluent is a source of hydrocarbons, pharmaceuticals, and illicit drugs that WWTPs are not designed to remove during the wastewater treatment process (Bridgeman et al. 2014). Typically anthropogenic sources are expected to be more labile than terrestrial sources, but their relative lability compared to autochthonous sources is not quantified. Therefore, understanding the ecological effects of increased labile OM loads to rivers, is necessary to advance watershed management paradigms from simple sanitation to sustainable urban landscapes (Kaushal and Belt 2012, Parr et al. 2016).

I have introduced OM as a pool divided into unknown proportions of three sources: terrestrial, autochthonous, and anthropogenic. The source of OM may predict OM composition and quality (Chen and Jaffé 2014). Throughout the literature, aquatic OM composition of terrestrial origin is described as high in aromatic and humic content,

which is correlated with lower proportions of amino acids and protein-like OM (Findlay and Sinsabaugh 1999, del Giorgio and Davis 2003). Consequently, terrestrially derived aquatic OM has a high organic carbon to organic nitrogen ratio (C:N; range of 20 to 100 in aquatic ecosystems) compared to autochthonous sources (5 to 20 C:N range; Knapik et al. 2015, Parr et al. 2015). It is also typically composed of larger, more complex OM constituents than autochthonous sources, which makes it less likely to be assimilated and/or respired by microbes (Guillemette et al. 2013). Therefore, terrestrially derived OM in rivers is characterized as a low quality carbon source for microbial consumption. In contrast, autochthonous OM sources have greater proportions of small, simple, aliphatic, nitrogen rich, protein-like compounds, and are classified as high quality OM (Findlay and Sinsabaugh 1999, del Giorgio and Davis 2003, Mostofa et al. 2013). Measures of OM composition and quality are also used as proxies of OM bioavailability, where high quality OM is considered more bioavailable than low quality OM. Bioavailable (or labile) OM is "preferred" by microbes, that is, rapidly consumed within hours, days, or weeks in aquatic ecosystems versus semi-labile (or recalcitrant) OM, which is lost over months, years, or centuries (Cory and Kaplan 2012).

Current estimates of microbial consumption or OM decay rates are highly variable among OM sources and across aquatic ecosystems. Decay rates calculated from natural sources of DOM in rivers, such as soil or algal leachate, range from 0.0003/d to 62.8/d (Webster and Meyer 1997, Kaplan et al. 2008). One reason for this wide range is due to the many methods used to quantify DOM decay, including bioassays, reach-scale tracer experiments, and ecosystem models. Bioassays, which include any closed system incubation (e.g., dark bottles and plug-flow reactors), are commonly used to measure

DOM decay as bacterial respiration and/or organic carbon loss. However, most incubations do not include a proxy for the benthic zones of lotic ecosystems (Catalán et al. 2016, Mineau et al. 2016, Bengtsson et al. 2018), and benthic habitats are responsible for at least half of DOM consumption (Cory and Kaplan 2012, Risse-Buhl et al. 2012, Mineau et al. 2016). Further, results are difficult to compare across studies because incubation times vary from days to years (Mineau et al. 2016), and are often conducted in the dark, so bioassays do not account for effects of photodegradation, an important abiotic driver of DOM decay (Moran and Zepp 2000, Findlay and Parr 2017). Thus to better estimate DOM processing rates in streams, more empirical measures of autochthonous and terrestrial OM decay that include benthic OM consumption are needed (Mineau et al. 2016, Bengtsson et al. 2018).

The effects of increased proportions of autochthonous and/or anthropogenic OM sources on river ecosystem function remains unclear. Increased human influence within a watershed has increased the proportion of labile OM compared to semi-labile OM in freshwater ecosystems (Hosen et al. 2014, Parr et al. 2015, Williams et al. 2016). It is proposed that the smaller proportion of labile, autochthonous OM has non-additive effects on the decay rates of semi-labile OM, such that when labile and semi-labile OM are mixed, labile OM stimulates microbial consumption of semi-labile OM resulting in a positive non-additive effect or “priming” effect (Bengtsson et al. 2018). Terrestrial studies of OM non-additive effects identified positive non-additive effects over 50 years ago (Kuzyakov et al. 2000), but results remain unclear for aquatic ecosystems (Guenet et al. 2010, Bengtsson et al. 2018). In theory, increased anthropogenic inputs of labile OM may increase mineralization of terrestrial OM in rivers due to non-additive effects of

labile and semi-labile DOM. Or, if labile OM does not accelerate semi-labile decay, the addition of labile DOM may saturate demand for semi-labile DOM, and consequently semi-labile, terrestrial OM loads would increase to downstream lakes and estuaries (Wollheim et al. 2018).

Based on these gaps in OM research, the objectives for my dissertation were to:

1) Identify seasonal sources of OM to an urban river, and provide proportional estimates of terrestrial, autochthonous, and anthropogenic sources of POM and DOM.
2) Identify sources, and characterize composition of POM and DOM in watersheds at base flow with varying degrees of human impact and mixed land cover including urban development, natural ecosystems (e.g., forest and shrublands) and agriculture.
3) Measure decay rates of labile and semi-labile DOM in experimental streams with a benthic microbial community and compare these decay rates to bottle-bioassays without a benthic microbial community. Then, use measured decay rates of labile and semi-labile DOM to model the non-additive effects of mixing labile and semi-labile DOM in experimental streams and bottle-bioassays.

It is important to identify sources of OM, characterize OM composition, and quantify OM decay rates to better to inform models of OM flux between terrestrial and aquatic ecosystems, and from headwaters to downstream waterbodies. Aside from its relation to carbon budgets, it is important to have baseline estimates of stream OM

transformations for managers who aim to reduce OM loads, as well as to mitigate for pathogens and contaminants associated with OM in human-altered watersheds (Edmonds and Grimm 2011, Stanley et al. 2012). DOM can contribute to biochemical oxygen demand, the formation of disinfection by-products, and adsorb metal contaminants (Stanley et al. 2012, Kaushal et al. 2014). Also, OM inputs to rivers from terrestrial and human altered landscapes needs further study at the reach, and watershed scale (as in this study) to understand OM dynamics within larger aquatic networks of wetlands, lakes, reservoirs, and urban or agricultural infrastructure (as in Williams et al. 2016). The study of novel sources of DOM in anthropogenically altered landscapes is just beginning (Stanley et al. 2012, Creed et al. 2015), and estimates of the proportional contributions of autochthonous and terrestrial sources, as well as empirical measures of DOM decay, will help put the ecological consequences of less studied sources of DOM in perspective. My study provides proportional estimates of anthropogenic sources of OM in rivers and empirical measurements of OM decay and carbon spiraling metrics that will help predict the implications of DOM processing in streams with respect to downstream water quality.

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CHAPTER II

ORGANIC MATTER IS A MIXTURE OF TERRESTRIAL, AUTOCHONOUS, AND ANTHROPOGENIC SOURCES IN AN URBAN RIVER

Abstract: The first step to reducing organic matter (OM) loads that contribute to poor water quality in urban watersheds is to identify the sources of OM inputs. Autochthonous sources of OM are predicted to increase compared to terrestrial sources in urban rivers due to higher nutrient concentrations and light availability than reference watersheds, and anthropogenic sources of OM to urban rivers (e.g. wastewater effluent) are hard to distinguish from other sources. Our objective was to identify sources of three size-classes of OM to an urban river, the Jordan River, in the Salt Lake Basin, Utah, USA. Stable isotopes of carbon, nitrogen and hydrogen were used as tracers of OM sources for samples of coarse particulate OM (CPOM), fine particulate OM (FPOM), and dissolved OM (DOM). Isotopes were used in a Bayesian mixing model and a graphical gradient-based mixing model to identify autochthonous, terrestrial, and anthropogenic sources of OM. optical properties of DOM were also used to identify the sources and composition of DOM. We found CPOM was mostly terrestrially derived with increased autochthonous inputs in warm months. FPOM was a mixture of terrestrially derived OM, wastewater influenced OM, and OM from the eutrophic Utah lake. DOM was primarily from Lake-

DOM with increasingly significant contributions from WWTP effluent in fall. Based on proportional estimates of autochthonous, terrestrial, lake and wastewater effluent sources managers can better target specific sources of problematic OM loads to the Jordan River. Additionally, baseline estimates of terrestrial versus autochthonous OM sources in an urban river will inform developing theoretical frameworks (e.g. Urban Watershed Continuum) that aim to understand ecosystem functions of urban watersheds.

Keywords: urban ecology, wastewater, water quality, dissolved organic matter, particulate organic matter, natural abundance stable isotope tracer, mixing models, deuterium

Introduction

Rivers and streams are hotspots of organic matter (OM) transport and transformation (McClain et al. 2003, Battin et al. 2008). River metabolism is often fueled by terrestrial inputs, and rivers have high metabolic efficiency considering their surface area at the global scale (Fisher and Likens 1973, Duarte and Prairie 2005, Raymond et al. 2013). Recent data revealed the global surface area of streams and rivers was previously underestimated by 40%, so they likely contribute significantly more to global carbon cycling than previously thought (Allen and Pavelsky 2018). By storing, transporting, and transforming OM, rivers provide important ecosystem services, such as nutrient retention and removal that maintain water quality and ecological integrity of downstream lakes, estuaries, and oceans. For example, river networks efficiently transform terrestrial inputs

into biomass that are used as energy for organisms occupying higher trophic levels (Wallace 1997, Kominoski and Rosemond 2012). Rivers also store or mineralize terrestrial inputs which helps to mitigate excessive nutrients (Alexander et al. 2009, Kaushal et al. 2014) and sediment loads (Larsen and Harvey 2017) to downstream waterbodies.

Increased urbanization has altered river geomorphology, flow regimes, and biological community structure, potentially reducing the capacity of urban watersheds to retain and transform OM (Meyer et al. 2001, Kominoski and Rosemond 2011, Smith and Kaushal 2015). Hydrologic connectivity among streets, storm drains, pipe networks, and ditches results in high drainage densities (i.e., stream length per unit watershed area) in urban watersheds compared to natural watersheds (Baruch et al. 2018). As a result, OM loads to urban rivers are larger than to their reference counterparts (Kaushal and Belt 2012). Excessive particulate OM (POM) loads in rivers increases nutrient concentrations associated with POM (Larsen and Harvey 2017), thereby exacerbating symptoms of eutrophication in urban rivers. Greater light availability and higher inorganic nutrient concentrations in urban rivers may also increase autochthonous OM production (Bernot et al. 2010, Smith and Kaushal 2015). A greater proportion of autochthonously derived OM compared to terrestrially derived, is problematic because autochthonous OM sources are more bioavailable than terrestrial sources (Kaplan and Bott 1989, del Giorgio and Pace 2008, Parr et al. 2015). More bioavailable OM in urban watersheds compared to reference watersheds augments microbial activity (McCallister and del Giorgio 2012) again exacerbating symptoms of eutrophication such as increased dissolved oxygen demand.

In addition to increased autochthonous sources, urban OM loads include less studied OM sources such as storm water, impervious surface and lawn runoff (Edmonds and Grimm 2011, Hosen et al. 2014), as well as hydrocarbons and pharmaceuticals (Griffith et al. 2009, McElmurry et al. 2013), all of which occur at unknown quantities in urban watersheds. Effluent from wastewater treatment plants (WWTPs) is another possible source of labile DOM (Westerhoff and Anning 2000, Figueroa-Nieves et al. 2014) which again, would spur primary production and microbial metabolism in reaches downstream of WWTPs. Anthropogenic OM released from wastewater treatment has been studied for decades (Ma et al. 2001, Debryyn and Rasmussen 2002, Gücker et al. 2006), the downstream consequences of OM are often ignored (Wassenaar et al. 2010). Also, due to the interacting effects of landuse, geomorphology, and climate it remains difficult to quantify the downstream ecological impact of a single WWTP (Wassenaar et al. 2010).).

Robust estimates of autochthonous, terrestrial, and anthropogenic OM sources is important information for watershed managers to reduce excess OM loads in impaired urban rivers. Studies have estimated the proportion of terrestrial versus autochthonous particulate OM (POM) in pristine freshwater ecosystems and found terrestrial sources dominated POM (Karlsson et al. 2003, Mohamed and Taylor 2009, Solomon et al. 2011), or was a mixture of autochthonous and terrestrial sources (Wilkinson et al 2013). Reported proportions autochthonous dissolved OM (DOM) in lakes, ranges from 0 to 20% , and the remainder of DOM is considered terrestrial (Kritzberg et al. 2004, Bade et al. 2007, Ostapenia et al. 2009, Wilkinson et al. 2013).

Proportional estimates of autochthonous, terrestrial and WWTP effluent OM sources in rivers are limited. Autochthonous dissolved organic carbon (DOC) accounted for upwards of 25% of total primary production per day in a nutrient-rich stream (Lyon and Ziegler 2009), and almost 16% in a reference stream (Hotchkiss and Hall 2015). Autochthonous sources of POM were found to increase with greater watershed area, and represent at least half of POM in large rivers of the United States (drainage area >10,000 km^2; Kendall et al 2001). In small urban streams, POM was derived from both agricultural (15%) and WWTP (85%) sources (Gücker et al. 2011), or contributions of autochthonous sources ranged from 20 to 50% all POM and the remainder was terrestrial (Imberger et al. 2014). However, estimates remain uncertain because source proportions were based on carbon and nitrogen isotope mixing models with endmember $\delta^{13}C$ values that overlapped.

Reference watershed DOM is dominated by terrestrial sources (Palmer et al. 2001, Hood et al. 2005, Cartwright 2010, Wilkinson et al. 2013), while urban watersheds have an unknown proportion of laabile (Hosen et al. 2014, Imberger et al. 2014), recently derived (Williams et al. 2016), and autochthonous DOM sources (Parr et al. 2015). Labile DOM in urban waterways can originate from anthropogenic sources, such as runoff from lawns and impervious surfaces, leaky septic tanks, and treated wastewater (Smith and Kaushal 2015, Fork et al. 2018), but the proportions of anthropogenic, autochthonous, and terrestrial sources of DOM in urban rivers remains unknown. In addition to informing management strategies to reduce OM loads, baseline estimates of terrestrial versus autochthonous OM sources in an urban river will inform current theoretical frameworks, for example the urban watershed continuum that aim to extend conceptual

models of organic matter in reference watersheds to urban ecosystems (Vannote et al. 1980, Kaushal and Belt 2012, Kominoski and Rosemond 2012).

Our objective was to provide proportional estimates of terrestrial, autochthonous, and anthropogenic sources of POM and DOM to an urban river, and identify how these sources may vary across 4 watersheds within a matrix of land covers. We collected CPOM (POM, >1mm), FPOM (POM, 1mm-0.7μm and DOM throughout the year in the Jordan River, an urban river in the Great Salt Lake Basin (Fig. 1). Optical properties of DOM were used to identify sources and characterize DOM composition, and naturally occurring stable isotopes of carbon, nitrogen, and hydrogen were used as tracers in mixing models to identify OM sources. Proportional estimates of OM sources can test the hypothesis that urbanization increases autochthonous OM in rivers, and this study provides one of few proportional estimates of terrestrial, autochthonous, and anthropogenic sources in a river.

Methods

Study sites and sampling regime

The Jordan River begins at Utah Lake, a shallow, eutrophic lake in the southern portion of the Great Salt Lake Basin, and flows north 82 km where it terminates in wetlands that connect to the Great Salt Lake. Utah Lake receives water from the Provo River, Spanish Fork River, and American Fork River as well as wastewater effluent from 6 WWTP in these drainages (Psomas, 2009). Three WWTPs discharge effluent into the Jordan River and are located 22, 37, and 50 km downstream from Utah Lake (Fig. 1).

Discharge from Utah Lake to the Jordan River is highly regulated for irrigation, and flood control in the Salt Lake metropolitan area; average daily discharge has ranged from 0.05 to 8.9 $m^3 s^{-1}$ since 1985 (Cirrus and Stantex 2009; Supplement 1). Since 1985 the river has been regulated never to exceed 9.8 cubic meters per second (CMS) as a result of extensive flooding in 1983-1985 (Supplement 1; Hooten 2011). Depth and width range from 0.57 m and 16 m in the first 50 km below Utah Lake to 1 m depth and 39 m width at lower reaches (Epstein et al. 2016). The dominant substrate is gravel in the upper reaches and fine sediments in lower reaches (Epstein et al. 2016).

Three size-classes of OM were collected at 9 sites. OM in the Jordan River is dominated by the dissolved size-class, which makes up 94% of total annual carbon transport, compared to 6% and 1% of FPOM and CPOM (Epstein et al. 2016). CPOM, FPOM, and DOM were collected in April, July, September, and November of 2014, and December of 2015 for $\delta^{13}C$, $\delta^{15}N$, and $\delta^{2}H$ stable isotope analysis. We collected OM in April and July to characterize OM before and after snowmelt-runoff which typically occurs in mid-June. OM was collected in September, November, and December to characterize OM before and after leaf senescence in October. We also collected Jordan River water for deuterium ($\delta^{2}H$-water), and carbon isotopes of DIC ($\delta^{13}C$-DIC), at the same time as OM (but DIC was not collected in December 2015).

Organic matter isotope sampling of CPOM, FPOM and DOM

In addition to samples collected in 2014 and 2015, CPOM samples collected from a previous study of the Jordan River were also analyzed for $\delta^{13}C$, $\delta^{15}N$, and $\delta^{2}H$. Samples from Epstein et al. (2016) were collected in February, May, July, August, and October of

2013. All CPOM was sampled with bedload samplers based on the Helley-Smith bedload sampler design (Helley and Smith 1971). One-mm mesh nets were attached to the bottom and top of a steel pole. Nets were held perpendicular to flow for 6 minutes to collect CPOM in transit along the bottom and on the surface of the river. CPOM was then picked from the nets and transported back to the laboratory in a cooler.

FPOM was collected as grab samples in the field with a 1-liter bottle from each site and then transported back to the laboratory for filtering. FPOM for $\delta^{13}C$ and $\delta^{15}N$ isotope analysis was filtered on 25 mm diameter glass fiber filters of 0.7 µm pore size (Whatman GF/F, Maidstone, UK). Filters were dried at 50 °C, rewet with deionized water, and acidified by fumigation in a desiccator with 25% HCl for 6 hours (Brodie et al. 2011). FPOM for $\delta^{2}H$ isotope analysis was collected on 0.45 µm nylon filters (Whatman polyamide membrane filters, Maidstone, UK) then backwashed into deionized water, and dehydrated at 50 °C in a drying oven (Wilkinson et al. 2013). The remaining solid was scraped from glass dishes and sent for $\delta^{2}H$ isotope analyses.

DOM was collected as grab samples in the field with two, 1-liter bottles at each site and filtered in the laboratory through 0.7 µm glass fiber filters (Whatman GF/F, Maidstone, UK). One liter was acidified to pH 2.5-3 with concentrated HCl to remove inorganic carbon. Acidified DOM was then evaporated in 8-inch diameter glass dishes at 50 °C, residue was scraped from plates (Wilkinson et al 2013), and stored in scintillation vials. DOM from November 2014 and December 2015 was freeze dried because several previously collected DOM samples congealed after dehydration and were not submitted for isotope analysis. Non-acidified DOM was also dehydrated and residue was sent for $\delta^{2}H$ isotope analysis.

Organic matter source sampling

Five endmember categories were evaluated as possible sources for each size-class of OM: terrestrial, autochthonous, benthic organic matter (BOM), WWTP effluent and lake sources. Except for WWTP and lake sources, 1 to 2 samples of each source were collected from each site and dried at 50°C for stable isotope analysis. Terrestrial sources included leaf-litter (senesced), tree leaves (not senesced), and *Phragmites.* Autochthonous sources included macrophytes, biofilm, and algae. Macrophytes were cut from large submerged aquatic vegetation anchored to the benthic zone. Biofilm was scraped from benthic rocks, and algae were collected from green mats floating on the water surface. Autochthonous sources were transported back to the laboratory, rinsed with DI water, and large macroinvertebrates (>1 mm) were removed. BOM was collected by sinking a stove-pipe 5 to 10 cm into river sediment, agitating with a meter stick, then a 100 mL sample of the sediment-water mixture was collected and stored in coolers for transport (Wallace et al. 2006). WWTP and lake sources included OM of each-size-class from Utah Lake (Lake-CPOM, Lake-FPOM, Lake-DOM) and WWTP effluent (WWTP-CPOM, WWTP-FPOM, WWTP-DOM), and were collected identically to each size-class of OM at sampling sites. Lake OM was collected directly below the Utah Lake pumping station in a large depositional area below the pumping station (Supplement 2).

WWTP and lake sources included OM of each-size-class from Utah Lake (Lake-CPOM, Lake-FPOM, Lake-DOM) and WWTP effluent (WWTP-CPOM, WWTP-FPOM, WWTP-DOM), and were collected identically to each size-class of OM at sampling sites.

Lake OM was collected in a large depositional area below the Utah Lake pumping station (Supplement 2). WWTP effluent was sampled directly below the effluent outfall of the Central Valley Water Reclamation Facility on Mill Creek (Mille Creek WWTP) *ca.* 2 km from the confluence of the Jordan River (Supplement 2). Effluent was only collected from the Mill Creek WWTP because the effluent stream of the most upstream WWTP, South Valley Water Reclamation Facility (South Valley WWTP) was difficult to distinguish from irrigation return flows, and was very small compared to mainstem river flow. The 3 most downstream WWTPs on the Jordan River were outside our study domain. The South Valley and Mill Creek WWTPs are both tertiary treatment facilities with UV disinfection, and were constructed in the early 1980s (Mill Creek 1981-1989 www.svwater.com, South Valley 1985 www.cvwrf.org). The South Valley WWTP has a smaller capacity (25 million gallons per day) than Central Valley WWTP (75 million gallons per day), and contributes up to half of total discharge to the Jordan River, or more during low flow periods (Cirrus and Stantex 2009).

Stable isotope analysis

Organic matter samples for isotope analysis were prepared and analyzed using standard methods (Hershey et al. 2017). Briefly, acidified OM samples were packed in silver, and non-acidified samples were packed in tin capsules for stable isotope analysis. All dried POM samples were ground in a coffee bean grinder. Samples for $\delta^{13}C$ and $\delta^{15}N$ analysis were sent to the Stable Isotope Facility (SIF) at University of California Davis on a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) with a long term standard

deviation of 0.2 ‰ for ^{13}C and 0.3‰ ^{15}N. Deuterium analysis was conducted at the Colorado Plateau Stable Isotope Laboratory (CPSIL) at Northern Arizona University. Samples were pyrolyzed to H_2 gas following the procedures of Doucett et al (2007) and analyzed with a Thermo-Finnigan TC/EA and DeltaPLUS-XL (Thermo Electron Corporation, Bremen, Germany; precision 2‰). Samples analyzed for δ^2H were corrected for exchange of H atoms between sample and ambient water vapor using the bench top equilibration method (Doucett et al. 2007). The $\delta^{13}C$ of DIC was obtained by filling helium-flushed, 12 mL exetainer vials with 1 mL of 85% phosphoric acid and 4 mL of filtered river water (Taipale and Sonninen 2009). DIC samples were analyzed using a GasBench II system interfaced to a Delta V Plus IRMS (Thermo Scientific, Bremen, Germany) with a long term standard deviation of 0.1 ‰. Jordan River water was analyzed for δ^2H (precision 2‰) and $\delta^{18}O$ (precision 1‰) isotopes at the Utah State University Stable Isotope Lab. Samples were run using a GasBench II with GC PAL auto-sampler interfaced to a Delta V Plus IRMS (Thermo Scientific, Bremen, Germany; precision 2‰ ^2H and 1‰ ^{18}O).

Isotope mixing model

The Stable Isotope Mixing Model in R package (SIMMR) provided a Bayesian inference mixing model designed to estimate the proportional contribution of sources to a mixture (Parnell and Inger 2016)**.** SIMMR incorporates variability of end-members into the model and estimates source contributions to a mixture regardless of the number of isotope tracers (Parnell et al. 2013). Three isotope tracers ($\delta^{13}C$, $\delta^{15}N$, δ^2H) were used to

estimate source contributions to CPOM and FPOM, but only $\delta^{13}C$ and $\delta^{2}H$ isotopes were used in the DOM mixing model since $\delta^{15}N$ values of DOM included nitrate.

CPOM samples were collected in 9 different months and were grouped into 4 seasons for SIMMR analysis. Fall included samples collected in November and September, winter included February and December, spring included April and May, and summer included June, July, and August. FPOM and DOM were collected in April, July, September, November of 2014, December 2015, and were grouped by month for analysis.

Source identification SIMMR was first run for each OM size-class, CPOM, FPOM, and DOM, using all potential sources (13 total). The high density intervals (HDI) of estimated source contribution were compared to identify significant sources to OM. Estimated values within the HDI have higher probability density than values outside the HDI and the total probability of values in the 95% HDI is 95% (Kruschke 2018). Within the 95% HDI, a 75% HDI was delimited to convey skewness of the 95% HDI, and further constrain the most credible contribution estimates. Similar to the 95% HDI, values within the 75% HDI are more probable than outside the 75% HDI.

Sources were excluded from a subsequent mixing models for 2 reasons. First, if the 75% HDI of feasible solutions was less than 10%, the source was considered too small a contributor and was excluded from subsequent models. Second, if the 75% HDI of feasible solutions estimated a contribution greater than 60% of OM, isotope values were considered too variable, and the source was excluded. Sequential models were run and sources were excluded until a model with 4 or less sources was resolved. While

SIMMR can estimate any number of sources, we constrained our CPOM and FPOM models to 4 sources since we had 3 isotope tracers ($\delta^{13}C$, $\delta^{15}N$ and $\delta^{2}H$). Models for DOM were constrained to 3 sources since we had only 2 isotope tracers for DOM ($\delta^{13}C$ and $\delta^{2}H$) because dehydrated DOM contained ^{15}N from nitrate.

FPOM and DOM gradient-based mixing model

In addition to the Bayesian mixing model, a graphical, gradient-based mixing model was used to partition OM sources as either terrestrial or autochthonous (Mohamed and Taylor 2009, Rasmussen 2010, Wilkinson et al. 2013). If DOM was primarily derived from terrestrial inputs, $\delta^{13}C$-DOM or $\delta^{2}H$-DOM would not vary systematically with $\delta^{13}C$-DIC or $\delta^{2}H$-water, and yield a flat line with a y-intercept at the average $\delta^{13}C$ or $\delta^{2}H$ terrestrial isotope values. If DOM was primarily derived from autochthonous production, the $\delta^{13}C$ and $\delta^{2}H$ values would vary linearly with aqueous $\delta^{13}C$-DIC or $\delta^{2}H$-water values (Wilkinson et al. 2013).

Water quality metrics

DOC, total dissolved nitrogen (TDN), and Chlorophyll *a* (Chla) were collected in April, July, September, November, and December along with OM samples. DOC and TDN samples were filtered through 0.7 µm glass fiber filters into 40 mL amber vials and acidified with HCl to a pH of 2.5 for storage until carbon analysis. Acidified DOC and TDN samples were run on a Shimadzu TOC-L analyzer via catalytic oxidation combustion at 720 °C (DOC MDL 0.2 mg/L, TDN MDL 0.1 mg/L; Shimadzu Corp., Kyoto, Japan). Chla was collected on glass fiber filters, in-stream, with a drill-pump

(Kelso and Baker 2015), wrapped in foil, frozen, and subsequently analyzed on a Turner handheld fluorometer (Turner Designs, Sunnyvale, CA; MDL 0.1 mg/L) following Steinman et al (2007).

DOM spectroscopic indices

Six spectroscopic indices were calculated from excitation emission matrices (EEMs), which were produced on a Horiba Aqualog spectrofluorometer (Horiba Scientific, Edison, New Jersey). EEMs were collected over excitation wavelengths 248-830 nm at 6 nm increments and over emissions 249.4-827.7 nm at 4.7 nm (8 pixel) increments. All samples were collected in ratio mode (S/R), and run at an integration time resulting in a maximum emission intensity of 5,000 to 50,000 counts per second, typically 0.25 to 1 second. Samples that exceeded 0.3 absorbance units at excitation 254 nm were diluted with deionized water. All samples were corrected for inner filter effects, Rayleigh scatter, and blank subtracted in MATLAB^{TM} (version 6.9; MathWorks, Natick, Massachusetts) as described in Murphy et al (2013).

The fluorescence index (FI), Yeomin fluorescence index (YFI), freshness index (BIX), humification index (HIX), peak T to peak C ratio (TC), and $SUVA_{254}$ were calculated from corrected EEMs in MATLAB^{TM} (Table 1). The FI was calculated at excitation 370 nm as the ratio of emission intensities at 470 and 520 nm (Cory and McKnight 2005). The YFI was calculated as the average intensity over emission 350-400 nm divided by the average intensity over emission 400-500 nm at excitation 280 nm (Heo et al 2016). YFI was calculated in addition to the FI because the YFI can better differentiate fluorophore precursor materials than the FI, and it is less sensitive to

concentration-dependent effects (Heo et al. 2016). For example, the YFI has a wide index range for fulvic, humic, aminosugar-like, and protein-like fluorophores (0.30-6.41). In contrast, the FI has a narrower index range (0.82-2.14), and cannot distinguish between protein-like and aminosugar-like standards (Heo et al. 2016). The β:α index (BIX), also called the freshness index, was calculated as the intensity at excitation 380 nm divided by the max intensity between emission 420-435 nm, where higher values represent more recently derived DOM (Parlanti et al. 2000). The HIX was calculated at excitation 254 nm as the area under emission 435-480 divided by the area under emission 300-450 nm + 435-480 nm; higher HIX values represent more humic-like material (Zsolnay et al. 1999). The TC index is the ratio of maximum fluorescence in the peak T region (protein-like) versus peak C region (humic-like) with higher values representing more protein-like DOM, which are also associated with WWTP effluent (Baker 2001). TC was calculated as the ratio of maximum fluorescence at excitation 275/em350 nm to max intensity within excitation 320-340nm/emission 410-430 nm (Gabor et al. 2014). Last, $SUVA_{254,}$ an indicator of aromaticity, was calculated from DOM absorbance at 254 nm normalized by DOC concentration (Weishaar et al. 2003). Nitrate and iron interferences with fluorescence and absorbance indices were ruled out following Weishaar et al. (2003) given iron concentrations were < 1 mg/L (Jordan River maximum 0.08 mg/L) and nitrate concentrations were < 40 mg/L (maximum 20.4 mg/L TDN this study, maximum NO_2^- +NO_3-N 8 mg/L, Epstein et al. 2016).

Spectroscopic indices were correlated to water quality metrics with all months combined. Correlations were conducted with the GGally package in R (Schloerke et al.

2014). Correlations were considered significant when correlation coefficients were greater than 0.35 (Rohlf and Sokal 1995).

Results

Source isotope values

Deuterium was the only isotope that sufficiently separated autochthonous and terrestrial sources (Fig. 2). Biofilm, algae, and macrophytes had the most negative δ^2H values (-222.6 ‰, standard deviation (sd) 35.9; Table 2). WWTP-FPOM, WWTP-DOM, and Lake-DOM had the most positive δ^2H values (Fig. 2). All other sources had average δ^2H values between -150 to -200‰. Variation in $\delta^{13}C$ and δ^2H values of autochthonous sources (mean coefficient of variation, 0.22 $\delta^{13}C$ ‰ and 0.12 δ^2H ‰) was greater than terrestrial sources (mean coefficient of variation, 0.04 $\delta^{13}C$ ‰ and 0.07 δ^2H ‰). Average $\delta^{15}N$ for all sources were between 5 ‰ and 10 ‰ except for WWTP-DOM which had more positive values (29.4 $\delta^{15}N$ ‰) because it included enriched WWTP-derived nitrate. Average $\delta^{13}C$ values from autochthonous sources overlapped the range of terrestrial $\delta^{13}C$ values, again highlighting that only δ^2H isotopes may be able to differentiate between autochthonous and terrestrial sources (Table 2).

Carbon and hydrogen isotope values were similar between leaf-litter and tree leaf sources (Table 2). Therefore if SIMMR did not distinguish sources depending on the $\delta^{15}N$ isotope value of an OM size-class, as was the case with FPOM and DOM, these leaf sources were averaged together and modeled as one terrestrial source (Litter+TreeLeaves). However, because leaf-litter had depleted $\delta^{15}N$ values (mean 3.9, sd

2.4‰) compared to living tree leaves (mean 6.9, sd 3.5‰), SIMMR was able to distinguish litter and tree leaves as different sources to CPOM (see below).

CPOM

Bayesian model Three possible sources of CPOM were identified: biofilms, macrophytes and leaf-litter. Algae, BOM, living tree leaves, Lake-FPOM, Lake-DOM, WWTP-FPOM, and WWTP-FPOM were excluded from the model because proportional estimates were <10%, and all other excluded sources had proportional estimates with variability >60% (Supplement 3.1). Leaf-litter always represented the greatest feasible proportion of CPOM, except in summer when leaf-litter and macrophyte contributions were roughly equal (Fig. 3). Macrophytes were the second most likely source of CPOM; contributions ranged from 4 to 38% in fall, increased in winter and spring, and greatest feasible proportions were in summer (15-64%). Biofilm was the least likely source of CPOM with higher contributions estimated in spring (3-34%), and summer (5 to 26%) compared to fall and winter.

FPOM

Bayesian model Four potential sources of FPOM were identified by SIMMR, including Lake-FPOM, WWTP-FPOM, Litter+TreeLeavess and BOM. Autochthonous sources, *Phragmites*, and WWTP-DOM were excluded from the model because proportional estimates were <10%, and all other excluded sources had proportional estimates with variability >60% (Supplement 3.1). BOM and Lake-FPOM had higher feasible proportions in July and September, than November and December, ranging from

9 to 82% in July and 8 to 58% in September (Fig. 4). Litter+TreeLeaves increased from July to December with median percent contributions of 12 % in July and 18% in December. WWTP-FPOM was greatest in September and November, and ranged from 16 to 69% over both months. In sum, terrestrial sources of FPOM increased in autumn, with possible autochthonous contributions from Lake-FPOM in July and September, and from WWTP-FPOM in September and November. April was not included because there was not enough particulate for analysis of δ^2H.

Graphical gradient model If FPOM was derived from 100% autochthonous sources, we expected δ^2H-FPOM and $\delta^{13}C$-FPOM values to have a positive relationship with δ^2H-water and $\delta^{13}C$-DIC. Lake samples were excluded from $\delta^{13}C$ gradient models because Lake DIC-$\delta^{13}C$ values were extremely high compared to all other OM (Fig. 5).There were no significant linear relationships between δ^2H-FPOM and δ^2H-water within months, or among all months combined (Fig. 5 top, Supplement 4). FPOM δ^2H values averaged -166.3 ‰ (sd 13.6) which was similar to average terrestrial sources (-163.8 ‰, sd 11.5). WWTP FPOM had δ^2H-FPOM values (mean -140‰, sd 16.2) that were more positive than terrestrial δ^2H values (Fig. 5 top). Several FPOM samples from July had lower δ^2H values than terrestrial sources, suggesting autochthonous contributions to FPOM in July. November $\delta^{13}C$-FPOM and $\delta^{13}C$-DIC values had a positive relationship ($r = 0.44$, $p = 0.04$); all other months were not significantly correlated. The results of both models indicated FPOM was primarily terrestrial in November and December with possible autochthonous contributions from Lake-FPOM and BOM in July, and increased contributions from WWTP-FPOM in September and November.

DOM

Bayesian model DOM was composed of 3 sources, Lake-DOM, WWTP-DOM and Litter+TreeLeaves. SIMMR predicted average terrestrial contributions of 16%, and WWTP-DOM contributions averaged 27% throughout the year. Lake-DOM was always the most likely DOM source and averaged 57% throughout the year. Autochthonous sources, *Phragmites*, BOM, Lake-CPOM, Lake-FPOM, and WWTP-CPOM were excluded from the model because proportional estimates were <10%, and WWTP-FPOM was excluded because proportional estimates of WWTP-FPOM were too variable (75% HDI >60%; Supplement 3.1). Lake-DOM was the primary source of Jordan River DOM, with median contributions that ranged from 48 to 70 % throughout the year (Fig. 6). WWTP-DOM was the second most likely source of DOM, with median values ranging from 20 to 33% in all months. Litter+Tree leaves contributions were similar among July, November, and December (mean 11%, sd 7), but were greater in September (mean 29%, sd 10).

Graphical-gradient model If DOM was derived from 100 % terrestrial sources, we expected no relationship between δ^2H-DOM and δ^{13}C-DOM versus δ^2H-water and δ^{13}C-DIC, and a flat line near terrestrial values. All δ^2H-DOM values were more positive (mean –103.6 ‰, sd 19.3) than average δ^2H values of terrestrial sources (Fig.7), and there were no significant linear relationships between δ^2H-DOM and δ^2H-water (Supplement 4**).** There were positive relationships between δ^{13}C-DOM and δ^{13}C-DIC in April and November (Fig. 7), but these relationships were dependent on WWTP-DOM values,

which had more positive δ^{13}C-DOM values than other sites in each month. Both models indicated Lake-DOM was a major source of DOM in the Jordan River, and DOM was neither autochthonous nor terrestrial but had major contributions from WWTPs throughout the year.

Relationships between spectroscopic indices and water quality

Correlations of spectroscopic indices and water quality metrics indicated DOM was microbial derived but not necessarily autochthonously derived. Chla was negatively correlated with FI (r = -0.43) and YFI (r = -0.48) values (Table 3, Fig. 8). This negative relationship was due to higher Chla concentrations and low FI/YFI values in July, compared to higher FI/YFI values and low Chla in November and December (Table 3, Fig. 8). DOC was positively correlated with FI (r = 0.51) and YFI (r = 0.45) values and negatively correlated with HIX (r= -0.28) and SUVA (r = -0.42; Table 3, Fig. 8). Therefore, samples with high DOC concentrations were more microbial-derived, and less aromatic, than samples with low DOC concentrations. SUVA values were also significantly higher in September than all other months, indicating increased aromatic content of DOM in September (Supplement 5). TC values were too variable to interpret as biologically significant, likely due to highly correlated Peak T and Peak C.

Discussion

The POM sources we identified were consistent with previous OM studies in urban watersheds, which found POM was a mixture of sources including periphyton,

leaves, and grass (Newcomer et al. 2012), WWTP effluent (Gücker et al. 2011), as well as algae and macrophytes (Imberger et al. 2013). In the Jordan River, CPOM was primarily terrestrial with a greater proportion of autochthonous sources in warm months. Macrophytes and biofilms contributed the most to CPOM in summer, an average of 40% and 18%, respectively (Fig. 3). FPOM was at least 12% terrestrially-derived throughout the year and increased to an average of 56% in December (Fig. 4). SIMMR predicted 3 other sources of FPOM including WWTP-FPOM, Lake-FPOM, and BOM. WWTP-FPOM contributions were greatest in fall due to less dilution from Lake-FPOM after irrigation season (Supplement 1). Water is released from Utah Lake during spring to late summer to regulate spring runoff and meet irrigation requirements and then water released from Utah lake decreases in fall (Cirrus and Stantec 2009). Similarly, a recent study of the Jordan River found Utah Lake accounted for roughly 50% of discharge in the upstream reach in summer, versus 20% in fall, and WWTP effluent was consistently between 30 and 50% throughout the year (personal communication, Jennifer Follstad Shah, University of Utah).

Consistent with lake discharge to the river, Lake-FPOM contributions were greatest in July, and we assumed Lake-FPOM was mostly autochthonous for two reasons. First, Chla concentrations were highest at all sites in July and reached up to 30 µg/L in Utah Lake (Fig. 8). Second, δ^2H-FPOM values were lower than average terrestrial δ^2H values in July indicative of autochthonous sources which have lower δ^2H values than terrestrial sources (Fig. 5; Doucett et al. 2007).

We found the majority of DOM was neither autochthonous nor terrestrial throughout the year. Median terrestrial contributions from Litter+TreeLeaves averaged

15% for all 4 months, and the highest average contributions were in September (29%, sd 12.5; Fig. 6). Fluorescence indices and δ^2H isotope values indicated the remainder of DOM was microbial-derived, but not from autochthonous sources. High FI/YFI values (>2) indicated microbial derived DOM (Heo et al. 2016, Ateia et al. 2017), and high FI/YFI were associated with WWTP river locations, and were negatively correlated to Chla (Fig. 8). The FI was designed to distinguish between autochthonous and terrestrial endmembers, based on fulvic acids isolated from a black water river in Georgia (the Suawannee, FI = 1.2), and a productive lake in Antarctica (Pony Lake, FI = 1.5; Cory and McKnight 2005, Cory et al. 2010). The FI has since been broadly applied to bulk DOM samples across ecosystem types with typical values ranging between 1.1 and 1.8 (Jaffé et al. 2008). However, at high DOC concentrations the relationship between fluorescence intensity and DOC concentration is not linear and therefore when comparing samples over a wide range of concentrations the change in FI may not represent the degree of change in DOM composition (Korak et al. 2014). FI values above 2 have been attributed to WWTP-sourced DOM specifically (Dong and Rosario-Ortiz 2012, Hansen et al. 2016, Ateia et al. 2017).

In addition to high FI and YFI, all δ^2H-DOM and most $\delta^{13}C$-DOM values were more positive than average terrestrial isotope values collected in this study (Fig. 7), as), as well as more positive than terrestrial values in a similar study of Midwestern lakes (Wilkinson et al. 2013). In the literature, terrestrial sources range from -124 to -161 δ^2H ‰ which is much more negative than Jordan River δ^2H-DOM values (Doucett et al. 2007, Collins et al. 2016). We concluded DOM was primarily microbial derived from

WWTP effluent sources and Utah Lake, or a combination of the 2 considering Utah Lake receives effluent from 6 WWTPs.

We cannot know the source or mechanism for enriched δ^2H-DOM values, but we propose 3 possible explanations. First, assuming WWTP OM is primarily derived from humans, δ^2H-DOM would reflect human δ^2H values. Human hair directly correlates with local tap water δ^2H values (Ehleringer et al. 2008) which range from -131.9 to -93.6‰ in the Salt Lake Valley (Jameel et al. 2016). Additionally, one other study reported a δ^2H-WWTP value of -52 ‰ (Spies et al. 1989), but this value was produced prior to development of standard methods that account for exchangeable hydrogen of OM and may not be comparable to other δ^2H ‰ values (Wassenaar and Hobson 2000). Second, Lake-DOM was the primary source of DOM which also had enriched δ^2H-DOM values (-86.1‰, sd 18.2) compared to all other sources (Table 2). While we expected Utah Lake DOM to have more negative δ^2H values due to autochthonous production of DOM, Utah Lake had enriched δ^2H-DOM values due to evaporative enrichment of δ^2H-water in Utah Lake (Jameel et al. 2016). While water was retained in Utah Lake, microorganisms likely used enriched lake water for photosynthesis which would enrich microbial-derived δ^2H-DOM. However, Utah Lake also receives effluent from 6 WWTPs, and therefore, WWTP as a source of DOM in Utah Lake cannot be discounted. Third, since δ^2H-DOM samples were not acidified, DOM may have included bicarbonate, which might make δ^2H-DOM more positive. We believe bicarbonate contamination was minimal because δ^{13}C-DOM samples were acidified, and also had more positive δ^{13}C values than other sources. Additionally, FPOM δ^2H would have contained bicarbonate contamination as well, but

FPOM δ^2H values were in the same range as terrestrial values suggesting minimal bicarbonate contamination even though samples were not acidified.

This study highlights a gap in evolving urban aquatic ecosystem frameworks which have yet to incorporate the role of higher order streams/rivers (e.g. > 1000 km^2), as well as the effects of reservoirs or inlet/outlet lakes within urban watersheds on OM source and quality. The Urban Stream Syndrome (Walsh et al. 2005) characterized urban stream hydrology of engineered headwaters and stream networks as flashy, which is the opposite of urban rivers like the Jordan River which are highly regulated, and largely sourced as a lake outlet. Likewise the Urban Watershed Continuum is based on low order streams of the Baltimore Long Term Ecological Research (Kaushal and Belt 2012, Smith and Kaushal 2015) and calls for further research in OM dynamics from human influenced headwaters, to rivers, and estuaries to better mitigate the effects of urban pollution that result in hypoxic dead zones, as observed in the Chesapeake Bay (Baskin et al. 2002) or in the case of the Jordan River, pollution of the Great Salt Lake (Naftz et al. 2008). There are many examples of studies of OM quality and quantity in large, urban rivers with WWTP inputs, including foundational work in the Santa Cruz and Gila Rivers of Phoenix, AZ (Westerhoff and Anning 2000, Edmonds and Grimm 2011), Hudson River, NY (Findlay 2005, del Giorgio and Pace 2008, Caraco et al. 2010) and Sacramento River, CA (Sickman et al. 2007), but the results of these studies have yet to be incorporated into a larger framework that links headwaters to estuaries in human impacted watersheds (Kaushal and Belt 2012). Evidence from studies on the Jordan River indicate reaches directly downstream of the dam-controlled lake are metabolically autotrophic, and lower reaches are heterotrophic because of fine sediments and turbidity that limit light

penetration in the water column (Epstein et al. 2016). Our findings suggest heterotrophic activity in lower reaches may also be spurred by labile WWTP effluent inputs.

Specifically, this study informs the total maximum daily load (TMDL) plan developed by the state of Utah. The plan identifies OM as the cause of low dissolved oxygen concentrations in the lower section of the Jordan (Cirrus and Stantec 2009). The TMDL identified 35 possible sources of POM to the Jordan River, primarily from storm water runoff and tributaries. We narrowed primary sources of POM and DOM throughout the year, and found sources from Utah Lake and WWTPs contributed greatly to DOM, the largest pool of OM (Epstein et al. 2016). Dilution from non-WWTP water is a common mechanism to mitigate adverse effects of excessive nutrient and OM loads from (Edmonds and Grimm 2011, Gücker et al. 2011), and this study can help water companies and managers to effectively plan and allocate water released from Utah Lake throughout the year to mitigate excessive OM loads of concern (Cirrus and Stantex 2009). Since Utah Lake was the primary DOM source to the Jordan River, reducing OM loads or improving water quality in the river would also require improved water quality of Utah Lake.

OM load reduction and regulation begins with source identification, and therefore, this study informs future management of urban river water quality. Excessive OM loads may increase the cost of wastewater treatment and make treatment less effective (Chow et al. 2005). For example, algal-derived DOM reduces WWTP effectiveness through increased coagulant demand and membrane fouling (Nyguen et al. 2005, Henderson et al. 2008). Likewise, microbial and algal-derived DOM is produced and persists throughout the treatment process, and upon chlorination may form hazardous disinfection-products

by (Nyguen et. al. 2005, Bridgeman et al. 2014). To prevent increased WWTP costs and energy use in the future managers could consider strategies that may reduce autochthonous sources in the Jordan River such as reducing autochthonous inputs from Utah Lake, decreasing inorganic nutrient inputs at base flow, and/or mitigating inorganic nutrient pulses during storms. Increased habitat heterogeneity through construction of riffle and pool sequences along the Jordan River could increase retention and microbial processing of OM. However, this strategy would have to balance the benefits of increased OM retention with flood hazards, and construction of new depositional areas that may increase primary production in oxic habitats or methanogenesis in anoxic habitats. This study can inform efforts to effectively manage OM loads in urban ecosystems, as well as inform future studies that aim to understand the ecological consequences of anthropogenic OM inputs to rivers and streams.

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Tables

Table 1. Fluorescence indices used to characterize and identify potential sources of DOM in the Jordan River, Salt Lake City, Utah. High and low values represent index ranges expected in developed watersheds[a] and do not encompass all possible values of each index.

Index	Abbreviation	high values indicate:		Low values indicate:		Reference
Fluorescence index	FI	1.8	microbial derived	1.2	terrestrial derived	Cory and McKnight 2005
Yeomin fluorescence index	YFI	2-7	aminosugar and protein-like	0-2	humic-like	Heo et al. 2016
Freshness index (β:α)	BIX	0.7-0.9	recently derived	0.3-0.5	less recently derived	Parlanti et al. 2000
Humification index	HIX	variable	lower H/C ratios indicative of humification	variable	lower degree of humification	Zsolnay et al. 1999
Peak T to Peak C ratio	TC	1	wastewater-like, high biochemical oxygen demand	0	low biochemical oxygen demand	Baker 2001
Specific UV absorbance at 254 nm	SUVA	3-6	greater proportion aromatic content	0-3	lower proportion aromatic content	Weishaar et al. 2003

a See Hosen et al. 2014, Parr et al. 2015, Williams et al. 2016

Table 2. Mean isotope values and standard deviation for potential sources of Jordan River organic matter (OM) including autochhtonous and terrestrial sources, OM from Utah Lake and WWTP effluent, and average isotope values for each size-class of OM. Stable Isototpe Analsysis In R (SIMMR) was conducted on all size-classes, and gradient-based mixing models were conducted for FPOM and DOM. Nitrogen isotope values were not used as a tracer in the SIMMR DOM model due to nitrate contamination of DOM.

Sources	n	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰	$\delta^{2}H$ ‰
Average Autochthonous		-25.5 ± 5.7	8.7 ± 4.9	-222.6 ± 27.7
Macrophytes	24	-26.5 ± 4.6	10.4 ± 5.4	-198.0 ± 21.1
Biofilm	30	-22.4 ± 5.6	9.3 ± 3.8	-244.2 ± 29.4
Algae	10	-29.6 ± 7.1	6.3 ± 5.4	-255.6 ± 32.6
Average Terrestrial		-27.2 ± 1.2	5.8 ± 3.1	-163.8 ± 11.5
Senesced leaf-litter	11	-27.8 ± 0.6	3.9 ± 2.4	-165.8 ± 10.0
Living tree leaves	17	-28.5 ± 1.4	6.9 ± 3.5	-159.4 ± 9.1
Phragmites	11	-28.4 ± 1.7	9.6 ± 3.5	-170.4 ± 15.4
BOM	21	-22.9 ± 4.8	5.1 ± 2.1	-202.3 ± 24.0
Lake-CPOM	2	-25.6 ± 0.5	7.4 ± 1.8	-164.4 ± 5.3
Lake-FPOM	5	-19.1 ± 6.1	6.8 ± 1.8	-186.7 ± 19.3
Lake-DOM	6	-25.9 ± 2.0	5.0 ± 3.9	-86.1 ± 18.2
WWTP-CPOM	5	-25.6 ± 1.7	10.4 ± 3.2	-182.4 ± 12.4
WWTP-FPOM	5	-23.9 ± 0.5	8.5 ± 1.2	-140.4 ± 16.2
WWTP-DOM	5	-23.5 ± 3.5	29.4 ± 12.4[a]	-121.5 ± 15.2
Jordan River OM				
CPOM	49	-27.0 ± 1.4	8.6 ± 2.5	-182.2 ± 28.3
FPOM	28	-22.1 ± 2.9	7.2 ± 1.6	-166.8 ± 13.6
DOM	30	-25.4 ± 1.7	25.1 ± 15.4 [a]	-117.2 ± 19.3
DIC and water				
River-DIC	34	-9.4 ± 0.9		
Lake-DIC	8	-2.7 ± 0.9		
WWTP-DIC	8	-8.3 ± 0.6		
River-water	49			-98.0 ± 15.9
Lake-water	8			-77.6 ± 30.9
WWTP-water	11			-111.7 ± 9.2

a - DOM nitrogen isotope values include nitrate and were not included in the Bayesian mixing models

Table 3. Pearson's correlations between spectroscopic indices FI, YFI, BIX, HIX, and SUVA and water quality metrics Chla, DOC, and TDN. Correlations were run between indices and water quality metrics for all months combined (see Fig. 8).

	Chla µg/L	DOC mg/L	TDN mg/L
BIX	0.05	-0.2	-0.43
HIX	0.15	-0.28	-0.29
FI	-0.43	0.51	0.86
YFI	-0.48	0.45	0.63
SUVA	-0.11	-0.42	-0.12

Figures

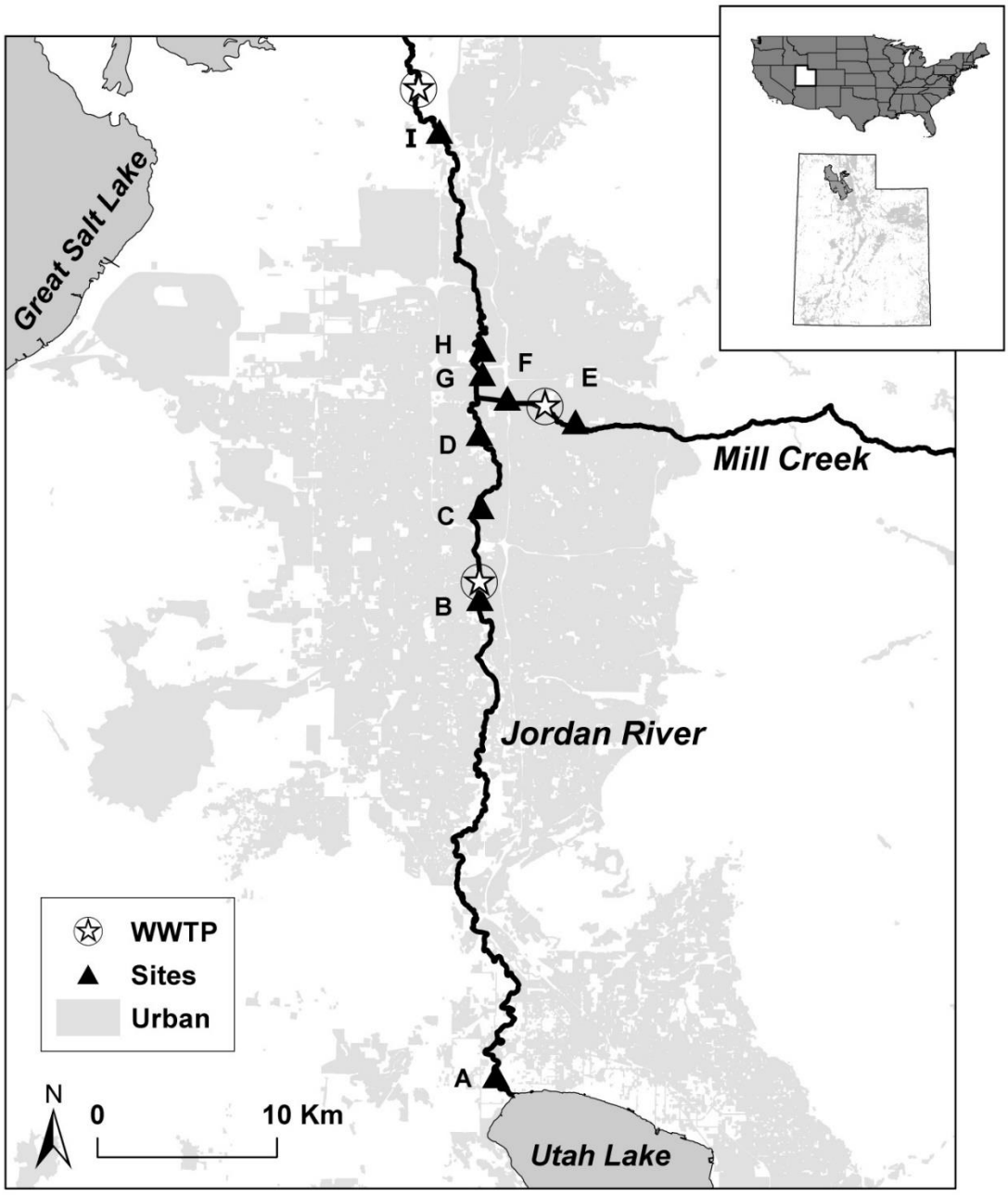


Figure 1. Study sites (A-I) and wastewater treatment plant (WWTP) located along the Jordan River from Utah Lake to terminus in wetlands of the Great Salt Lake. Light grey represents urban land-cover.

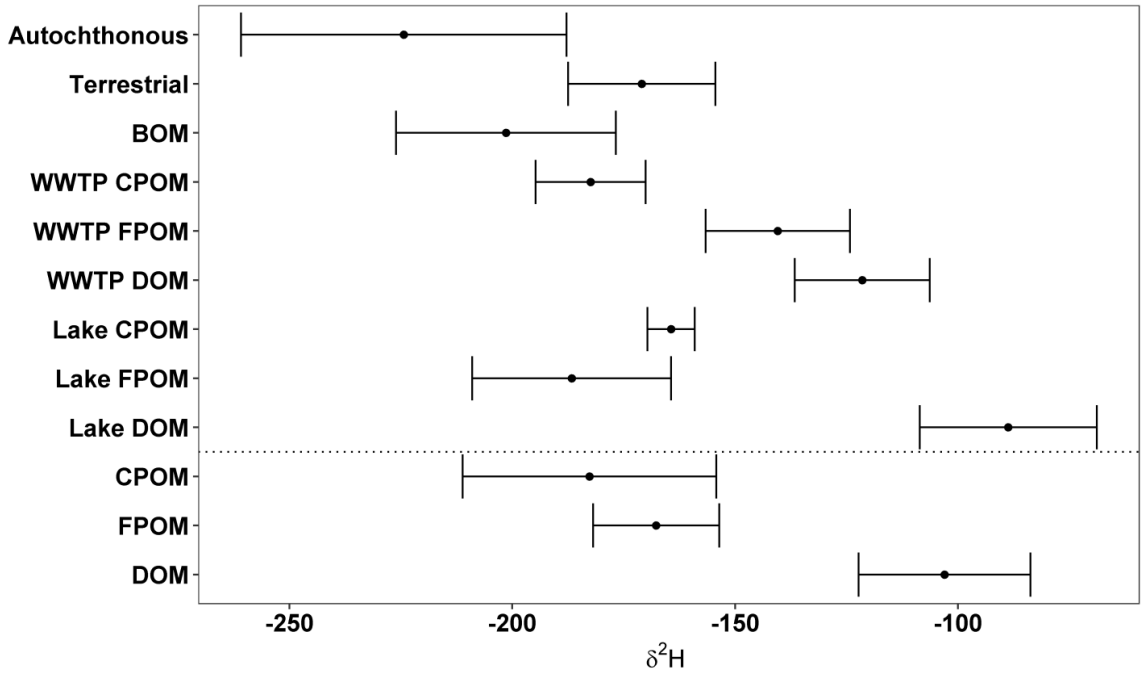


Figure 2. Above the dotted line are average δ^2H values of potential sources. Below the dotted are average δ^2H values of 3 size-classes of organic matter. Dots represent the means and whiskers are 1 standard deviation. Autochthonous sources were the average of macrophytes, biofilms and algae. Terrestrial sources were the average of senesced leaf-litter, living tree-leaves and *Phragmites* (Table 2).

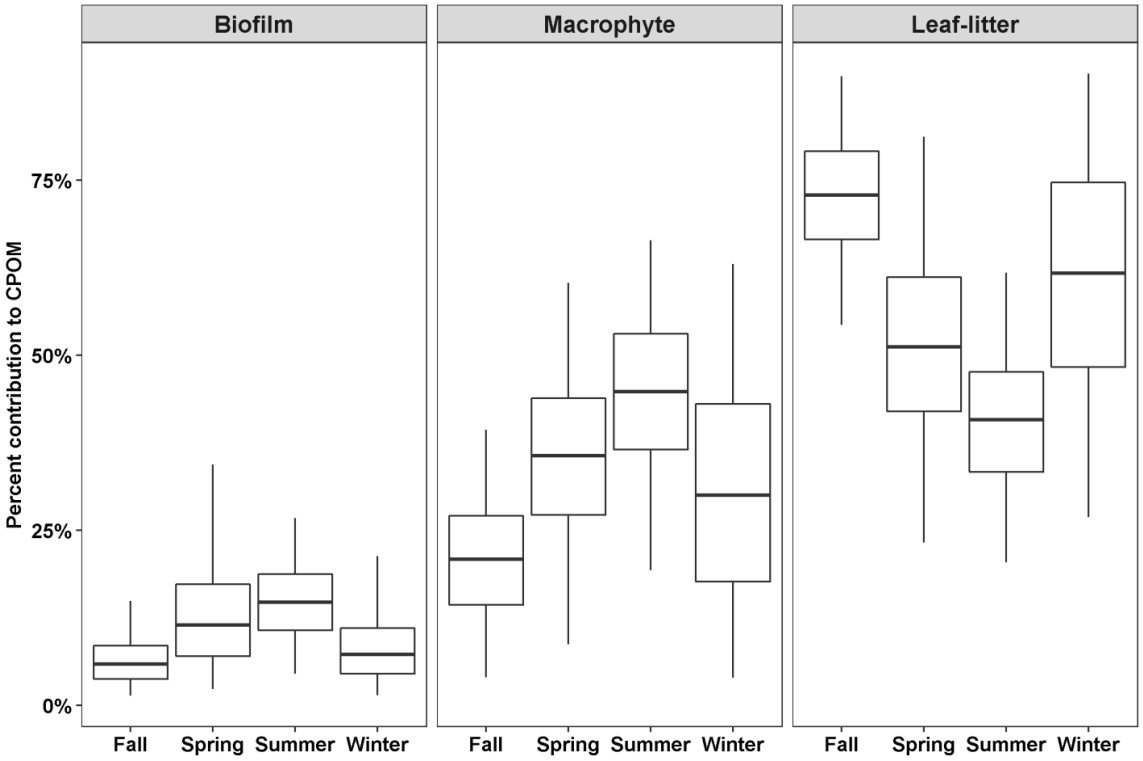


Figure 3. The percent feasible contributions of 3 sources to CPOM depending on season. Contributions were estimated using SIMMR with 3 isotope tracers, $\delta^{13}C$, $\delta^{15}N$, and $\delta^{2}H$. Boxes represent the 75% high density interval; whiskers represent the 95% high density interval.

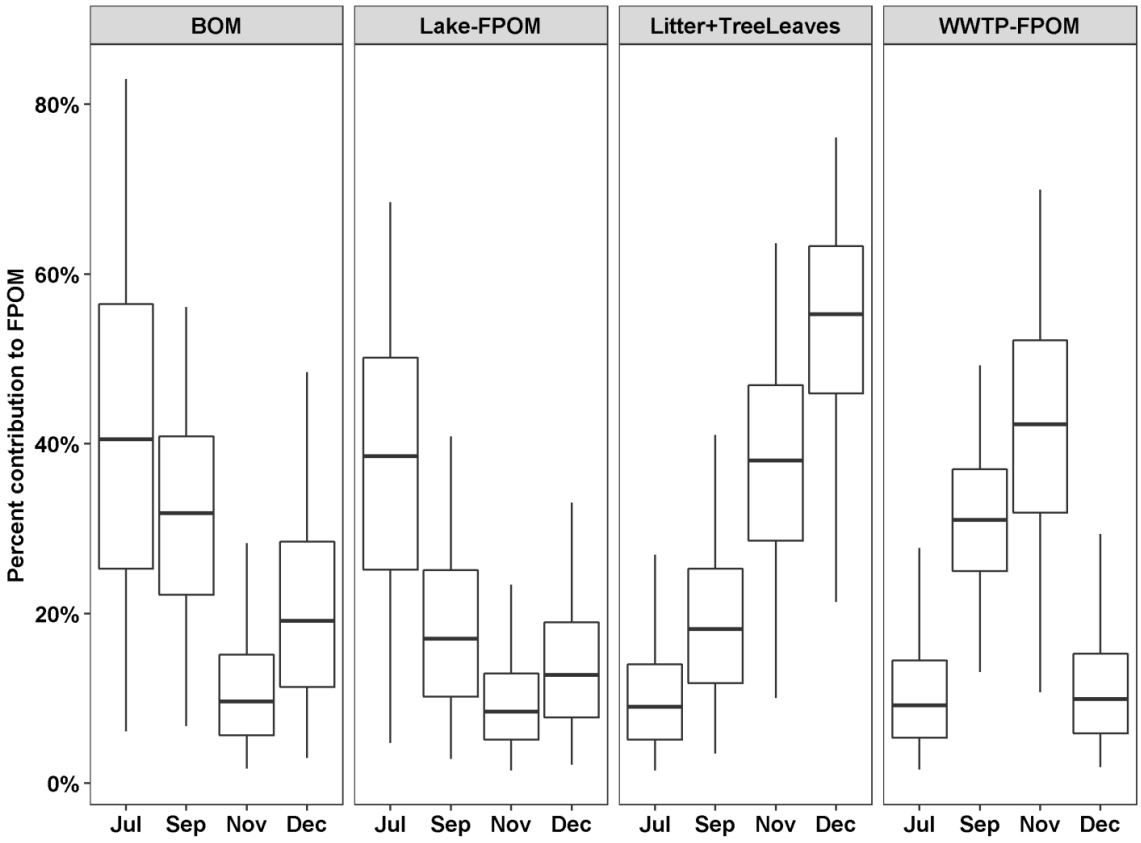


Figure 4. Percent feasible contributions to FPOM from 4 sources depending on the month. Contributions were estimated using SIMMR with 3 isotope tracers, $\delta^{13}C$, $\delta^{15}N$, and $\delta^{2}H$. Boxes represent the median and 75% high density interval; whiskers represent the 95% high density interval.

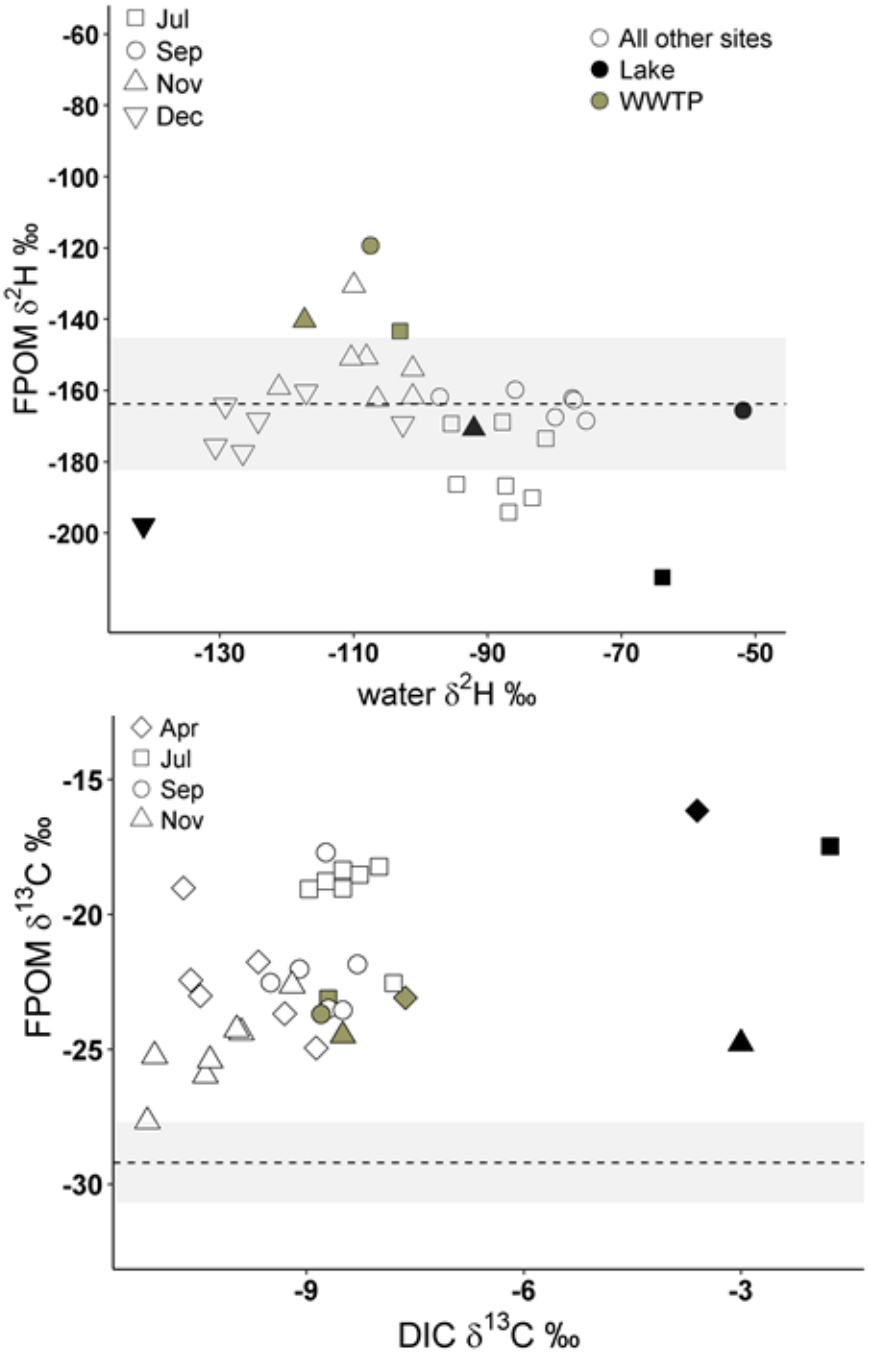


Figure 5. Deuterium values of FPOM compared to δ^2H-water (top) and δ^{13}C-FPOM compared to δ^{13}C of dissolved inorganic carbon (DIC; bottom). The dashed lines and grey areas represent the average deuterium and carbon isotope values of terrestrial sources collected in this study (see Table 2). Grey circles represent FPOM collected from WWTP effluent, black circles are FPOM collected from Utah Lake and open circles are all other sites.

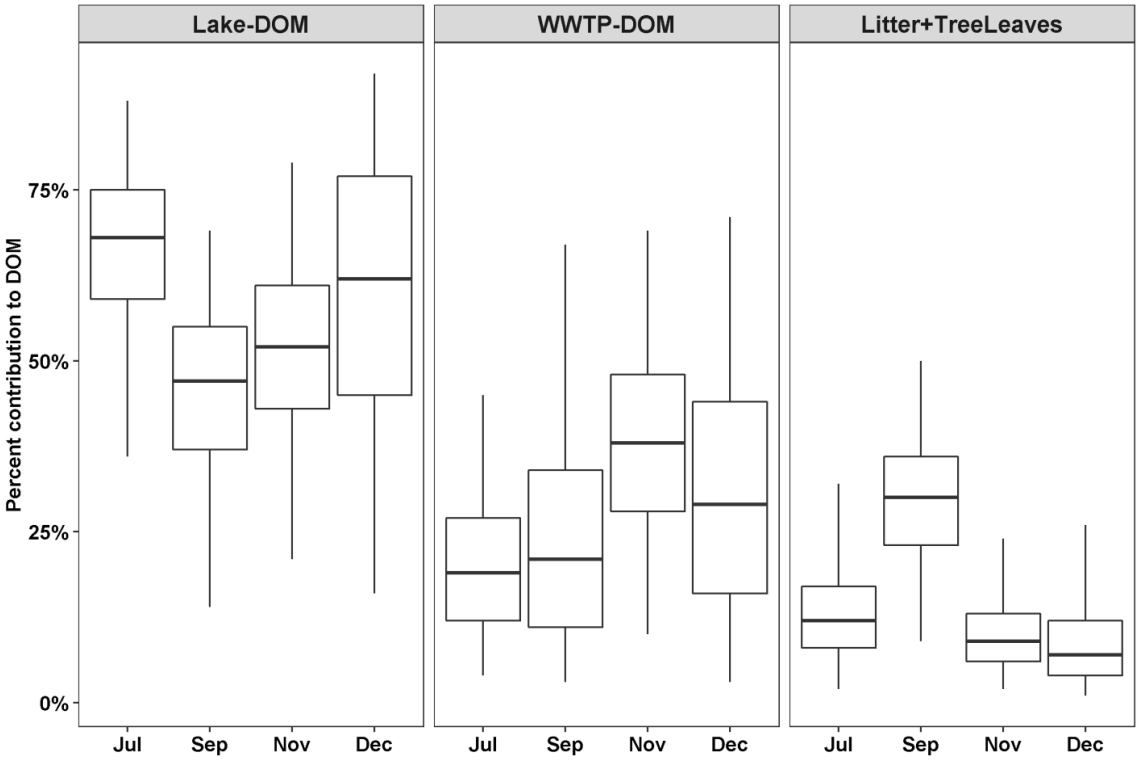


Figure 6. Percent feasible contributions to DOM from 4 sources depending on the month collected. Contributions were estimated using SIMMR with 2 isotope tracers, $\delta^{13}C$ and $\delta^{2}H$. Boxes represent the median and 75% high density interval; whiskers represent the 95% high density interval.

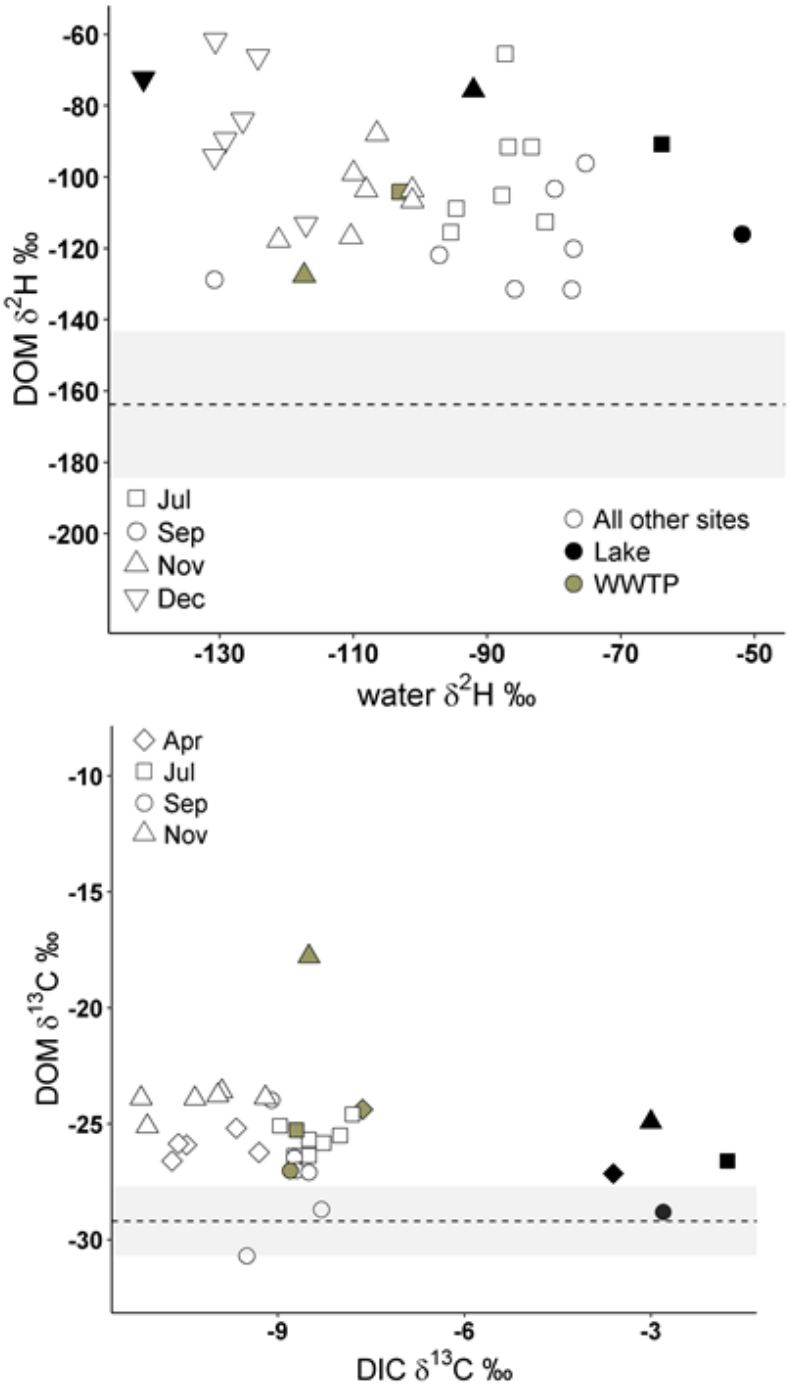


Figure 7. Deuterium values of DOM compared to δ^2H-water (top) and δ^{13}C-DOM compared to δ^{13}C of dissolved inorganic carbon (DIC; bottom). The dashed lines and grey area represent the average δ^2H and δ^{13}C values of terrestrial sources collected in this study (see Table 2). Grey circles represent FPOM collected from WWTP effluent, black circles are FPOM collected from Utah Lake and open circles are all other sites.

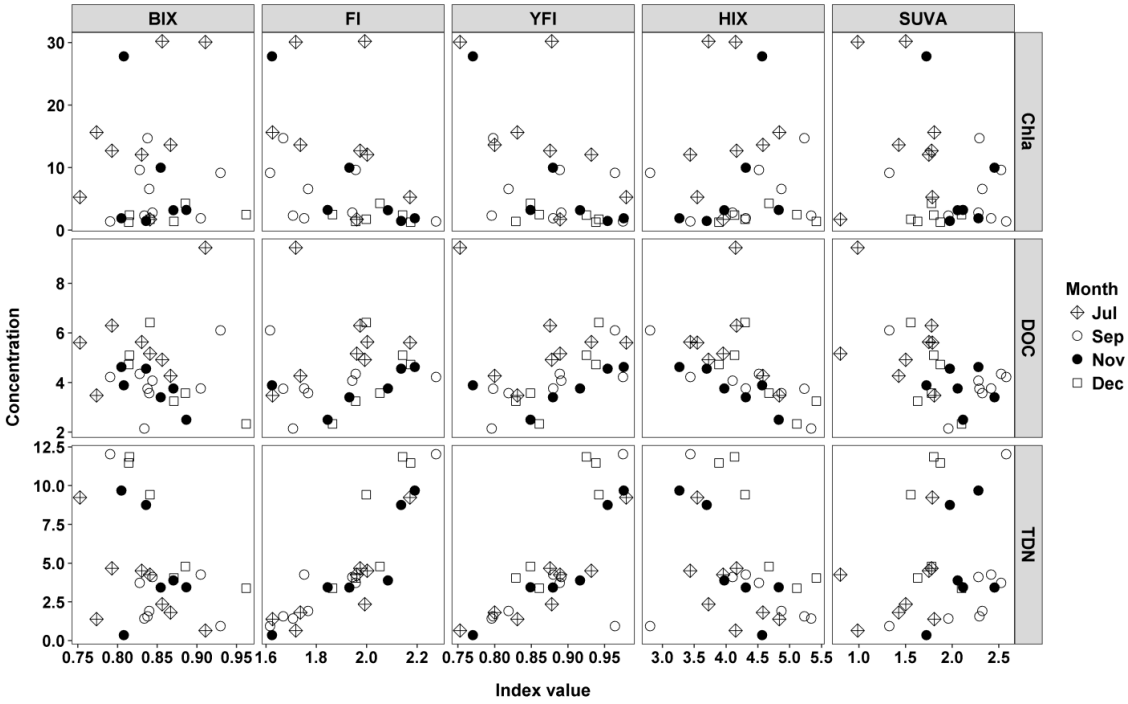
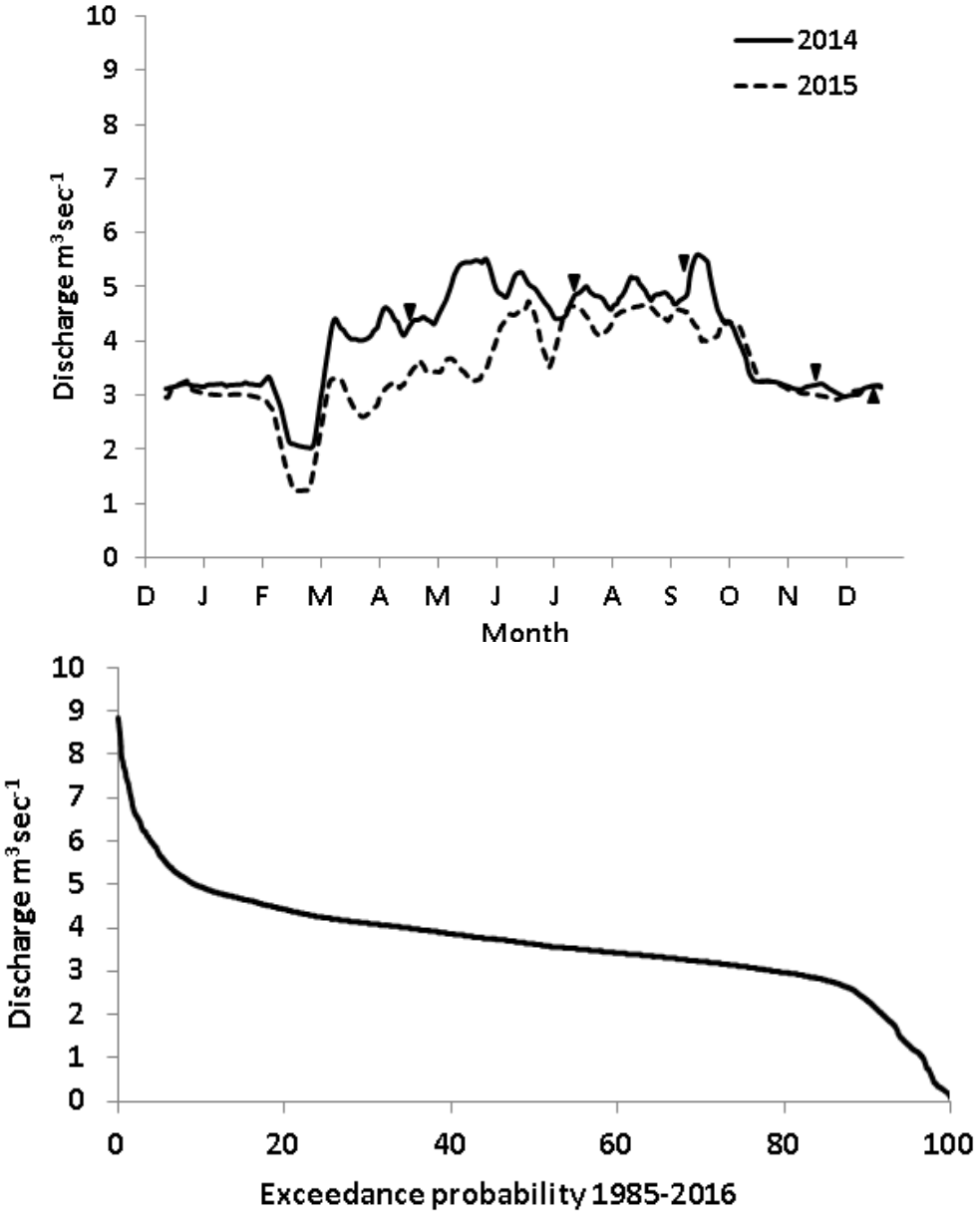


Figure 8. Water quality metrics, chlorphyll *a* (Chla µg/L), dissolved organic carbon (DOC mg/L), and total dissolved nitrogen (TDN mg/L), correlated to 5 fluorescence indices,freshness index (BIX), flourescence index (FI), Yeomin index (YFI), humification index (HIX) and SUVA.

Supplement

Supplement 1. Top: Mean daily discharge for the Jordan River (JR) at site H (Figure 1) in 2014 and 2015 (gage 10171000). A 10-day moving average was calculated for each year of daily discharge. Upside-down triangles (4) represent sampling dates in 2014 and the triangle represents the sampling date in 2015. Bottom: Flow duration curve since 1985 until sampling period. After 1985 Utah Lake was regulated so the JR would never exceed 9.8 m^3/s (Hooten 2011). Discharge exceedance probability represents the percent of time discharge is predicted to be met or exceeded over the period of record.



Supplement 2. Locations where Lake and WWTP OM endmembers were collected. Top: just below the Jordan River pumping station Lake samples were collected by wading into the thalweg. Bottom: WWTP OM collection site at Central Valley Water Reclamation Facility on Mill Creek just below effluent outfall. Samples were collected by floating into the thalweg on a one-man raft.

Supplement 3. Table of sources that were included and excluded for each SIMMR model. If a source had a 75% HDI that was <10% it was excluded, and if the 75% HDI had a range >60% the source was excluded.

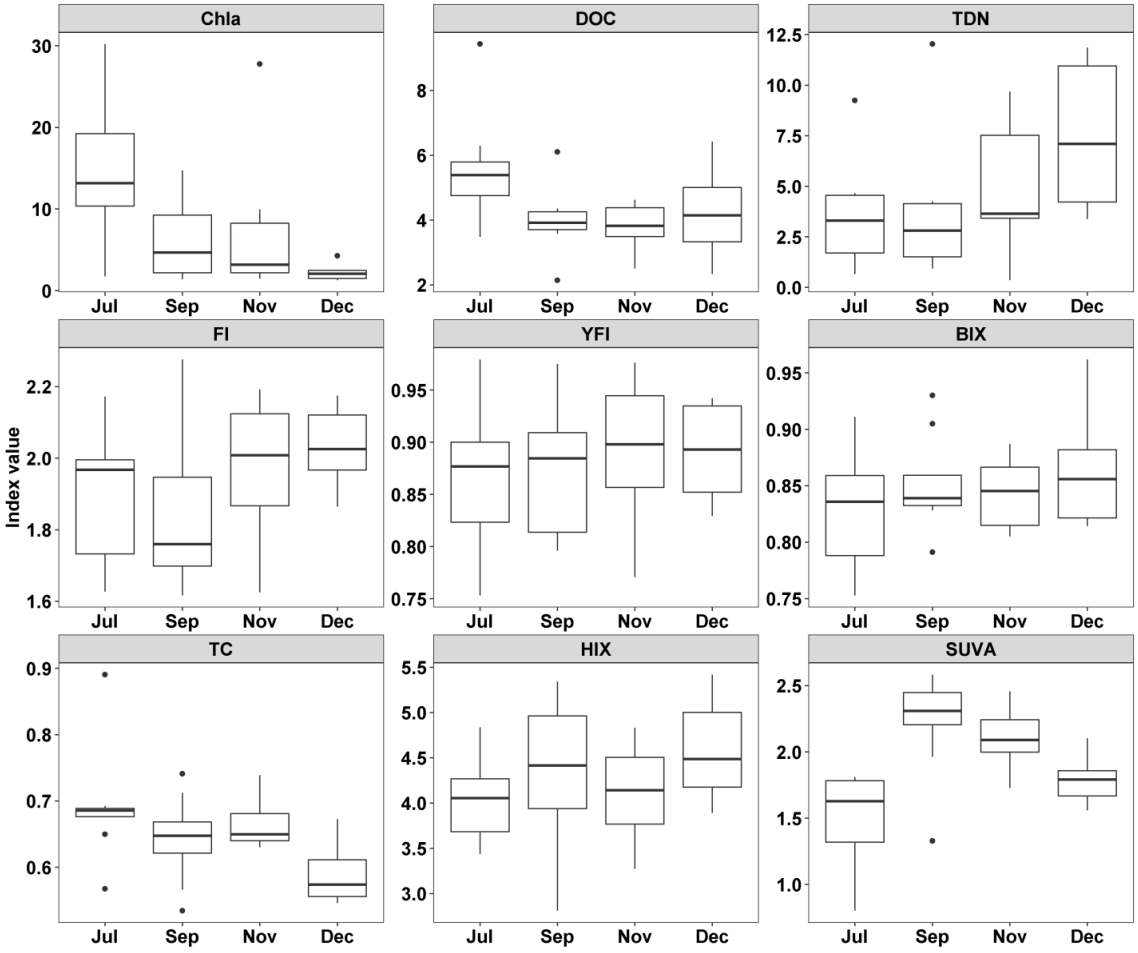
	CPOM	FPOM	DOM
Macrophytes	**Included**	<10%	<10%
Biofilm	**Included**	<10%	<10%
Algae	<10%	<10%	<10%
Senesced leaf-litter	**Included**	**Included**	**Included**
Living tree leaves	0-80%	**Included**	**Included**
Phragmites	0-60%	<10%	<10%
BOM	<10%	**Included**	<10%
Lake-CPOM	0-60%	0-60%	<10%
Lake-FPOM	<10%	**Included**	<10%
Lake-DOM	<10%	0-100%	**Included**
WWTP-CPOM	0-100%	0-60%	<10%
WWTP-FPOM	<10%	**Included**	0-60%
WWTP-DOM	<10%	<10%	**Included**

Supplement 4. Table of linear regressions results for graphical analysis of gradient based mixing models of FPOM (top) and DOM (bottom). Analyses were run for each month and for all months combined.

	δ^2H-FPOM vs δ^2H-Water				δ^{13}C-FPOM vs δ^{13}C-DIC			
Month	n	slope	r	p	n	slope	R	p
Apr	-	-	-	-	7	-0.33	0.16	0.2
Jul	8	-0.29	0.35	0.07	8	-0.29	-0.14	0.72
Sep	7	-0.59	0.627	0.02	7	-0.69	-0.19	0.95
Nov	8	-0.17	-0.08	0.51	8	0.45	0.44	0.04
Dec	6	0.45	-0.15	0.58	-	-	-	-
All Months	29	-0.29	0.05	0.12	30	0.17	0.19	0.01

	δ^2H-DOM vs δ^2H-Water				δ^{13}C-DOM vs δ^{13}C-DIC			
Month	n	slope	r	p	n	slope	r	p
Apr	-	-	-	-	6	1.18	0.55	0.05
Jul	8	0.13	-0.07	0.49	8	0.21	-0.03	0.41
Sep	8	0.82	0.09	0.24	7	0.03	-0.16	0.71
Nov	6	0.38	0.41	0.09	7	0.31	0.49	0.05
Dec	7	-0.12	0.03	0.32	-	-	-	-
All Months	29	-0.19	0.05	0.13	28	-0.02	0.04	0.82

Supplement 5. Boxplots of water quality metrics, Chlorophyll *a* (Chla, µg/L), dissolved organic carbon (DOC, mg/L), and total dissolved nitrogen (TDN, mg/L) and index values for Fluorescence Index (FI), Yeomin Flourescence Index (YFI), Biological index (BIX), PeakT to PeakC ratio (TC), humification index (HIX) and SUVA grouped by month.



CHAPTER III

ORGANIC MATTER SOURCES AND COMPOSITION IN RIVERS WITH MIXED LAND COVER

Abstract: As human dominated landscapes have expanded, the diversity of organic matter (OM) sources to rivers has increased and knowledge of the composition and quality of these sources is lacking. The source and quality of OM regulate ecosystem functions that affect material retention and transport within a watershed. Aquatic OM is a complex mixture of thousands of organic molecules, which makes OM source difficult to identify within a matrix of land covers. We collected fine particulate OM (FPOM) and dissolved OM (DOM), in 4 watersheds of north-east Utah with a mixture of urban, forest, and agricultural land cover. We used the natural abundance of ^{13}C, ^{15}N, and ^{2}H isotopes in mixing models to quantify the proportion of terrestrial, autochthonous, and anthropogenic OM. We also used the fluorescence and absorbance properties of DOM to characterize OM composition as microbial versus humic derived, and bioavailability based on percent protein-like DOM. Percent land cover within a watershed did not explain differences in proportional sources of OM among sites. The greatest differences in OM composition was due to the influence of wastewater treatment plants (WWTP) at a subset of the urban sites. FPOM and DOM were primarily derived from terrestrial sources, except at sites influenced by wastewater which had significant contributions

from WWTP derived OM. In addition, sites influenced by WWTPs had more homogenous DOM that consistently had ~ 35% protein-like DOM. All other sites had much more percent protein-like DOM. Further study is needed to understand landscape drivers of DOM bioavailability and composition, and studies in watersheds with WWTPs should incorporate direct measures of WWTP OM when comparing OM composition across land covers.

Keywords: dissolved organic matter, fine particulate organic matter, mixing models, land cover, water quality, urban ecology, PARAFAC, wastewater

Introduction

Organic matter (OM) across aquatic and terrestrial ecosystems is a complex mixture of thousands of organic molecules and exists in in every compartment of the hydrologic cycle. OM source, composition, and bioavailability to microbes (i.e. quality) are directly linked. Identification of OM sources is a challenge, due to the multiple origins of OM in rivers, including inputs from terrestrial and anthropogenic sources, as well as OM produced *in situ* through primary production. OM source identification is helpful so watershed managers can understand the origins of excessive OM loads, and infer its bioavailability. OM produced in-stream, autochthonous OM, is considered more bioavailable (i.e. labile) to microbes compared to terrestrial sources because microbial activity associated with photosynthesis produces exudates of simple, low molecular weight compounds that are easy for microbes to consume (Guillemette et al. 2013, Wyatt

et al. 2014). Autochthonously derived OM has proportionally more nitrogen rich compounds (e.g. amino acids, DNA), than terrestrial sources and therefore is also considered high quality OM that is preferentially consumed in nutrient limited conditions (Knapik et al. 2014, Guenet et al. 2010).

The quality of OM in rivers regulates functions such as decomposition and nutrient assimilation that affect material retention and transport within watersheds. Excessive labile OM and inorganic nutrient loads to rivers can saturate microbial demand for high quality OM, thereby reducing transformation and retention of semi-labile OM (Edmonds and Grimm 2011, Wollheim et al. 2018). Consequently, OM and associated nutrients and pathogens are transported downstream to lakes and estuaries causing pollution and eutrophication which pose significant public health risks, and increase the cost of drinking water treatment (Chow et al. 2005, Shutova et al. 2014). Therefore, it is important to identify the sources and composition of OM in rivers to inform management strategies aimed at improving water quality in both rivers and downstream water bodies.

With increased urbanization and other land-use changes, the diversity of anthropogenic OM inputs to rivers has increased (Stanley et al. 2012, Fork et al. 2018) adding to the complexity, and difficulty, of characterizing OM sources and composition. For example, conversion of wetlands to agriculture was thought to destabilize fossil-aged soil OM, which contributed large OM loads to the Sacramento River (Sickman et al. 2007). However, the same indicators of fossil soil OM (radiocarbon values) may also signify the contribution of anthropogenic sources of petroleum products from wastewater effluent, urban runoff, or pesticides (Sickman et al. 2010, Butman et al. 2015). Other anthropogenic sources of OM include detergents, pharmaceuticals (Kolpin et al. 2002),

microplastics (McCormick et al. 2016), leaky sewage pipes and septic tanks (Kaushal and Belt 2012), grass clippings, and pet waste (Mallin et al. 2006). Many of these anthropogenic sources are discharged from wastewater treatment plants (WWTPs), which are not equipped to remove pharmaceuticals and petroleum products (Bridgeman et al. 2014). The 'ecological footprint' of wastewater effluent on downstream organic matter processing and production, and effects at higher trophic levels needs further study in rivers to understand the consequences of anthropogenic sources of OM to downstream lakes and estuaries (Wassenaar et al. 2010, Figueroa-Nieves et al. 2014, Hansen et al. 2016).

Numerous studies have aimed to describe OM sources and quality in watersheds with different land covers and gradients of human impact. Fine particulate OM (FPOM), OM between 0.45 and 1000 μm (Hutchens et al. 2017), was more autochthonously derived in agricultural and urban watersheds compared to watersheds with less human influence (Newcomer et al. 2012, Imberger et al. 2014). Dissolved OM (< 0.45 μm) in urban watersheds was more bioavailable (Hosen et al. 2014,), autochthonous (Petrone et al. 2011, Parr et al. 2015), and had greater proportions of hydrophobic/petroleum OM (McElmurry et al. 2013), than DOM in non-urban watersheds. Agricultural land use was associated with less complex, more microbial-derived OM compared to forest land cover (Wilson and Xenopoulos 2008, Williams et al. 2010). But, only one study has successfully distinguished DOM associated with urban versus agricultural land cover, and differences were dependent on the scale of comparison, and type of waterbody (e.g. lake vs. river, Williams et al. 2016).

The ability to link OM sources and composition to OM bioavailability is an exciting frontier in OM research. Traditional methods to assess bioavailability with bioassays that measure dissolved organic carbon (DOC) decay, biochemical oxygen demand (BOD), or bioavailable dissolved organic carbon (BDOC), are informative but labor intensive. Development of spectrofluorometers that can rapidly analyze DOM samples and produce 3-dimensional fluorescence excitation-emission matrices (EEMs) has driven advancements in characterizing DOM character and function (Shutova et al. 2014). EEMs produce peaks over a range of excitation and emission wavelengths, and depending on peak location, DOM can be characterized as humic-like or protein-like (Coble 1996). The percent protein-like DOM in a sample has been directly correlated to DOC decay rate (Parr et al. 2015), BOD (Baker and Inverarity 2004), and BDOC (Fellman et al. 2008, Balcarczyk et al. 2009, Petrone et al. 2011, Hosen et al. 2014), making spectrofluorometry an inexpensive and efficient tool to describe DOM bioavailability.

Our first objective was to identify sources of FPOM and DOM in watersheds with varying land covers including urban, suburban, forest, shrub/scrub, and agriculture. We hypothesized that OM at sites with urban or agricultural development would have a greater proportion of autochthonously derived DOM due to increased inorganic nutrient concentrations and primary production, compared to forest and shrub/scrub land covers. Our second objective was to use spectrofluorometric properties of DOM to infer DOM composition and relative lability at sites with varying land use. We used fluorescent properties of DOM, and the natural abundance of carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), and deuterium ($\delta^{2}H$) stable isotopes, to estimate the proportion of autochthonous, terrestrial,

and anthropogenic sources of OM collected in rivers across 4 watersheds with a mixture of land cover.

Methods

Study sites and land cover

Four watersheds located in the Central Basin and Wasatch Mountain Ecoregions (Woods et al. 2001) were sampled in Northeastern Utah. The Logan River, Provo River, and Red Butte Creek watersheds all transition from forested, nationally protected areas (USDA National Forest and Wilderness Areas) to downstream reaches surrounded by either urban or suburban/rural land covers (Hall et al. 2015). The Jordan River flows north through the Salt Lake Valley metropolitan area. The source of the Jordan River is Utah Lake, a shallow, eutrophic lake that receives wastewater effluent from 6 WWTPs in the Orem, Provo, and Spanish Fork urban areas (Hogsett 2015; Fig. 1). The Jordan River also receives effluent from 3 WWTPs located 22, 37, and 50 km downstream of Utah Lake. It also receives runoff from six major tributaries with headwaters in the Wasatch Range (Epstein et al. 2016). There were 8 to 9 sampling sites within each of the 4 watersheds (Supplement 1). Nine sites were sampled on the Jordan River, 2 of which were above and below a WWTP on Mill Creek, a Jordan River tributary 37 km downstream of Utah Lake. Study site locations were chosen to sample river reaches that represented either, or both natural and developed land covers.

Watersheds and sub-watersheds were delineated for each site in ArcGIS (version 10.4.1; Environmental Systems Research Institute, Redlands, California) and the USGS

StreamStats web application (https://water.usgs.gov/osw/streamstats). Land cover metrics were derived from the 2011 National Land Cover Dataset (Homer et al. 2015); 18 land covers were reduced to 6 types expected to explain DOM concentrations and composition at a site (Petrone et al. 2011, Williams et al. 2016). Initial land cover classes included forest, scrub-grassland, wetland, pasture, cultivated crops, and developed. Percent land cover within a sub-watershed was calculated for each the 8 or 9 sites within a watershed.

Correlations of percent land cover classes among the 34 sites sampled revealed land covers indicative of human influence were positively correlated. For example, percent crop and pasture were correlated ($r = 0.97$), and both crop and pasture were correlated with development ($r = 0.56$ and $r = 0.54$; Supplement 2A). Percent development within a sub-watershed was negatively correlated with percent forest ($p = 0.73$) and percent scrub-grassland was positively correlated with both crop ($p = 0.31$) and pasture land cover ($p = 0.27$). A principal components analysis (PCA) of percent land cover within sub-watersheds of 34 sites revealed forest-dominated sites were different from development-dominated sites, but there were no significant differences between sites with agricultural versus urban development, or scrub versus forest land cover (Supplement 2B). Furthermore, a PCA of water quality and land cover metrics among sites also revealed differences in OM composition among sites were better explained by watershed than land cover (see below). Therefore, further analysis of OM composition and quality at each site were compared by watershed and not land cover.

Isotope mixing models

Two isotope mixing models were used to identify the sources of FPOM and DOM, a Bayesian mixing model, and a graphical gradient-base mixing model. The Stable Isotope Mixing Model in R package (SIMMR) used three isotope tracers ($\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$) to estimate source contributions to FPOM and DOM. SIMMR is a Bayesian inference mixing model that can incorporate variability of end-members into the model, and estimate source contributions to a mixture regardless of the number of isotope tracers (Parnell and Inger 2016). Significant differences among source contributions for each land cover classification were assessed by comparing the 95% high density intervals (HDI) of the posterior probability densities of each source. Parameter values within the HDI have higher probability density than values outside the HDI and the total probability of values in the 95% HDI is 95% (Kruschke 2018). Within the 95% HDI, a 75% HDI was delimited to convey skewness of the 95% HDI, and further constrain the most credible estimates.

A graphical, gradient-based mixing model was used to partition OM sources as either terrestrial or autochthonous (Mohamed and Taylor 2009, Rasmussen 2010, Wilkinson et al. 2013). If OM was primarily derived from terrestrial inputs, OM- $\delta^{13}C$ or OM- $\delta^{2}H$ will not vary systematically with DIC $\delta^{13}C$ or water-$\delta^{2}H$, yielding a flat line with a y-intercept at the average $\delta^{13}C$ or $\delta^{2}H$ terrestrial isotope values. If OM was primarily derived from autochthonous sources, the $\delta^{13}C$ and $\delta^{2}H$ values will vary linearly with aqueous DIC- $\delta^{13}C$ or water- $\delta^{2}H$ values since autochthonous sources (e.g. algae) used river water to fix carbon, and terrestrial sources did not (Wilkinson et al. 2013).

OM sampling

FPOM and DOM were collected at 34 sites in all 4 watersheds (Fig. 1). Samples were collected during baseflow in September and November of 2014, and November of 2015. Five OM endmembers were evaluated as possible sources of FPOM and DOM for the SIMMR mixing model. Endmembers included benthic organic matter (BOM), autochthonous sources (macrophytes, biofilm, and algae), tree leaves (both senesced and live), soil, and WWTP-DOM or WWTP-FPOM. All OM samples were analyzed for $\delta^{13}C$, $\delta^{15}N$, and $\delta^{2}H$ stable isotopes.

DOM was collected with 2, 1-liter grab samples at each site and filtered in the laboratory through 0.7 µm glass fiber filters (Whatman GF/F, Maidstone, UK). One liter was acidified to pH 2.5-3 with concentrated HCl to remove inorganic carbon. Acidified DOM was then evaporated in 8-inch diameter glass dishes at 50 °C, residue was scraped from plates (Wilkinson et al 2013), and stored in coin envelopes or scintillation vials. DOM was then freeze dried, packed in silver capsules, and sent for $\delta^{13}C$ and $\delta^{15}N$ analysis. One liter of non-acidified DOM was also dehydrated in glass dishes, stored in coin envelopes or scintillation vials, and residue was sent to be packed and analyzed for $\delta^{2}H$ analysis.

FPOM for $\delta^{2}H$ samples was collected instream with a 1-liter bottle from each site and transported back to the laboratory for filtering. FPOM was collected on 0.45 µm nylon filters (Whatman polyamide membrane filters, Maidstone, UK) then backwashed into deionized water, and dehydrated at 50 °C in a drying oven (Wilkinson et al. 2013). This material was packed in tin capsules. FPOM for $\delta^{13}C$ and $\delta^{15}N$ isotope analysis was collected instream with a drill-pump (Kelso and Baker 2015) and filtered onto a 25-mm diameter glass fiber filters of 0.7 µm pore size (Whatman GF/F, Maidstone, UK). Filters

were transported back to the laboratory in foil, dried at 50 °C, rewet with deionized water, and acidified by fumigation in a desiccator with 25% HCl for six hours (Brodie et al. 2011) before being packed into silver capsules.

OM endmembers were collected in all watersheds throughout the 3 sampling efforts, but not all sources were sampled in each sampling effort. Autochthonous sources of OM were collected in July and September of 2014 in the Jordan River and September of 2014 in all other watersheds (Table 1). The autochthonous endmember was represented by the average isotope values of macrophytes, algae, and biofilm. Large submerged aquatic vegetation was classified as macrophytes, biofilm was scraped from benthic rocks, and algae were collected from green mats floating on the water surface. Tree leaves were sampled as a proxy for terrestrial vegetation in all watersheds in either November of 2014 or December of 2015 at sites that had Elm trees (*Ulmus pumila*) because elm trees were a deciduous tree present in all 4 watersheds (Hall et al. 2015). Senesced tree leaves were collected from riparian zones and tree leaves were collected from live elm trees. BOM and soil was collected in December 2015. BOM was collected at two sites, a reference site, and a development-dominated site in each of the four watersheds. BOM was collected by sinking a stove-pipe 5 to 10 cm into river sediment, agitating with a meter stick, and then a 100 mL sample of the sediment-water mixture was collected, transported back to the laboratory, and filtered through 0.7 µm glass fiber filters. Soil was collected at four sites along the Jordan, two upstream, and two downstream of the WWTP effluent input on Mill Creek, and four sites on the Logan River at two forested, and two urban sites. Soil was collected by inserting a 10 x 1 inch soil auger into soil at the riparian zone of sites. One inch of soil was removed from the

bottom of the of the auger. WWTP-FROM and WWTP-DOM were collected instream at the WWTP effluent outfall of the Central Valley Water Reclamation Facility on the Mill Creek tributary of the Jordan River. WWTP-DOM and WWTP-FPOM were collected in all three sampling efforts. WWTP OM was processed for isotopes as described for all FPOM and DOM isotope samples. In the laboratory all isotope samples were dried for at least 48 hours in a drying oven at 50°C, ground in a coffee grinder, and packed for isotope analysis.

Isotope analysis

OM stable isotope analysis Samples were sent to the Stable Isotope Facility (SIF) at University of California Davis for $\delta^{13}C$ and $\delta^{15}N$ analysis on a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Deuterium analysis was conducted at the Colorado Plateau Stable Isotope Laboratory (CPSIL) at Northern Arizona University. Samples were pyrolyzed to H_2 gas following the procedures of Doucett et al (2007),and analyzed on a Thermo-Finnigan TC/EA and DeltaPLUS-XL IRMS (Thermo Scientific, Bremen, Germany).

Samples analyzed for deuterium were corrected for exchange of H atoms between sample and water vapor using the bench top equilibration method (Wassenaar and Hobsob 2000). To account for exchangeable hydrogen of a sample OM is equilibrated in a vacuum, at a high temperature (> 100º C), using water vapor with a known δ^2H value. This equilibration process effectively replaces all exchangeable hydrogen with non-exchangeable hydrogen of a known δ^2H value (Wassenaar and Hobsob 2000). Then a 2

endmember isotopic equilibration procedure is used to calculate the proportion of exchangeable hydrogen.

OM isotope analysis challenges Many DOM samples collected in the first sampling effort could not be successfully analyzed for carbon and nitrogen isotopes because some acidified samples that were stored in coin envelopes turned into gel, which degraded coin envelopes and could not be packed for isotope analysis. Additionally, DOM samples from low DOC sites (e.g. < 1 mg/L) did not produce enough DOM solid when dehydrated for deuterium isotope analysis. Likewise, for FPOM, it was often hard to backwash and dehydrate sufficient FPOM material for deuterium analysis. These issues were rectified for subsequent samples by freeze-drying DOM, storing OM in scintillation vials, and collecting more water to filter for FPOM at low DOC sites. However, only samples that were successfully analyzed for all three isotopes could be included in the SIMMR mixing models. Because of these issues the DOM and FPOM SIMMR models included 50 and 75 samples, respectively.

Organic nitrogen isotope correction The ^{15}N content of DOM samples was corrected for ^{15}N of nitrate. First, TDN-$\delta^{15}N$ values obtained from DOM residue were converted to TDN-^{15}N atom percent (AP), and then values were corrected with nitrate-^{15}N AP to obtain DON-^{15}N AP. TDN-^{15}N AP was corrected for ^{15}N of nitrate using the following equation,

$$\text{TDN-}^{15}\text{N AP} * [\text{TDN}] = \text{DON-}^{15}\text{N AP} * [\text{DON}] + \text{nitrate-}^{15}\text{N AP} * [\text{nitrate}]$$

where TDN-^{15}N AP was the ^{15}N AP value of residue submitted for ^{15}N analysis, and the concentration of DON was calculated by subtracting the concentration of nitrate, from TDN. The corrected DON-^{15}N AP value were then converted to DON-δ^{15}N values for DOM stable isotope mixing models. TDN residue was not corrected for ammonium-^{15}N isotope values, so DON concentrations and DON-δ^{15}N included ammonium. However, we assumed the influence of ammonium was minimal because, on average, ammonium was 6.4% of TDN (sd 5.6), while nitrate was 56% of TDN (sd 39.2).

For nitrate-δ^{15}N analysis filtered water was frozen in 40 mL centrifuge tubes and sent to the UC Davis Stable Isotope Facility. Samples were prepared by bacterial denitrification (Sigman et al. 2001) and measured with a GasBench + PreCon trace gas concentration system (Thermo Scientific, Bremen, Germany) interfaced to a Delta V Plus IRMS. Filtered samples, collected concurrently with DOM, were frozen in 60 mL high density polyethylene bottles for analysis of nitrate and ammonium. Nitrate was determined by nitrate-nitrite calorimetric, automated, cadmium reduction, and ammonium nitrogen was determined by semi-automated colorimetry on an Astoria Autoanalyzer (nitrate method detection limit (MDL) 0.005 mg/L, ammonium MDL 0.001 mg/L).

Inorganic tracers of OM Carbon isotopes of dissolved inorganic carbon (DIC) and deuterium isotopes of river water were collected in September and November 2014 for use in the graphical gradient-based mixing models. The DIC-δ^{13}C was obtained by filling helium-flushed, 12 mL Exetainer® vials (Labco, Lampeter, United Kingdom) with 1 mL of 85% phosphoric acid and 4 mL of 0.7µm filtered river water (Taipale and Sonninen

2009). DIC samples were analyzed at SIF using a GasBench II system interfaced to a Delta V Plus IRMS (Thermo Scientific, Bremen, Germany). Unfiltered river water was collected in scintillation vials and stored at 6º C until analyzed. δ^2H and $\delta^{18}O$ isotopes of water were obtained with a GasBench II with GC PAL auto-sampler interfaced to a Delta V Plus IRMS at the Utah State University Stable Isotope Lab.

Water quality metrics

We collected samples for analysis of chlorophyll *a* (Chla) dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concurrently with organic matter sampling described above. DOC and TDN samples were filtered through 0.7 µm glass fiber filters into 40 mL amber vials and acidified with HCl to a pH of 2.5 for storage until carbon analysis. Acidified DOC and TDN samples were run on a Shimadzu TOC-L analyzer via catalytic oxidation combustion at 720 °C (DOC MDL 0.2 mg/L, TDN MDL 0.1 mg/L; Shimadzu Corp., Kyoto, Japan). Chla was collected on glass fiber filters, in-stream, with a drill-pump, wrapped in foil, frozen, and subsequently analyzed on a Turner handheld fluorometer (Turner Designs, Sunnyvale, CA) following Steinman et al. (2007).

DOM fluorescence

Fluorescence characteristics of DOM were collected to characterize DOM as microbial derived versus terrestrially derived using fluorescence indices and protein-like versus humic-like fluorophores identified by parallel factor analysis (PARAFAC). Filtered water from each site and sampling effort was analyzed for DOM spectrofluorometric properties obtained from EEMs collected on a Horiba Aqualog

spectrofluorometer (Horiba Scientific, Edison, New Jersey). EEMs were collected over excitation wavelengths 248-830 nm at 6 nm increments and over emissions 249.4-827.7 nm at 4.7 nm (8 pixel) increments. All samples were collected in ratio mode (S/R), and run at an integration time resulting in a maximum emission intensity of 5,000 to 50,000 counts per second. Samples that exceeded 0.3 absorbance units at excitation 254 nm were diluted with deionized water. All samples were corrected for inner filter effects, Rayleigh scatter, and blank subtracted in MATLAB™ (version 6.9; MathWorks, Natick, Massachusetts) as described in Murphy et al. (2013).

Five optical indices were calculated from EEMs: the fluorescence index (FI), Yeomin fluorescence index (YFI), freshness index (BIX), humification index (HIX), peak T to peak C ratio (TC), and one index, $SUVA_{254}$ (SUVA) was calculated from sample absorbance. The FI was calculated at excitation 370 nm as the ratio of emission intensities at 470 and 520 nm (McKnight et al. 2001, Cory et al. 2010). The YFI was calculated as the average intensity over emission 350-400 nm divided by the average intensity over emission 400-500 nm at excitation 280 nm (Heo et al. 2016). The YFI differs from FI in that it has a wider range of values used to characterize fulvic, humic, aminosugar-like and protein-like fluorophores (0.30-6.41), the last two of which are prevalent in WWTP effluent (Heo et al. 2016). In contrast, the FI has a narrower index range (0.82-2.14), and cannot distinguish between protein-like and aminosugar-like standards (Heo et al. 2016). The β:α index (BIX), also called the freshness index, was calculated as the intensity at excitation 380 nm divided by the max intensity between emission 420-435 nm, where higher values represent more recently derived DOM (Parlanti et al. 2000). The HIX was calculated at excitation 254 nm as the area under

emission 435-480 divided by the area under emission 300-450 nm + 435-480 nm; higher HIX values represent more humic-like material (Zsolnay et al. 1999). The TC index is the ratio of maximum fluorescence in the peak T region (protein-like) versus peak C region (humic-like) with higher values representing more protein-like DOM, which are also associated with WWTP effluent (Baker 2001). TC was calculated as the ratio of fluorescence intensity of peak T, at excitation 275/emission 350 nm, to the maximum intensity of peak C within excitation 320-340nm/emission 410-430 nm (Gabor et al. 2014). Lastly, $SUVA_{,}$ an indicator of aromaticity, was calculated from DOM absorbance at 254 nm normalized by DOC concentration (Weishaar et al. 2003). In addition to fluorescence indices, we calculated a DOC:TDN ratio to compare the proportion of organic carbon to inorganic plus organic nitrogen in DOM samples.

PARAFAC was used to identify humic and protein-like fluorescent components of DOM to elucidate differences in DOM that varied by watershed and water quality within a watershed. PARAFAC decomposes a collection of EEMs into groups of organic compounds with similar fluorescent characteristics (Stedmon and Bro 2008, Murphy et al. 2013) The drEEM toolbox was used to create a PARAFAC model in MATLAB^{TM} following Murphy et al. (2013). Resolved PARAFAC components were then compared to previously found fluorophores in the open source library OpenFluor (Murphy et al. 2014). A total of 499 EEMs, collected as part of a previous synoptic sampling effort from July 2014 to December 2015, were used to create the PARAFAC model. The model included EEMs from all 4 watersheds, each of which composed 11-36% of all EEMs used for the model. Of the EEMs from the model, 97 were collected concurrent with OM for this study, and were used for further analysis.

DOM source and composition analysis

Wilcoxon sign-ranked t-tests were conducted in R to identify water quality and DOM composition indices that differentiated high and low human impact sites (version 3.4.3; R Project for Statistical Computing, Vienna, Austria). Multi-way ANOVAs were conducted in R and significant differences among watersheds were assessed with Tukey's HSD post-hoc test. Metrics included four water quality variables (DOC, TDN, DOC:TDN, Chla), 6 indices (BIX, FI, YFI, HIX, SUVA, TC), and four PARAFAC components (C1, C2, C3, C4). Metrics that were significantly different between high and low human impact sites were used in a principal component analysis (PCA) of DOM. However, DOC and TDN were excluded from the PCA to emphasize DOM composition and not concentration. Prior to conducting the PCA all variables were Z-score standardized. The PCA was conducted with using the FactoMineR package (Lê et al. 2008), and visualized with the factoextra package (Kassambara 2015).

Pearson's correlations were conducted among water quality metrics, isotope values, fluorescence indices, and PARAFAC components for DOM grouped by watershed to identify variables that revealed the source or character of DOM among watersheds. Correlations were conducted with the GGally package using all DOM samples and grouped by watershed (Schloerke et al. 2014). Correlations were considered significant when correlation coefficients were greater than 0.35 (Rohlf and Sokal 1995)

Results

Watershed characteristics

The 4 watersheds differed substantially in area and less so in land cover. The Jordan River had the most human developed land cover and largest watershed area of all 4 watersheds equal to1191 km^2 upstream of the Mill Creek confluence, and 1683 km^2 at the most downstream site. The Provo and Logan Rivers were similar in area, 1900 km^2 and 1526 km^2 respectively, and Red Butte Creek was the smallest watershed (186 km^2; Table 2). The Jordan River watershed was the most human impacted watershed with the greatest percent urban development within a sub-watershed (mean 26%, sd 6%) and agriculture land cover (mean 7%, sd 3%) compared to other watersheds. The 3 other watersheds had similar levels of percent development (mean 3%) and agriculture (1%) and were dominated by forest (mean 73%) and scrub-grassland (mean 21%) land covers. Average DOC (4.0 mg/L sd 1.5), TDN (5.1 mg/L sd 3.2) and Chla (3.9 µg/L sd 3.7) concentrations were all highest among Jordan River sites and lowest among Logan River sites (DOC 0.7 mg/L sd 0.2), TDN (0.2 mg/L sd 0.1) and Chla (1.4 µg/L sd 1.1)

Deconstructing influence of land cover on watershed DOM composition

PARAFAC A 4 component PARAFAC model was resolved and validated with split-half analysis (Supplement 3). Components 1 and 2 (C1, C2) were humic-like, and components 3 and 4 (C3, C4) were protein-like (Table 3). Previous studies identified C1 and C2 as fulvic-acid derived (Walker et al. 2009, Yamashita et al. 2011), and C2 was also characterized as terrestrial with high molecular weight content (Amaral et al. 2016). Protein-like C3 was identified as tryptophan-like (Graeber et al. 2012) and protein-like

C4 was identified as both tyrosine and tryptophan- like (Walker et al. 2009, Murphy et al. 2011, Yamashita et al. 2013). In this study, percent C2 and C4 were correlated with percent forest land cover within a sub-watershed and percent C1 and C3 were correlated with developed land cover (Supplement 4).

DOM by watershed analysis To better understand variability in DOM composition among watersheds we assessed differences in water quality, fluorescence indices, and PARAFAC components grouped by watershed with multi-way ANOVAs and a PCA. DOC, TDN, and Chla were significantly higher for the Jordan River than all other watersheds (ANOVAs, Supplement 5). The FI, YFI, BIX, percent humic-like C1, and percent protein-like C3 were also higher for the Jordan River than all other watersheds. The Provo River had the highest HIX (range 5 to 10 and lowest percent protein (22 to 35%) compared to all other watersheds, and had high SUVA values (range 2.2 to 5.3) compared to all watersheds except for Red Butte Creek which had variable SUVA (range 0.3 to 5.4).

The first 3 components of the PCA explained 45%, 21% and 10% of variation among DOM samples (Fig. 2, Supplement 6). The FI, YFI, TC, BIX and percent protein-like C3 had significant positive correlations with PC1, and SUVA, HIX, DOC:TDN, and percent C2 were negatively correlated to PC1 (Table 4). The FI and percent humic-like C1, which were greatest at Jordan River sites, were positively correlated with PC2. Positive PC1 coordinate values separated Jordan River sites with more microbial-derived DOM (high FI, YFI, TC, and BIX) from negative PC1 coordinate values and Provo sites with more humic-like DOM (high SUVA and HIX). DOM at sites in the Logan and Red

Butte Creek watersheds were more humic-like than Jordan River DOM, but not as humic-like as Provo DOM as indicated by overlap of 95% confidence ellipses. Chla was only significantly correlated to PC3 (Supplement 6). Positive C3 coordinate values were correlated with Chla, and distinguished Utah Lake and upstream Jordan River sites from WWTP sites and lower reaches with negative PC3 coordinates. Significantly more microbial-derived and protein-like DOM at Jordan River sites compared to all others was attributed to the influence of Utah Lake and WWTP effluent.

Attribution of OM sources

DOM isotope mixing models DOM in the Jordan River was primarily WWTP-derived while DOM from all other watersheds was primarily terrestrially-derived (Fig. 3). WWTP-derived DOM ranged from 8 to 85% in the Jordan River and terrestrial contributions from tree leaves ranged from 3 to 68%. In other watersheds, contributions from tree leaves ranged from 53 to 93% in the Provo River and Red Butte Creek, with slightly lower tree leaf contribution estimated for the Logan River (95% HDI 26 to 79%). Maximum feasible autochthonous contributions were estimated for the Jordan River (95% HDI 1 to 46%, median 11%), but median feasible autochthonous contributions were highest for the Logan River (95% HDI 3 to 43%, median 18%). Estimated contributions of BOM as a source of DOM were similar to estimates of autochthonous sources across watersheds likely due to similar mean $\delta^{13}C$ and $\delta^{2}H$ values between these sources (Table 1).

DOM carbon gradient-based mixing models indicated most DOM was terrestrially derived, while DOM hydrogen gradient-based mixing models indicated

DOM was only terrestrial at some Provo and Red Butte sites and not terrestrial in other watersheds. DOM-$\delta^{13}C$ and DIC-$\delta^{13}C$ were in the same range as terrestrial $\delta^{13}C$ values and were not positively correlated in any watershed or among all watersheds (Fig. 4A, Supplement 7) indicating terrestrial sources of DOM. All DOM $\delta^{2}H$ values were more positive than terrestrial $\delta^{2}H$ values for the Jordan River, as were over half of Red Butte samples and all but one Logan DOM sample (Fig. 4B). A wide range in $\delta^{2}H$ values of water was due to differences in water-$\delta^{2}H$ values in each of the 4 watersheds (Supplement 8). Water $\delta^{2}H$ values in the Logan and Provo rivers averaged -128.4 ‰ and -122.9 ‰ (sd 3.4 and sd 4.4) which were lower than values in Red Butte Creek (mean -115.8 ‰, sd 10.3) and the Jordan River (mean –97.4 ‰, sd 21.9). DOM- $\delta^{2}H$ values were higher at WWTP sites than all other sites (Fig. 4B). Carbon isotope values between autochthonous and terrestrial sources were not different (means -25.5 versus -25.4), but hydrogen isotope values were different (mean -222.6 versus -176.5 $\delta^{2}H$), and therefore the hydrogen gradient based mixing models were considered more informative. Results from SIMMR and the hydrogen gradient-based mixing model indicated most sites had primarily terrestrially-derived DOM, except in the Jordan River primarily a WWTP-derived DOM.

Microbial versus autochthonous DOM sources We expected microbial derived DOM to be derived from autochthonous DOM, and therefore expected a positive relationship between Chla and microbial indices of DOM, Chla, and percent protein-like DOM, and a negative relationship between Chla and DOC:TDN. In contrast to this expectation, Chla and FI/YFI microbial indices were negatively correlated for the Jordan

River (r = -0.69, r = -0.62), and there were no strong relationships between Chla and FI/YFI in other watersheds (Fig. 5; Supplement 9). Also counter to our expectation, there was a positive relationship between Chla and DOC:TDN for the Jordan River, but DOC:TDN was extremely low for the Jordan River (mean 0.9, sd 0.6) compared to all other watersheds (mean 6.1, sd 4.9). Chla and percent protein-like DOM were positively correlated at WWTP sites (r = 0.52), but this relationship was driven by one very low Chla concentration (0.45 µg/L) at the WWTP site. We reasoned that autochthonous sources were present at WWTP sites, but a different microbial source also contributed to significant portion of DOM at WWTP sites.

FPOM isotope mixing models Similar to DOM results, FPOM was primarily from terrestrial sources in all watersheds except the Jordan River (Fig. 6). Estimated contribution of WWTP-FPOM for the Jordan River ranged from 47 to 77% and ranged from 1 to 34% for other watersheds. Compared to all other watersheds the Logan River had the greatest variability in estimated source contributions with autochthonous and BOM sources ranging from 2 to 69% and terrestrial contributions ranging from 5 to 85%. In contrast, autochthonous and BOM sources ranged from 1 to 30% for all other watersheds, and terrestrial sources ranged from 33 to 91% in the Provo and Red Butte Creek watersheds.

Graphical gradient-based isotope mixing models were consistent with SIMMR mixing model results and indicated FPOM was terrestrially derived across watersheds except for the Jordan River. FPOM $\delta^{13}C$ and $\delta^{13}C$-DIC isotope values were positively correlated for the Jordan River (r = 0.68), and $\delta^{13}C$ values were not in the terrestrial range

suggesting autochthonous sources of OM (Fig. 4A, Supplement 7). The Logan River also had positively correlated $\delta^{13}C$ and $\delta^{13}C$-DIC ($r = 0.53$), but, FPOM $\delta^{13}C$ values were clustered within the range of terrestrial $\delta^{13}C$ values, and therefore we assumed FPOM was primarily terrestrial. In contrast to the carbon graphical gradient-based model, the hydrogen gradient-based model suggested Jordan River FPOM were primarily terrestrial, and from a variety of sources in all other watersheds as indicated by a variable range of $\delta^{2}H$-FPOM values (-198 to -120 $\delta^{2}H$ ‰; Fig 4B).

Discussion

The greatest differences in OM composition among sites were not elucidated by differences in land cover. OM composition was significantly different in the Jordan River due to the influence of WWTP effluent and autochthonously derived OM from Utah Lake, and OM composition was more variable for the Logan River due to human activities at forested sites (e.g. cattle grazing and recreation).

Despite numerous studies, it remains difficult to detect differences in DOM composition in response to gradients of urban development, and across multiple land covers. Studies of DOM quality among multiple land covers (e.g. agriculture, wetland, forest) (Petrone et al. 2011, Parr et al. 2015, Williams et al. 2016), and watersheds that included WWTP effluent, or leaky sewage infrastructure, have found human impact increased DOM lability (Harbott and Grace 2005, Newcomer et al. 2012, Hosen et al. 2014). But, only one study has successfully distinguished the effect of agricultural versus urban land cover on DOM composition and results were dependent on landscape scale of analysis (Williams et al. 2016). Several studies that reported a WWTP influence did not

directly sample WWTP effluent OM (Stedmon et al. 2003, Sickman et al. 2007, Petrone et al. 2011, Hossler and Bauer 2012, Lambert et al. 2017) or did not consider wastewater effluent sources in the initial study design (Harbott and Grace 2005, Newcomer et al. 2012, Hosen et al. 2014). A few studies directly sampled DOM from WWTPs to compare to other land uses and found DOM was less aromatic, (Westerhoff and Anning 2000), and had lower C:N ratios (Gücker et al. 2011) than non-WWTP or agricultural DOM. Duan et al. (2014) compared wastewater OM stable isotopes to surrounding urban, non-urban, and storm water DOM, and found terrestrial derived OM was replaced by wastewater and autochthonous sources of DOM. We had similar results to Duan et al. (2014), but ours is the first study to report proportional contributions of autochthonous, terrestrial, and WWTP sources in watersheds with multiple land covers. Proportional estimates of OM sources can then inform OM reduction strategies to focus on WWTP effluent versus autochthonous sources, non-point sources from agriculture, or terrestrial sources within a watershed.

Identifying relative proportions of DOM sources can also help to characterize the quality of DOM, or bioavailability to microbes. The composition of DOM at sites influenced by WWTP effluent were likely of high quality for microbial assimilation and mineralization. DOM in the Jordan River was directly correlated with indices of microbial-derived DOM including FI, YFI, BIX, and had very low DOC:TDN values indicating it was more bioavailable than DOM of other watersheds. It is important to note that FI values are based on the assumption that OM concentration varies proportionally with fluorescence intensity, which is generally true except at high DOC concentrations (e.g. >5 mg/L , and FI values above 2 are rarely, if ever, reported for non-human

impacted water bodies. However, several studies have reported FI values greater than 2 from samples of algal leachate and WWTP effluent (Dong and Rosario-Ortiz 2012, Hansen et al. 2016, Ateia et al. 2017). Furthermore, Ateia et al. (2017) described DOM with FI values between 1.2 and 1.8 as a mixture of terrestrially- and microbial-derived DOM and values above 1.8 represented entirely microbial-derived DOM. We concluded DOM from the Jordan River was dominated by microbial-derived DOM, some from Utah Lake and some from wastewater effluent.

It was likely autochthonous sources of DOM from high primary production in Utah Lake contributed some degree to indicators of DOM bioavailability at Jordan River sites, but several lines of evidence suggest significant sources of microbial-derived DOM from WWTP effluent. First, Chla was not significantly correlated to Jordan River sites along the axis that explained the most variation of the DOM PCA, and Chla was negatively correlated to WWTP effluent sites along PC3. Second, the gradient-based mixing model did not indicate contributions from autochthonous sources, and δ^2H values of WWTP DOM were much higher than both terrestrial and autochthonous δ^2H values. Third, Chla was negatively correlated with FI, and YFI, and positively correlated with the DOC:TDN ratio, which was lower for the Jordan River compared to other watersheds (e.g. <2.5). Although percent protein was significantly correlated to Chla at for the Jordan River, percent protein never exceeded 35% in that watershed. Thus, we characterized DOM at WWTP sites as a more consistently produced, protein-like, homogenous source of microbial DOM compared to other watersheds that had a wider range of DOM composition. Previous studies in watersheds with mixed land cover identified wastewater effluent as a likely source of DOM, or estimated 25% of DOM was petroleum-based,

through sources such as WWTP effluent (Griffith et al. 2009, McElmurry et al. 2013). We posit DOM at WWTP sites was derived from a consistent, homogenous, microbial derived source, such as lysed microbes or microbial exudates from a "microbe factory" like a WWTP.

The primary indications that WWTP DOM was a homogeneous, protein-like source was percent protein was never above 35%; and SUVA and DOC:TDN values were less variable than for other watersheds. DOM from other watersheds was characterized as more variable because percent protein values ranged from 21 to 54%, and DOC:TDN and SUVA values were also more variable than at Jordan River sites. Surprisingly, the site with lowest percent protein was one of the WWTP-DOM samples, and the 3 highest percent protein values were on the Logan River from forested sites (54 and 46 % percent protein), and an urban site (52% percent protein). A possible source of labile DOM at forested sites on the Logan River is cattle grazing. Forested sites in the along the Logan River were historically grazed by cattle from 1935 to 2005, and currently have cattle trailed up tributaries of the river each fall (Hough-Snee et al. 2013). In addition, the National Forest in the southern portion of the Logan River watershed includes a network of trails and two-track dirt roads used for recreation throughout the year. Sediment from dirt roads or exhaust from vehicles could contribute inorganic nutrients to upper sites of the Logan River, stimulating microbial activity, resulting in possible increases in the proportion of protein-like DOM.

Similar to DOM, FPOM at all sites was primarily terrestrially-derived, except for the Jordan River, which was dominated by contributions from WWTP effluent derived FPOM. WWTP effluent has enriched nitrate- $\delta^{15}N$ values due the $\delta^{15}N$ signature of

human waste, and wastewater treatment processes that induce isotopic fractionation such as ammonia volatilization and denitrification (Ulseth and Hershey 2005, Finlay and Kendall 2007, Gücker et al. 2011). FPOM is a mixture of detritus and microorganisms (DeBruyn and Rasmussen 2002, Gücker et al. 2011) and therefore, 2 possible pathways for enriched $\delta^{15}N$ FPOM values below WWTP sites were FPOM discharged in effluent, or microbial assimilation of enriched nitrate-$\delta^{15}N$.

FPOM at WWTP influenced sites also had contributions from autochthonous and BOM sources (ranging from 2-27%) which was consistent with previous studies that found FPOM in urban streams was a mixture of autochthonous, terrestrial, and BOM sources (Newcomer et al. 2012, Imberger et al. 2014), and had significant WWTP contributions at WWTP influenced sites (Duan et al. 2014). A positive relationship between FPOM-$\delta^{13}C$ and DIC-$\delta^{13}C$ for the Jordan River indicated autochthonous sources of FPOM, but there was no linear relationship between FPOM-$\delta^{2}H$ and water-$\delta^{2}H$. This was due to a wider range of water-$\delta^{2}H$ than expected for the Jordan River (range -120 to -40 $\delta^{2}H$ ‰), compared to other watersheds (range -130 to -100 $\delta^{2}H$), and compared to values of precipitation across Utah (range -127 to -92 $\delta^{2}H$‰, Bowen et al. 2007). More positive and variable $\delta^{2}H$ values for the Jordan Rivers may be attributed to the enriched $\delta^{2}H$ values of humans (Ehleringer et al. 2008), and a wide range of OM sources processed within WWTPs. We concluded there were small contributions of autochthonous, terrestrial and BOM derived sources for the Jordan River, but WWTP-FPOM was the dominant source. In contrast, FPOM in the Provo and Red Butte Creek watersheds was dominated by terrestrial sources, and a mixture of sources for the Logan watershed. Greater variability in FPOM source estimates for the Logan River could have

been due to cattle grazing activity or recreation in forested reaches of the watershed. We did not have a metric to assess FPOM lability (e.g. C:N or BOD), but similar studies found that WWTP FPOM was preferred by microbes compared to autochthonous and terrestrial sources (DeBruyn and Rasmussen 2002), and considering the very high FI and YFI values combined with very low DOC:TDN values we concluded WWTP-FPOM was likely more labile than other FPOM sources.

We did not identify a human land cover metric that could adequately predict OM composition or bioavailability. Typical land cover metrics that predict DOM quality include wetland land cover (Wilson and Xenopoulos 2008, Williams et al. 2010, Petrone et al. 2011, Williams et al. 2016) and impervious surface area (Harbott and Grace 2005, Hosen et al. 2014, Parr et al. 2015). Impervious surface area within a sub-watershed might have better distinguished low and high human impact sites in this study. However, the influence of impervious surface area can vary greatly depending on the degree of hydrologic connection above and below ground, and within urban infrastructure (Baruch et al. 2018), and therefore, measures of impervious surface may also be meaningless unless detailed water infrastructure information is available. More importantly, land cover in this study did not account for stark differences in DOM quality due to the influence of WWTPs, and human activity in forested reaches of the Logan River. We recommend all OM studies in watersheds with WWTP effluent obtain a representative WWTP sample, and incorporate wastewater OM into study designs that compare land cover across watersheds.

We also did not consider how storms or seasonal changes in hydrology could influence DOM source and bioavailability. The effect of storms in urban watersheds may

supersede the influence of urban land cover as storms may replace autochthonous derived OM with terrestrial OM (Imberger et al. 2013, Smith and Kaushal 2015). In general, lower flows in summer result in more autochthonous OM compared to terrestrial OM in other seasons (Kendall et al. 2001, Hudson et al. 2007). Autochthonous sources during low flow in summer transition to terrestrial sources in autumn due to allochthonous inputs in temperate ecosystems (Kendall et al. 2001). In contrast, terrestrial sources are greater in spring during runoff in snowmelt driven ecosystems with little deciduous riparian cover (Hornberger et al. 1994, Hood et al. 2005). In addition, the influence of WWTP effluent can increase during low flows in summer due to decreased dilution from other sources (e.g. tributaries and groundwater), and results in greater autochthonous OM production (Wassenaar et al. 2010, Edmonds and Grimm 2011, Duan et al. 2014 While there has been extensive research on the effect of hydrology to OM sources and composition, studies of OM at large spatial scales that include multiple land cover and aquatic ecosystem types (e.g. Spencer et al. 2012, Williams et al. 2016), will help elucidate anthropogenic controls on OM composition.

DOM composition of freshwaters in wet, temperate ecoregions, such as the Eastern United States, is controlled by different parameters than in the arid west, such as the influence of reservoirs and large dams, legacy land cover, and differences in urban growth patterns (Grimm et al. 2000). In this study, percent and total area of wetland land cover was near zero, and therefore had little influence on DOM composition. Wetland land cover is less extensive in the west (4% of sites sampled by EPA in 2011) compared to eastern ecoregions (EPA 2016). This could be due to the arid climate, sparse assessment of western wetlands, or incomparable wetland typology between western and

eastern ecoregions. Regardless of the reason for low wetland cover in west, wetlands appear to play a smaller role in DOM composition in the arid west compared to regions such as the Great Lakes (Wilson and Xenopoulos 2008, Williams et al. 2016), the boreal forest (Kothawala et al. 2014), eastern U.S (Newcomer et al. 2012, Parr et al. 2015), and coastal ecosystems (Sickman et al. 2007, Yamashita et al. 2008, Fellman et al. 2011).

It is important to identify and quantify the sources and lability of OM in rivers to better understand controls on OM supply and demand within and among watersheds. OM is a common currency of energy across watersheds that influences biological processes such as nutrient retention and primary production (Smith and Kaushal et al. 2015), as well as abiotic processes such as metal sorption and sediment transport (Casas-Ruiz et al. 2017). Knowing OM source can inform management decisions to reduce supply of OM through point and non-point sources, or increase retention and removal or OM by altering flow regimes or stream geomorphology. Constituent removal, a common goal of watershed management is tightly linked with OM supply and demand (Wollheim et al. 2018) which also depends on OM quality. For example, the ratio of dissolved iron and copper to DOM increases with increased aromatic DOM content (Kikuchi et al. 2017). Therefore, management practices aimed at reducing labile OM inputs (e.g. WWTP effluent or autochthonous sources) would not sufficiently address iron and copper constituent transport and accumulation. Similarly, if in-stream nutrient reduction is the primary management goal, targeted reduction of labile OM might be effective, but identification of the primary labile OM source, e.g. point sources or urban/agricultural runoff would be crucial. Thus for constituents of concern, whether it be transport to

downstream waters or accumulation within the watersheds, management of constituent fluxes can be improved through knowledge of OM source, composition and quality.

Conclusions

Traditional land use metrics, such as percent developed land cover within a watershed, did not account for the greatest differences in FPOM and DOM composition. Sites influenced by WWTP effluent had OM with significant WWTP-OM contributions, and WWTP-DOM was a consistent source of microbial derived, protein-like DOM. Likewise, greater variability in OM composition in forested sub-watersheds of the Logan River associated with cattle grazing or recreational activity were also not accounted for by land cover. This study also highlights that arid regions have different drivers of DOM composition compared to wetter ecoregions, and further study is needed to link, hydrology, land cover and OM source and composition.

As human dominated landscapes increase it will become more important to understand the sources and quality of OM in rivers. Depending on source and composition OM can degrade or improve river ecosystem functions such as constituent removal and retention. With increased human development, impervious surfaces, dams, and diversions, sources of OM to rivers will increase and become more variable (Kaushal and Belt 2012). Therefore, scientists and watershed managers need access to information that describes OM composition in rivers with varying land cover to predict how OM composition will influence ecosystem functions such primary production, decomposition, pollutant transport, and nutrient retention and transformation. In addition to management implications, understanding OM source and composition will also provide baseline

estimates of organic carbon flux from terrestrial to aquatic ecosystems and inform ecosystem models of carbon cycling.

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Yamashita, Y., J. N. Boyer, and R. Jaffé. 2013. Evaluating the distribution of terrestrial dissolved organic matter in a complex coastal ecosystem using fluorescence spectroscopy. Continental shelf research 66:136-144.

Tables

Table 1. Carbon, nitrogen and hydrogen isotopes values of sources used in the SIMMR isotope mixing model. Tree leaves were the average of both sceneced and living tree leaves collected in site riparian zone. Macrophytes were defined as rooted, submerged aquatic vegetation, biofilms were scaped from benthic rocks, and algae was collected from floating matts.

Sources	n	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰	$\delta^{2}H$ ‰
Avg. Autochthonous		-25.5 ± 6.2	8.7 ± 4.9	-222.6 ± 35.9
Macrophytes	24	-26.5 ± 4.6	10.4 ± 5.4	-198.0 ± 21.1
Biofilm	30	-22.4 ± 5.6	9.3 ± 3.8	-244.2 ± 29.4
Algae	10	-29.6 ± 7.1	6.3 ± 5.4	-255.6 ± 32.6
Avg. Terrestrial		-25.4 ± 6.1	5.2 ± 3.0	-176.5 ± 29.8
Soil	4	-27.8 ± 0.6	3.9 ± 2.4	-168.2 ± 14.4
Tree leaves	25	-28.5 ± 1.4	6.9 ± 3.7	-165.1 ± 14.0
BOM	21	-22.9 ± 4.8	5.1 ± 2.1	-202.3 ± 24.0
WWTP-FPOM	5	-23.9 ± 0.5	11.9 ± 1.2	-140.4 ± 16.2
WWTP-DOM	5	-23.5 ± 3.5	38.4 ± 11.9[b]	-121.5 ± 15.2
FPOM	75	-26.2 ± 3.3	5.6 ± 2.1	-168.9 ± 16.9
DOM	50[a]	-27.2 ± 1.9	11.9 ± 20.4[b]	-140.2 ± 32.6

[a] There were less DOM than FPOM samples because only samples that were successfully analyzed for all 3 isotopes were included in mixing models (see methods).
[b] $\delta^{15}N$-DOM and $\delta^{15}N$-WWTP-FPOM includes a correction for $\delta^{15}N$-nitrate that was included in the DOM sample.

Table 2. Watershed characteristics, water quality, and DOM optical metrics averaged among sub-watersheds within each watershed. Percent agriculture was the sum of crop and pasture land cover within each sub-watershed. Percent protein was the sum of protein-like PARAFAC components C3 and C4 (see table 3).

	Jordan	Logan	Provo	Red Butte
Mean % development	20.6 (7.0)	0.5 (0.4)	0.6 (0.3)	3.6 (6.5)
Mean % Agriculture	7.6 (4.3)	0.7 (0.8)	3.6 (2.0)	0.1 (0.1)
Mean % Forest	34.0 (19.6)	68.7 (4.2)	71.0 (5.9)	79.0 (10.6)
Mean % Scrub	21.3 (10.1)	28.4 (3.1)	18.9 (5.7)	16.5 (3.4)
Mean % Wetland	1.1 (0.8)	0.2 (0.1)	0.4 (0.3)	0.1 (0.1)
Mean sub-watershed area (km)	1175 (307)	725 (501)	893 (655)	40 (60)
DOC (mg/L)	4.0 (1.5)	0.7 (0.2)	2.4 (1.2)	1.6 (1.2)
TDN (mg/L)	5.1 (3.2)	0.2 (0.1)	0.5 (0.3)	0.4 (0.6)
Chlorophyll *a* (µg/L)	3.9 (3.7)	1.4 (1.1)	1.7 (1.7)	1.2 (1.8)
BIX	0.8 (<0.01)	0.8 (<0.01)	0.7 (0.1)	0.8 (0.0)
FI	1.9 (0.2)	1.7 (<0.01)	1.6 (0.1)	1.7 (0.1)
YFI	0.9 (0.1)	0.7 (0.1)	0.6 (0.1)	0.7 (0.1)
TC	0.7 (0.1)	0.7 (0.2)	0.5 (0.1)	0.7 (0.2)
SUVA	2.0 (0.3)	2.3 (1.1)	3.2 (1.0)	2.6 (1.5)
HIX	4.3 (0.9)	4.9 (1.5)	7.4 (1.5)	5.7 (1.9)
Percent.protein	32.3 (3.8)	34.5 (6.3)	27.1 (3.8)	31.2 (6.0)

Table 3. PARAFAC components and descriptions from references matched in the OpenFluor database and descriptions for this study.

Component	Excitation/ Emission (nm.)	Reference	Description- Reference	Description - This study
C1	320/415	Yamashita et al. 2011 Walker et al. 2009 Amaral et al. 2016	Humic, fulvic-acid-type Humic Humic, fulvic-acid-type	Humic-like:
C2	368/490	Amaral et al. 2016 Walker et al. 2009	Humic, terrestrial, aromatic Humic-like	Humic-like,
C3	290/355	Graeber 2012 Bittar et al. 2016	Tryptophan-like Protein-like	Protein-like
C4	275/315	Yamashita et al. 2011 Walker et al. 2009 Yamashita et al. 2013 Murphy et al. 2011	B peak; Tyrosine-like Tryptophan-Tyrosine mixture Tyrosine-like Tryptophan-like	Protein-like

Table 4. PCA correlation coefficients (r) for DOM water quality metrics, PARAFAC components, and optical indices. Variables are listed in order of correlation to PC1 and were considered significantly correlated to an axis (bold) with correlation coefficients >0.35 (Rohlf and Sokal 1995).

Variable	PC1 45% r	PC2 21% r	PC3 10% r
percentC2	**-0.90**	-0.33	0.13
HIX	**-0.89**	0.22	0.14
DOC:TDN	**-0.48**	0.08	0.22
SUVA	**-0.47**	-0.09	-0.04
percentC1	-0.08	**0.96**	-0.13
Chla	0.20	0.02	**0.76**
percentC4	0.31	**-0.87**	-0.24
FI	**0.64**	**0.47**	-0.41
TC	**0.72**	**-0.55**	0.09
percentC3	**0.76**	0.29	**0.42**
BIX	**0.87**	0.06	0.20
YFI	**0.96**	0.05	-0.06

Figures

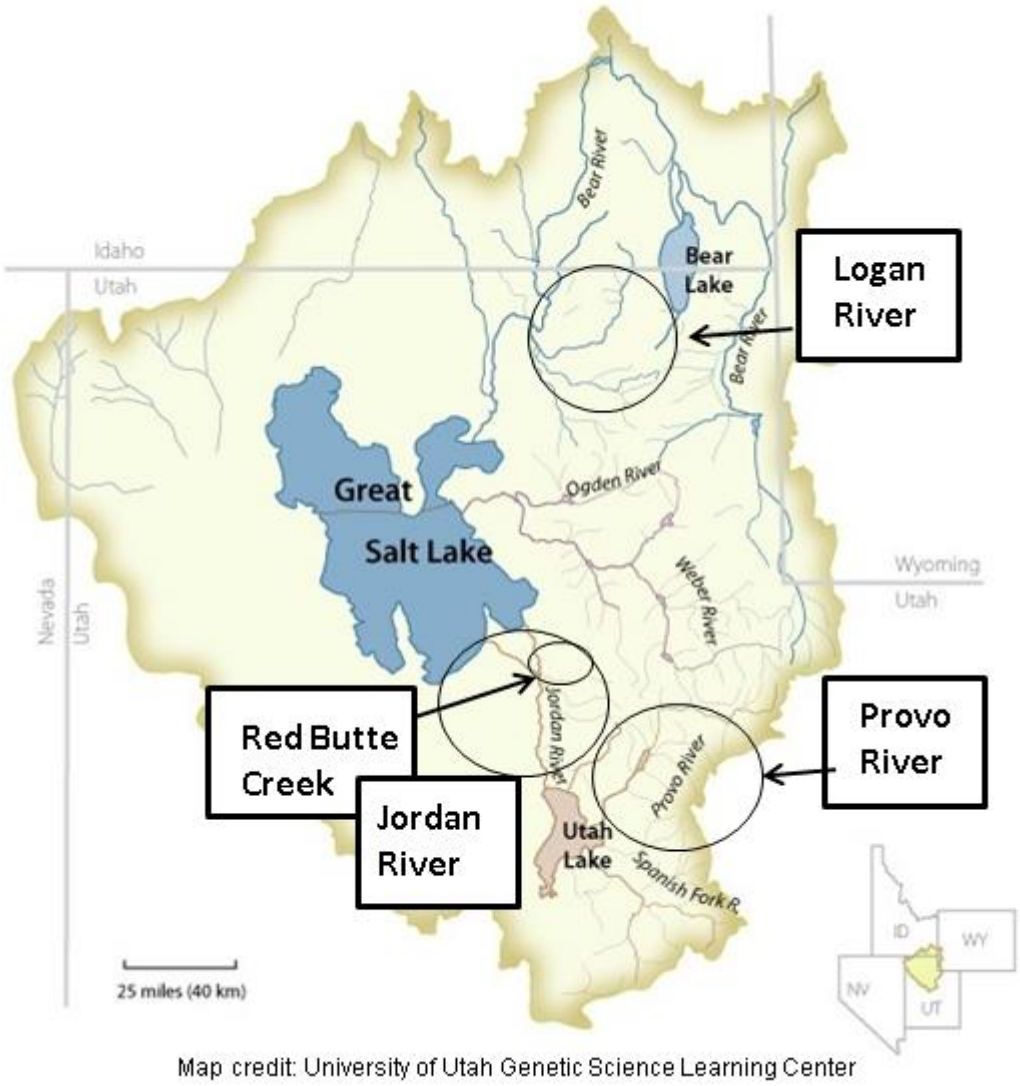


Figure 1. Eight to 9 sites were sampled in each of 4 watersheds, the Logan River (watershed area 1756 km^2), Provo River (1810 km^2), and Red Butte Creek (189 km^2), a tributary of the Jordan River (2067 km^2). Sites were sampled in each watershed in September and November of 2014 and November of 2015.

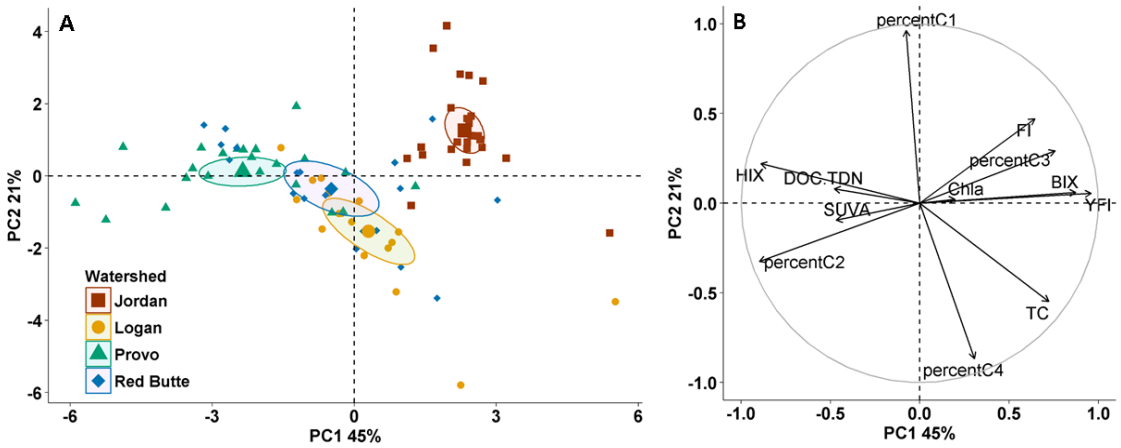


Figure 2. Principle components 1(PC1) and 2 (PC2) of a PCA with 82 DOM samples from 34 sites (A). The larger symbol at the center of the 95% confidence ellipses represents the mean of PC1 and PC2 values within a watershed. If 95% confidence ellipses do not overlap DOM composition between watersheds was different. Covariates inlcuded 2 humic-like flourescent components (percent C1 and C2), 2 protein-like components (percet to C3 and C4), Chla concetrations, the ratio of DOC and TDN concentrations (DOC:TDN), and flourescence indices of microbial derived DOM (FI, BIX), protein-like peak T to :humic-like peak C ratio (TC), and humic DOM (SUVA, HIX).

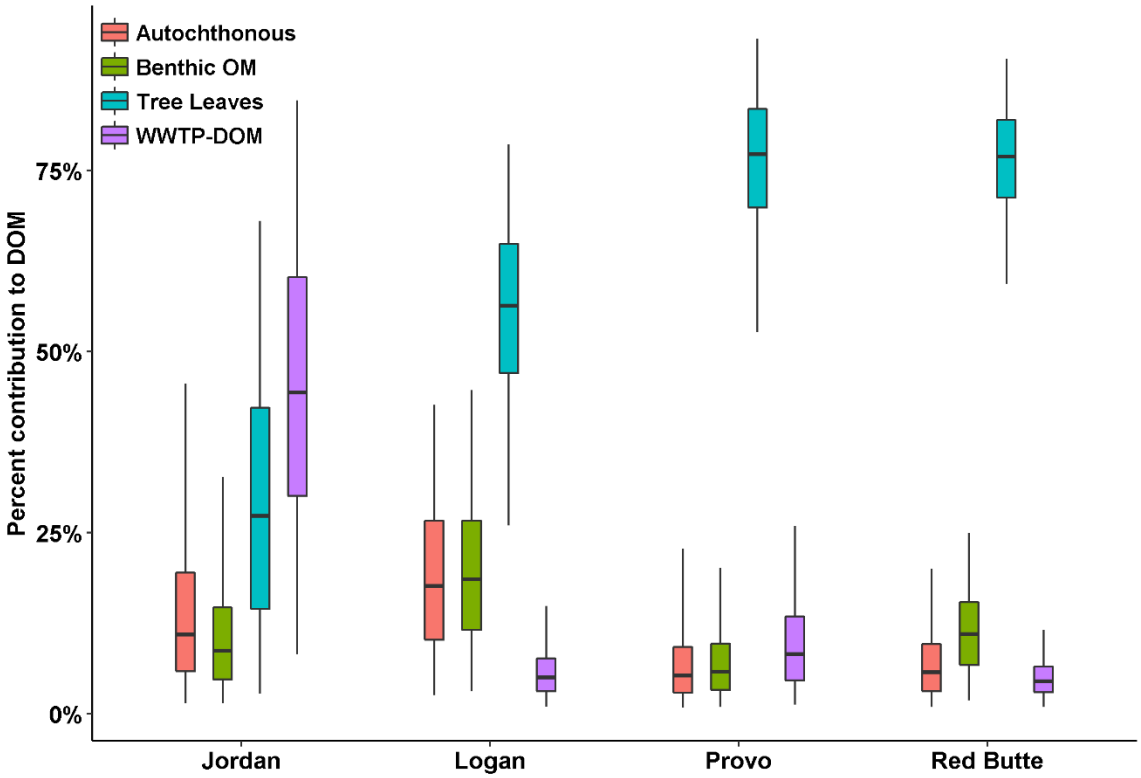


Figure 3. Percent feasible contributions of 4 sources to 50 DOM samples collected in all watersheds. Contributions were estimated with 3 isotope tracers, $\delta^{13}C$, $\delta^{15}N$, and $\delta^{2}H$. The autochthonous endmember was the average of algae, biofilm and macrophyte isotope values (Table 1). Boxes represent 75% high density interval (HDI), the 75% most credible values, and whiskers represent the 95% HDI.

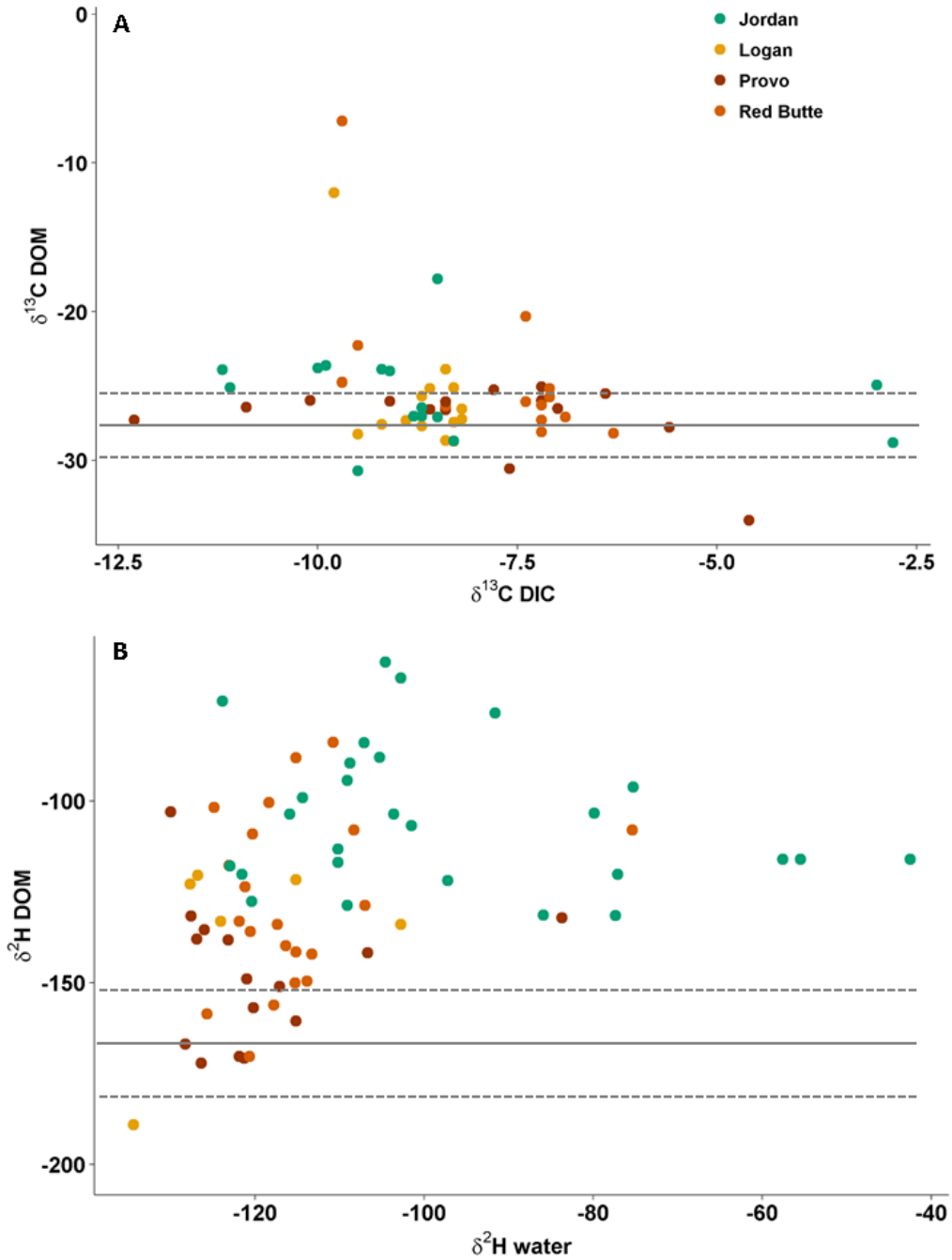


Figure 4. DOM-$\delta^{13}C$ values compared to DIC-$\delta^{13}C$ of river water (A), and DOM-$\delta^{2}H$ values compared to $\delta^{2}H$ value of river water (B). The solid and dashed lines represent the average and standard deviation of $\delta^{2}H$ and $\delta^{13}C$ values of tree leaves (Table 1). If DOM was dominated by autochthonous sources, DOM-$\delta^{13}C$ and DOM-$\delta^{2}H$ would vary linearly with aqueous $\delta^{13}C$ and $\delta^{2}H$.

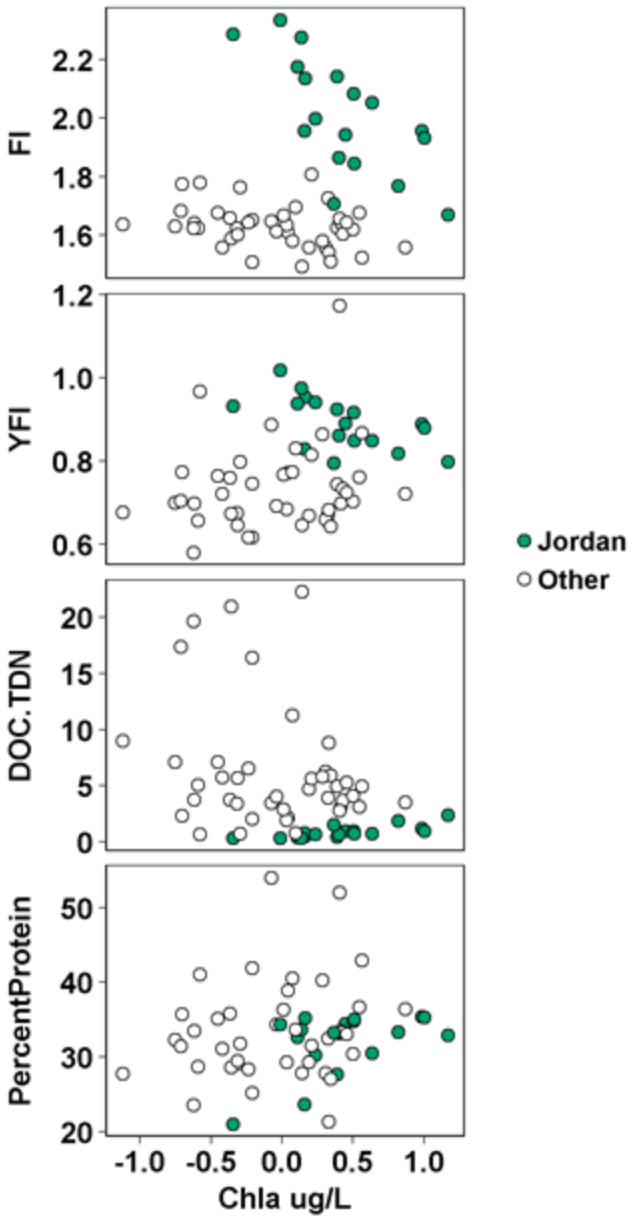


Figure 5. Correlations between chlorophyll *a* (µg/L) and fluorescence indices of microbially- derived DOM (FI, YFI), dissolved organic carbon to total dissolved nitrogen ratio (DOC:TDN), and percent protein-like DOM. Chla concentrations were log transformed. Percent protein was the sum of percent C3 and C4 PARAFAC components (Table 3). For pearson's correlation significance results see Supplement 9.

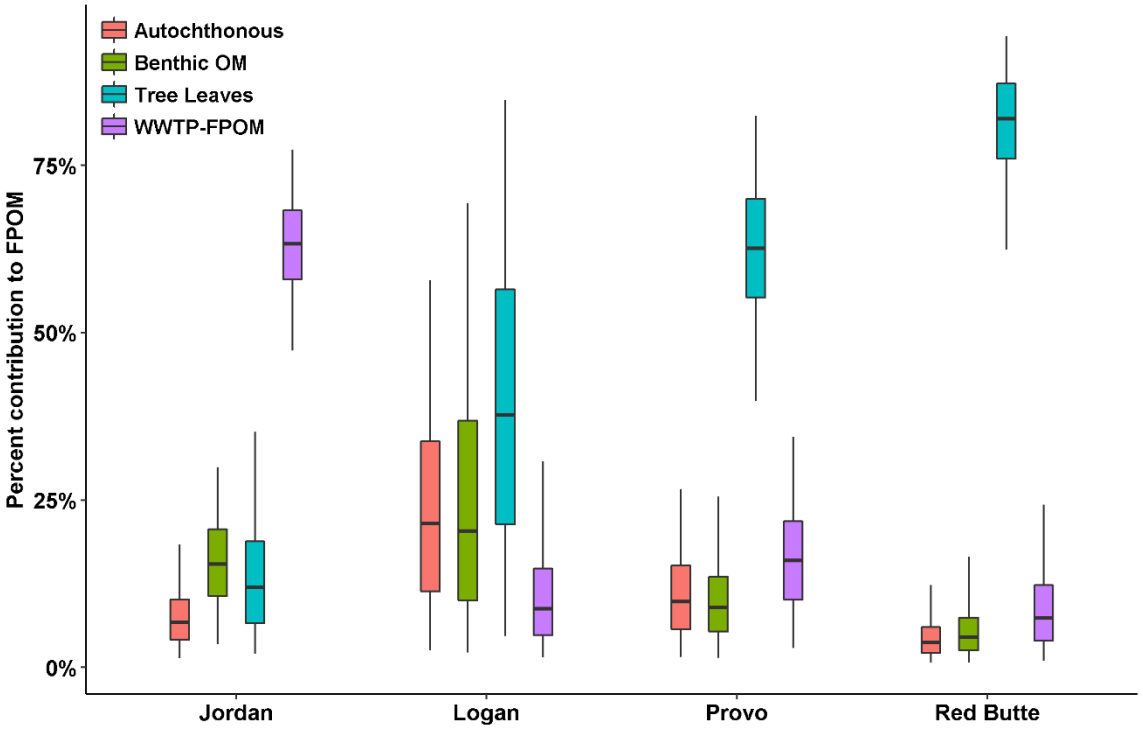


Figure 6. Percent feasible contributions of 4 sources to 75 FPOM samples collected in all watersheds. Contributions were estimated with 3 isotope tracers, $\delta^{13}C$, $\delta^{15}N$, and $\delta^{2}H$. The autochthonous endmember was the average of algae, biofilm and macrophyte isotope values (Table 1). Boxes represent 75% high density interval (HDI), the 75% most credible values, and whiskers represent the 95% HDI.

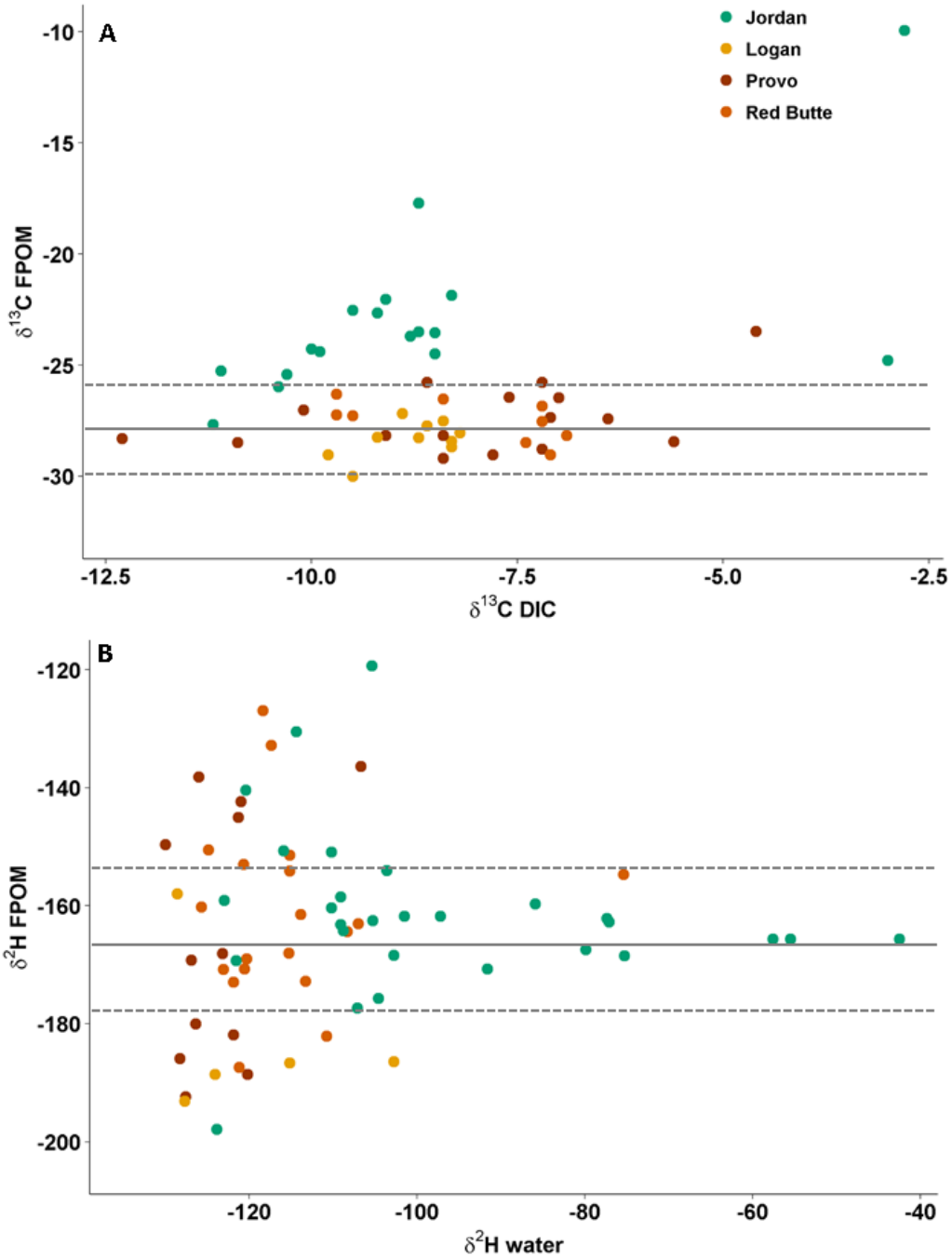
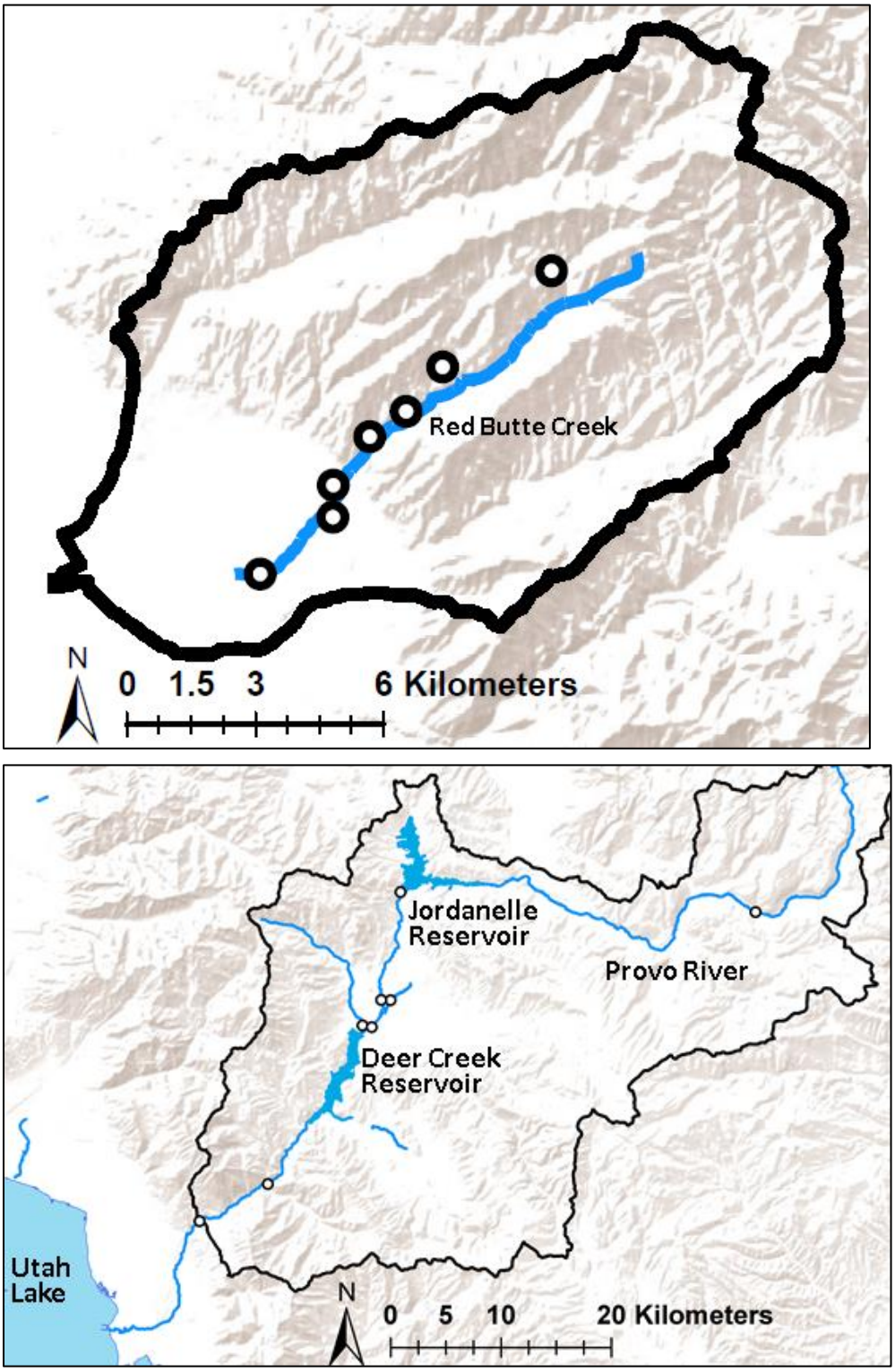


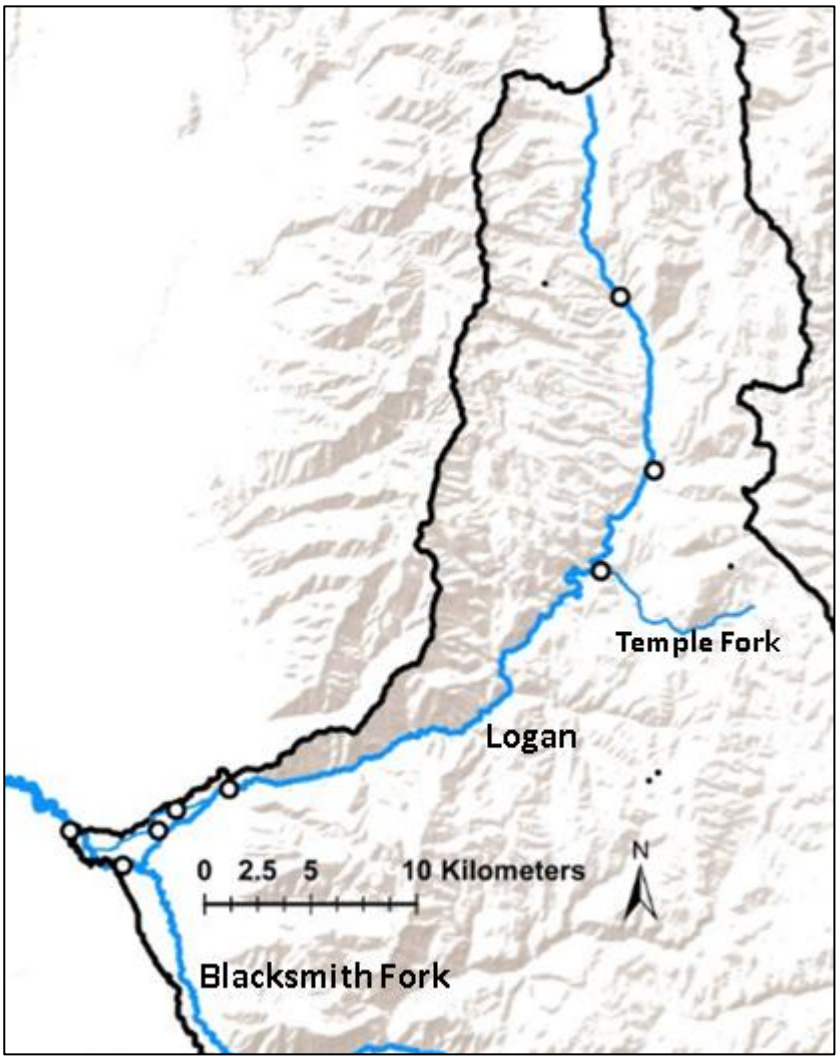
Figure 7. FPOM-$\delta^{13}C$ values compared to DIC-$\delta^{13}C$ of river water (A), and FPOM -$\delta^{2}H$ values compared to $\delta^{2}H$ of river water (B). The solid and dashed lines represent the average and standard deviation of $\delta^{2}H$ and $\delta^{13}C$ values of tree leaves; Table 1). If FPOM was dominated by autochthonous sources, FPOM-$\delta^{13}C$ and FPOM-$\delta^{2}H$ would vary linearly with aqueous $\delta^{13}C$ and $\delta^{2}H$.

Supplement

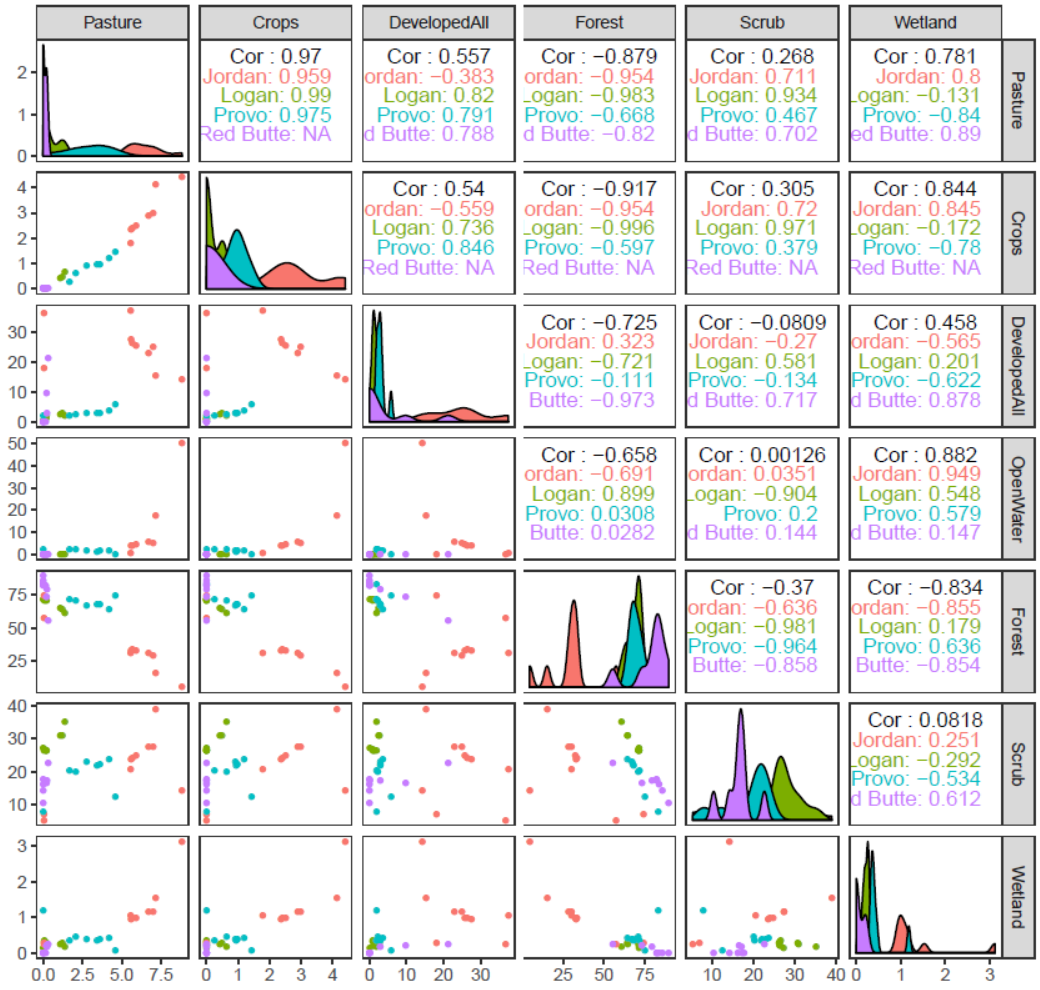
Supplement 1A. Maps of study sites for Red Butte Creek (n=8, 2nd highest site not shown) and the Provo River (n=8).



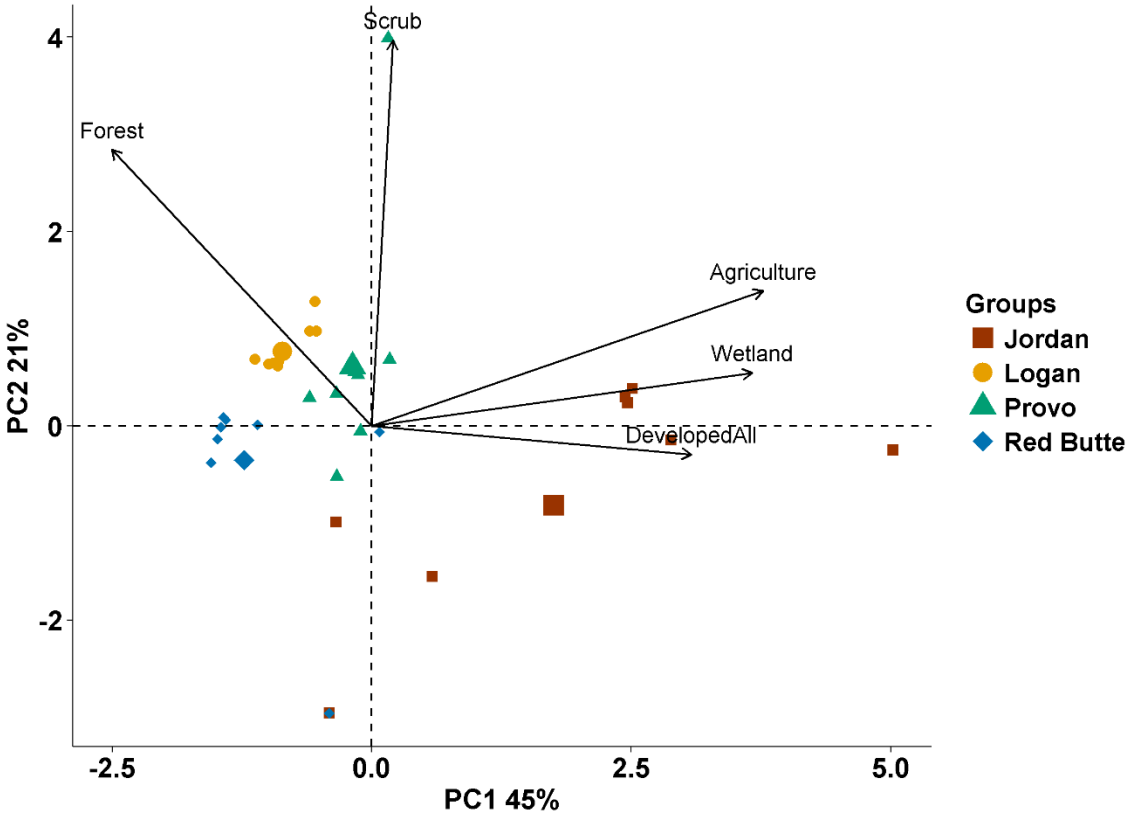
Supplement 1B. Study sites on the Logan River (n=8) and Blacksmith Fork (n=1).



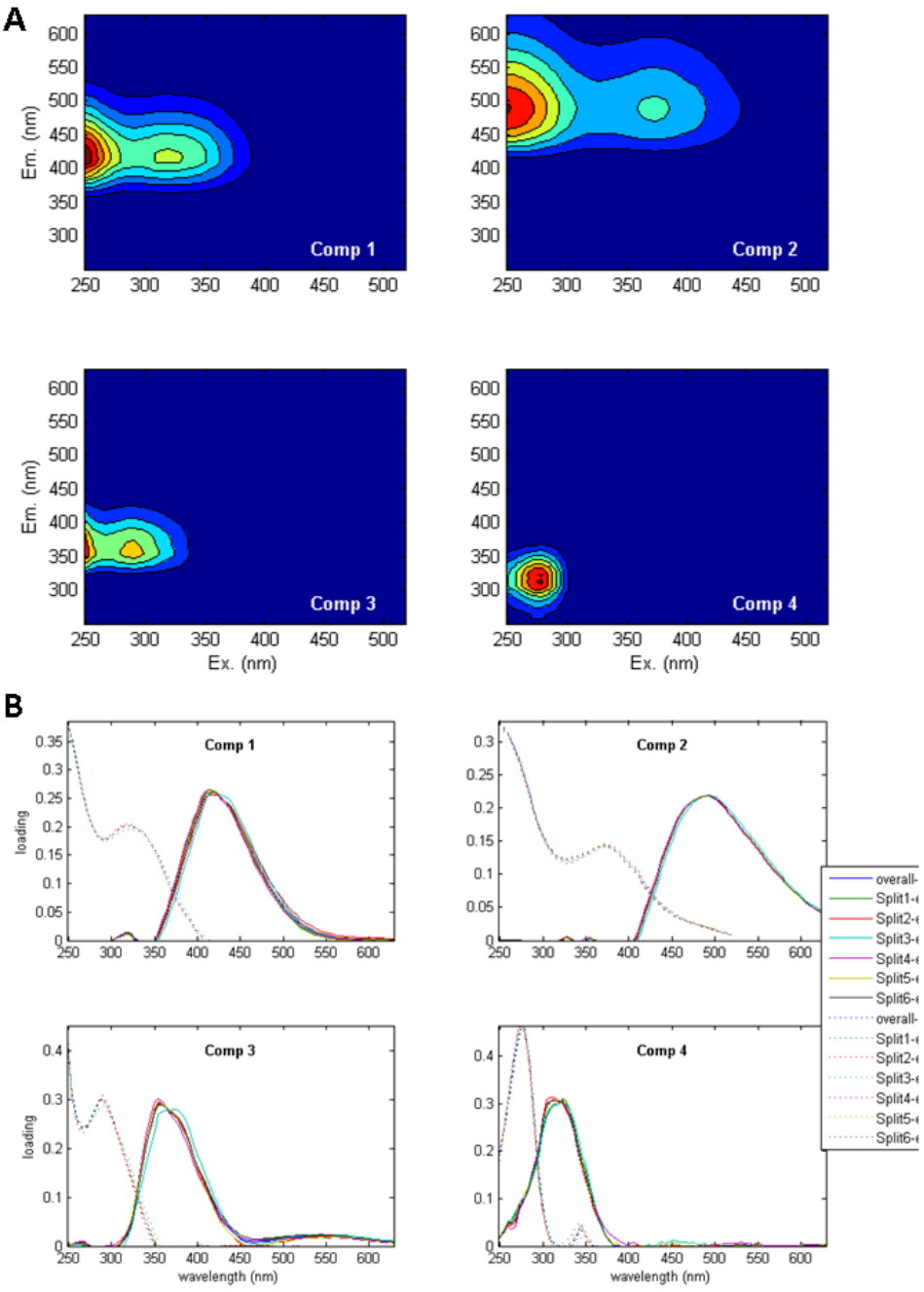
Supplement 2A. Six land covers were expected to influence OM composition including wetland, forest, cultivated cropland (crops), pasture, scrub-grassland and development. These land covers were derived by summing land covers that were ecologically similar and positively correlated with each other including developed (open+ low+ medium+ high), forest (deciduous + evergreen + mixed), wetland (woody + emergent), scrub-grassland (Shrub/Scrub + Grassland).



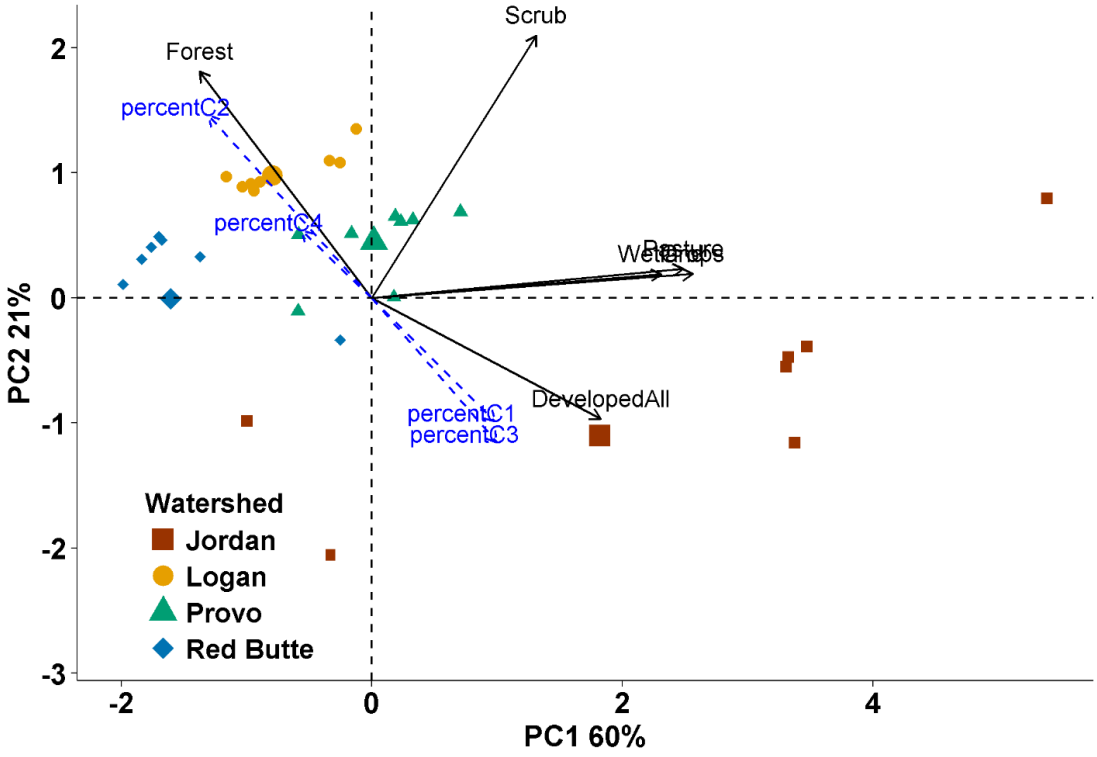
Supplement 2B. PCA of land cover by site grouped by watershed.



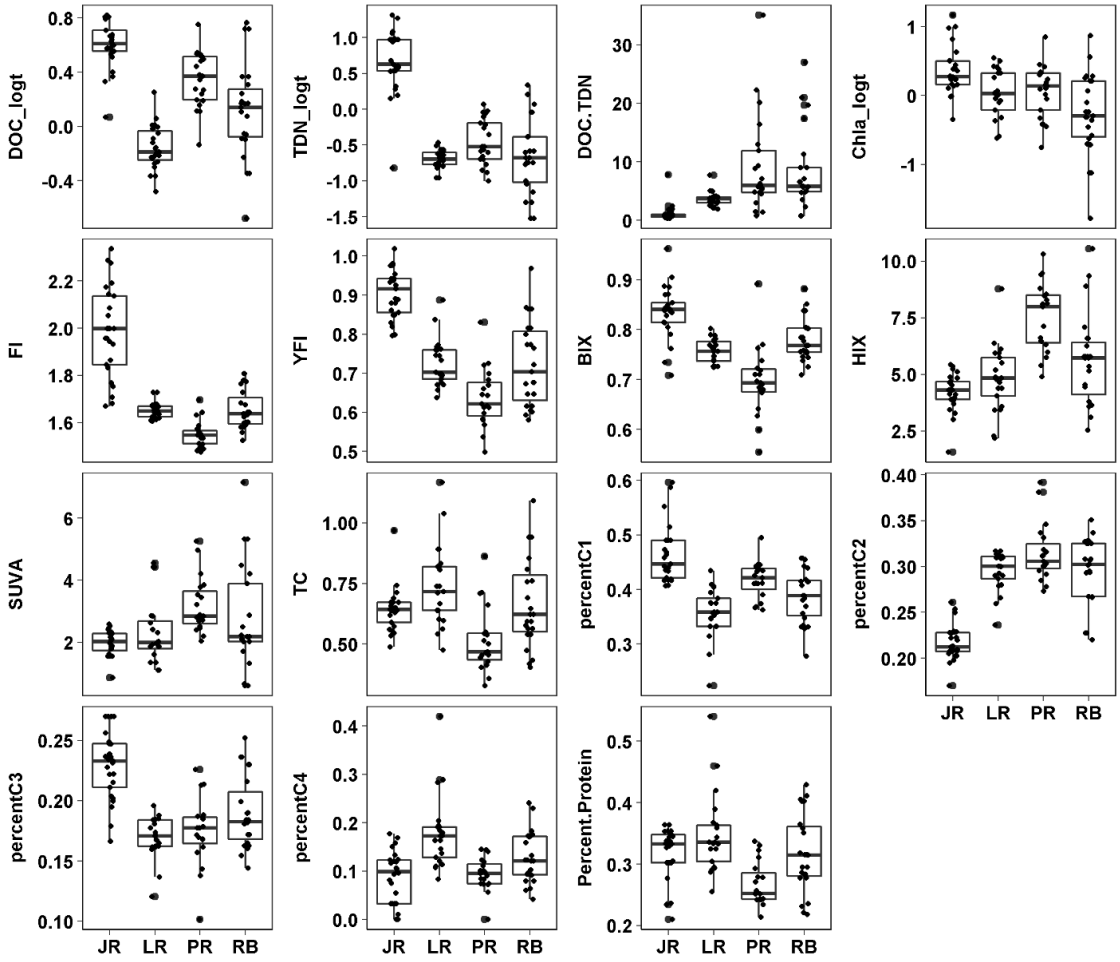
Supplement 3. Contour maps of excitation and emission intensities of the 4 components resolved by a PRAFAC model with 213 EEMs. Intensities are in Raman units. Components 1 and 2 (C1, C2) were humic-like and components 3 and 4 (C3,C4) were protein-like. (B) Split half validation of excitation (dotted lines) and emission (solid lines) loadings. Validation indicates samples were split into 6 halves and recombined into 3 models and all components in the split models found a match with Tucker correlation coefficient > .95 (Murphy et al. 2013).



Supplement 4. PCA of land cover and sites grouped by watershed and percent PARAFAC components projected onto the PCA. C1 and C2 were humic-like components and C3 and C4 were protein-like components (See table 3).



Supplement 5.1. Multi-way ANOVAs of water quality metrics, fluorescence indices and PARAFAC components among watersheds. Tukey HSD significant differences are in the multiple comparisons table below.

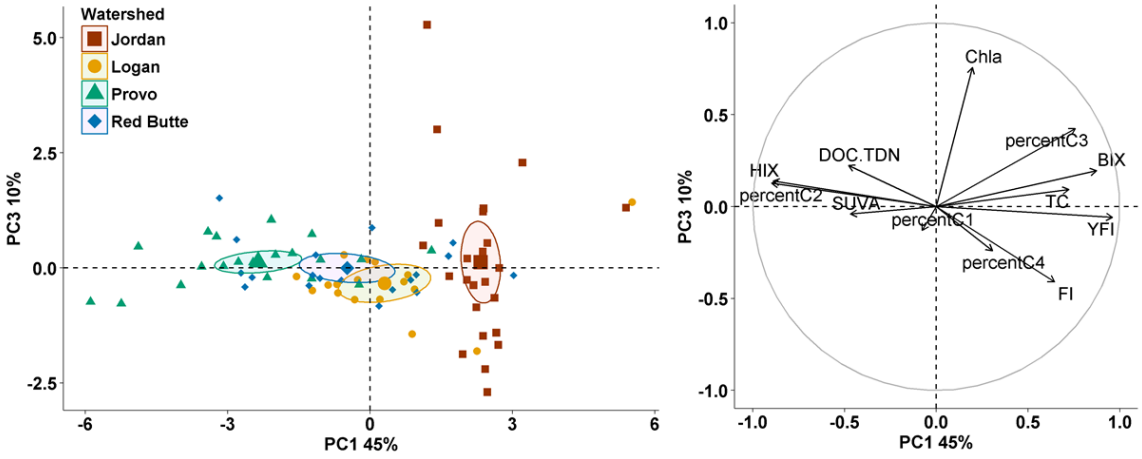


Supplement 5.2. Table of Tukey HSD multiple comparisons for ANOVAs of water quality and DOM fluorescence metrics. DOC and TDN units were mg/L and Chla units were µg/L.

Watershed Comparison	DOC	TDN	DOC:TDN	Chla	FI	YFI	BIX	HIX	SUVA	TC
JR v LR	0	0	0.4	0.03	0	0	0	0.45	0.68	0.11
JR v PR	0	0	0	0.05	0	0	0	0	0	0.03
JR v RB	0	0	0	0	0	0	0	0.01	0.08	0.91
LR v PR	0	0.19	0	1	0.05	0	0	0	0.08	0
LR v RB	0	0.99	0.02	0.11	1	1	0.3	0.28	0.61	0.39
RB v PR	0.01	0.31	0.94	0.06	0.03	0	0	0	0.59	0.01

Watershed Comparison	% C1	% C2	% C3	% C4	% Protein
JR v LR	0	0	0	0	0.36
JR v PR	0.01	0	0	1	0.01
JR v RB	0	0	0	0.12	0.99
LR v PR	0	0.12	0.95	0	0
LR v RB	0.14	1	0.07	0.02	0.22
RB v PR	0.19	0.12	0	0.23	0.02

Supplement 6. PCA graphs of DOM grouped by watershed and table of covariate correlations to PC1, PC2, and PC3. Principle components 1(PC1) and 2 (PC2) explained 66% of variation total variation in DOM composition (Figure 2), and PC3 explained 10%. Larger points in 95% confidence ellipses represent the mean of PC1 and PC3 values for sites in a watershed. The table was sorted by correlation to PC1 and values in bold are signifianct correlations (r > 0.35; Rohlf and Sokal 1995).

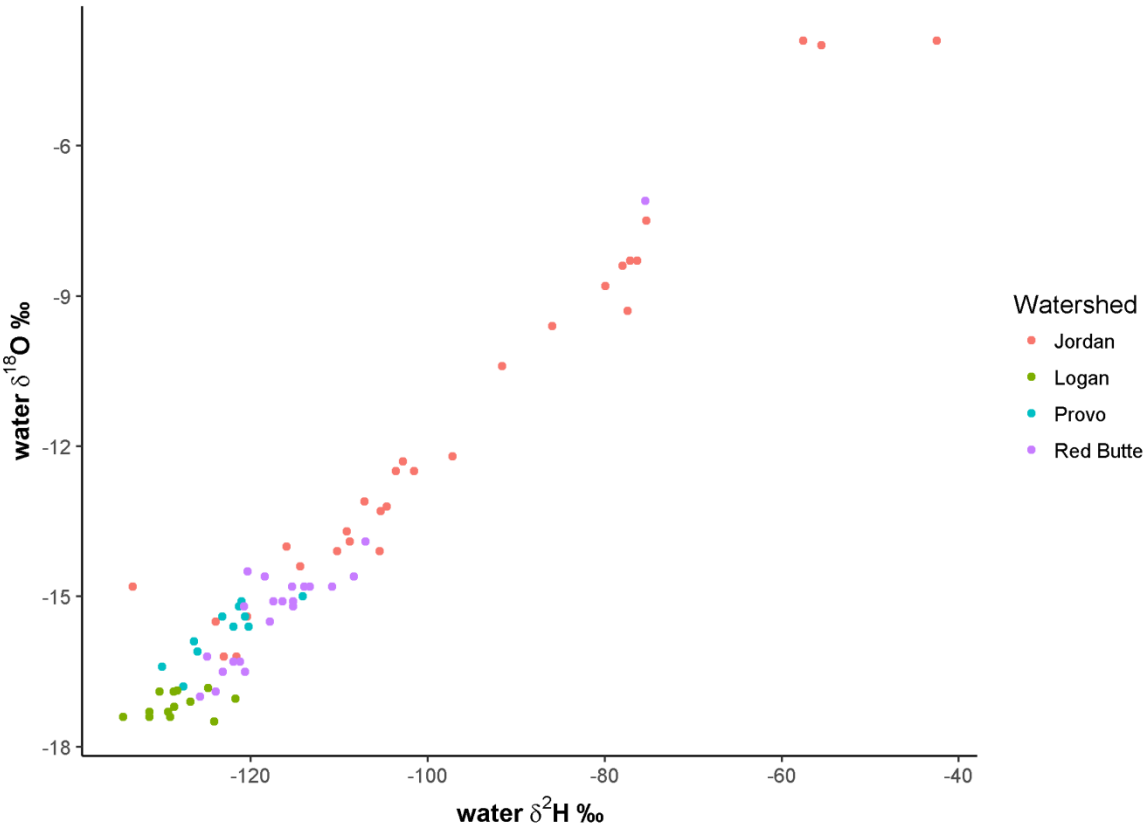


Variable	PC1 45% r	PC2 21% r	PC3 10% r
percentC2	**-0.90**	-0.33	0.13
HIX	**-0.89**	0.22	0.14
DOC:TDN	**-0.48**	0.08	0.22
SUVA	**-0.47**	-0.09	-0.04
percentC1	-0.08	**0.96**	-0.13
Chla	0.20	0.02	**0.76**
percentC4	0.31	**-0.87**	-0.24
FI	**0.64**	**0.47**	-0.41
TC	**0.72**	**-0.55**	0.09
percentC3	**0.76**	0.29	**0.42**
BIX	**0.87**	0.06	0.20
YFI	**0.96**	0.05	-0.06

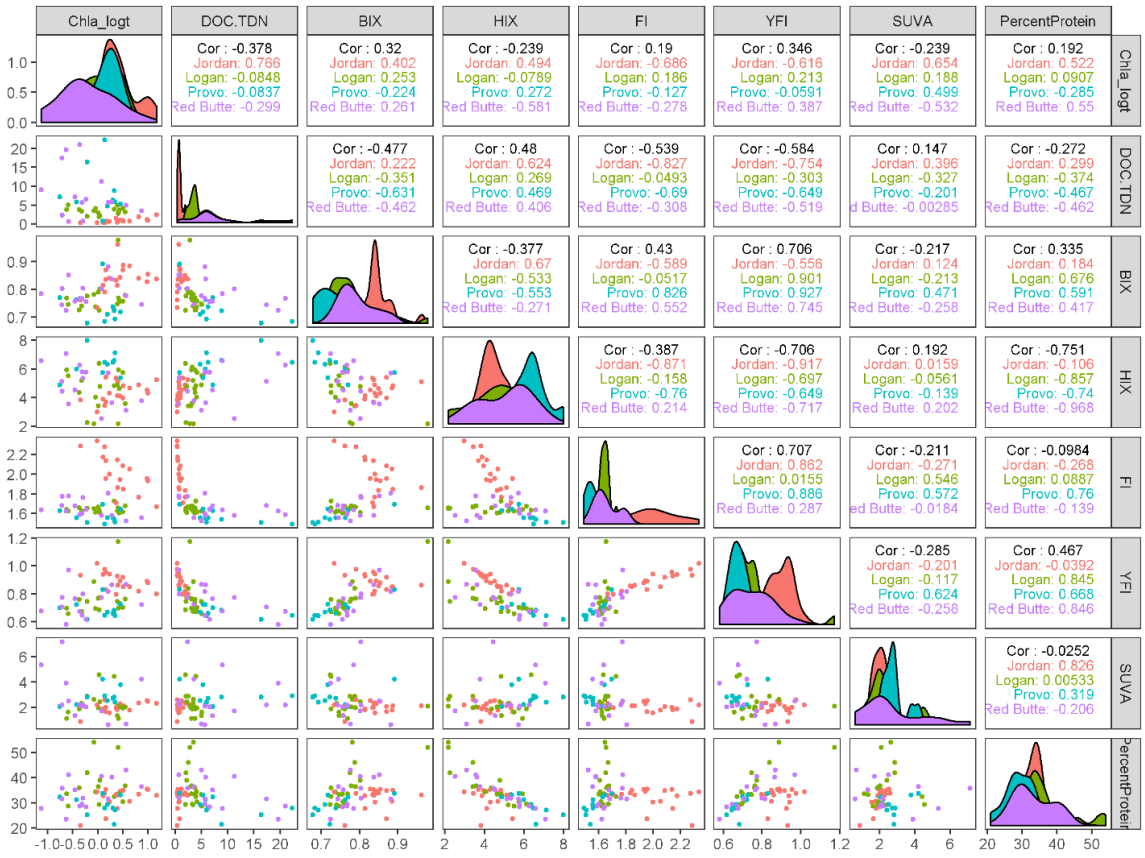
Supplement 7. Correlation r squared values for OM-$\delta^{13}C$ versus DIC-$\delta^{13}C$, and OM- $\delta^{2}H$, versus water-$\delta^{2}H$ for DOM and FPOM.

DOM	OM-$\delta^{13}C$ v DIC-$\delta^{13}C$	OM- $\delta^{2}H$ v water- $\delta^{2}H$
Jordan	-0.16	-0.23
Logan	-0.54	0.49
Provo	-0.4	0.06
Red Butte	-0.56	0.13
FPOM		
Jordan	0.68	-0.19
Logan	0.53	0.03
Provo	0.17	0.39
Red Butte	-0.61	-0.11

Supplement 8. River water $\delta^{18}O$ and $\delta^{2}H$ values of 4 watersheds sampled. Most sites fall along the local meteoric water line ($\delta^{2}H = 7.45 \text{ X } \delta^{18}O\text{-}1.66$). Groundwater dominated sites that receive snow melt at higher elevations had lower $\delta^{18}O$ and $\delta^{2}H$ values (Logan River and Provo River) compared to sites at lower elevations (Red Butte) that also received water with an evaporative signature from Utah lake (Jordan River).



Supplement 9. Pearson's correlation values for chlorophyll *a* and fluorescence indices by watershed.



CHAPTER IV

DOM DEMAND AND NON-ADDITIVE EFFECTS OF AUTOCHTHONOUS AND TERRESTRIAL LEACHATES IN BIOASSAYS AND EXPERIMENTAL STREAMS

Abstract: Dissolved organic matter (DOM) is the largest pool of OM in aquatic systems, and as a primary substrate for microbial respiration in streams, it is important to understand the drivers of DOM decay. Often, DOM decay measurements are based on proxies of DOM (e.g. sugar or leaf-litter leachate) or by compartmentalizing DOM into 2 pools of labile and semi-labile DOM. Many DOM decay rates were quantified with bioassays, which may underestimate DOM decay in streams because they do not include a benthic zone, and do not account for downstream transport of DOM. In both experimental streams and dark bottle bioassays we measured decay of 2 types of labile DOM, algae and light-degraded soil and light-degraded plant leachates, and 2 types of semi-labile DOM, plant and soil leachates. We also quantified decay rate constants of labile and semi-labile pools of DOM when mixed to test for non-additive effects, or priming, of semi-labile DOM by labile DOM. We compared dissolved organic carbon (DOC) decay from bioassays and experimental streams to previous studies that quantified DOC loss in bioassays or stream reaches. Bioavailable DOC (BDOC) was greater in experimental streams (mode 52.6 % ± 20.3),compared to bottle bioassays (mode 22.8% ± 12.3), but there was no significant difference in DOC decay rate constants between

bottles and experimental streams. Mixing of labile and semi-labile DOM resulted in both positive and negative non-additive effects. Consistent non-additive effects were difficult to quantify due to extremely fast decay of algal (2.06/d ± 0.66), and light-degraded, terrestrial DOM (1.54/d ± 0.74). Decay rates calculated in this study are needed for models that aim to estimate the proportion and quantity of OM transformed and evaded to the atmosphere by rivers at the interface of terrestrial and aquatic ecosystems.

Keywords: priming, dissolved organic matter, non-additive effects, light degradation, first order decay, biexponential decay, biphasic decay, PARAFAC

Introduction

Dissolved organic matter (DOM) is the largest pool of organic matter (OM) in aquatic ecosystems (Webster and Meyer 1997, Wetzel 2001) and the flux of DOM from terrestrial ecosystems to inland waters is recognized as an important component of organic carbon budgets at watershed (Moody et al. 2013) to global scales (Battin et al 2008, Butman et al. 2016). Continental and global estimates show that carbon dioxide evasion from streams and rivers (hereafter streams) is at least as large as terrestrial net ecosystem production (Battin et al. 2008, Butman et al. 2016). However, empirical measures of whole-ecosystem DOM transformations are lacking, and the rate at which streams process terrestrial DOM inputs remains poorly understood (Battin et al. 2009, Mineau et al. 2016).

Aside from its relation to carbon budgets, it is important to have baseline estimates of stream DOM transformations for managers who aim to reduce OM loads, as well as to mitigate for pathogens and contaminants associated with OM in human-altered watersheds (Edmonds and Grimm 2011, Stanley et al. 2012). DOM can contribute to biochemical oxygen demand, the formation of disinfection by-products, and adsorb metal contaminants (Stanley et al. 2012, Kaushal et al. 2014). DOM decay in streams is controlled by several factors, including hydrologic dilution, sorption to sediments, microbial metabolism, and photodegradation (Edmonds and Grimm 2011). Managers may not have control of all these factors, but dilution is a relatively common DOC reduction strategy (Gücker et al. 2006, Edmonds and Grimm 2011) that may decrease stream ecosystem functions such as nutrient, pollutant, and pathogen retention, (Bunch and Bernot 2011, Kaushal et al. 2014). More reach-scale measures of DOM removal, such as DOC decay, that are valid for use at the watershed scale are needed (Mineau et al. 2016, Seybold and McGlynn 2018), and will inform OM management in streams, as with similar investigations into nitrate removal in streams (Mulholland et al. 2008).

Bioassays, which include any closed system incubation (e.g. dark bottles, Erlenmeyer flasks), are commonly used to measure DOM decay as bacterial respiration and/or organic carbon loss. Bioassay decay rates are problematic because most incubations do not include a proxy for the benthic zones (benthos) of aquatic systems (Catalán et al. 2016, Mineau et al. 2016, Bengtsson et al. 2018). These habitats contribute to at least half of DOM consumption in marine and lake sediments (Bengtsson et al 2018), and at least half of stream DOM demand (Cory and Kaplan 2012, Risse-Buhl et al. 2012, Mineau et al. 2016). In addition, bioassays typically are conducted in the dark, so

they do not account for effects of photodegradation. Further, results are difficult to compare across studies because incubation times vary from days to years, and may or may not include sediment (van Nugteren et al. 2009), inorganic substrates (e.g. glass beads; Catalán García et al. 2015, Ward et al. 2016), or circulation to maintain realistic dissolved oxygen concentrations (Lock and Hynes 1976, Qualls and Haines 1992).

DOM decay rates are difficult to constrain because DOM is a complex, highly variable mixture of compounds (Seitzinger et al. 2005, Kaplan et al. 2008). The chemical composition and quality of DOM influences the ability of microbes to consume DOM, and is therefore an important control of decay rate (Koehler et al. 2012, Mostovaya et al. 2016). The majority of DOM is considered semi-labile (i.e. recalcitrant), derived from terrestrial sources, such as soil and plant leachates, and is typically rich in humic constituents (Findlay and Sinsabaugh 2003). The quality of terrestrial DOM can also change because of exposure to sunlight. Photodegradation can reduce the molecular weight of DOM constituents but the degree of degradation depends greatly on DOM chemical composition (Moran and Zepp 2000, Chen and Jaffé 2014). For example, the greater the proportion of aromatic content, the greater the effect of sunlight on bioavailability (Moran and Zepp 2000, Tranvik and Bertilsson 2001). The effects of photodegradation can increase (Moran and Zepp 1997), decrease (Tranvik and Bertilsson 2001), or have no effect (Wiegner and Seitzinger 2001) on DOM lability to microbes. Autochthonous DOM, OM produced instream by biofilms, filamentous algae, and/or macrophytes, is considered extremely labile because it consists of low molecular weight, protein-rich cellular exudates produced during photosynthesis (Guillemette et al. 2013).

We do not understand the interactions between labile and semi-labile DOM pools. When mixed, these two pools are hypothesized to have non-additive effects on microbial degradation rates (Guenet et al. 2010, Bengtsson et al. 2018). Non-additive effects refer to a change in decay rates, usually of the semi-labile pool, when 2 pools are mixed compared to when the 2 pools remain separate (Bengtsson et al. 2018). The concept of non-additive effects, also referred to as the priming effect, originated in soil science, but has been proposed by aquatic ecologists as a possible mechanism to explain the rapid transformation of semi-labile DOM over short distances in stream networks (Hotchkiss et al. 2014, Mineau et al. 2016). The priming effect in streams is predicted to occur when a small pool of autochthonous DOM is mixed with the semi-labile pool, which then accelerates microbial degradation of semi-labile DOM to a faster decay rate than without the labile DOM (Guenet et al. 2010, Danger et al. 2013).

We had 2 objectives, first to compare decay rate constants of labile and semi-labile DOM in experimental streams that included a benthic zone, exposure to sunlight, and constant reaeration versus bottle bioassays that did not include these effects. Second, we aimed to quantify the non-additive effects of mixing labile and semi-labile DOM in experimental streams and bioassays. We designed experiments to test 2 hypotheses: 1) that bioassays in bottles underestimate stream DOM decay because they exclude benthic microbes, and 2) that semi-labile DOM decay rates are increased by addition of labile DOM (i.e. priming).

Seven consecutive 3-day experiments were conducted in experimental streams and in dark-bottles (bioassays). To confirm that semi-labile sources of DOM decayed at a faster rate than labile DOM we conducted 5 single-source experiments which measured

decay of 2 types of semi-labile DOM (soil and plant leachates) and 3 types of labile DOM (algal derived, light-degraded plant leachate, and light-degraded soil leachate). Then we converted decay rate constants to uptake lengths and uptake velocities, to compare DOM uptake in bottles, experimental streams, and previously reported DOM uptake metrics from previous studies. Following single-source experiments we conducted 2 priming experiments by mixing labile DOM, either algae or light-degraded plant DOM, with semi-labile, plant DOM (Fig. 1). Decay rates calculated from single-source experiments were then used to inform 2-compartment models of semi-labile and labile decay when mixed. We expected DOM decay rates to be faster in streams compared to bottles, and we expected that DOC decay rates of semi-labile DOM would be faster when mixed with labile DOM, compared to semi-labile decay rates without labile DOM.

Methods

Experimental streams

Experiments were conducted in 8 experimental streams at the Cary Institute of Ecosystem Studies Artificial Stream Facility in Millbrook, New York. Streams were housed in a greenhouse covered with eight mm high-impact double skinned acrylic and estimated to transmit 84% of photosynthetically active radiation (Acrylic Building Products, Mississauga, Canada). In all experiments the fiberglass artificial streams (4 x 0.3 x 0.15 m) were filled with 33 L of groundwater that had low levels of DOC (< 1.0 mg/L, Fig. 1). Water in the streams was circulated at 45 rotations/min using stainless steel paddle wheels propelled by Dayton DC gear motors (Dayton, Niles, Illinois),

yielding a mean velocity of 0.6 m/sec. Forty cobbles covered with periphyton were added to each stream to compare DOC consumption in experimental stream with benthic biofilms versus bottle-bioassays without biofilms. Cobbles were collected from an open canopy section of East Branch Wappinger Creek within the Cary Institute of Ecosystem Studies conservation research area.

Experimental design and leachates

We conducted 5 single-source experiments followed by 2 priming experiments over the course of 22 days in July 2016. One dark-bottle was incubated in each stream to compare decay in bottles-bioassays and experimental streams during each 3-day experiment (Fig. 1). To ensure DOC concentrations declined over time, 4 experimental streams were covered with cardboard and designated as dark treatments. The remaining 4 streams were not covered and were designated as light treatments. Light streams experienced natural daily fluctuations in sunlight to observe more realistic decay rates than in dark treatments, and dark streams were used to eliminate labile DOM production from photosynthesis and to be more comparable to dark bottles. At the beginning of single-source experiments, 12 liters of leachate were added at sunset resulting in 26% of total stream volume as leachate (Fig. 1). Leachates were added at sunset to maximize the duration of darkness at the beginning of each experiment, and ensure DOC decline in light treatment streams prior to sunrise when DOC production would begin in light streams. Single-source experiments were referred to as algae, soil, light-degraded soil (soil-light), plant, and light-degraded plant (plant-light). For each priming experiment 10 liters of plant leachate were mixed with 4 liters of labile DOM, either as algae (prime-

algae experiment) or light-degraded plant leachate (prime-light experiment). After leachate was added and allowed to mix, 500 mL dark-bottles were filled with experimental stream water and sampled for constituents at the same time as experimental streams.

Algal leachate was made by scrubbing the biofilm off cobbles from East Branch Wappinger Creek within the Cary Institute of Ecosystem Studies conservation research area and mixing this slurry with groundwater. The leachate was then incubated in 5 gallon buckets for 1-2 hours. Soil leachate was made by mixing 4 liters of soil with 10 liters of groundwater, stirred and allowed to settle for 2-4 hours. Plant leachate was made from concentrated roasted barley leachate. Barley concentrate was made by adding 60 g of ground, roasted barley to one liter of groundwater. Plant leachate was then made by adding 5 mL of concentrate to a liter of groundwater. Light-degraded soil and plant leachates were made by incubating leachate in 0.5 x 1 x 0.2 m trays in full sun for 3-4 hours. Terrestrial leachates were exposed for what we considered the minimum amount of time DOM would be exposed to natural sunlight in a temperate stream with a short travel time (<1 day). All leachates were filter-sterilized using 0.2 μm pore size in-line cartridge filters (Waterra, Mississauga, Ontario, CA).

DOC was sampled prior to adding leachate and 1, 3, 6, 24, and 70 hours after leachate additions (Fig. 1). Experimental stream and bottle samples were filtered with 0.7 μm glass fiber filters (Whatman GF/F) into 40 mL amber vials and acidified to a pH of 2.5 for storage until carbon analysis. Acidified DOC samples were run on a Shimadzu TOC-L analyzer via catalytic oxidation combustion at 720 °C (MDL 0.62 mg/L DOC; Shimadzu Corp., Kyoto, Japan). Streams and bottles were sampled for

spectrofluorometric analysis after 1, 24, and 70 hours. Samples were filtered and stored in amber vials at 6°C until analysis. Periphyton in the experimental streams were also collected after 1, 24, and 70 hours to obtain chlorophyll *a* and ash-free dry mass of benthic biomass.

DOM fluorescence

Excitation emission matrices (EEMs) were collected on an Aqualog spectrofluorometer to assess changes in DOM character though each 3-day experiment and to calculate DOM fluorescence indices that characterized DOM as either microbial or humic-like. EEMs were collected with excitation wavelengths from 248 to 830 at 6 nm increments and over emissions 249.4 to 827.7 at 4.7 nm (8 pixel) increments. All samples were collected in ratio mode (S/R) and run at an integration time resulting in a maximum emission intensity of 5,000 to 50,000 counts per second. Samples that exceeded 0.3 absorbance at excitation 254 nm were diluted with deionized water. All samples were corrected for inner filter effects, Rayleigh scatter, and blank subtracted in MATLAB™ (version 6.9; MathWorks, Natick, Massachusetts) as described in Murphy et al (2013).

From EEMs, the fluorescence index (FI), β:α index or freshness index (BIX), humification index (HIX), and peak T to peak C ratio (TC) were calculated. High versus low FI values indicate microbial versus terrestrially derived DOM (Cory and McKnight 2005). Higher values of the BIX indicate more recently derived DOM (Parlanti et al. 2000), and more humic-like DOM for higher values of the HIX (Zsolnay et al. 1999). The TC index represents the ratio of the protein-like peak (T) to humic-like peak (C) intensities (Baker 2001). SUVA (SUVA), an indicator of DOM aromatic content, was

calculated by normalizing the absorbance at 254 nm by the DOC concentration of each sample (Weishaar et al. 2003).

Parallel factor analysis (PARAFAC) was used to identify fluorescence components of DOM to assess changes in DOM throughout each experiment (e.g., a decline in humic-like components due to light exposure). PARAFAC decomposes a collection of EEMs into groups of organic compounds with similar fluorescent characteristics (Stedmon and Markager 2005). MATLAB was used to create a PARAFAC model with 213 EEMS using the drEEM toolbox following Murphy et al. (2013). The model was then validated with split-half analysis, and resolved components were compared to previously found fluorophores in the open source library OpenFluor (Murphy et al. 2014). Percentage of each PARAFAC component was correlated with fluorescence indices using Pearson correlations in R with the psych v1.7.8 package (Revelle 2017).

Five linear models were run to identify treatments that best described variation in fluorescence indices and PARAFAC components. Linear models tested the fixed effects of 1) treatment, 2) treatment plus bottles versus streams, 3) treatment light streams versus dark streams, and 4) the interaction of treatment and light versus dark streams. Samples collected after 70 hours were used to assess differences in fluorescence indices and PARAFAC components since that is when differences were greatest. Bayes factors were calculated to identify the linear model that best described variation in dependent variables. The Bayes factor (B_{01}) can be generalized as the probability ratio between two models (M_0, $M_{1)}$ (Eqn. 1).

$$B_{01} = \frac{\Pr(\text{Data}|M_0)}{\Pr(\text{Data}|M_1)} \quad (1)$$

The R package BayesFactor was used with uninformative priors (Morey et al. 2018). Bayes factors were calculated for models normalized by the effect of treatment alone. Significant differences in treatments were then tested using multiple comparisons of means and Tukey HSD.

DOC decay models

To estimate decay rates constants for single-source experiments we used an inverse modeling approach with Bayesian parameter estimation. Decay rates constants were calculated for all experiments after 6, 24, and 70 hours. Single-source decay rates were estimated using a first order exponential decay model (Eqn. 2):

$$C_t = C_0 e^{-k_{tot} t} \quad (2)$$

where C_0 and C_t represent DOC concentrations at the start and end of the period over which $-k_{tot}$ was calculated over time (t). The difference in mean decay rates for labile and semi-labile DOM estimated from single-sources models were then used to test the hypothesis that labile sources of DOM (algae, soil-light, plant-light) decayed faster than semi-labile sources (soil, plant). The difference was calculated by subtracting the 95% high density interval (HDI) of semi-labile DOM from the 95% HDI of labile DOM. If the median difference was greater than zero the decay rates were considered significantly different (Hotchkiss et al. 2014). Parameter values within the 95% HDI are more likely than outside the HDI, and all values within the HDI represent 95% of all possible values (Kruschke 2015).

Two different models were used to estimate DOC decay rates in priming experiments. First, a two-compartment, biexponential decay model assumed the labile (k_{fast}), and semi-labile (k_{slow}), pools of DOC decayed simultaneously starting at time zero t_0 (Eqn. 3):

$$C_t = p_1 C_{1(t_0)} e^{-k_{fast} t} + p_2 C_{2(t_0)} e^{-k_{slow} t} \quad (3)$$

where C_t is the total concentration of both labile (C_1), and semi-labile (C_2), pools at the start of the experiment, and $p_1$and p_2 are the proportional volumes of each leachate (Hotchkiss et al 2014; Supplement 1).

Second, a 2-compartment, biphasic decay model assumed there was a fast period of decay, followed by a slow period of decay (Eichmiller et al. 2016, Brouwer et al. 2017). For the biphasic model, k_{fast} was estimated using first order exponential decay up to a breakpoint at time t^* (Eqn. 4), and $k_{slow}$was estimated for the period of decay after the breakpoint using the value estimated for k_{fast} prior to the breakpoint (Eqn. 5; Supplement 1).

$$C_{t*} = C_0 e^{-k_{fast} t} \qquad t < t^* \quad (4)$$

$$C_t = C_0 e^{-k_{fast} t*} e^{-k_{slow}(t - t*)} \qquad t > t^* \quad (5)$$

There were not enough time points to identify the breakpoint between fast and slow periods of decay using traditional methods of breakpoint analysis (e.g., segmented or changepoint analysis). Therefore, breakpoints were estimated visually from raw DOC concentrations plotted over 70 hours.

The decay rates of each compartment were estimated using Bayes Rule where the posterior probability distribution of k_{fast} and k_{slow}, given the DOC data, is proportional to the product of the likelihood of the decay model, and the prior probability distributions

of the decay parameters (Hotchkiss et al 2014). The posterior probability distributions of k_{fast} and k_{slow} were simulated with the rjags package using Markov Chain Monte Carlo (MCMC) sampling from an informed prior distribution (Plummer 2018). Each model was run for 150,000 iterations, using three different starting values for each chain, and the first 10,000 samples were not included in parameter estimation. Model fit was assessed through linear regression of measured versus predicted values of DOC concentrations at the last modeled time point.

To determine if positive non-additive effects were significant (priming effect), we subtracted the posterior probability distribution for single-source plant decay (k_{tot}) from the posterior distribution of the slow-decay compartment (k_{slow}). A positive non-additive was considered significant if the median difference in the 95% HDI of the two distributions ($k_{slow} - k_{tot}$) was greater than zero (Hotchkiss et al. 2014).

Bioassay versus experimental stream DOC decay

To test the hypothesis that bioassays underestimate DOC decay, differences in single-source DOC decay constants and BDOC were compared using the BEST test (Bayesian estimation superseded t-Test) in R (Kruschke 2013). If the difference in posterior probability densities estimated for the mean of each group includes zero, the BEST test is considered not significant. BDOC was calculated as the percent loss in DOC concentration from 3 to 70 hours in streams (Fellman et al. 2008). BDOC in bottles and streams was calculated from 6 to 70 because, for the first 6 hours of 4 experiments, DOC concentrations increased due to DOM production, (as seen previously Hosen et al. 2014) after which concentrations declined for the duration of the experiment. To further

compare bioassays and stream DOM decay, we compared DOM decay rate constants from studies that used bottles (Hotchkiss et al. 2014) to decay rate constants calculated from stream reach additions (Webster and Meyer 1997, Griffiths et al. 2012, Epstein et al. 2016, Hall et al. 2016; Supplement 2).

Benthic biomass

Benthic biomass was measured to assure that any differences in DOM decay were due to differences in DOM source rather than biomass effects. To collect periphyton biomass one cobble was taken from each experimental stream after 1, 24, and 70 hours, scrubbed with a toothbrush and washed with an aliquot of groundwater. Periphyton slurry from each cobble was subsampled and filtered through GF/F filters and analyzed for chlorophyll *a* and ash free dry mass (AFDM) analysis following Steinman et al. (2007). A picture of each cobble was taken to calculate surface area using ImageJ (Schneider et al. 2012). Chlorophyll *a* and AFDM then were normalized by area of each cobble sampled. We detected no significant differences across experiments in benthic biomass measured as AFDM which confirmed that biomass did not factor into differences among experiments (Supplement 3). Chlorophyll *a* concentrations were lower in priming experiments than single-source experiments, but did not differ among other experiments (Supplement 3). As priming experiments occurred at the end of the 22 day period during which the experiments were conducted, we interpret this to indicate aging of the biofilm. Benthic biomass data are not discussed further in this paper (see Supplement 3).

Results

Were decay rates of algal labile DOM faster than semi-labile DOM?

To confirm the hypothesis that labile DOM decay rates (algae and light-degraded) were faster than semi-labile DOM decay rates (soil and plant) we tested the difference between estimated values of labile and semi-labile decay rates (Table 1, Supplement 4). The difference in mean decay rates of light versus dark treatments of experimental streams were not significantly different after 6 hours (95 %, HDI -2.61, 3.96), 24 hours (HDI -0.99, 0.45) or 70 hours (HDI -0.38, 0.23; Supplement 5). Therefore, we assessed decay rates among treatments for all 8 streams combined.

Algal DOM decay rates were always faster than soil and plant DOM decay rates in both bottles and streams, except after 70 hours, algal decay was not faster in streams (Table 1, Supplement 4). Soil and soil-light DOM decay rates were highly variable in streams, and there was little to no decay of both treatments in bottles. Light-degraded plant DOM decay rates were faster than soil and plant decay rates over the first 6 hours of the experiment but were not significantly faster after 24 and 70 hours in both bottles and streams. Overall labile DOM decay rates of algal and plant-light DOM were hard to estimate (i.e. high variation) in the first 6 to 24 hours of each experiment, and their decay rates declined significantly after 70 hours.

Did sunlight alter DOM composition?

DOM composition Fluorescence indices were calculated to characterize DOM from different leachates and to identify changes in DOM composition during each experiment. In all experiments, FI values were higher in light streams (mean 1.65, sd 0.09) than dark

streams (mean 1.61, sd 0.09) indicating more microbial-derived DOM in light streams (Fig. 2). SUVA and HIX values were significantly lower in the soil-light experiment than the soil experiment indicating a decrease in aromatic content of soil-derived DOM after exposure to sunlight (Fig2, Supplement 6). Likewise, indices of recently derived DOM (BIX) and protein-like DOM (TC) were higher in the soil-light than soil experiment (Supplement 6). Plant DOM had lower aromatic content (SUVA mean 0.63, sd 0.19) than algal and soil derived DOM (SUVA mean 3.02 sd 2.9; mean 2.6, sd 0.29; Fig. 2).

A 5 component PARFAC model (hereafter C1 to C5) was resolved and validated with split-half analysis to identify major fluorophores (Supplement 7). Components 1 through 5 were at least 95% identical to fluorophores identified within the OpenFluor library (Murphy et al. 2014). C1, C2, and C3 were described as humic-like in previous studies and this study (Table 2). Earlier studies described C4 as recently transformed or microbial-derived (Murphy et al. 2013). In this study, percent C4 was greatest for plant derived DOM (Fig. 3) which had less aromatic content than soil DOM (Fig. 2), and was more recently derived than soil DOM as indicated by higher BIX values than soil derived DOM (Supplement 6). C5 was protein derived, tryptophan-like DOM in both this, and previous studies (Coble et al 1996, Yamashita and Tanoue 2003).

Percent C2 was lower in light streams at the end of all experiments, except the algae experiment, indicating it was susceptible to light degradation in terrestrially derived DOM (Fig. 3). The greatest concentrations of C3 were in the soil and soil-light experiments (range 23-29%) were associated with older humic DOM because C3 was positively correlated with the HIX and SUVA ($r = 0.64$, $r = 0.75$; Supplement 8). C3 appeared to be “produced” from light exposure as it increased in proportion to other

components in the light streams of all plant experiments (Fig. 3). But, C3 also increased slightly in dark streams with plant DOM, therefore microbial activity that consumed C2 may have created C3 in the process. C4 had highest concentrations in plant experiments (range 24 to 31%) and was negatively correlated with the HIX and SUVA ($r = -0.72$, $r = -0.81$; Supplement 8). C5 the protein-like component, declined in all experiments except for the soil experiment which had the lowest percent protein out of all experiments (range 10-16%).

Do bioassays underestimate microbial DOM demand when compared to experimental or real streams?

To assess whether DOM consumption measured in bioassays was comparable to that measured in experimental streams, we compared DOC decay rate constants, and BDOC between bioassays versus experimental streams, and bioassay versus experimental streams and real streams. Decay rate constants were excluded from comparisons if the coefficient of variation (CV) among 8 streams and bottles within a treatment were greater than 100% to ensure only consistently estimated decay rates were used in comparisons. Excluded decay rate constants included 2 experimental stream decay rates calculated after 24 hours (CV SoilLight 128% and Soil 287%) and 4 bottle decay rates (Plant -24 hrs 183%, Soil-70 hrs 377%, SoilLight-70 hrs 612%, Soil-24 hrs 866%). Again, there was no difference in mean decay of light versus dark experimental streams, so results from light and dark experimental streams were pooled (Supplement 4).

Decay rate constants Decay rates constants from single-source experiments of experimental streams (n= 13, mode 0.23/d, sd 0.89) were not different from decay rate

constants of bioassays (n = 11, mode 0.199 /d, sd 0.527; 95 % HDI -0.426, 0.901; Fig. 4). Decay rate constants of bioassays in previous studies tended to be lower (n = 33, 0.041/d, sd 0.028), than for real streams (n = 25, mode 0.003/d, sd 0.004), but the probability density of difference in means included zero (95 % HDI -0.004, 0.057), and therefore was not significant.

Bioavailable DOC BDOC was calculated to compare the proportion of DOC lost during each single-source experiment between bottles and experimental streams. Soil leachate BDOC in streams was significantly lower (<0 %) than all other experimental stream experiments, and there were no other significant differences in BDOC among treatment experiments in streams ($F = 0.94$, $p = 0.46$). Overall, percent BDOC was greater in streams (mode 52.6 %, sd 20.3) than bottles (mode 22.8%, sd 12.3; 95 % HDI 22.6, 36.7; Fig. 5).

Do positive non-additive effects result from mixing DOM pools?

We used plant-leachate as the semi-labile source of DOM in priming experiments because single-source soil leachate experiments reached maximum concentrations of *ca.* 4 mg/L DOC so it was difficult to detect significant declines in DOC concentrations and estimate decay rates for soil leachate. Variation in single-source estimates of plant leachate decay in bottles were extremely high (CV mean 111%) compared to experimental streams (CV mean 20%), so meaningful effect sizes for non-additive effects in bottles could not be calculated, and are not discussed further.

Mixed algal and plant leachates Non-additive effects were inconsistent among experiments with mixed algal and plant leachates (prime-algae). The biexponential models detected a negative non-additive effect on DOC decay (Table 3). This may have been due to difficulty in estimating decay rates of the labile pool as a result of DOM production in some streams. For example, biexponential estimates of k_{fast} for algal-leachate were -1.23/d (sd 0.31) and 0.06/d (sd 0.15) after 6 and 24 hours. These values were slower than estimates of k_{slow} (1.25/d and 1.73/d) for the same models. The prime-algae biphasic model had a better fit than the biexponential model as indicated by predicted versus observed DOC concentration regressions (Supplement 9). The biphasic model technically detected a positive non-additive (priming) effect with a median effect size greater than zero (0.032/d), but this effect size is very small (Table 3). BDOC for the prime-algae experiment was not significantly different than the plant single source experiment (ANOVA F = 0.94, p = 0.46, Supplement 10), consistent with little decay or DOC production in algal treatments resulting in negative non-additive effects.

Mixed photodegraded plant and plant leachates In the prime-light experiment, the 6-hour biexponential model and the biphasic model both predicted a positive non-additive effect of light-degraded plant DOM on plant leachate. The 6-hour biexponential model estimated a non-additive effect size of 4.93/d (95% HDI 1.65, 9.87). Despite being statistically significant, biexponential model estimates of both fast and slow decay constants were highly variable (CV mean 123%). The biphasic model, while statistically significant, could not constrain estimates of non-additive effect size as indicated by the

broad posterior probability density around the estimated median of 0.88/d (95% HDI -0.76, 2.99). While BDOC tended to be higher in streams in the prime-light versus plant experiment, there was no significant difference between experiments (Supplement 10).

Discussion

Bioassays may underestimate DOC demand in streams

Average BDOC in experimental streams was 2 times greater than in bottles, which suggests bioassays underestimated DOC decay in experimental streams. Experimental stream BDOC was similar to the estimated percent DOC consumed at the watershed scale which ranged from 27 to 45% for 7 north-east watersheds (Mineau et al. 2016). Bioassay decay rate constants also tended to be slower than decay rates calculated from mass balance models at the watershed scale, but the ideal comparison to test our hypothesis would compare bioassay decay rates constants calculated from mass balance models to decay rate constants calculated for ambient DOM in bioassays from the same watershed. While we cannot conclude if bioassays underestimated DOC demand in real streams, evidence suggests given then same OM substrate, bioassays would likely underestimate DOM demand compared to a lotic system with a benthic component.

In addition, first order decay rates estimated from bioassays and experimental streams include products of microbial production less than 0.7 µm, or whatever filter pore size is used to collect DOM. As a result, decay rate constants estimated were based on net changes in DOC concentration, not gross DOC consumption, another factor to suggest such experiments underestimate DOM demand. Without an isotope tracer, DOC demand

estimated from bulk DOM additions is likely not comparable to DOM demand in lotic ecosystems. Thus, the role of bioassays and experimental streams as a tool to predict carbon cycling at the watershed scale needs further study (Mineau et al. 2016) to help further constrain estimates of DOM transformation in rivers.

We recommend future studies of stream DOM supplement bioassay decay rates with additional measures of DOC mineralization such as reach-scale measurements and/or mass balance models. Bioassays not only exclude DOC consumption by benthic biofilms, they also exclude the effect of abiotic factors that increase DOC decay such as photodegradation, adsorption, and sedimentation (Cory and Kaplan 2012, Catalan et al. 2016). As noted by Catalan et al. (2016), field studies better integrate all processes of DOC loss and production which may have minimal consequences for bioassays of aquatic systems with long water residence times (e.g. > 1 year), but could significantly influence bioassay decay rates in water bodies with short residence times such as streams. Our study would have benefitted from an experimental stream control without benthic periphyton to help elucidate physical versus biological drivers of DOC decay. Supplementing bioassays with field studies, or lotic mesocosms, such as experimental streams or plug-flow reactors, would help account for all physical and biological factors that influence DOC decay in streams.

Extremely fast labile DOM decay

Our estimates of decay for labile sources of DOM in experimental streams, (i.e. algae and light-degraded plant) were an order of magnitude greater than estimates of labile pools calculated from previous bioassays and field-based models (Griffiths et al.

2012, Hotchkiss et al. 2014, Epstein et al. 2016, Hall et al. 2016). For both bottles and experimental streams, decay rate constants were faster when calculated within the first 6 or 24 hours of the experiment compared to 70 hours. Few studies have estimated DOM decay within the first 12 to 24 hours of incubation (but see Lyon and Zeigler 2009, Cory et al. 2007). Incubation durations range over days (Bernhardt and Likens 2002, Hotchkiss et al. 2014), weeks (Guillemette and del Giorgio 2011, Catalan et al. 2015), months (Danger et al. 2013) and years (Vahatalo and Wetzel 2008, Evans et al. 2017). The only study to report a decay rate constant faster than this study was for the labile portion of stream DOM incubated in bioreactors with an empty bed contact time < 15 min. resulting in a decay rate constant of 1.59/day and uptake velocity of 1.23 mm/min (Kaplan et al. 2008). While most DOM decay studies assume a constant first order decay rate (Guillemette et al. 2013), if differences in decay rate constants depend on the time over which decay is calculated, as in this study, first order decay may not be an appropriate model of DOC decay. Recent DOM decay studies have investigated the reactivity continuum model that assumes overall decay is the result of an infinite number of reactive pools with decay constants that decrease over time and indeed found that decay rates vary over time (Koehler et al. 2012, Guillemette et al. 2013).

Regardless of the model used to describe decay, labile DOM pools in freshwater are known to decay within hours to one day (Guillemette and del Giorgio 2011, Cory and Kaplan 2012, Hotchkiss et al. 2014, Mostovaya et al 2016, Ward et al. 2016), or even within minutes (Pollard et al 2013). Future studies that aim to quantify consumption of autochthonous DOM, or other labile DOM, should increase sampling frequency and replication within the first 24 hours of experiments. Furthermore, it may be impossible to

measure the most bioavailable DOM in streams since it is consumed so quickly (Hotchkiss et al. 2014). Bulk DOM samples that are typically collected from streams likely constitute only the semi-labile DOM that remains "leftover" after labile DOM has been consumed (Hotchkiss et al. 2014, Findlay and Parr 2017).

Light reduced aromatic content in soil leachate

Exposure to natural sunlight decreased aromatic content in DOM and increased BDOC of light-degraded soil compared to the single-source soil experiment. Our indices of DOM degradation by natural sunlight may differ from previous studies because sunlight exposure time was much shorter than previous experiments. One other study, conducted in streams, found significant changes in tyrosine-like DOM within 4 to 7 hours of sunlight exposure (Cory et al. 2007), but most studies investigated the effect of light over 24 to 48 hours (Skully et al. 2004, Bittar et al. 2015) or up to 5 weeks (Guillemette and del Giorgio 2011, Catalán et al. 2015). Our study highlights the effect sunlight had on DOM quality after just 3 to 4 hours of exposure, a duration that represented the minimum duration of sunlight exposure for a stream in the warm months, of a temperate ecosystem.

Non-additive effects were difficult to quantify

It was hard to quantify the non-additive effect of mixing labile and semi-labile DOM because it was difficult to measure net DOM decay. All but 2 experiments included DOM production after leachate was added resulting in highly variable decay rates that may have underestimated the total amount of DOM assimilated or mineralized. We did not account for DOM production (as in Hosen et al. 2014), which may have reduced

variation in estimates of single-source decay, and therefore could have better informed biexponential models. The biphasic model better predicted final DOC concentrations for both non-additive effects experiments because, as opposed to the biexponential model, the labile and semi-labile pool were distinctly separated by the modeler. A stable isotope tracer of terrestrially derived DOM would have helped differentiate fast and slow pools and therefore models could have better estimated fast versus slow decay rates.

While non-additive effects on DOM decay have been studied in soil ecosystems since the mid 1900s (Bingeman et al. 1953), interactive effects of labile and semi-labile DOM in aquatic ecosystems have only been studied over the last decade (Guenet et al. 2010, Bengtsson et al. 2018). A recent review identified 17 studies since 2010 that explicitly tested for non-additive effects in aquatic ecosystems, and found 7 studies measured a positive non-additive effect, 6 did not, and 4 had mixed results (Bengtsson et al. 2018). It is worth noting that all studies were conducted as lab incubations, and 65% of studies used naturally occurring labile OM such as algal leachates, while the other studies used glucose or other simple compounds (Bengtsson et al. 2018). Laboratory conditions and the use of non-natural DOM reiterate the difficulty of separating labile and semi-labile pools due the high variability and complexity of DOM. In addition, studies of non-additive effects that include a benthic component are vastly underrepresented in the literature (Bengtsson et al. 2018). We conclude if positive non-additive effects do occur in aquatic systems, it is extremely hard to detect because variation in DOM lability is so great that it remains difficult to model separate decay rates of 2 different DOM pools.

Conclusions

It is important to quantify DOM decay and compare decay rates among ecosystems to better estimate carbon fluxes to the atmosphere from freshwater ecosystems. The relative lability and processing rate of autochthonous and terrestrial OM sources remains elusive. Our results emphasize the need to better quantify both fast and slow decaying OM pools in streams. Direct measurements of known sources of DOM in an experimental setting can help define the lability of DOM along a continuum of minutes to years, rather than from correlations of chemical and biological parameters of DOM to infer lability (Cory and Kaplan 2012, Koehler et al. 2012). More empirical measurements of OM decay and carbon spiraling metrics for pools with varying lability will help predict the biological implications of DOM processing in streams.

Excessive OM in streams is a problem worldwide that contributes to cultural eutrophication, the transport of contaminants to downstream waters, and can increase the cost of wastewater treatment (Chow et al. 2005, Volkmar and Dahlgren 2006, Solomon et al. 2015). In addition to informing models of organic carbon flux from streams, better estimates of DOM decay in streams from varying sources can inform management decisions aimed at reducing DOM loads at the watershed-scale. If autotrophic production in human altered watersheds is increased, it is likely the proportion of autochthonously derived, labile DOM compared to the proportion of semi-labile DOM is also increased. A greater proportion of labile DOM could saturate microbial demand, and therefore more semi-labile DOM would remain untransformed and transported downstream to receiving waters. If managers are to mitigate increased OM loads in rivers, the rate at which labile and semi-labile DOM is transformed, and the interactive effects of these pools on bulk

DOM transformation are useful information for managers. The study of novel sources of DOM in anthropogenically altered landscapes is just beginning, and baseline measures of autochthonous and terrestrial rates of DOM decay will help put the ecological implications of less studied sources of DOM in perspective.

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Tables

Table 1. Single source decay rates (k_{tot}/d) calculated after 6, 24, and 70 hours using equation 2. Values are reported as the mean (n=8) and standard deviation in parentheses. Positive values represent decay and negative values indicate no decay or net DOC production.

	Algae	Soil	Soil- light	Plant	Plant-light
Bottles					
Decay rate after 6 hours	1.17 (0.64)	0.53 (0.3)	0.06 (0.36)	-0.72 (0.45)	1.31 (0.95)
Decay rate after 24 hours	0.27 (0.09)	0.13 (0.03)	0.2 (0.04)	0.1 (0.18)	-0.09 (0.18)
Decay rate after 70 hours	0.09 (0.03)	<0.01 (0.03)	0.07 (0.01)	0.05 (0.04)	<0.01 (0.03)
Streams					
Decay rate after 6 hours	2.06 (0.66)	-0.32 (0.26)	0.25 (0.17)	0.21 (0.07)	1.54 (0.74)
Decay rate after 24 hours	0.39 (0.13)	-0.02 (0.04)	-0.27 (0.35)	0.12 (0.02)	-0.32 (0.26)
Decay rate after 70 hours	0.23 (0.06)	-0.04 (0.02)	0.2 (0.08)	0.25 (0.02)	0.23 (0.02)

Table 2. Descriptions of 5 components identified by PARAFAC and references that had a tucker's congruency coefficient of 0.95 or more for previously identified fluorophores in the OpenFluor library (Murphy et al. 2014).

	Excitation emission (nm)	References	Reference description	This study description
C1	ex 340 em 435-440	Osburn et al 2011; Stedmon et al 2007	Humic-like	Humic-like
C2	ex 255-260 em 495-500	Walker 2009, Yamashita et al 2008	Humic-like	Humic-like, susceptible to light degradation
C3	ex 248 em 430-440	Shutova et al 2014; Osburn et al 2016	Humic-like	Humic-like, product of light degradation
C4	ex 315 em 385-390	Osburn et al 2011; Shutova et al 2014	Recently derived or microbial-derived	Recently derived, terrestrial
C5	ex 278 em 330-335	Coble et al 1996; Yamashita and Tanoue 2003	Protein-like, tryptophan-like	Protein-like

Table 3. Estimated decay rates (1/d) for the labile, k_{fast} and semi-labile, k_{slow} pools of DOM in the prime-algae and prime-light experiment at 6, 24 and 70 hours. Biexponential models were fit using equation 2 and biphasic models were fit using equations 3 and 4. Model fit was assessed through linear regression of measured versus modeled final DOC concentrations (Supplement 9). The high density interval (HDI) of effect-size was calculated as the difference in the HDI of the posterior probability distribution of $k_{slow}$and k_{plant} where a positive median effect size indicated a positive non-additive (priming) effect.

	t	Model	k_{slow}	k_{fast}	Model fit	Effect size		
	Hours		mean (1/d),	mean (1/d),	slope, r^2	2.50%	50%	97.50%
Prime-Algae	6	Biexponential	1.25, 2.88	-1.23, 0.31	0.36, '0.94	-1.835	-1.459	-0.887
	24	Biexponential	1.73, 1.89	0.06, 0.15	0.11, '0.61	-0.258	-0.068	0.235
	70	Biexponential	2.55, 2.14	0.12, 0.05	0.13, 0.95	-0.180	-0.136	-0.037
	70	Biphasic	fixed = 0.31	0.28, 0.06	0.43, 0.88	-0.041	0.032	0.134
Prime-Light	6	Biexponential	3.19, 2.67	5.37, 2.18	0.20, 0.56	1.655	4.931	9.871
	24	Biexponential	2.68, 2.32	4.52, 3.96	0.42, 0.13	-4.252	4.634	11.702
	24	Biphasic	fixed = 2.0	1.05, 0.96	0.55, 0.83	-0.764	0.880	2.990

a k_{fast} was fixed at 0.31 /d which was estimated from time zero to the breakpoint at 0.5 days using equation 3.

b k_{fast} was fixed at 2.0 /d which was estimated from time zero to the breakpoint at 0.25 days using equation 3.

Figures

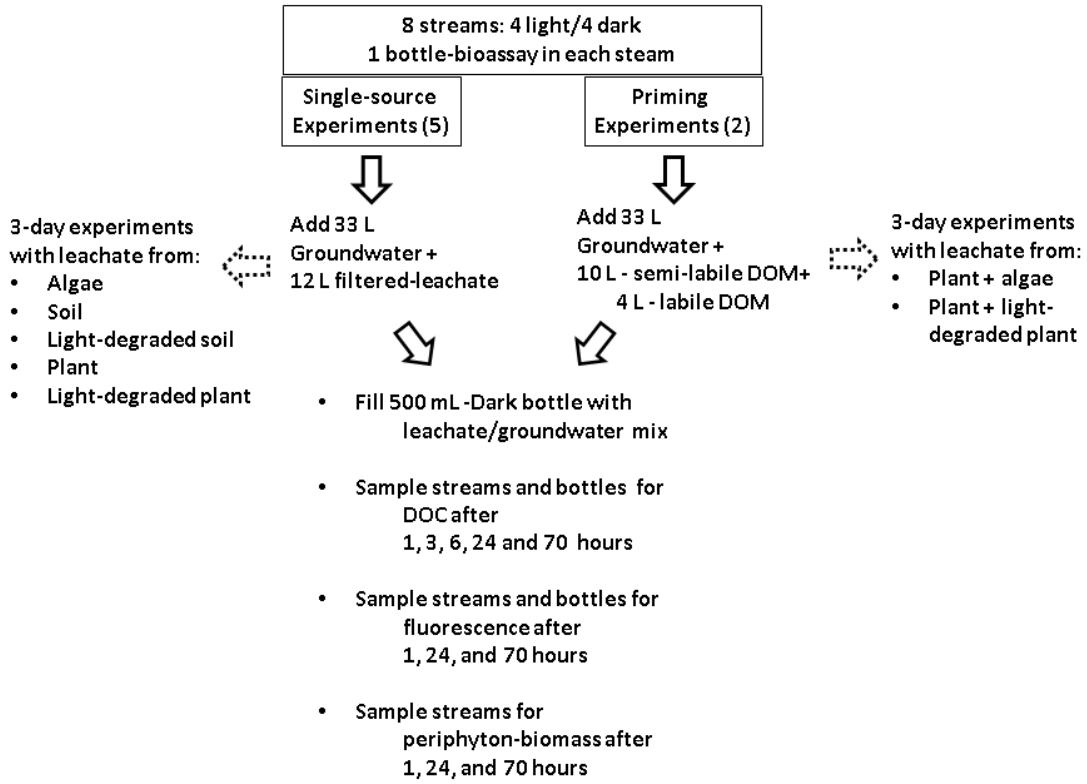


Figure 1. Eight experimental streams and 8 bottle-bioassays were used to compare decay in bioassays versus experimental streams and test the hypothesis labile DOM would increase the decay rate of semi-labile DOM. Streams were in a greenhouse; half of streams were covered with cardboard for the dark treatment (4 replicates), and half were not for the light treatment (4 replicates; see picture of light treatments). Seven, 3-day experiments were conducted as, 5 single-source experiments and 2 priming experiments.

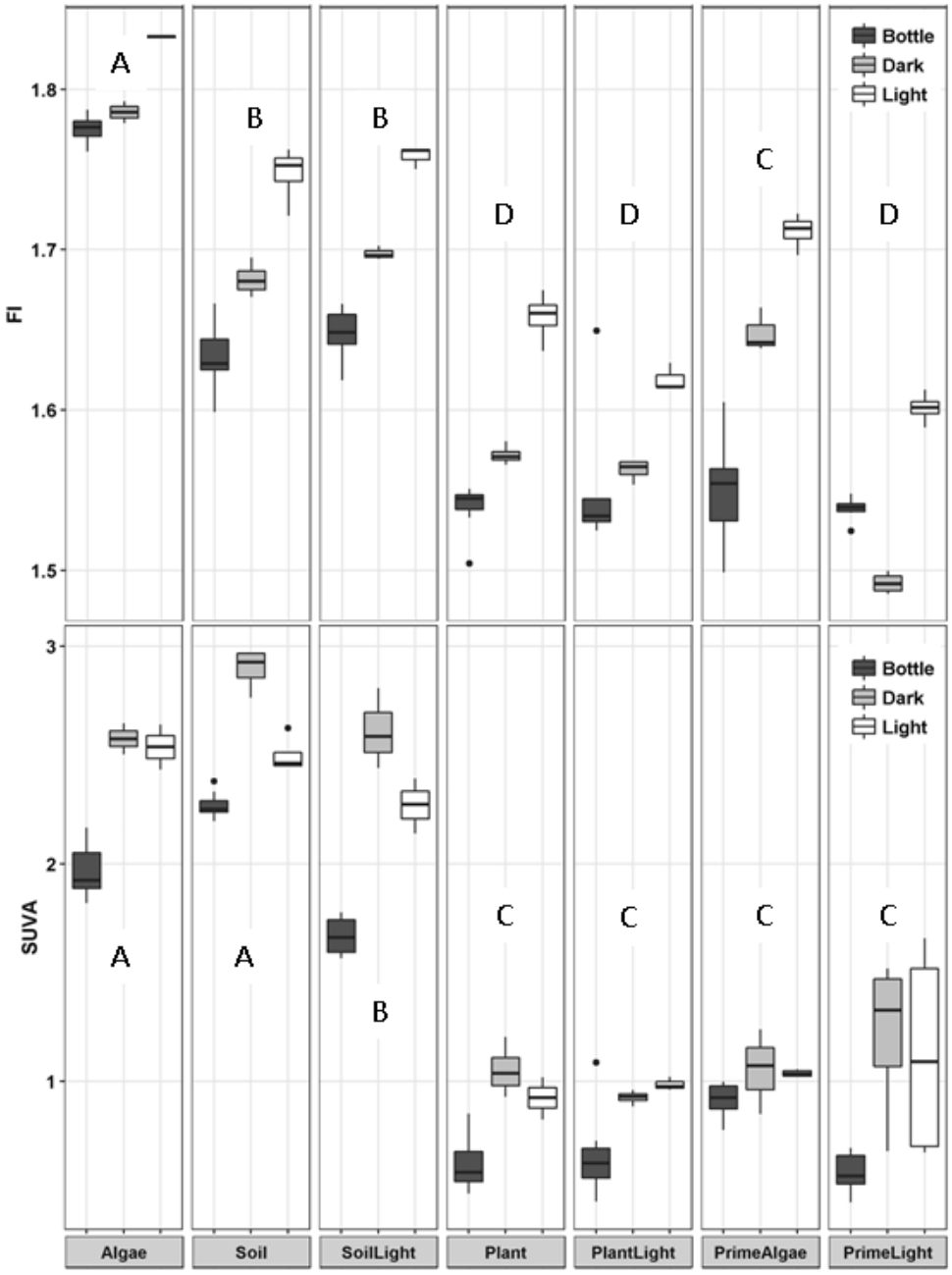


Figure 2. Light streams (n=4) had significantly higher fluorescence index (FI) values than dark streams (n=4) and all streams had higher FI values than bottles (n=8). SUVA was not significantly different among bottles and streams. Letters indicate treatments that differed by average FI or SUVA values. High FI values indicated more microbial derived DOM and high SUVA values represented greater aromatic content of DOM.

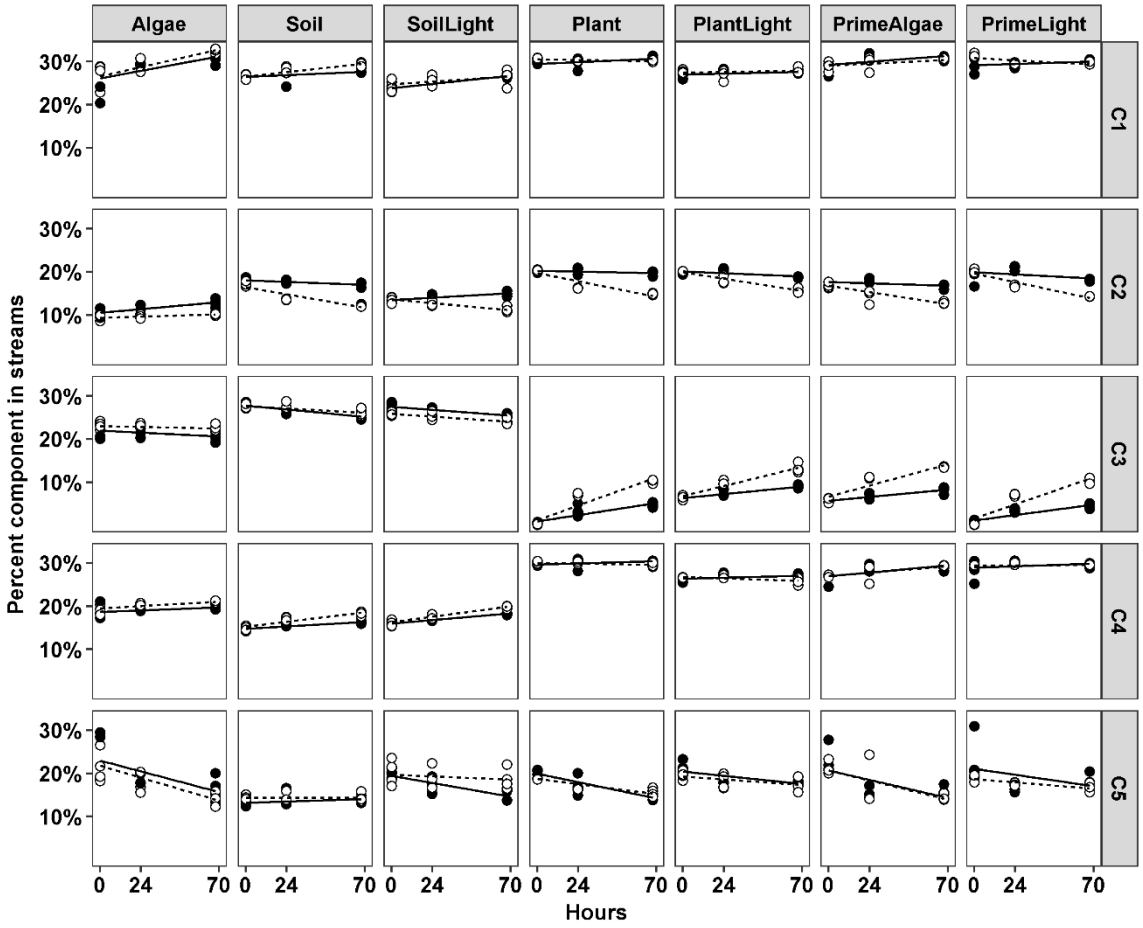


Figure 3. Percent fluorescence contribution compared among components 1 through 5 (C1, C2, C3, C4, C5) after 1, 24 hours and 70 hours. Black lines represent dark streams; dashed lines represent light streams. C1, C2 and C3 were humic-like, C4 was recently derived humic-like, and C5 was protein-like (Table 2). All components were significantly different by treatment, except C2 which had an interactive effect between dark (n=4) and light streams (n=4).

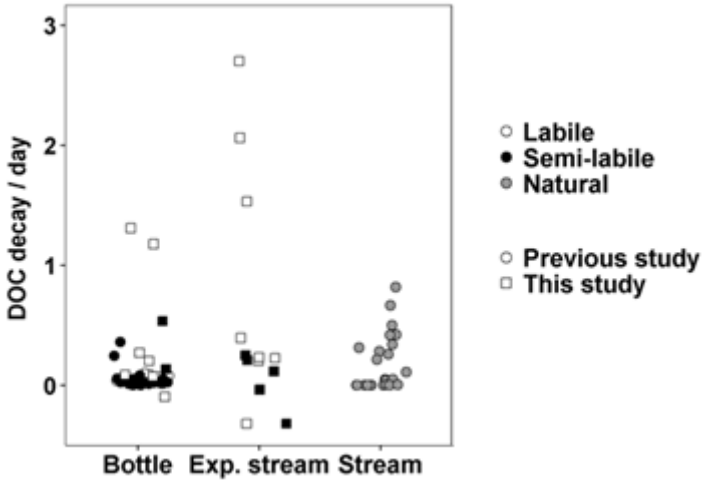


Figure 4. Dissolved organic carbon (DOC) decay rates for bioassays, experimental streams, and natural streams. Bottles include decay rate constants calculated for DOM leachates from this study and Hotchkiss et al. 2015. Experimental streams values are from this study, and streams values were calculated from modeled decay rates for real streams (Griffiths et al. 2009, Epstein et al. 2016, Hall et al. 2016).

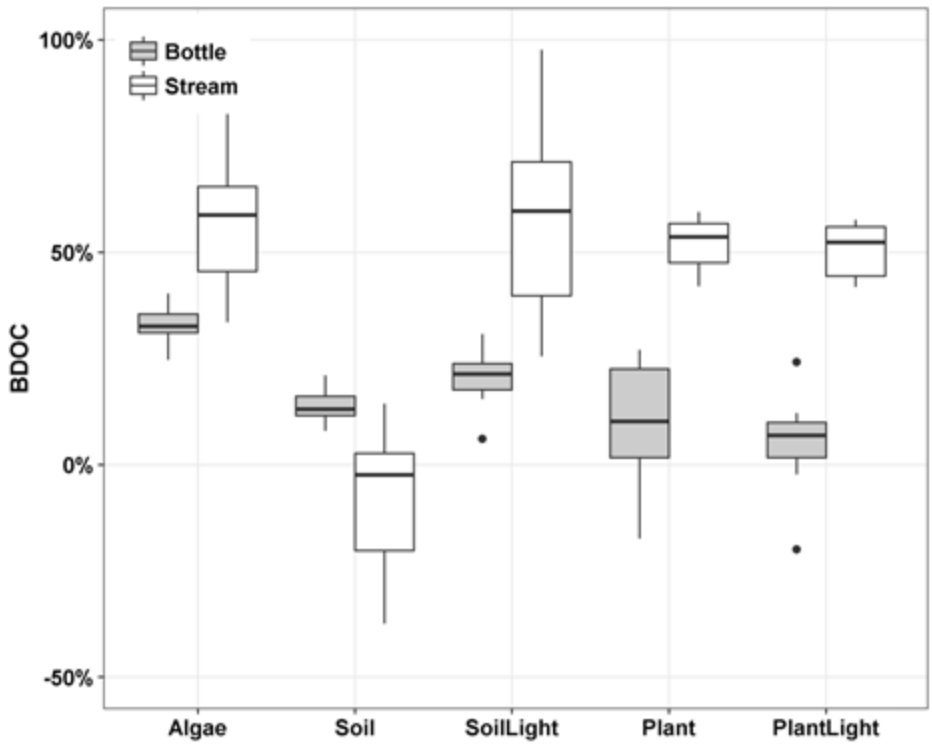


Figure 5. Average bioavailable DOC (BDOC) was significantly greater for experimental streams compared to bottles across all experiments except soil, which had significantly higher BDOC in bottles compared to experimental streams, and there were no other significant differences among experiments. Boxes represent the median and interquartile range, whiskers represent 2.5 and 97.5, and dots are outliers.

Supplement

Supplement 1. Text file of R code for biexponential and biphasic models.

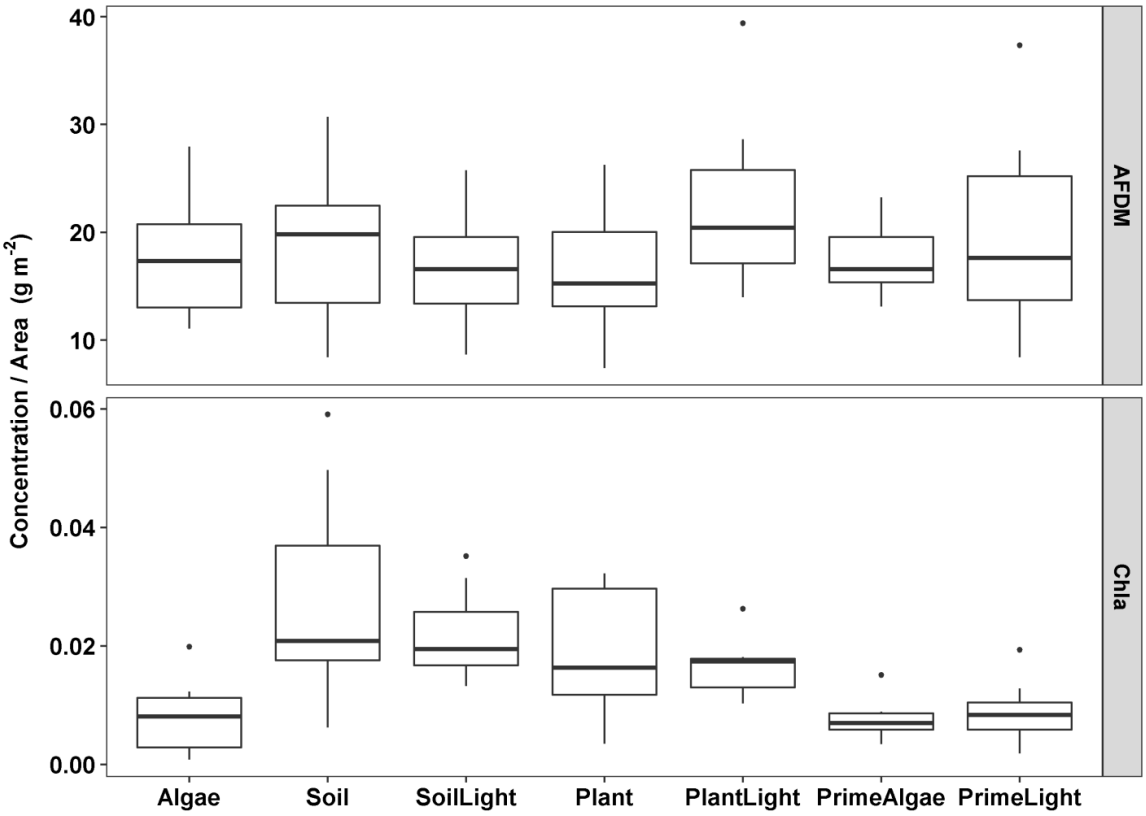
```
### Biexponential model ###
modelString = "
  model {
    for ( i in 1:Ntotal ) {
      y[i] ~ dt(mu[i], 1/sigma^2, nu)
      mu[i] <- pr1*C1*exp(k1[s[i]]*x[i]) + pr2*C2*exp(k2[s[i]]*x[i])
    }
    for ( j in 1:Nsubj ) {
      k1[j] ~ dnorm( k1mu , 1/(k1sigma)^2)
      k2[j] ~ dnorm( k2mu , 1/(k2sigma)^2 )
    }
    # Priors
    k1mu ~ dnorm( -1.57, 0.05 )
    k2mu ~ dnorm( -0.21,0.05 )
    sigma ~ dgamma( 1 , 0.05 )
    k1sigma ~ dgamma( 1 , 0.05 )
    k2sigma ~ dgamma( 1 , 0.05 )
    nu ~ dexp(1/30.0)
}

### Biphasic model ###
modelString = "
  model {
    for ( i in 1:Ntotal ) {
      y[i] ~ dt(mu[i], 1/sigma^2, nu)
      mu[i] <- Co*exp(k1[s[i]]*tp)*exp(k2[s[i]]*(x[i]-tp))
    }
    for ( j in 1:Nsubj ) {
      k1[j] ~ dnorm( k1mu , 1/(k1sigma)^2)
      k2[j] ~ dnorm( k2mu , 1/(k2sigma)^2 )
    }
    # Priors
    k1mu ~ dnorm( -2, 0.5 )
    k2mu ~ dnorm( -0.21, 0.05 )
    sigma ~ dgamma( 1 , 0.05 )
    k1sigma ~ dgamma( 1 , 0.05 )
    k2sigma ~ dgamma( 1 , 0.05 )
    nu ~ dexp(1/30.0)
}
```

Supplement 2. References and values used to create figure 4. Depth and velocity are for the stream or experimental stream DOM was collected from.

Reference	DOM source	Stream Assay	Decay (1/d)	Depth (m)	Velocity (m/s)
Epstein et al 2016	Natural	Stream	0.6	1.04	0.36
Epstein et al 2016	Natural	Stream	1.6	0.57	1.22
Epstein et al 2016	Natural	Stream	2	0.7	0.86
Griffiths et al 2012	Natural	Stream	0.001	-	-
Griffiths et al 2012	Natural	Stream	0.002	-	-
Griffiths et al 2012	Natural	Stream	0.002	-	-
Griffiths et al 2012	Natural	Stream	0.002	-	-
Griffiths et al 2012	Natural	Stream	0.003	-	-
Griffiths et al 2012	Natural	Stream	0.004	-	-
Griffiths et al 2012	Natural	Stream	0.007	-	-
Griffiths et al 2012	Natural	Stream	0.008	-	-
Griffiths et al 2012	Natural	Stream	0.009	-	-
Griffiths et al 2012	Natural	Stream	0.01	-	-
Griffiths et al 2012	Natural	Stream	0.013	-	-
Griffiths et al 2012	Natural	Stream	0.019	-	-
Hall et al 2016	Natural	Stream	0.041	1.3	0.57
Hall et al 2016	Natural	Stream	0.045	1.3	0.39
Hall et al 2016	Natural	Stream	0.048	1	0.45
Hall et al 2016	Natural	Stream	0.109	0.6	0.53
Hall et al 2016	Natural	Stream	0.258	1.1	0.49
Hall et al 2016	Natural	Stream	0.337	1	0.98
Hall et al 2016	Natural	Stream	0.416	1.4	0.52
Hall et al 2016	Natural	Stream	0.495	0.6	0.59
Hall et al 2016	Natural	Stream	0.819	0.8	0.36
Hotchkiss et al 2014	Algae	Bioassay	0.038	0.6	0.59
Hotchkiss et al 2014	Algae	Bioassay	0.074	0.8	0.36
Hotchkiss et al 2014	Algae	Bioassay	0.075	1.1	0.49
Hotchkiss et al 2014	Algae	Bioassay	0.092	1.2	0.43
Hotchkiss et al 2014	Algae	Bioassay	0.098	1.4	0.52
Hotchkiss et al 2014	Soil	Bioassay	0.001	1.1	0.49
Hotchkiss et al 2014	Soil	Bioassay	0.004	0.8	0.36
Hotchkiss et al 2014	Soil	Bioassay	0.011	1	0.45
Hotchkiss et al 2014	Soil	Bioassay	0.017	1	0.98
Hotchkiss et al 2014	Soil	Bioassay	0.023	1.4	0.52
Hotchkiss et al 2014	Soil	Bioassay	0.024	0.6	0.59
Hotchkiss et al 2014	Soil	Bioassay	0.024	1.2	0.43
Hotchkiss et al 2014	Soil	Bioassay	0.026	1.3	0.39

Hotchkiss et al 2014	Soil	Bioassay	0.052	1.3	0.57
Hotchkiss et al 2014	Soil	Bioassay	0.058	0.6	0.53
This study	Algae - 24 hr	Stream	0.39	0.07	-
This study	Algae - 6 hr	Stream	2.06	0.07	0.6
This study	Algae - 70 hr	Stream	0.234	0.07	-
This study	Algae -24 hr	Bioassay	0.27	0.07	-
This study	Algae -6 hr	Bioassay	1.18	0.07	0.6
This study	Algae -70 hr	Bioassay	0.088	0.07	-
This study	Light-plant - 6 hr	Bioassay	1.31	0.07	0.6
This study	Light-plant - 6 hr	Stream	1.53	0.07	0.6
This study	Light-plant - 70 hr	Stream	0.225	0.07	-
This study	Light-soil - 24 hr	Bioassay	0.2	0.07	-
This study	Light-soil - 6 hr	Bioassay	0.06	0.07	0.6
This study	Light-soil - 70 hr	Bioassay	0.074	0.07	-
This study	Light-soil - 70 hr	Stream	0.202	0.07	-
This study	Plant - 24 hr	Stream	0.12	0.07	-
This study	Plant - 6 hr	Stream	0.21	0.07	0.6
This study	Plant - 70 hr	Stream	0.25	0.07	-
This study	Plant-24 hr	Bioassay	0.1	0.07	-
This study	Plant-70 hr	Bioassay	0.048	0.07	-
This study	Soil - 24 hr	Bioassay	0.13	0.07	-
This study	Soil - 6 hr	Bioassay	0.54	0.07	0.6
This study	Soil - 70 hr	Bioassay	0.014	0.07	-

Supplement 3. Benthic biomass measured as ash free dry mass (AFDM) and chlorophyll *a* (Chla) for each experiment. Boxplots represent the average concentration per area of AFDM and Chla for 3 samples collected during each experiment from each stream. Concentration of each variable was multiplied by the total volume of slurry produced from scrubbing the cobble and normalized by the area of the cobble.



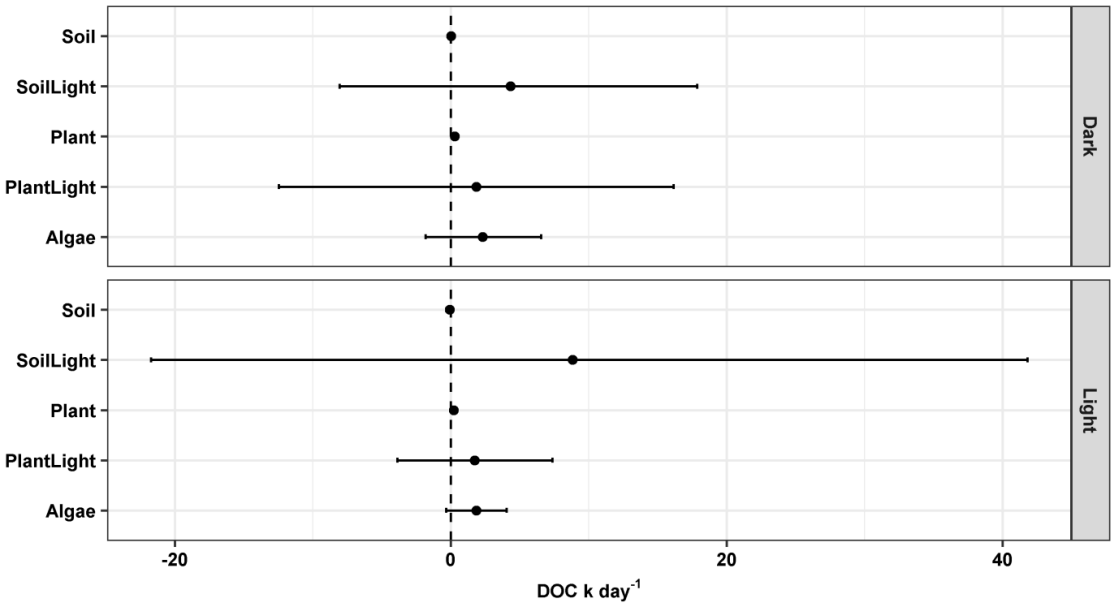
Supplement 4. High density intervals (HDI) of the difference between labile (algae, soil-light, plant-light) and semi-labile (soil, plant) decay rate HDIs. A positive median difference in decay rate indicated a significant difference in decay rate constants (bold) estimated by the single-source model (Eqn. 2).

	Algae-Soil			**Algae-Plant**		
Streams	**2.5%**	**50%**	**97.5%**	**2.5%**	**50%**	**97.5%**
6 hours	**0.75**	**1.18**	**1.60**	**0.25**	**0.90**	**1.53**
24 hours	**0.08**	**0.20**	**0.29**	**-0.03**	**0.13**	**0.25**
70 hours	**-0.09**	**0.05**	**0.15**	-0.18	-0.07	0.02
Bottle						
6 hours	**--0.05**	**0.30**	**0.66**	**0.76**	**0.94**	**1.14**
24 hours	**-0.03**	**0.06**	**0.12**	**0.28**	**0.13**	**-0.02**
70 hours	**0.00**	**0.03**	**0.05**	**0.09**	**0.05**	**0.02**

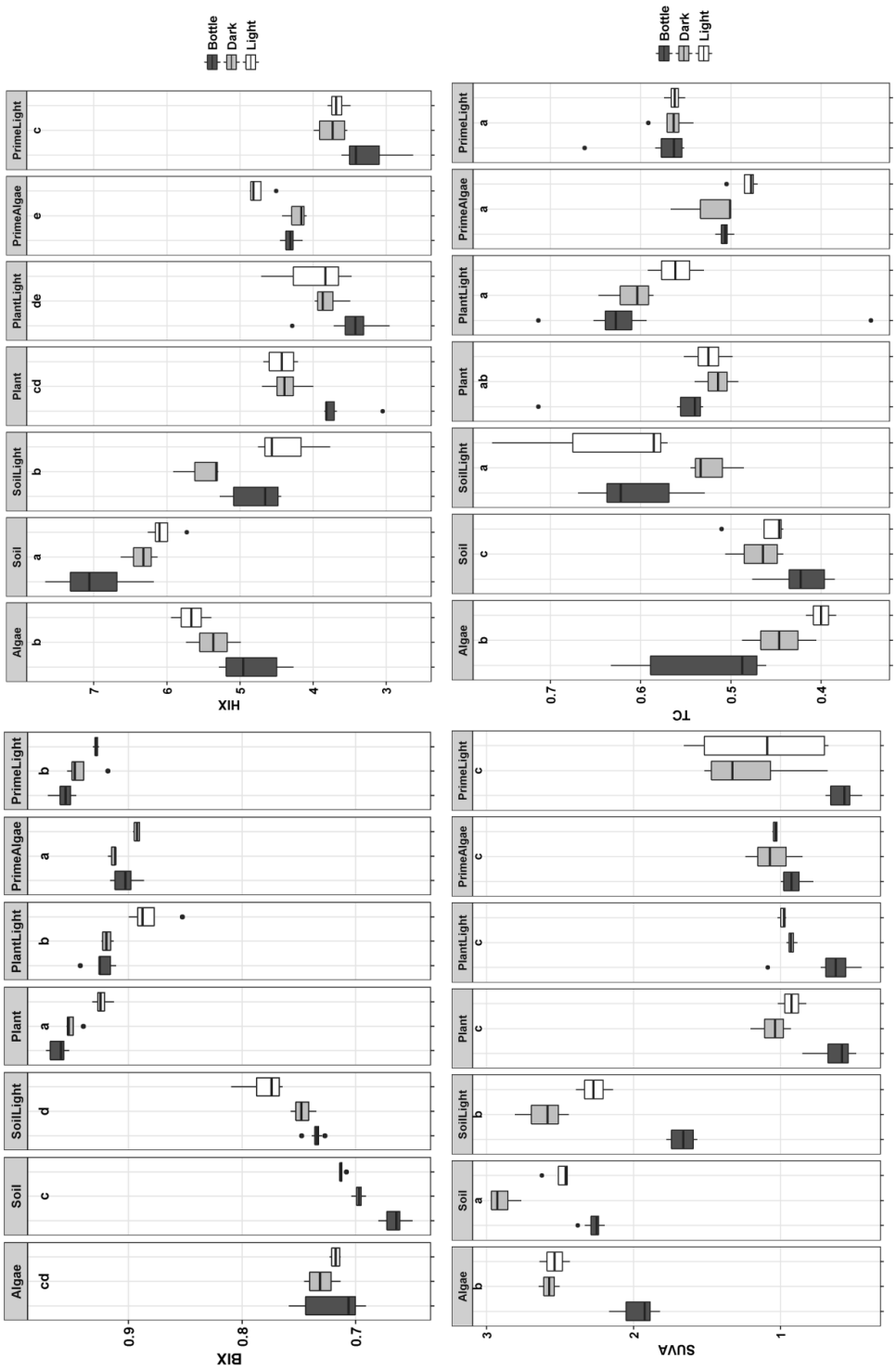
	Plant-light-Soil			**Plant-light-Plant**		
Streams	**2.5%**	**50%**	**97.5%**	**2.5%**	**50%**	**97.5%**
6 hours	**0.39**	**0.90**	**1.43**	**-0.11**	**0.62**	**1.36**
24 hours	-0.39	-0.16	0.06	-0.50	-0.23	0.02
70 hours	0.00	0.00	0.00	-0.09	-0.11	-0.12
Bottle						
6 hours	**-0.31**	**0.36**	**1.02**	**0.50**	**0.99**	**1.51**
24 hours	-0.18	-0.12	-0.07	0.13	-0.05	-0.21
70 hours	-0.10	-0.05	-0.02	0.00	-0.03	-0.05

	Soil-light-Soil			**Soil-light-Plant**		
Streams	**2.5%**	**50%**	**97.5%**	**2.5%**	**50%**	**97.5%**
6 hours	**-0.17**	**1.45**	**3.21**	**-0.67**	**1.17**	**3.13**
24 hours	-0.75	-0.20	0.17	-0.86	-0.28	0.12
70 hours	**-0.19**	**0.05**	**0.15**	-0.28	-0.07	0.03
Bottle						
6 hours	-0.30	-0.24	-0.17	**0.50**	**0.39**	**0.31**
24 hours	**0.02**	**0.03**	**0.04**	**-0.10**	**0.10**	**0.33**
70 hours	**0.00**	**0.01**	**0.02**	**-0.01**	**0.03**	**0.10**

Supplement 5. Comparison of decay rates calculated over 6 hours for light and dark streams.



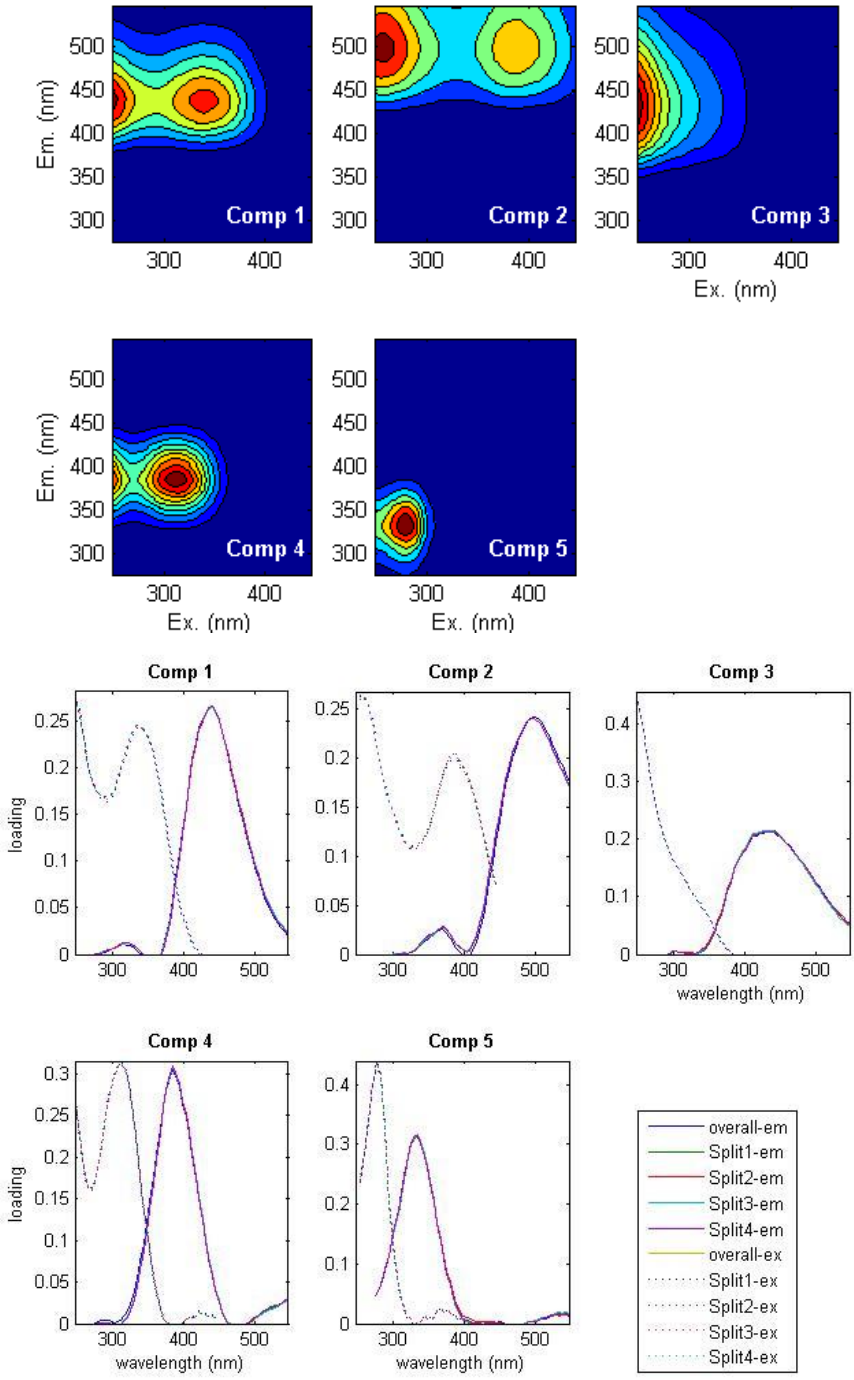
Supplement 6.1. Differences in the BIX, HIX, FI and SUVA between treatments. Letters at the top of panels represent results of the Tukey HSD test.



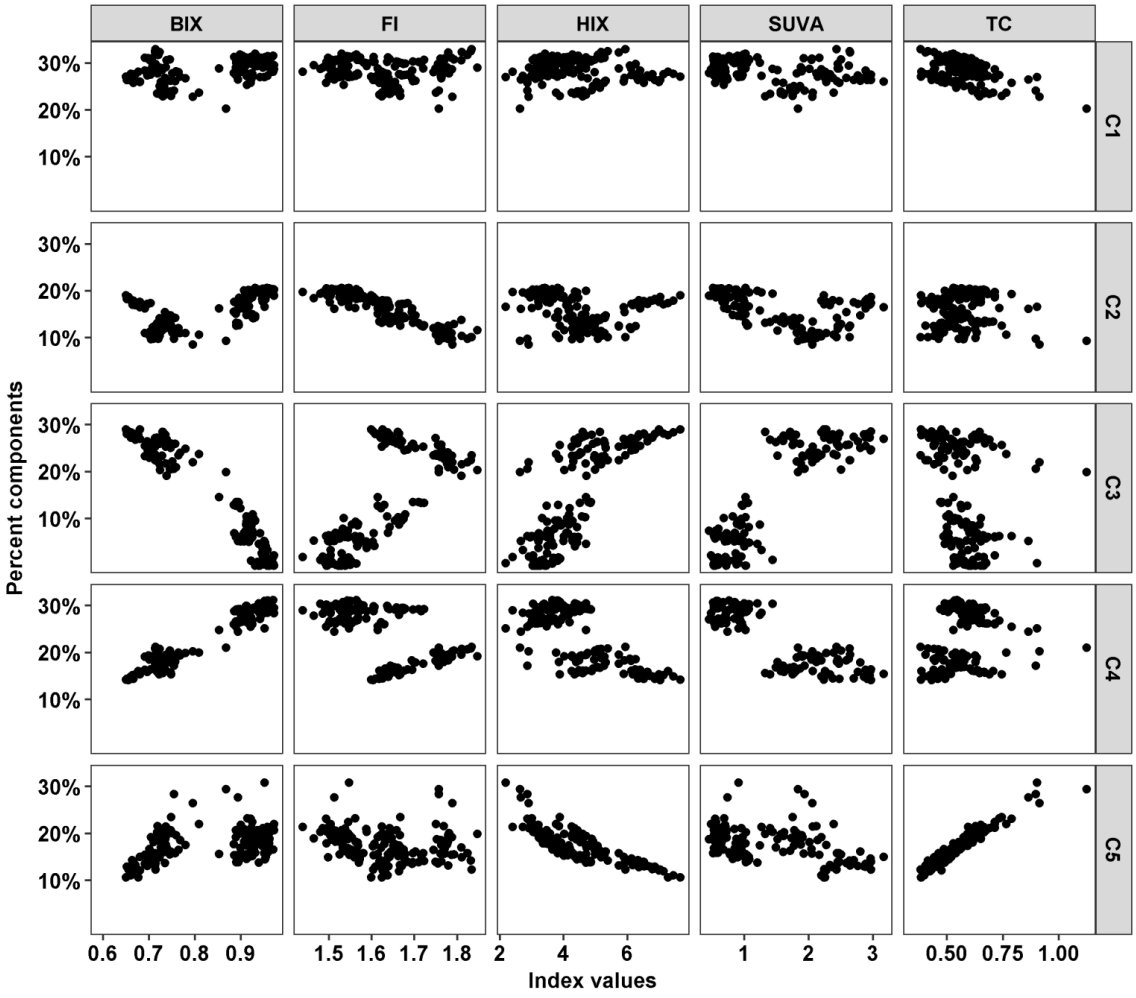
Supplement 6.2. Bayes factor results for 5 linear models that described variation in fluorescence indices. The biological index (BIX), the humification index (HIX), the fluorescence index (FI), the peak T to peak C ratio (TC) and SUVA at absorbance wavelength 254 nm (SUVA), were compared after 70 hours in each experiment. Linear models were also fit using the percent contribution of each component from the PARAFAC model (C1-C5). The higher the Bayes Factor the better the model explained variation in the dependent variable. Bold cells are the highest Bayes Factor in each row.

	Treatment	Treatment + Bottle/Stream	Treatment + Bottle/Stream + interaction	Treatment + Dark/Light/Bottle[b]	Treatment + Dark/Light/Bottle[a] + interaction
BIX	**2.1 E 44**	0.3	0.3	0.2	0.1
HIX	**3.3 E 31**	4.4	1.5 E 3	1.9	2.5 E 4
FI	1.6 E 19	1.5 E 11	9.6 E 11	3.7 E 25	**1.5 E 30**
TC	**9.7 E 8**	1.2	0.55	0.8	1.1
SUVA	7.6 E 31	1.3 E 14	1.2 E 17	2.5 E 47	**2.5 E 49**
Percent C1	**1.6 E 27**	22.6	2.2 E 3	29.6	1.7 E 3
Percent C2	4.4 E 15	4.5 E 8	6.1 E 9	6.6 E 17	**2.7 E 20**
Percent C3	**1.2 E 51**	3.4E 2	3.5 E 13	6.1 E 4	2.2 E 21
Percent C4	**2.4 E 70**	61.3	4.6 E 9	38.1	4.4 E 10
Percent C5	**7.7 E 10**	4.5	21.2	3.1	8.7

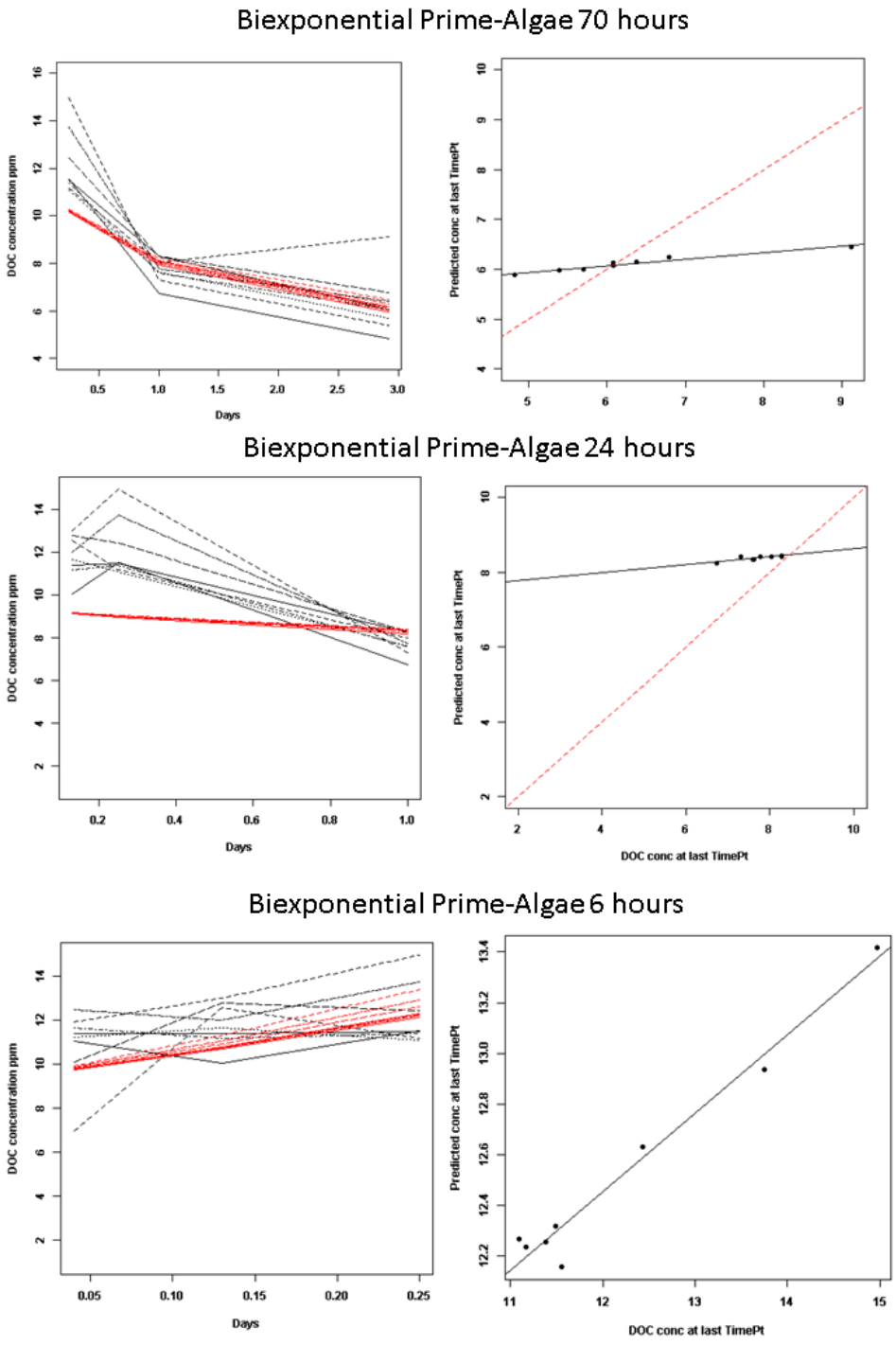
Supplement 7. Spectral characteristics of five components resolved by PARAFAC. Fluorescence intensities are in Raman units (top). Ex = excitation and Em = emission wavelengths. Split-half validation of reverse normalized model that produced components 1 to 5 (bottom).



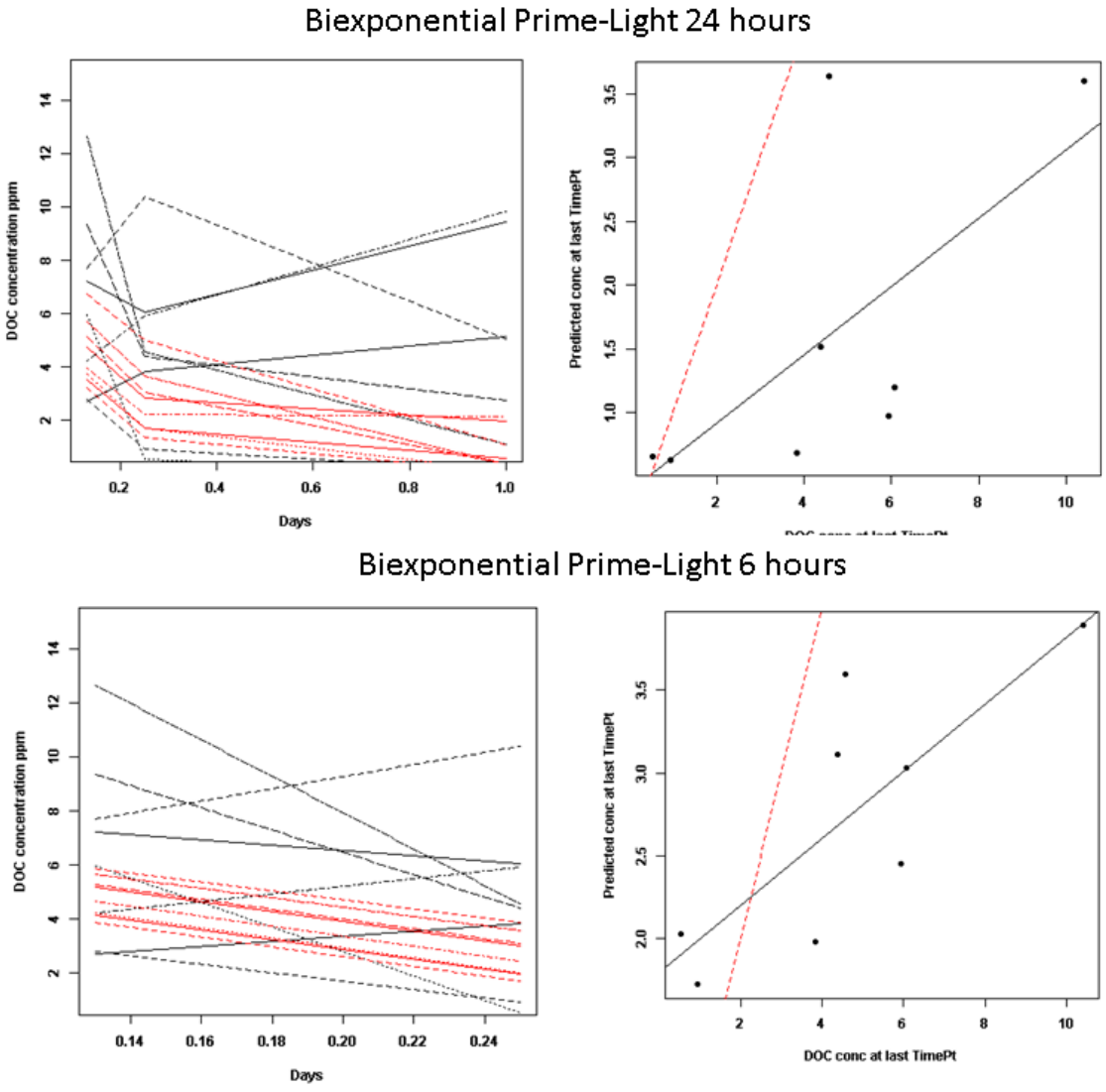
Supplement 8. Pearson's correlations between components and fluorescence indices. All fluorescence samples were included.



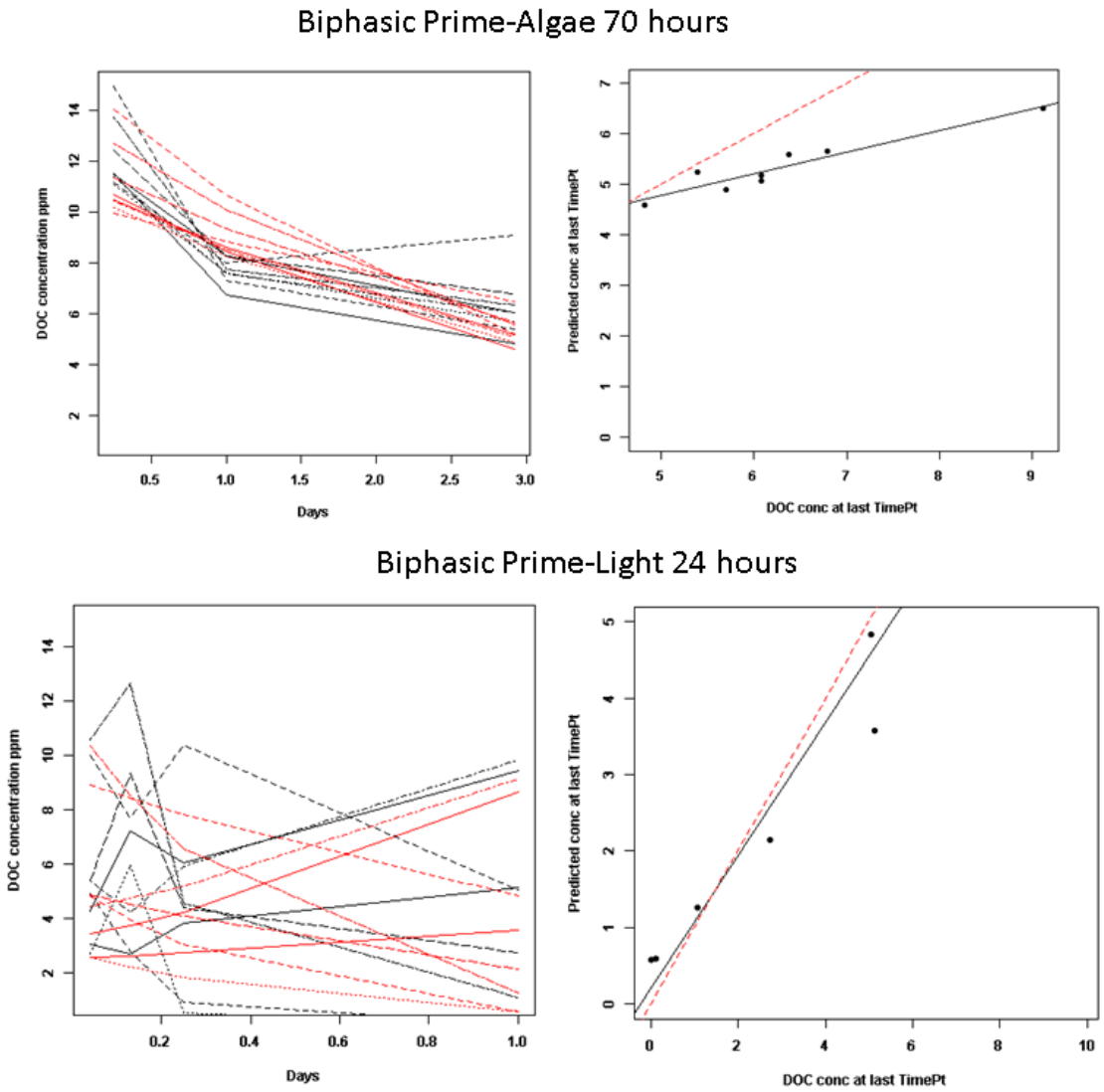
Supplement 9.1. Left panels are modeled biexponential DOC decay (red) and actual DOC decay (black) for the prime algae experiment after 70, 24, and 6 hours. Right panels are the modeled data points in black and the modeled versus actual 1:1 line in red.



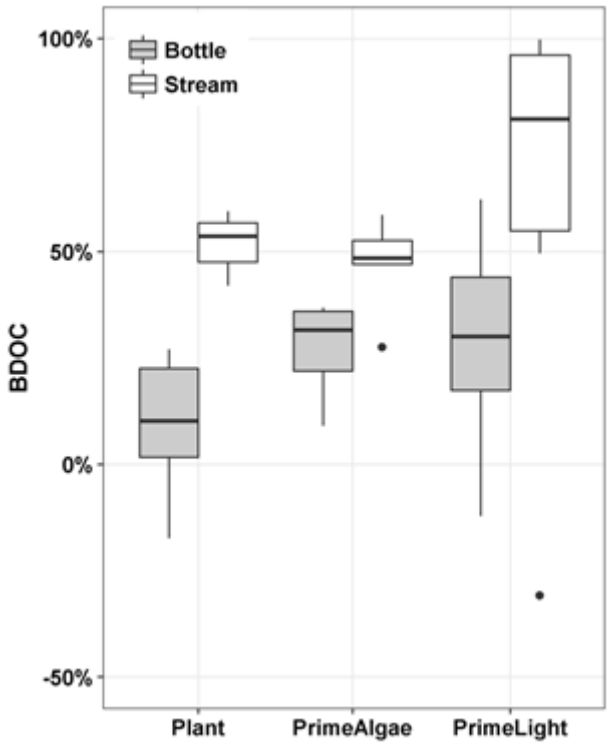
Supplement 9.2. Left panels are modeled biexponential DOC decay (red) and actual DOC decay (black) for the prime-light experiment after 24 and 6 hours. Right panels are the modeled data points in black and the modeled versus actual 1:1 line in red.



Supplement 9.3. Left panels are modeled biphasic DOC decay (red) and actual DOC decay (black) for the prime-algae experiment (top) and prime-light experiment (bottom). Right panels are the modeled data points in black and the modeled versus actual 1:1 line in red.



Supplement 10. Bioavailable DOC (BDOC) in the single-source plant experiment and the 2 priming experiments. More BDOC in priming experiments than in the plant experiment would indicate a possible positive non-additive effect. While BDOC was higher in the streams of the prime-light experiment there was not significant difference across treatments (ANOVA F = 0.94, p = 0.46).



CONCLUSIONS

Despite the difficulty in distinguishing sources of OM in watersheds with mixed land use, I identified major sources of OM to the Jordan River including WWTP effluent, OM derived from Utah Lake, and autochthonous and terrestrial sources. WWTP effluent OM sources were incorporated into FPOM in the Jordan River and had increased influence on FPOM during low flow periods in fall. There were also increased autochthonous sources of CPOM in spring and summer. These results support the hypothesis outlined in the Urban Watershed Continuum (Kaushal and Belt 2012) that urbanization can increase the proportion of autochthonous sources of OM and in effect, replace terrestrial OM with more labile sources of OM.

I did not identify any land cover metrics that correlated with OM source or composition across multiple watersheds. The greatest differences in OM were due to the influence of WWTP effluent, OM sources from Utah Lake, and human activity within federally designated national forests. None of these human activities were accounted for in land cover categories of the National Land Cover Dataset. Further study is needed to understand the influence of landcover on OM source and composition, especially in arid regions which have different flow regimes than temperate systems, and are influenced by large lakes and reservoirs within multiple land cover types. While some previous studies have specifically compared WWTP OM to other OM sources within the landscape (Wassenaar et al. 2010, Gucker et al. 2011, Duan et al. 2014), I think more OM studies conducted in watersheds with wastewater effluent should directly incorporate OM samples from WWTPs into their sampling regimes. Likewise, researchers of wastewater treatment engineering and biogeochemistry are disconnected from sociology, biology and

ecology researchers, areas of study that all inform watershed management. Increased collaboration across disciplines could rapidly advance our understanding of the sources and composition of OM within a matrix of land cover, and the ecological impacts of differences in land cover on rivers.

It is important to identify and quantify the sources and lability of OM in rivers to inform management decisions aimed at OM load and associated pollutant reduction. Here, I outline how OM source identification can help reduce OM loads of either autochthonous or terrestrial sources. Possible strategies to reduce terrestrial OM loads include geomorphic alterations of riparian and benthic habitat to increase OM retention time within a reach. Greater habitat heterogeneity through the addition of bio swales, large benthic substrates (e.g. boulders), and wood additions may increase OM retention and/or reduce benthic embeddedness, consequently increasing hyporheic exchange (Hester and Gooseff 2010). Greater retention and hyporheic exchange increase the amount of habitat and time available for microbial OM processing, thereby reducing OM export from a reach (Wollheim et al. 2018). However, geomorphic alterations should be considered with extreme caution because reach-scale restoration studies suggest they are not effective at improving ecosystem function (Bernhardt and Palmer 2011).

To reduce autochthonous OM sources, effective reduction strategies must occur at the multi-watershed scale. As is the case with the Jordan River, the primary source of problematic OM is from Utah Lake, which receives water from 6 other major watersheds (Psomas 2009). Reduced inorganic nutrients could reduce in-stream primary production. Potential nutrient reduction strategies include updating stormwater infrastructure to reduce urban and agricultural runoff during storms, and encouraging best management

practices when applying fertilizer in urban and agricultural areas (Parr et al. 2016). Other possible, but costly, nutrient reduction strategies in urban watersheds are wastewater treatment facility updates, such as upstream filtration for membrane treatment and UV disinfection (Henderson et al. 2009).

However, replacing infrastructure is expensive, and changing human behavior is hard. I think future research to reduce OM loads in the Great Salt Lake Basin should focus on how reservoirs and diversions have altered the natural flow regime (Miller et al. 2018, Wurtsbaugh et al. 2017). A recent study identified consumptive use of water in the Great Salt Lake Basin as the cause of reduced lake levels (Wurtsbaugh et al. 2017). This implies that water available to dilute OM loads is lacking. A study to assess the effect of reservoirs and diversions on river flow regimes before and after impoundment installations could reveal alterations to organic matter source and transport dynamics. It is not realistic to remove dams and diversions, but knowledge of the flow regimes prior to impoundment could outline strategies to return portions of the watershed to their natural flow regimes. Then, management strategies could be specifically tailored to flow regimes and problematic OM for each watershed. For example, if floodplain areas were lost, perhaps constructed wetlands would help simulate ecological services provided by floodplains.

In addition to knowledge of source identity and quantity, understanding OM bioavailability can directly inform regional and global models of organic carbon cycling (Cole et al. 2007, Raymond et al. 2013). Decay rates for terrestrial sources of DOM span 10 orders of magnitude due to variation in OM substrate, and methods used to quantify dissolved organic carbon uptake (Cory and Kaplan 2012, Mineau et al. 2016). Likewise,

microbial transformation rates of labile DOM sources, especially naturally derived labile DOM, are poorly constrained. Uncertainty of DOM transformation rates, combined with unknown proportions of labile OM within the DOM pool, has limited robust estimates of inorganic carbon evasion to the atmosphere from rivers (Wollheim et al. 2015).

Autochthonous and terrestrially derived DOM decay rates from this study can inform future studies that aim to constrain OM transformation rates in rivers. DOM reactivity and removal from rivers has been described as moderate (Wollheim et al. 2015) to high (Hall et al. 2016). Uncertainty of DOM removal rates is derived from the portion of the DOM pool for which removal is measured. For example, removal rates are calculated for the entire DOM pool (Hall et al. 2016 and references), the terrestrial portion (Mineau et al. 2016), or fractions separated by molecular weight (Skully et al. 2004) or hydrophobicity (Wollheim et al. 2015). My results emphasize the need to better quantify both fast and slow decaying OM pools in rivers. Many measures of OM decay are based on bioassays which likely underestimate OM demand in rivers. Direct measurements of known sources of DOM in an experimental setting can help define the lability of DOM along a continuum of minutes to millennia.

I have highlighted that the study of OM source, composition, and quality can inform both watershed management and the study of carbon cycling at the watershed scale. The management implications I discussed focused on source identification of OM loads such as labile versus semi-labile sources of autochthonous, anthropogenic, or terrestrial inputs. It is important to note these are water quality issues largely faced by developed nations that have wastewater treatment infrastructure, while many developing nations do not treat wastewater. I also believe estimates of OM demand for

autochthonous and terrestrial DOM from this study may inform models of OM transformation and carbon dioxide evasion to the atmosphere. But, I emphasize that further study is needed to standardize metrics and definitions of OM demand across disciplines, and to identify measures of anthropogenic influence within watersheds that can predict OM composition at a specified spatial scale.

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Wassenaar, L., J. Venkiteswaran, S. Schiff, and G. Koehler. 2010. Aquatic community metabolism response to municipal effluent inputs in rivers quantified using diel 18O values of dissolved oxygen. Canadian Journal of Fisheries and Aquatic Sciences 67:1232-1246.

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Wollheim, W., S. Bernal, D. Burns, J. Czuba, C. Driscoll, A. Hansen, R. Hensley, J. Hosen, S. Inamdar, and S. Kaushal. 2018. River network saturation concept: factors influencing the balance of biogeochemical supply and demand of river networks. Biogeochemistry: doi:10.1007/s10533-018-0488-0.

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JULIE KELSO

Utah State University, Department of Biology, Ph.D. Ecology
juliekelso.weebly.com

EDUCATION

Utah State University, Logan, UT - Ph.D., Biology and Ecology
2013 - present

University of Central Arkansas, Conway, AR - M.S. Biology
2010 - 2012

Tulane University, New Orleans, LA - B.A. Environmental Policy
2002 - 2005

RESEARCH AND RELATED EXPERIENCE

Research and Teaching - Utah State University, Logan, UT……Jan-13 to Dec 18

- Collected and analyzed water quality metrics of the Jordan River to for the Utah Division of Water Quality to develop recommendations for Total Maximum Daily Load allocations of phosphorus and organic matter
- Developed research questions and managed all water quality data collected for the NSF funded project, iUTAH – *innovative* Urban Transitions and Aridregion Hydro-sustainability
- Responsibilities included sampling of surface waters for nutrients and other water quality constituents, QA-QC of water quality data for iUTAH database, maintenance and sample analysis of Shimadzu carbon and total dissolved nitrogen analyzer and Aqualog spectrofluorometer
- Teaching assistant for human anatomy, elementary microbiology, and introductory biology

Science Reporter - Utah Public Radio, Logan, UT……...Jan-17 to Dec-17

- Researched, wrote, recorded, mixed audio and published online content for weekly news segment on science related topics in Utah
- Feature writer on issues related to global climate change and water

Research and Teaching - University Central Arkansas, Conway, AR….Aug-10 to Dec-12

- Monitored macroinvertebrate communities in 17 streams in north central Arkansas for potential effects of natural gas drilling
- Installed and maintained photo-monitored gages in 6 stream reaches to characterize intermittent stream hydrology
- Compiled and analyzed macroinvertebrate density and biomass data for 3-year sampling effort
- Collected storm samples of total and volatile suspended solids from siphon samplers
- Teaching assistant for non-majors biology lab

PROFESSIONAL EXPERIENCE

Biological Technician
Wildlife Conservation Society, Prudhoe Bay, AK…….Apr-10 to Jun-10

- Banded migrating shorebirds for research investigating the effect of gas drilling on nest predation
- Assisted with game camera monitoring of nest predators

Assistant Outreach Coordinator
Alliance for the Great Lakes, Chicago, IL…….Apr-08 to Sep-08

- Helped recruit and coordinate volunteers in Illinois and Indiana for annual Great Lakes beach cleanup in collaboration with the Ocean Conservancy's international beach cleanup day
- Organized and conducted three team leadership trainings for principal volunteers
- Maintained an online database to track volunteers and citizen science data
- Promoted event to media outlets including web, radio, print, and television

Noxious Weed Inventory Intern
U.S. Forest Service, Salmon, ID……..May-06 to Nov-06

- Inventoried wilderness sites for US Forest Service noxious week inventory program
- Used ESRI ArcPad and GIS to document and map noxious weed sites.

Fisheries Intern
U.S. Army Corps of Engineers, Bonneville Lock and Dam, OR Feb-06 to May-06

- Monitored sea lion predation of fishes from Bonneville Dam
- Identified predated fishes including shad, lamprey, Chinook, or Steelhead

Wildland Fire Prevention Intern
Bureau of Indian Affairs, Cloquet, MN Jun-05 to Nov-05

- Assessed over 1000 homes for risk to wildland fire on the Fond du Lac Reservation
- Developed and implemented wildland fire prevention curriculum for grades K-5

PUBLICATIONS

Austin, J.B., **J. E. Kelso**, M. A. Evans-White, S.A. Entrekin. 2018. Can high volume hydraulic fracturing effects be detected in large watersheds? A case study of the South Fork Little Red River. Current Opinion in Environmental Sciences & Health. DOI:10.1016/j.coesh.2018.04.003

Kelso, J.E. and S.A. Entrekin. 2017. Intermittent and perennial macroinvertebrate communities had similar richness but differed in species trait composition depending on flow duration. Hydrobiologia. DOI:10.1007/s10750-017-3393

Epstein, D.M., **J.E. Kelso**, and M.A. Baker. 2016. Beyond the urban stream syndrome: Organic matter budgets for diagnostics and restoration of an impaired urban river. Urban Ecosystems. 19:1041-1061. DOI:10.1007/s11252-016-0556

Kelso, J.E. and M.A. Baker. 2015. Filtering with a drill pump: an efficient method to collect suspended sediment and filtrate. Journal of American Water Resources Association. 52:1536-1541. DOI:10.1111/1752-1688.12368

PUBLISHED DATASETS

Kelso, J., M.A. Baker (2017). Dissolved organic matter spectrofluorometric properties along a mountain to urban gradient in North East Utah, HydroShare, http://www.hydroshare.org/resource/7722d73be4b348a9ad874fe29086c1fb

Kelso, J., M.A. Baker (2017). FPOM and DOM isotope values, HydroShare, http://www.hydroshare.org/resource/4eb5c9c871e34aa4ae6951ce6d15020d

PRESENTATIONS

Kelso, J., and M.A. Baker. Characterization of organic matter sources within a matrix of land use in Northeast Utah. Ecological Society of America. August 2017.

Kelso, J., E.Rosi, and M.A. Baker. Light-degraded dissolved organic matter increased the decay rate of terrestrial organic matter in experimental streams. Society for Freshwater Science Meeting. June 2017.

Kelso, J., and M.A. Baker. Characterization of dissolved organic matter sources along a mountain to urban gradient. Society for Freshwater Science Meeting. May 2016.

Kelso, J., D.M. Epstein, and M.A. Baker. Characterization of riverine organic matter in an urban landscape. Society for Freshwater Science Meeting. May 2015.

Epstein, D.M., J. Kelso and M.A. Baker. Organic matter budget for an impacted urban river stream. Society for Freshwater Science Meeting. May 2014.

Kelso, J., D.M. Epstein, and M.A. Baker. Characterization of sources of organic matter to an urban river. Society for Freshwater Science Meeting. May 2014.

Kelso, J., D.M. Epstein, and M.A. Baker. Characterization of sources of organic matter to the Jordan River, UT. Symposium on Urbanization and Stream Ecology. May 2014.

Musto, A., S.A. Entrekin, N. Jensen, J.E. Kelso, B. Haggard, C. Gallipeau, E. Inlander, and L.Massey, The relationship between land disturbance and trace elements in streams of north-central Arkansas. Society for Freshwater Science Meeting. May 2013.

Kelso, J.E. and S.A. Entrekin. Use of the hyporheic zone as refuge by macroinvertebrates in an intermittent and perennial Ozark stream. Society for Freshwater Science Meeting. May 2013.

Kelso, J.E. and S.A. Entrekin. Macroinvertebrate communities in intermittent and perennial Ozark streams. Great Plains Limnology Association. October 2012.

Kelso, J.E., and S.A. Entrekin. Macroinvertebrate communities in intermittent and perennial Ozark streams. Society for Freshwater Science Meeting. May 2012.

POSTERS

Kelso, J., M.A. Baker. Characterization of riverine organic matter within a matrix of land use in northeast Utah. American Geophysical Union, December 2017.

Gabor, R., R.M. Smith, J.F. Shah, J.E. Kelso, M.A. Baker, P.D. Brooks. The urban watershed as a transformer of dissolved organic matter chemistry. American Geophysical Union, December 2017.

Kelso, J., D. Epstein, M.A. Baker. Light-degraded dissolved organic matter may have increased the decay rate of terrestrial organic matter in experimental streams. Utah State University, Spring Runoff Conference. March 2017.

Kelso, J., D. Epstein, M.A. Baker. Characterization of dissolved organic matter along a mountain to urban gradient. Utah State University, Spring Runoff Conference. March 2016.

Capito, L.M., J.E. Kelso, M.A. Baker. Diving into Utah's water with spectrofluorometry. Utah State University, Undergraduate Research Symposium. December 2015.

Entrekin, S.A., B. Austin, J.E. Kelso, S. Polaskey, A. Musto, and M. Evans-White. Does hydrology and activity from natural gas development interact to alter quality of communities in small streams? Society for Freshwater Science Meeting. May 2015.

Butterfield, A., J.E. Kelso, M.A. Baker. Photodegradation of dissolved organic matter in the Jordan River, UT. National Conference on Undergraduate Research, April 2015.

Kelso, J., D. Epstein, M.A. Baker. Spectrofluorometric and isotopic characterization of organic matter along a gradient of urban land use. Utah State University, Spring Runoff Conference. March 2015.

Kelso, J. and M.A. Baker. Characterization of sources of organic matter to an urban river. Utah State University, Spring Runoff Conference. April 2014.

Kelso, J. and S.A. Entrekin. Macroinvertebrate community structure in intermittent and perennial Ozark streams. UCA Student Research Symposium. April 2012.

Kelso, J. and S.A. Entrekin. Does refuge affect macroinvertebrate communities in intermittent Ozark streams? Society for Freshwater Science Meeting. May 2011.

Kelso, J. and S.A. Entrekin. Refuge use by macroinvertebrates in intermittent Ozark streams. University of Central Arkansas College of Natural Sciences and Mathematics Symposium. April 2011.

STUDENT MENTORING

Lindsay Capito, Utah State University, Logan, Utah – 2015-2016

- Trained in analytical laboratory methods including spectrofluorometric analysis of dissolved organic matter, chlorophyll *a*, isotope sample preparation, and volatile suspended solids analysis
- Assisted with experiment at the Cary Institute of Ecosystem Studies Experimental Stream Facility in July 2016

Simone Jackson, University of Utah, Salt Lake City – Summer 2015

- Trained to collect aquatic macroinvertebrates and periphyton for stable isotope analysis
- Helped identify macroinvertebrates to family
- Helped summarize data for poster presented at the Society for Freshwater Science meeting

Andrew Butterfield, Westminster College, Salt Lake City – Summer 2014

- Conducted an experiment on the Jordan River in which Andrew collected, analyzed and presented results at the National Conference on Undergraduate Research 2015

Chelsea Miller, Carolyn Pollard, David Hiltenbrand, Loren Biggs, University of Central Arkansas – 2011-2012

- Trained and managed undergraduate student workers hired to sort and identify macroinvertebrates and process organic matter biomass samples.
- Lead macroinvertebrate sampling field campaigns in headwater streams.

GUEST LECTURER

BIO 1010 Science for the Citizen, Ecosystem Ecology, April 21-24, 2016
BIO 2220 Ecology, Community Structure, November 7, 2017

GRANTS AND AWARDS

USU Student Association Enhancement Award Jan 2017 – $4,000
USU Dissertation Enhancement Award Jan 2016 – $10,000
USU Ecology Center Graduate Research Award, Apr 2015 – $3,700
Society for Freshwater Science, Mulholland Fund Research, Mar 2015 – $1000
USU Research and Graduate Studies Student Travel Award, Feb 2015 – $300
USU Ecology Center Graduate Research Award, Apr 2014 – $4000
Center for Woman and Gender Graduate Student Travel Award, Apr 2013 – $500

UCA University Research Council Student Research Grant, Sep 2011 – $800
Arkansas Game and Fish Conservation Scholarship, Jul 2011 – $1000
UCA Travel Award, Feb 2010 – $500
Outstanding Student Poster, Spring Runoff Conference, Logan, UT, Apr 2014

MEMBERSHIPS AND SERVICE

American Geophysical Union (2017-2018)
Biology Graduate Program Committee – Student representative (Jan 2014- Aug 2015)
USU Ecology Center Seminar Series Committee – (2013-2015)
American Water Works Association (2013-2014)
Society for Freshwater Science (2010 - present)
    Merchandise Committee Chair – 2017 Annual Meeting
American Fisheries Society (2010-2012)
Ecofest Volunteer (2010-2012)
    Annual public outreach event for city of Conway, AR
Backyard water quality sampling workshop, Clinton, AR – 2010

REVIEWER

Hydrobiologia
Science of the Total Environment

PROFESSIONAL DEVELOPMENT

Alan Alda Center for Communicating Science Workshop, Logan, UT, Oct 2016
Software Carpentry Workshop, Logan, UT, Mar 2015
Dissolved Organic Matter Fluorescence Workshop, Boulder, CO, Jul 2014
One-dimensional Transport with Inflow and Storage (OTIS) solute transport workshop, Portland, OR, May 2014
Getting Started as a Successful Proposal Writer and Academician, Logan, UT, Feb 2013
Aquatic GIS Workshop, St. Louis, MO, Jun 2011
Wilderness First Aid, Salmon, ID, Jun 2006