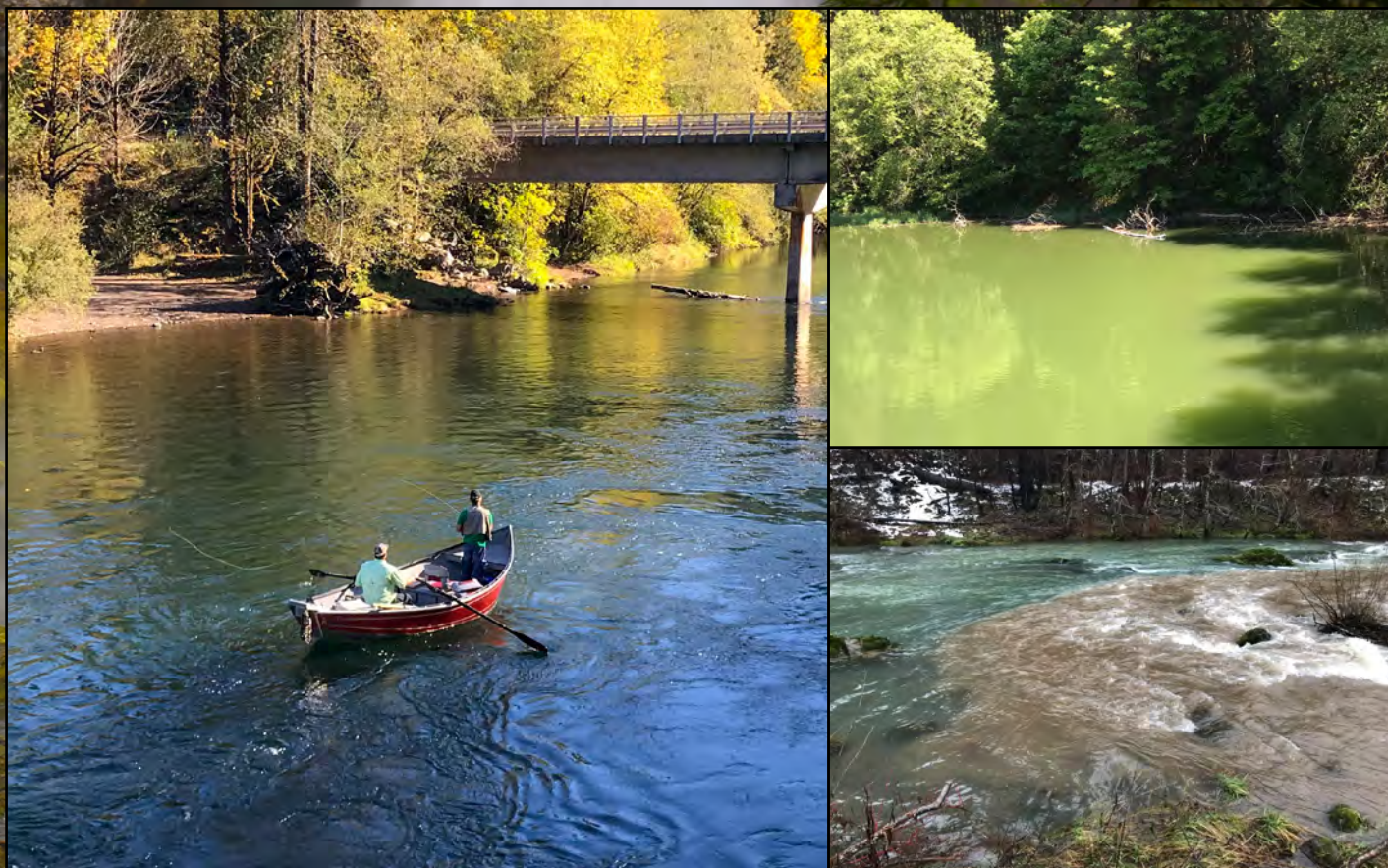


Prepared in Cooperation with Eugene Water & Electric Board

Sources and Characteristics of Dissolved Organic Carbon in the McKenzie River, Oregon, Related to the Formation of Disinfection By-Products in Treated Drinking Water



Scientific Investigations Report 2022–5010

U.S. Department of the Interior
U.S. Geological Survey

Cover:

Background:

Sahalie Falls pouring into the McKenzie River, near Eugene, Oregon. Photograph by David Donahue, Eugene Water & Electric Board, December 2019.

Foreground:

Left inset: McKenzie River at Finn Rock Landing, Lane County, Oregon. Photograph by David Donahue, Eugene Water & Electric Board, October, 2017. Right inset top: *Dolichospermum* bloom in Blue River Lake, Lane County, Oregon. Photograph by David Donahue, Eugene Water & Electric Board, December 2019, May, 2018.

Right inset bottom: Confluence of Blue River (left) and Simmonds Creek (right), Lane County, Oregon. Photograph by David Donahue, Eugene Water & Electric Board, January, 2022.

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Conversion Factors

U.S. International System of Units to U.S. customary units

Multiply	By	To obtain
Length		
mile (mi)	1.609	kilometer (km)
yard (yd)	0.9144	meter (m)
Area		
square mile (mi ²)	2.590	square kilometer (km ²)
Flow rate		
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as
 $^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$.

Datum and Other Supplemental Information

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L).

Absorbance is reported in absorbance units (AU) obtained directly from the instrument.

Abbreviations and Acronyms

AU	absorbance units
BQ	benchmark quotient
Br ₂ AA	dibromoacetic acid
BrAA	bromoacetic acid
C1, C2	PARAFAC component 1 (C1, C2, C3, etc.)
CHCl ₃	chloroform
DBP	disinfection by-product
DBP FP	disinfection by-product formation potential
DCAA	dichloroacetic acid
DOC	dissolved organic carbon
DOM	dissolved organic matter
DWTP	drinking-water treatment plant
EEM	excitation-emission matrix
EPA	U.S. Environmental Protection Agency
EWEB	Eugene Water & Electric Board
ex	excitation wavelength
em	emission wavelength
fDOM	fluorescent dissolved organic matter
FI	fluorescence Index
HAA	haloacetic acid
HAA5	total of five regulated haloacetic acids
HIX	humic index
MCAA	monochloroacetic acid
MCL	maximum contaminant level
NMDS	nonmetric dimensional scaling ordination
NLCD	National Land Cover Database
NWQL	U.S. Geological Survey National Water Quality Laboratory
PARAFAC	parallel factor analysis
Pct_C1	percent PARAFAC model component C1 (Pct_C2, Pct_C3, etc.)
POC	particulate organic carbon
POM	particulate organic matter
QA	quality assurance
RU	Raman units
SUVA ₂₅₄	specific ultraviolet absorbance at 254 nanometers

TA	Test America Laboratories
TCAA	trichloroacetic acid
THM	trihalomethane
THM4	total of four regulated trihalomethanes
USGS	U.S. Geological Survey
UVA ₂₅₄	ultraviolet absorbance at 254 nanometers
β:α	Freshness Index

Sources and Characteristics of Dissolved Organic Carbon in the McKenzie River, Oregon, Related to the Formation of Disinfection By-Products in Treated Drinking Water

By Kurt D. Carpenter¹, Tamara E. Kraus¹, Angela M. Hansen¹, Bryan D. Downing¹, Jami H. Goldman¹, Jonathan Haynes¹, David Donahue², and Karl Morgenstern²

Executive Summary

This study characterized the concentration and quality of dissolved organic carbon (DOC) in the McKenzie River, a relatively undeveloped watershed in western Oregon, and its link to forming disinfection by-products (DBPs) in treated drinking water. The study aimed to identify the primary source(s) of DOC in source water for the Eugene Water & Electric Board's (EWEB) conventional treatment plant on the McKenzie River near river mile 11, upstream of Hayden Bridge. The two classes of regulated compounds examined—trihalomethanes (THMs) and haloacetic acids (HAAs)—form when organic carbon in raw source water reacts with chlorine and (or) bromine during water treatment.

The objectives of the study were to:

- (1) characterize the amount and quality of DOC in the McKenzie River and select tributaries during storms;
- (2) identify the most common types of carbon using UV-vis spectroscopy and other methods;
- (3) evaluate optical properties for predicting DBP precursors in surface water; and
- (4) identify land cover classes or vegetation types that may be important sources of organic carbon and DBP precursors in EWEB's source water.

Eleven storms were sampled synoptically in upstream-to-downstream fashion to provide a “snapshot” of water quality conditions at four sites on the McKenzie River from Frissell Bridge (6 miles downstream from Trail Bridge Reservoir) to the EWEB water treatment plant at Hayden Bridge and nine contributing tributaries. Storms included late summer and early autumn “first flush” events and late autumn, winter, and spring storms spanning a range in streamflows from 3,000 to 26,000 cubic feet per second as measured in the main stem McKenzie River at the EWEB water intake.

Water samples were analyzed for DOC concentrations and optical properties (fluorescence and ultraviolet absorbance [UVA]) across a range of wavelengths to characterize the quantity and quality of dissolved organic matter (DOM) in the McKenzie River at the drinking water intake and upstream locations. Paired sets of source and finished water samples were collected at the EWEB treatment plant to identify DOC quality parameters in raw source water that might predict DBP concentrations in finished drinking water.

DOC concentrations were relatively low in the McKenzie River (0.4–3 milligrams per liter [mg/L]; average 1.5 mg/L) but much higher in the tributaries. The highest DOC concentrations occurred during “first flush” storms in October 2012 and September 2013; the highest value (16 mg/L) was measured at the 52nd Street stormwater outfall ([fig. 1](#)). The average DOC concentration in the lower basin-tributaries was 3.8 mg/L; three middle basin tributaries—Quartz, Gate, and Haagen Creeks, which drain private forestland with less coniferous forest compared with other higher elevation tributaries—had slightly lower average DOC concentrations (2.8 mg/L). These middle-basin watersheds may be important sources of DOC and DBP precursors to the McKenzie River, even more so than the lower basin tributaries, depending on their flows (and loads). This is particularly true after the September 2020 Holiday Farm fire, which burned much of this area.

DOC concentrations increased 68 percent in the McKenzie River between the uppermost reference site at Frissell Bridge and Vida; this includes drainage from Quartz Creek, Blue River Lake and Cougar Reservoir, which all contributed DOC to the main stem. In contrast, the lowermost tributaries draining most of the agricultural and urban land did not have a large effect on DOC in the McKenzie River despite their higher DOC concentrations because of their presumed relatively low streamflows and, consequently, DOC loads. Apart from the continuous flow monitors in the McKenzie River and some tributaries (Blue River and South Fork McKenzie River, and streamflow at Hayden Bridge and Vida, Camp Creek and some other locations), streamflow was not assessed during sample collection for this study. This lack of streamflow data precludes a detailed analysis of loads, which is discussed in the future studies section.

¹U.S. Geological Survey

²Eugene Water & Electric Board

2 Sources and Characteristics of Dissolved Organic Carbon in the McKenzie River, Oregon

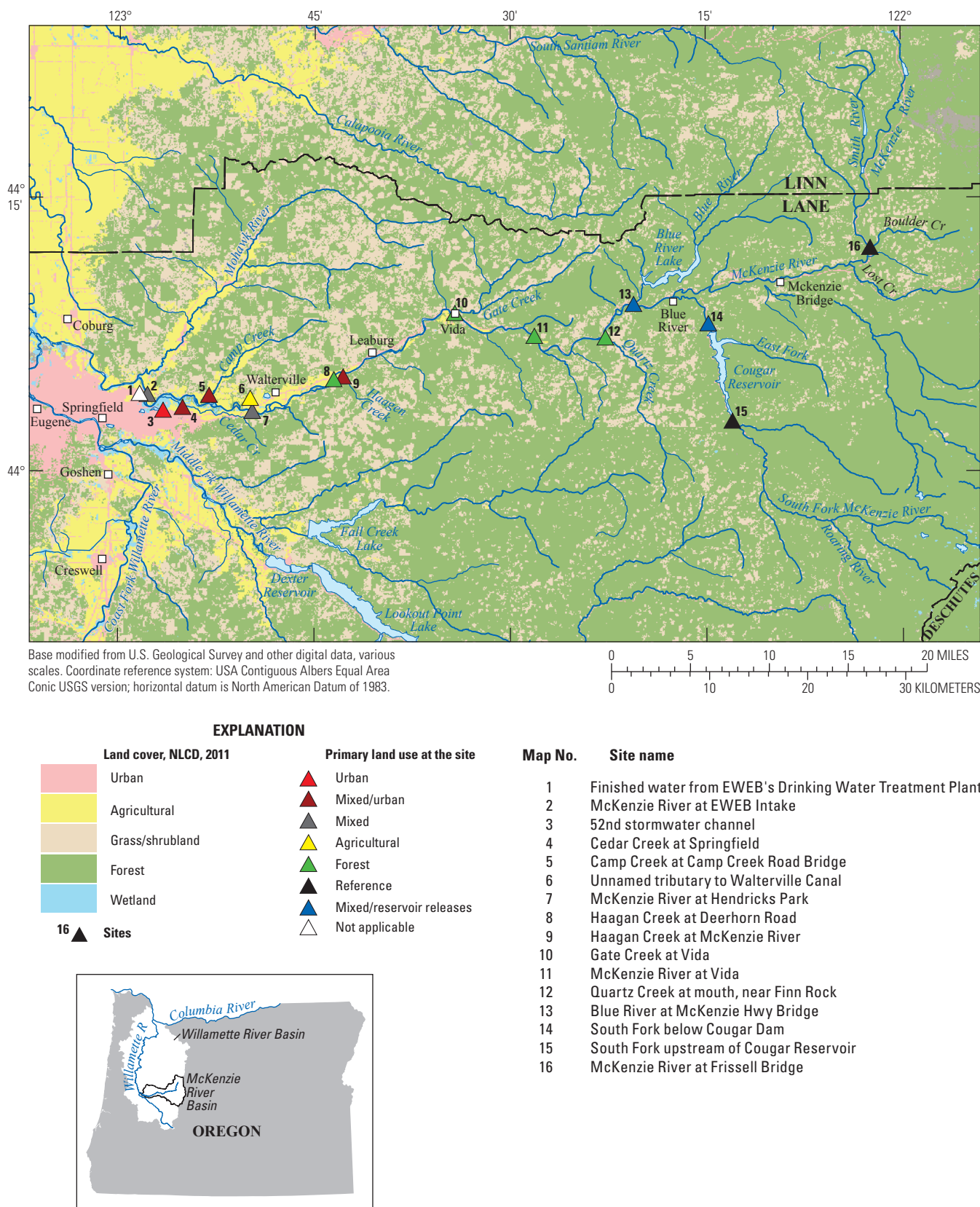


Figure 1. Land cover and site locations, McKenzie River Basin, Oregon. NLCD, National Land Cover Database.

All DBP concentrations in finished drinking water were less than EPA maximum contaminant levels (MCLs) of 0.080 mg/L for the four trihalomethanes (THM4) and 0.060 mg/L for five haloacetic acids (HAA5). During the 11 storm sampling events the maximum summed concentrations were about 0.040 mg/L for both THM4 and HAA5. Compliance monitoring samples, collected separately by EWEB, yielded some higher concentrations—0.046 mg/L THM4 and 0.047 HAA5—during the December 2012 storm. The corresponding benchmark quotient (BQ) values, which indicate how close a measured DBP concentration is to the MCL, were 0.58 and 0.78, respectively, for THM4 and HAA5. Compared with a similar 2007–08 McKenzie River study that did not target storm events, concentrations of THM4 and HAA5 in finished water were 68 percent and 33 percent higher, respectively, during the current study.

Due to the high dilution rates in the McKenzie River main stem, many of the individual fluorescence excitation-emission measurements were low (<0.1 Raman units) and approached analytical detection limits. Parallel factor analysis (PARAFAC) resulted in a five-component model (C1–C5) that represents five unique organic fluorophores. Components C1, C2, and C3 represent DOM associated with soil-derived, humic-like, more degraded organic matter. In contrast, components C4 and C5 represent “fresher” DOM, derived from terrestrial and aquatic plants, including algae and cyanobacteria that are common in the McKenzie River and its tributaries and reservoirs. The fluorescence data and PARAFAC modeling suggest that most of the DOC in the McKenzie River originated from terrestrial sources (primarily components C1 and C2). The largest increases in DOC in the main stem occurred in the reach upstream of Vida, from inflows by Quartz Creek, Blue River, South Fork McKenzie River, and other tributaries.

Concentrations of DBPs in EWEB’s finished drinking water were positively correlated with DOC concentrations in raw source water (THM4, $p < 0.05$; HAA5, $p < 0.01$) for paired samples collected 12–24 hours apart. DOC concentrations were significantly positively correlated ($p < 0.001$) with laboratory-based fluorescent dissolved organic matter (fDOM) measurements, suggesting fDOM as a useful parameter for monitoring and predicting DOC concentration in surface water and DBP concentrations in finished water.

Of all the PARAFAC components in surface water, C5 had the highest correlations with DBPs in finished water ($\rho = 0.77$ – 0.84 , $p < 0.01$), followed by components C1 and C2 ($\rho = 0.75$ and 0.71 , respectively, $p < 0.01$). This C5 carbon is associated with recently produced DOM, possibly from decomposed terrestrial and aquatic vegetation. Model loadings of these three components were considerably higher in the sampled tributaries relative to the main stem McKenzie River, with most of the observed increases in the main stem apparent at Vida. This points to Quartz Creek or other tributaries in the reach between Frissell Bridge and the sampling site near Vida (South Fork McKenzie and Blue Rivers) as potentially key contributors of DOM source material that leads to the production of DBPs in treated drinking water. A limited load analysis

showed that the reservoirs contributed 8–37 percent of the instantaneous DOC loads observed at Vida at the time of sampling, which suggests other sources such as Quartz Creek and other streams in the reach between Frissell Bridge and Vida are more important.

Random forest analyses identified PARAFAC components C1 and C5 and fluorescence peaks A, C, M, T and N as the best predictors for HAA5 concentrations in finished drinking water, explaining 62.5 percent of the variation. The best predictors for THM4 were C1, C4 + C5, and peaks T, A, and N, which explained 33 percent of the variation.

Several land cover and vegetation classes were correlated with DOC concentration and other optical measurements. The percentage of evergreen forest in each of the subwatersheds sampled was negatively correlated ($p < 0.001$) with DOC concentration and many optical indicators of DOM quantity: UVA_{254} , fDOM, and all of the fluorescence peaks. In contrast, mixed (deciduous) forest was positively correlated ($p < 0.001$) with DOC, fDOM, UVA_{254} , and several fluorescence peaks, demonstrating the importance of deciduous leaf fall in generating DOC and DBP precursors.

The high level of human activities in the middle and lower portion of the basin—including timber harvesting and road construction on private forestland, agricultural, rural, industrial, and urban development—have resulted in the greatest loss in native coniferous and mixed deciduous forests in the basin. DOC loading from these tributaries and reservoir releases, which contain DOC from terrestrial and aquatic productivity, both enrich the McKenzie River. Concentrations of DOC increased an average of 71 percent (range 30–120 percent) in the McKenzie River between Frissell Bridge, the upstream reference site, and Vida. PARAFAC components C1, C2, and C5—which were correlated with DBPs in finished water—increased, on average, 109–136 percent (range 20–250 percent) in this same Frissell-to-Vida reach. These increases occur from input of tributaries in the middle basin such as Quartz Creek and others, as noted above.

Future monitoring, field, and lab studies can improve our understanding of seasonal and spatial sources of organic carbon contributing DBP precursors to the McKenzie River and allow detection of long-term trends resulting from the recent Holiday Farm Fire, which burned 173,393 acres of forestland, including riparian areas along the main stem, and numerous structures, homes, and outbuildings in September 2020. Future studies could examine DOC fluxes and flushing of carbon from the watershed, investigate the role of precipitation amount and intensity in mobilizing carbon and sediment, and evaluate impacts to aquatic communities and human health as part of a post-fire assessment. Other areas ripe for study include evaluating the impacts of potential temperature increases on carbon sequestration and decomposition in the burned and unburned forests and identifying practices that foster sequestration of carbon in forest soils.

The use of fluorescence sensors such as fDOM to monitor the concentration and composition of raw water supplies may be improved for detection of specific DBP precursors,

to provide continuous and real-time information to treatment plant operators. Future studies that monitor DOM amount and quality, and DBP Formation Potential (FP), particularly during storm events, paired with streamflow measurements, as suggested above, could help identify areas that contribute high DOC loads and thus help managers identify the key areas to focus restoration activities. Other studies could examine treatment options for currently regulated DBPs and potentially unregulated compounds, including advanced biological treatments for their removal.

This study was a collaboration between the U.S. Geological Survey (USGS) and EWEB in Eugene, Oregon, with additional funding provided from USGS Cooperative Matching Funds Program.

Introduction

One of the challenges facing drinking water utilities is managing treatment operations to minimize the formation of disinfection by-products (DBPs), organic compounds that form when dissolved organic matter (DOM) and particulate organic matter (POM) in raw water reacts with chlorine or other disinfectants (Croué and others, 1999). DBPs represent a diverse group of compounds that often contain chlorine or bromine; the heavier, brominated DBPs may contribute more to overall DBP concentrations than to the lighter chlorinated compounds. Several DBPs are mutagenic and carcinogenic (Krasner and others, 2006; Richardson and others, 2007), and their presence in finished drinking water is regulated by the Environmental Protection Agency (EPA). Currently there are nine regulated DBPs: four trihalomethanes (THMs) and five haloacetic acids (HAAs) (U.S. Environmental Protection Agency 2005, 2006, 2009). The maximum contaminant levels (MCLs) are 0.08 milligram per liter (mg/L) for total THMs (THM4) and 0.06 mg/L for total HAAs (HAA5). Included in the fourth Unregulated Contaminant Monitoring Rule (UCMR4) (U.S. Environmental Protection Agency, 2016) are five additional HAAs that have required additional monitoring since 2018. These additional HAAs were not included in the current study.

Conventional production of potable water typically includes a combination of settling and coagulation to remove sediments and precursors for DBPs, filtration, and chemical additions. Disinfectants are used to protect human health against pathogens and water-borne illnesses, but the DBPs that form are potentially toxic and frequently studied.

Although the dissolved organic carbon (DOC) concentration in source water is often a strong predictor of DBP formation in finished water, this is not always the case because only a fraction of the overall DOC pool reacts to form DBPs. Thus, the composition of the DOM pool—and more specifically the physiochemical composition of the compounds that form DBPs, commonly referred to as DBP precursors—affects the amount and types of DBPs that form. The physiochemical

properties of the DOM pool are not only functions of DOM source but also functions of environmental processing—bio- and photo-degradation, sedimentation, and sorption—that transforms DOM molecules during transport and affects their reactivity with coagulants and disinfectants.

The Cascade Range rivers, including the McKenzie, Santiam, and Clackamas Rivers, are important sources of drinking water for over 700,000 people. These three river basins are protected by Oregon's "Three Basin Rule," which restricts certain types of development. Their watersheds are mostly forested in the headwaters, and storage and flood control reservoirs regulate flows in the lower reaches of the Santiam and McKenzie Rivers. Previous studies on organic matter in Oregon's McKenzie River (fig. 1) (Kraus and others, 2010) and the Clackamas River to the north (Carpenter and others, 2013) revealed that riverine DOC is mostly soil derived from upstream terrestrial sources. Three DBPs—chloroform (a THM), tri- and dichloroacetic acids (TCAA and DCAA; two HAAs)—occur most frequently and at the highest concentrations in treated drinking water sourced from the rivers. TCAA and DCAA composed the majority (96 and 98 percent, respectively) of HAA5 in the McKenzie and Clackamas River studies (Kraus and others, 2010; Carpenter and others, 2013). Chloroform accounted for 78 percent of THM4 in the McKenzie River study, whereas a higher percentage (93 percent) was found in the Clackamas River study (Carpenter and others, 2013). The Clackamas River Basin has more agriculture (especially large nurseries) and urban development than the McKenzie River Basin, which is less developed and considered by many to be of even higher quality owing to its generous base flow even during summer when other rivers have notably lower streamflow. These three rivers have similar threats to drinking water quality: forestry, agriculture, industry, urban development, roads, and other activities that can degrade habitat and water quality.

DBPs are just one class of organic compounds that may threaten the quality of drinking water. A detailed study of organic compounds in treated drinking water from the Clackamas River (Carpenter and others, 2008) found numerous solvents, gasoline hydrocarbons, and pesticides, but concentrations of THMs and resulting benchmark quotients (BQs)—the ratio of the measured concentration to the EPA drinking-water standard—were highest for this class of compounds making DBPs a priority for water utility managers and researchers alike. BQs for the McKenzie River DBPs are similarly utilized in this report to estimate the risk posed by DBPs in finished drinking water. DBPs are typically present in drinking water at some levels if chlorination is part of the treatment process, and BQ provides a way to compare the relative risk to these two classes of DBPs that have different MCLs.

Understanding the source materials and seasonal patterns in DOC concentrations and DOM quality will allow water utilities to adapt to possible changes in source water quality and inform treatment plant design and operations (Cooke and others, 2001; Reckhow and others, 2004; Kraus and others, 2010, 2011; Carpenter and others, 2013). Understanding these

dynamics will help water utility managers develop source water protection strategies in response to changes in forest health (for example, forest fires), reservoir operations, climate, land use, or changes in the regulations.

Potential Sources of Organic Carbon Contributing Disinfection By-Product Precursors

Organic matter is present in all aquatic ecosystems and is made up of a heterogeneous mixture of compounds (Battin and others, 2009); some of it is transported to surface water from terrestrial environments (for example, decaying plants and soil organisms), and some of it (algae, cyanobacteria, and rooted macrophytes) is produced in the aquatic ecosystem (Aiken and Cotsaris, 1995; Reckhow and others, 2004). Autumn leaf fall, for example, is an important annual event bringing to streams carbon that is available to heterotrophic communities which drive key ecosystem processes (Triska and others, 1982). Deciduous trees including big leaf maple (*Acer macrophyllum*) and red alder (*Alnus rubra*) are common in the McKenzie River Basin, and “leaf packs” accumulate in streams and provide habitat for stone flies and other insects important for fish populations. However, decomposition of this organic matter may enrich waters with organic carbon that may contribute DBP precursors to source water intakes and degrade drinking water quality.

A comprehensive multiyear carbon budget for a forested headwater stream in the H.J. Andrews Experimental Forest, in the Blue River Basin, a tributary to the McKenzie River, found that DOC comprised about 11 percent of the total carbon budget, with particulate organic carbon (21 percent), dissolved inorganic carbon (40 percent), and effusion to the air (27 percent, as carbon dioxide [CO_2]) making up the balance (Argerich and others, 2016). Lee and Lajtha (2016) found carbon quality to differ between deep soil water and shallow soil water, the latter being mobilized during storms. Studies in the Clackamas and McKenzie Rivers (Hood and others 2006; Kraus and others, 2011; Carpenter and others, 2013; Lee and Lajtha, 2016) revealed that storm runoff transports organic matter from terrestrial environments to receiving streams and rivers. Compositional indicators suggest this carbon is derived from humified soils, as well as fresh or partly decomposed plant materials and fallen deciduous leaves. This is particularly evident during “first flush” storms in the late summer or early autumn, when relatively high concentrations of DOC and DBP precursors may occur at source water intakes, resulting in higher DBPs in finished drinking water.

Benthic and planktonic algae and cyanobacteria, which are important contributors to aquatic food webs, also yield DOC that can be DBP precursors (Graham and others, 1998; Jack and others, 2002; Kraus and others, 2011; Carpenter and others, 2013; Wert and Rosario-Ortiz, 2013; Korak and others, 2015). In addition to natural sources, DBP precursors can originate in anthropogenic sources of DOM including treated

and untreated human and animal wastes, septic tank leachates, erosion and runoff from agricultural/urban/rural/timber producing lands.

The observation of the late season “first flush” storm with associated mobilization of organic carbon and other contaminants is a common feature of watersheds in the Pacific Northwest (Hood and others, 2006; Carpenter and others, 2008, 2013; Goldman and others, 2012) and elsewhere (Saraceno and others, 2009; Jones and others, 2014). Soils “wet up” with the first rains after a typical long, dry summer buildup, and then decomposition products are “flushed” during the heavier rainfall that follows. As a result, concentrations of dissolved constituents including DOC and DBP precursors can be highest during these types of storms (Carpenter and others, 2013). This is also the time of year when annual maximum DBP concentrations in treated drinking water tend to occur in the Cascade Range streams. This flushing is followed by a period of lower DBP concentrations arising from the combined effects of higher streamflows during winter, lower primary productivity, and depleted easily mobilized carbon stores from the past grow season.

Use of Optical Properties to Characterize Dissolved Organic Matter

Much of the DOM pool interacts with light at varying wavelengths in the ultraviolet and visible spectrum—a portion may absorb light and then emit (fluoresce) at longer wavelengths—making optical measurements a valuable tool for assessing the quantity, composition, reactivity, and sources of DOM in aquatic systems (McKnight and others, 2001; Coble, 1996, 2007; Hudson and others, 2007; Downing and others, 2009).

Absorbance and fluorescence are optical measurements commonly used to determine DOM quality and quantity (Hudson and others, 2007; Fellman and others, 2010; Matilainen and others, 2011). Absorbance is the amount of light absorbed by a water sample at a specific wavelength. Absorbance scans are depicted in a two-dimensional array with wavelengths on one axis and the amount of light absorbed on the second axis. Information is gained from both the intensity and slope of decay of the curve with increasing wavelength. For example, the response at a single wavelength can be related to DOM concentration, while the slope between a range of wavelengths or the ratios of wavelengths provides information about DOM composition. Similarly, normalizing the absorbance response at a specific wavelength to DOC concentration provides information about how optically active the DOM pool is per unit carbon, which can be related to DOM composition.

Absorbance at the ultraviolet wavelength of 254 nanometers (nm) (UVA_{254}) has been used in the drinking-water industry as a proxy for DOC concentration for several decades (Weishaar and others, 2003), and UVA_{254} normalized by DOC concentration, known as the “specific UVA_{254} ” (SUVA_{254}),

is a useful proxy for DOM aromatic content (Weishaar and others, 2003), molecular weight (Chowdhury, 2013), and DBP precursor content (Carpenter and others, 2013, and references therein).

Fluorescence measures the intensity and wavelength of light emitted by a water sample following absorbance of incident light. Fluorescence scans may include thousands of excitation-emission pairs to enable three-dimensional visualization of the fluorescence, with excitation, emission, and intensity on separate orthogonal axes. The resulting signals from each sample are graphed into an excitation-emission matrix (or EEM) (fig. 2), which can be compared and analyzed in further detail to potentially link certain signals to particular sources. Individual diagnostic peaks within the EEMs (Coble and others, 1990; Coble, 1996, 1998; Stedmon and others, 2003), including fluorescent dissolved organic matter (fDOM) (excitation [ex] 370 nm /emission [em] 460 nm), are also used

by field instruments (table 1). Fluorescence intensity at a given excitation-emission pair is related to DOM concentration. Similar to absorbance, fluorescence can be used to gain insight into DOM source, composition, and reactivity (Coble, 2007; Hudson and others, 2007; Stedmon and Bro, 2008; Hansen and others, 2016). DOM composition can be inferred by the presence or absence of fluorophores, shifts in peak maxima, ratios of peaks, and calculated indices.

Although absorbance and fluorescence scans can generate large datasets, optical data are often distilled down to a few parameters that have been associated with specific pools of DOM (for example, degree of lability versus recalcitrant) or have proven informative in prior studies because they could be related to DOM composition (for example, aromaticity, molecular weight), source (for example, terrestrial and algal carbon, or wastewater), reactivity, or DBP-forming carbon (precursors) (fig. 2; table 1).

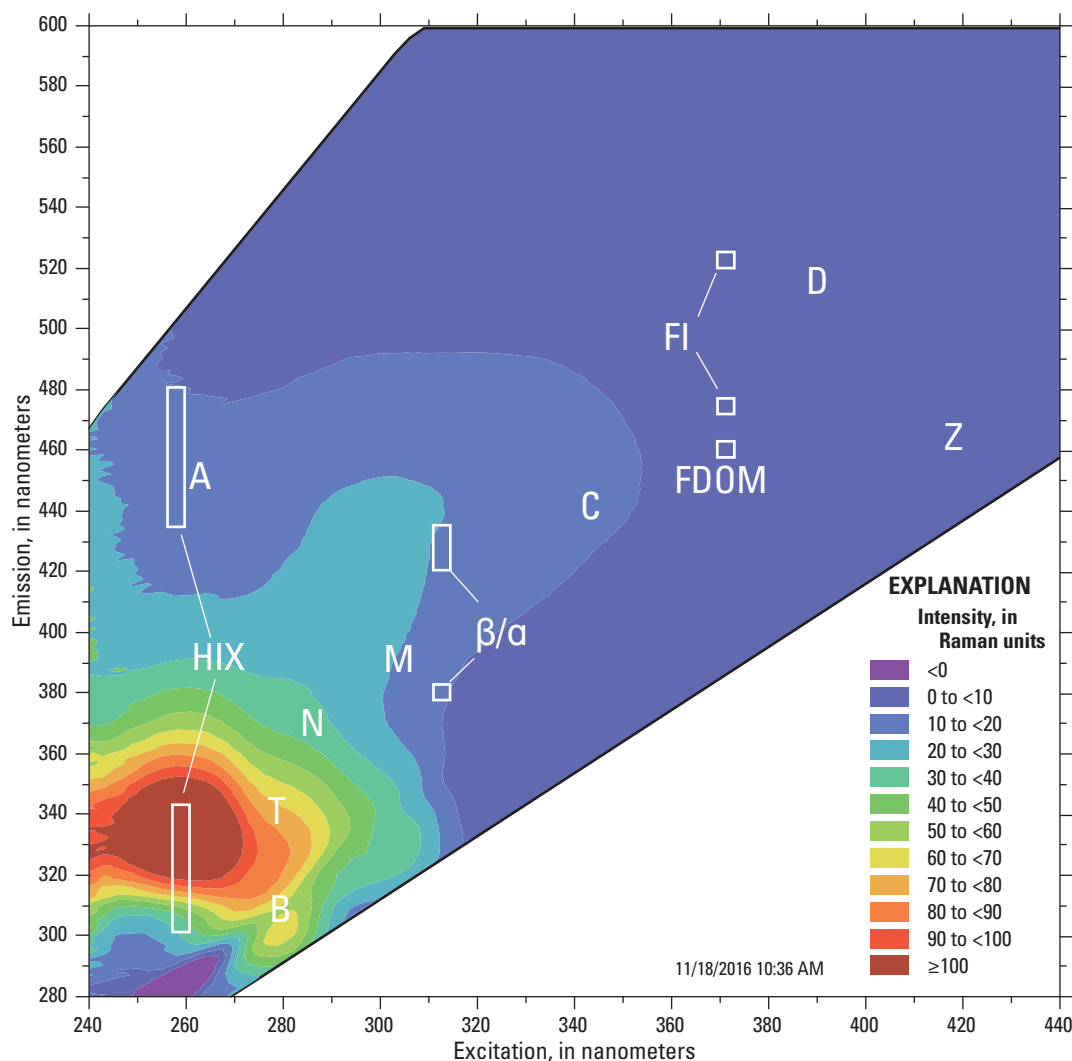


Figure 2. Example excitation-emission matrix showing the locations of selected fluorescence peaks, McKenzie River Basin, Oregon. <, less than; ≥, greater than or equal to.

Table 1. Description of commonly used optical properties for describing the composition of dissolved organic matter.

[Abbreviations: DOC, dissolved organic carbon; DOM, dissolved organic matter; em, emission; ex, excitation; L, liter; mg, milligram; m, meter; nm, nanometer]

Optical property	Calculated	Description	Reference
Specific ultraviolet absorbance (SUVA ₂₅₄)	Absorbance at 254 nm normalized to DOC concentration	Positively correlated with aromatic carbon content; in units of L/mg-m	Weishaar and others (2003)
Humification index (HIX)	Area under the em spectra 435–480 nm divided by the peak area 300–345 nm plus 435–480 nm, at ex 254 nm	Indicator of humic substance content or extent of humification; based on the idea that the emission spectra of fluorescing molecules will shift toward longer wavelengths due to lower H:C ratios as humification of DOM proceeds.	Ohno (2002)
Fluorescence index (FI)	The ratio of em wavelengths at 470 nm and 520 nm, obtained at ex 370 nm	Higher values associated with microbial sources such as extracellular release and leachate from bacteria and algae; lower values associated with terrestrially-derived soil and plant organic matter; typical values range from 1.3–1.9.	McKnight and others (2001), Cory and others (2010)
Freshness index (B:α)	The ratio of emission intensity at 380 nm divided by the maximum emission intensity between 420 nm and 435 nm at excitation 310 nm	An indicator of recently produced DOM, with higher values representing a higher proportion of fresh DOM.	Parlanti and others (2000), Wilson and Xenopoulos (2009)
Specific peak A	ex 260/ex 450 divided by DOC concentration	High molecular weight and aromatic humic, widespread, but highest in wetlands and forested environments.	Coble and others (1990), Coble (1996), Fellman and others (2010)
Specific peak C	ex 340/em 440 divided by DOC concentration	High-molecular-weight humic, widespread, but highest in wetlands and forested environments.	Coble and others (1990), Coble (1996), Fellman and others (2010)
Specific peak D	ex 390/em 510 divided by DOC concentration	Associated with DOM derived from soil fulvic acid.	Coble and others (1990), Coble (1996)
Specific peak M	ex 300/em 390 divided by DOC concentration	Low molecular weight, common in marine environments associated with biological activity but can be found in wastewater, wetland, and agricultural environments.	Coble and others (1990), Coble (1996), Fellman and others (2010)
Specific peak B	ex 275/em 304 divided by DOC concentration	Amino acids, free or bound in proteins, fluorescence resembles free tryptophan, may indicate intact proteins, polyphenols, or freshly produced DOM.	Coble and others (1990), Coble (1996, 1998), Fellman and others (2010), Hansen and others (2016)
Specific peak T	ex 275/em 340 divided by DOC concentration	Amino acids, free or bound in proteins, fluorescence resembles free tryptophan, may indicate intact proteins, polyphenols, or freshly produced DOM.	Coble and others (1990), Coble (1996, 1998), Fellman and others (2010), Hansen and others (2016)
Specific peak N	ex 280/em 370 divided by DOC concentration	Very labile, associated with freshly produced DOM.	Coble and others (1990), Coble (1996), Fellman and others (2010)

In situ fluorescence is a reliable surrogate for DOC concentration in many types of freshwater (Bergamaschi and others, 2005, 2012; Spencer and others, 2007; Saraceno and others, 2009; Pellerin and others, 2012; Carpenter and others, 2013). Fluorescent dissolved organic matter (fDOM, ex 370 nm / em 460 nm) is highly correlated with DOC concentration, even more so compared to traditional absorbance measurements (Nakajima and others, 2002; Coble, 2007; Kraus and others, 2010; Carpenter and others, 2013). For each system the relationship between DOC concentration and fDOM needs to be verified, however, because fDOM sensors measure at a single ex/em pair and therefore represent a specific fraction of the DOM pool. If the composition of the DOM pool changes, then the relationship between fDOM and DOC can vary. Monitoring fDOM can also be used as a surrogate or proxy for specific types of DBPs (Carpenter and others, 2013)—but this is again system dependent—but there is great potential for developing technology to monitor DBP precursors and eventually predict DBPs in treated drinking water in real-time.

Study Background

The McKenzie River in northwestern Oregon (figs. 1, 3) is the sole water source for the City of Eugene. The Eugene Water & Electric Board (EWEB) maintains and operates a drinking-water intake and conventional treatment plant on the lower-middle McKenzie River near river mile (RM) 11, just upstream of Hayden Bridge; the facility currently serves about 200,000 residents. As part of its management strategy, EWEB developed a drinking-water source protection and monitoring plan to assess all possible threats to drinking water that could impact this important regional water supply (Blair, 2000). Contaminants of potential concern included synthetic organic contaminants such as pesticides, metals, and organic carbon associated with the formation of DBPs during treatment.

The compliance monitoring by EWEB over the past 15 years has revealed a small upward trend in DBP concentrations in finished drinking water (fig. 4). The slope of the trends for THM4 is twice that for HAA5, suggesting source water concentrations of THM precursors are increasing more rapidly than HAA precursors. Although DBP concentrations remain well below EPA regulations, periodic increases in DBP concentrations have occurred during “first flush” types of storms in autumn (2005–07, 2009, and 2012) and coincided with a period of reservoir inundation following an extended drawdown and refilling of Cougar Reservoir on the South Fork McKenzie River (during 2005–07) (fig. 1).

Kraus and others (2010) were the first to characterize the organic carbon in the McKenzie River from the standpoint of identifying precursors for DBP formation during drinking water treatment. PARAFAC analysis of fluorescence spectra identified four primary pools of DOM, or “components,” in the watershed: two types of terrestrial, humic-like components (C1, C2), a “protein-like” pool associated with recently produced (less humified) material (C3), and a marine, humic-like

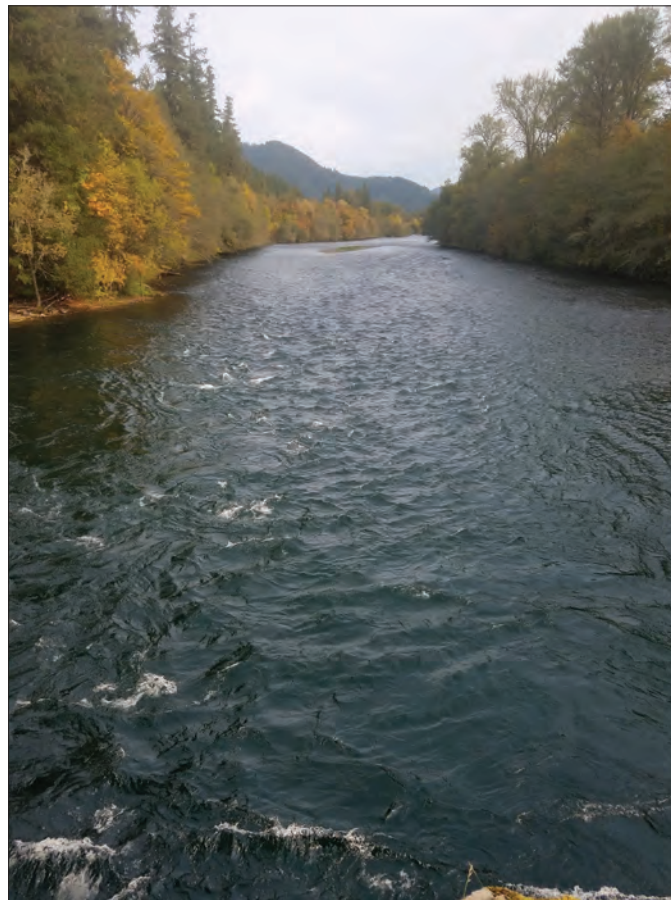


Figure 3. Main stem McKenzie River at Finn Rock, Lane County, Oregon. Photograph by Kurt Carpenter, U.S. Geological Survey.

pool that may represent algae-derived DOM (C4). Results from that study indicated watershed inputs of DOM originated primarily from upstream terrestrial sources (C1 and C2; Kraus and others, 2010). In the headwater streams of the H.J. Andrews Experimental Forest, in the McKenzie River Basin, Lee and Lajtha (2016) identified a “protein-like” type of DOM that was more prominent during base flow, which they associated with deep soil water. This signal was diluted during runoff events (Lee and Lajtha, 2016).

Other potential sources of DOC input to the McKenzie River include two U.S. Army Corps of Engineers flood control reservoirs—Blue River Lake and Cougar Reservoir (fig. 1)—which capture and release a substantial amount of flow from forested watersheds. Both reservoirs have blooms of cyanobacteria during summer (see fig. 5), which can move downstream if entrained in the discharge. Cougar Reservoir has a variable depth water release control that allows for blending, whereas discharge from Blue River Lake occurs at a regulating outlet at 220 ft depth during summer (Norman Buccola, U.S. Army Corps of Engineers, written commun., 2020). Flows out of these dams during summer augment flows in the Willamette River and help temperature management; they are drawn down in autumn to make room for winter rains and may enrich

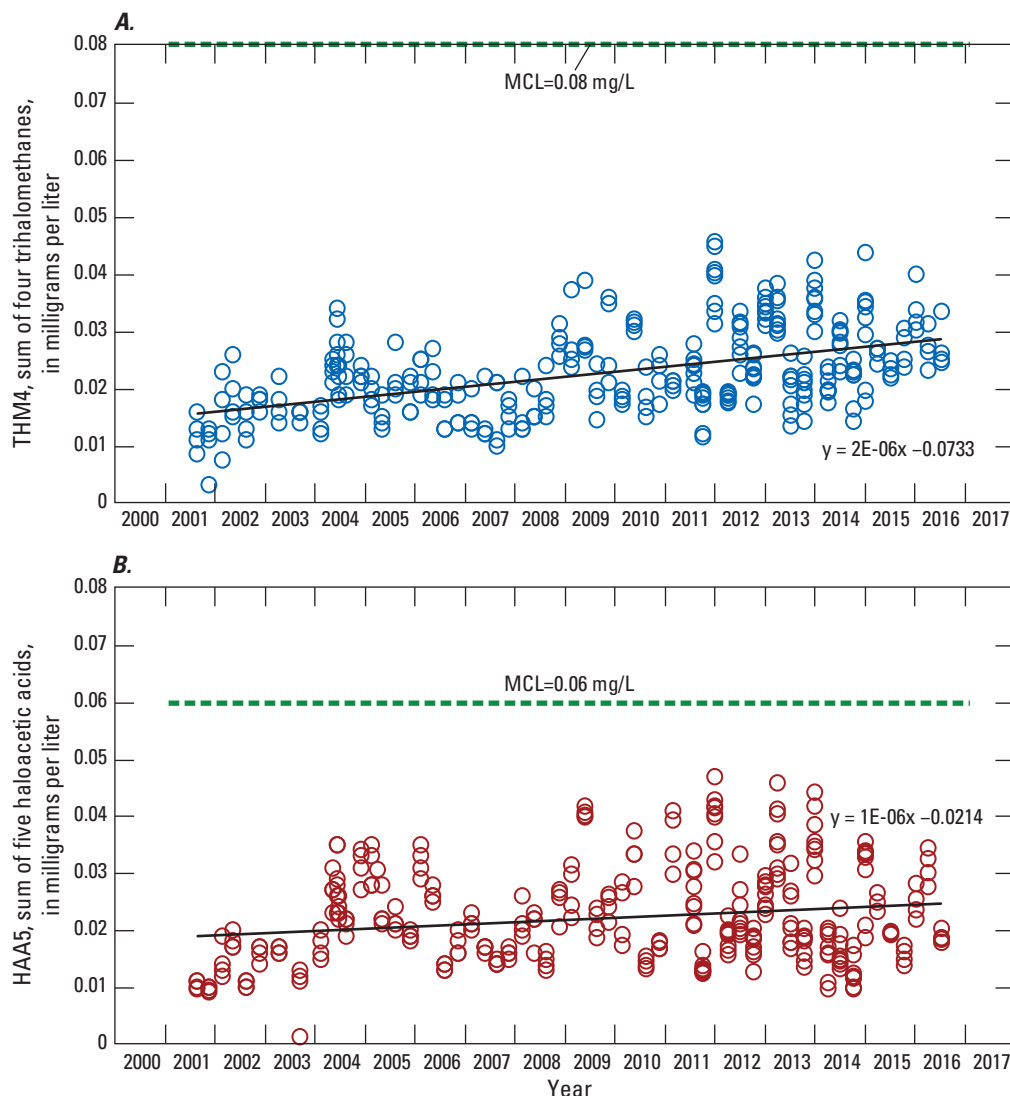


Figure 4. Historical trends in disinfection by-products, (A) trihalomethanes (THM4) and (B) haloacetic acids (HAA5), in finished water from the Eugene Water & Electric Board (EWEB) drinking water treatment plant on the McKenzie River, Oregon, 2002–17.

downstream reaches with organic carbon and cyanobacteria decomposition products at that time. Kraus and others (2010) found that, compared with the upstream reference site, DOC concentrations were 10–60 percent higher in the main stem river downstream from these two reservoirs.

Another major finding from the Kraus and others (2010) study was that, although smaller tributaries (including Camp and Cedar Creeks and Keizer Slough) farther downstream contributed relatively high DOC concentrations (and DBP precursors), these tributaries contributed less than 5 percent of the total flow in the lower McKenzie River.

This study was conducted in partnership with EWEB during 2012–14 to better understand sources of organic carbon in the McKenzie River that produce DBPs in treated drinking water, focusing on storms and the runoff that follows. The objectives of the study were to:

- (1) characterize the concentrations and quality of DOC in the McKenzie River and key tributaries during storms;
- (2) identify the most common types of DOC in the McKenzie River and selected tributaries during storms;
- (3) evaluate optical properties suitable as proxies for DBP precursors in surface water; and
- (4) identify land cover classes or vegetation types that are potentially important sources of DOC and DBP precursors in EWEB's source water for the Hayden Bridge Drinking Water Treatment Plant.



Figure 5. Bloom of cyanobacteria (likely *Dolichospermum*) in Cougar Reservoir, Oregon, August 2002. Photograph by Chauncey Anderson, U.S. Geological Survey.

The McKenzie River Basin Hydrology and Land Cover

The McKenzie River is a 144.8-km (90-mile) long tributary of the Willamette River in northwestern Oregon (fig. 1). The river is known for its clear and cold water and is valued for supplying high-quality drinking water to residents of Eugene and Springfield, Oregon. The upper basin contains extensive spring complexes (fig. 6), fed by expansive permeable volcanic aquifers in the High Cascades physiographic province (Tague and Grant, 2004). These provide a steady base flow of 2,000–3,000 cubic feet per second (ft³/s) during summer; streamflow in the upper McKenzie River downstream from Clear Lake shows little variability throughout the year. Despite its transparency and typically low concentrations of DOC, the McKenzie River can be impacted by turbid runoff from the tributaries, and from cyanobacteria blooms in the two reservoirs, as described above.

For the purposes of this report, the basin's hydrologic features and landscape can be grouped into the upper, middle, and lower reaches: the upper river extends from the headwaters down to Frissell Bridge; the middle reach is the area downstream of Frissell Bridge to the Gate Creek confluence, including several tributaries; the lower reach extends from Gate Creek to EWEB's intake.

Climate in the McKenzie River Basin is wet and cool during winter and dry and warm during summer. Mean annual precipitation (1961–90) in the study area ranges from about 50 inches near the river mouth to over 90 inches at higher elevations (Greenland, 1994), although average precipitation may have changed somewhat in recent decades; about 90 percent generally occurs between October and May (Western

Regional Climate Center, 2010). Following rainfall patterns, highest discharges occur in winter, with occasional pulses of flow in spring from snowmelt, with the lowest streamflows in late summer and autumn. Local topography also generates orographic lift and associated microclimatic variability during storms so that rainfall often falls inconsistently over the area (Kelly and others, 2012). Streamflow patterns in the McKenzie River are influenced by springs and other groundwater sources, five dams in the upper basin, and another dam and two canal diversions (Leaburg and Walterville) on the main stem (Blair, 2000; Risley and others, 2010). Cougar Reservoir and Blue River Lake on the South Fork McKenzie and Blue Rivers, respectively, are the largest reservoirs in the basin, and at times have considerable influence on McKenzie River streamflows. Downstream from Blue River, older and more dissected basins of the Western Cascades physiographic province (Tague and Grant, 2004) produce the majority of their streamflow during rainfall runoff (Risley and others, 2010). These streams respond quickly to rainfall but also recede quickly and, as a result, the flows at Hayden Bridge, at the EWEB intake, are more dynamic than the steady spring flows observed in the upper reaches of the McKenzie River (Kelly and others, 2012).

The McKenzie River Basin drains predominantly forestland (about 90 percent) that has a long history of logging, associated road construction, and wildfires. Land ownership is a mixture of private, State, and Federal. The middle portion of the McKenzie River Basin contains several tributaries that drain private industrial forestland, including three that were sampled as part of this study: Quartz, Gate, and Haagen Creeks. Although water in these tributaries typically is of higher quality compared with the lower basin tributaries that drain agricultural, industrial, or urban land uses, higher flows



Figure 6. Extensive springs in the upper McKenzie River Basin, Oregon. Photograph by David Donahue, Eugene Water & Electric Board.

during storms may result in substantial loading of constituents including carbon (Kraus and others, 2010), forestry pesticides (Kelly and others, 2012), sediment, and other compounds, to the main stem McKenzie River, particularly from steeper slopes disturbed by logging, and now wildfires.

The lower portion of the McKenzie River drains Quaternary alluvium—about 18 percent of the basin—where the river widens and agriculturally productive soils are found along the valley bottom (Sherrod and Smith, 2000). Rural residential development, urban neighborhoods, agricultural land, and industrial developments in the lower basin may be important sources of carbon and other contaminants (McCarthy and others, 2009; Kelly and others, 2012; McCarthy and Alvarez, 2014). Several small communities (rural residential) and pockets of agricultural land, primarily pastureland, orchards, nurseries, row crops, filberts, Christmas trees, grass seed, and blueberries are located in this alluvial floodplain (Morgenstern, 2006). These developed areas comprise 1.2 percent of the overall drainage basin area, yet can be significant because they discharge to the McKenzie River not far upstream from the EWEB water intake. The relatively undeveloped nature

of the McKenzie River also makes it susceptible to degradation from human activities within the riparian corridors. One small unnamed tributary to the Waltermire Canal has about 45 percent of its basin in cultivated crops (table 2) and could be an important source of carbon, although dilution from the McKenzie River, which feeds the canal, can obscure periodic inputs from these agricultural areas.

The stream network incorporates the stormwater drainage system for the City of Springfield (population 62,000), including five stormwater outfalls that drain into the McKenzie River. Three of these outfalls (at 72nd, 69th, and 64th Streets) discharge to Cedar Creek, a major tributary to the lower McKenzie River; these collectively represent most of the stormwater from the eastern portion of Springfield. The 52nd Street stormwater outfall drains into Keizer Slough, a slow-moving side channel that discharges to the McKenzie River about 0.25 miles upstream of the EWEB water intake (fig. 7). The 42nd Street stormwater outfall occasionally overflows into Keizer Slough and on to the McKenzie River and the EWEB water treatment plant downstream.

Table 2. List of sampling sites with estimated land cover and vegetation class percentages, McKenzie River Basin, Oregon, 2012–14.

[Watershed land cover percentages based on 2011 National Land Cover Data. Abbreviations: DWTP, drinking water treatment plant; mi², square mile; —, not applicable or “none” for table values]

					Land cover percentages																
Sampling site	Description	U.S. Geological Survey site identifier	Eugene Water & Electric Board site identifier	Basin area (mi ²)	Barren land	Cultivated crops	Deciduous forest	Developed, high intensity	Developed, low intensity	Developed, Medium intensity	Developed, open space	Emergent herbaceous wetlands	Evergreen forest	Hay/pasture	Herbaceous	Mixed forest	Open water	Perennial snow/ice	Shrub/scrub	Woody wetlands	
Finished (treated) water from Hayden Bridge DWTP	Finished water	440417122575701	E011	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
McKenzie River above Hayden Bridge	Raw water/main stem	14164900	E010	1,145	3.7	0.6	0.1	0.0	0.2	0.1	0.8	0.040	77.9	0.6	3.1	0.6	0.5	0.2	11.3	0.2	
52nd St. storm-water outfall at Highway 126	Lower basin outfall	440325122563600	E520	2.4	1.3	1.1	0.1	6.8	30.7	32.7	8.1	—	10.3	5.4	0.5	1.0	—	—	0.9	1.1	
Cedar Creek at Springfield	Lower basin tributary	14164700	E210	10.1	0.04	5.8	0.2	0.1	6.0	3.1	4.1	0.021	60.3	7.6	4.1	0.7	0.03	—	6.1	1.9	
Camp Creek at Camp Bridge	Lower basin tributary	14164550	E310	26	0.1	3.3	0.1	<0.01	0.1	0.03	0.02	—	50.3	7.6	9.1	1.5	<0.01	—	27.7	—	
Unnamed tributary to Walterville Canal	Lower basin tributary	440405122495600	E334	0.3	—	44.6	—	<0.01	3.0	0.1	0.2	—	0.7	50.8	—	—	0.6	—	—	—	
McKenzie River at Hendricks Park	Main stem	440322122494600	E020	1,094	3.8	0.3	0.1	<0.01	0.1	<0.01	0.8	0.036	79.6	0.2	2.8	0.6	0.5	0.2	11.0	<0.01	
Haagen Creek at Deerhorn Road	Forested tributary	440516122424900	E270	3.4	—	—	0.4	—	—	0.0	0.01	—	53.5	—	10.9	1.5	—	—	33.8	—	

Table 2. List of sampling sites with estimated land cover and vegetation class percentages, McKenzie River Basin, Oregon, 2012–14. —Continued

[Watershed land cover percentages based on 2011 National Land Cover Data. **Abbreviations:** DWTP, drinking water treatment plant; mi², square mile; —, not applicable or “none” for table values]

					Land cover percentages															
Sampling site	Description	U.S. Geological Survey site identifier	Eugene Water & Electric Board site identifier	Basin area (mi²)	Land cover percentages															
					Barren land	Cultivated crops	Deciduous forest	Developed, high intensity	Developed, low intensity	Developed, Medium intensity	Developed, open space	Emergent herbaceous wetlands	Evergreen forest	Hay/pasture	Herbaceous	Mixed forest	Open water	Perennial snow/ice	Shrub/scrub	Woody wetlands
Haagen Creek at McKenzie River	Forested tributary	440507122433100	E272	3.6	—	2.1	0.9	—	0.1	0.0	0.5	—	51.8	0.1	10.4	1.5	—	—	32.5	—
Gate Creek at Vida	Forested tributary	14163000	E393	48	0.2	—	0.04	<0.01	0.0	<0.01	0.1	—	69.8	—	9.1	1.1	—	—	19.7	—
McKenzie River near Vida	Main stem	14162500	E040	928	4.5	<0.01	0.05	<0.01	0.03	<0.01	0.7	0.043	82.6	<0.01	1.7	0.3	0.5	0.2	9.4	<0.01
Quartz Creek at mouth near Finn Rock	Forested tributary	440724122224300	E470	42	0.2	—	0.1	<0.01	0.02	<0.01	0.01	—	70.7	—	13.0	0.6	<0.01	—	15.4	—
Blue River at McKenzie Highway Bridge	Reservoir outflow	440915122203400	E540	92	0.9	—	0.0	<0.01	0.02	<0.01	0.04	—	84.4	—	0.2	0.2	0.5	—	13.7	—
South Fork McKenzie River near Rainbow	Reservoir outflow	14159500	E486	208	0.4	—	<0.01	<0.01	<0.01	<0.01	0.4	0.033	90.7	—	0.4	0.0	0.8	—	7.2	0.03
South Fork McKenzie River above Cougar Reservoir	Forested reference	14159200	E485	158	0.1	—	—	<0.01	<0.01	<0.01	0.4	0.043	92.5	—	0.1	—	0.5	—	6.3	0.04
McKenzie River at Frissell Bridge	Forested reference	441219122022400	E182	234	6.1	—	—	<0.01	0.1	<0.01	1.1	0.105	78.5	—	1.7	0.0	0.5	—	11.9	—



Figure 7. Keizer Slough upstream of the Eugene Water & Electric Board water treatment plant intake, Oregon. Photograph by Chauncey Anderson, U.S. Geological Survey.

Methods

Study Area/Sampling Sites

The study area extended from Frissell Bridge in the upper basin downstream to the EWEB water treatment plant at RM 11 (fig. 1). Eleven storm events were sampled over 2-day periods between October 2012 and April 2014, when streamflows at Hayden Bridge ranged from 3,000 to 26,000 ft³/s (fig. 8; table 3). Water samples were collected in an upstream-to-downstream fashion to provide a “snapshot” of conditions in the upper, middle, and lower reaches of the McKenzie River and selected tributaries (table 2). Sampling sites represented a range in land cover and included four main stem sites (the McKenzie River at Frissell Bridge, Vida, Hendricks Park, and the EWEB intake), eight tributaries (South Fork McKenzie and Blue Rivers, Haagen, Quartz, Gate, Cedar, and Camp Creeks plus one unnamed tributary of Walterville Canal), and one stormwater outfall channel at 52nd Street (fig. 1). Paired samples of raw source water (untreated water entering the treatment plant) and finished water (treated water exiting the plant) were analyzed to examine removal of organic carbon during treatment and to identify possible optical indicators, or surrogates, that might predict DBPs in finished water.

Water Sample Collection and Processing

Water samples were collected (fig. 8) and analyzed for DOC concentration and optical properties—absorbance and fluorescence spectroscopy—to characterize the amount and quality of DOM, including source and finished water. Personnel from EWEB and the USGS collected water samples from well-mixed locations in or near the river thalweg. Water samples were collected into pre-combusted 1-liter amber glass bottles, placed on ice, and kept in the dark until filtration

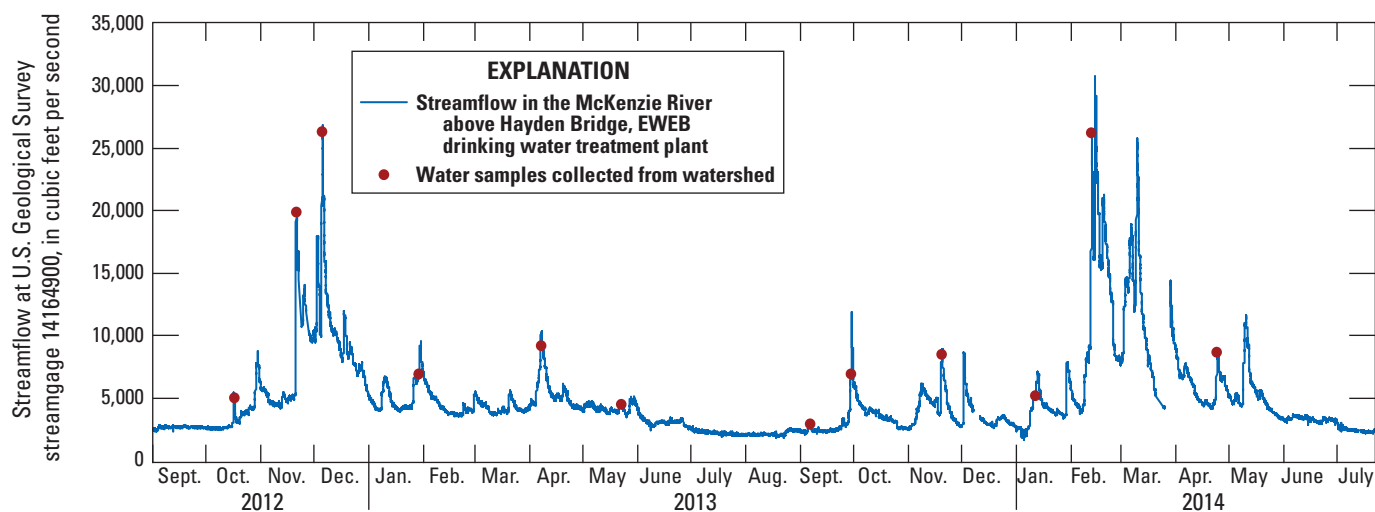


Figure 8. Timing of water sample collection and streamflow conditions in the McKenzie River above Hayden Bridge, Oregon, 2012–14. EWEB, Eugene Water & Electric Board.

Table 3. List of storm sampling events showing the average dissolved organic carbon concentration (DOC) for all sites and streamflow in the McKenzie River at Hayden Bridge at the time of source-water sample collection at the drinking-water treatment plant.

[Streamflow in cubic feet per second. **Abbreviation:** mg/L, milligram per liter]

Month and year	Description of storm event	Number of sites sampled	DOC concentration, in mg/L			Streamflow in the McKenzie River at Hayden Bridge
			Minimum	Average	Maximum	
October 2012	“First flush” autumn storm 1	15	0.82	4.0	10.0	5,010
November 2012	High flow autumn storm 2	16	1.40	3.7	5.7	19,800
December 2012	High flow autumn storm 3	15	1.00	2.1	4.2	26,300
January 2013	Moderate flow winter storm 4	15	0.38	1.3	4.0	6,950
April 2013	Moderate flow spring storm 5	15	0.49	1.4	4.1	9,140
May 2013	Low flow spring storm 6	11	0.53	2.8	13.0	4,470
September 2013	“First flush” summer storm 7	12	1.20	3.9	16.0	2,890
November 2013	Moderate flow autumn storm 8	15	0.82	2.7	4.2	8,480
January 2014	Moderate flow winter storm 9	14	1.00	1.9	2.7	5,170
February 2014	High flow winter storm 10	15	1.00	2.1	3.4	26,200
April 2014	Moderate flow spring storm 11	15	0.76	2.0	3.3	8,630

according to USGS protocols (Wilde and others, 2004). All data used in this report are available at USGS (2022) and USGS ScienceBase data release (Carpenter and others, 2022).

At the time of this study, conventional treatment at the EWEB plant consisted of coagulation with alum (7–17 mg/L) and sedimentation-filtration with chlorination (contact time 2–12 hrs) prior to filtration. Source-water samples were collected from taps inside the treatment plant. Finished-water samples were collected from inside the treatment plant prior to entry into the municipal distribution system. To account for travel through the treatment plant, finished-water samples were collected approximately 12–24 hours after source water samples were collected; the timing of finished-water sampling varied according to the flow rate and treatment plant operations and was determined on each sampling date by the EWEB treatment plant operators. Finished-water samples were collected for DBPs according to EPA protocols: sample bottles (40-mL pre-combusted amber glass vials fitted with a septum to prevent air entrapment) were inspected to ensure there were no bubbles or headspace. Samples were placed on ice in the dark until laboratory analyses. In addition to these finished water samples, EWEB also collected DBP samples for compliance purposes using the same methods, and some of these data are also utilized in this report.

Watershed samples for DOC concentration and optical properties were filtered within 24 hrs of collection using a borosilicate glass filtration unit and pre-combusted 0.7- μ m nominal pore size GF/F filters. DOC samples were acidified to pH < 2 with 1 mL of 4.5 N sulfuric acid and stored in the dark at 4 °C until analysis. Optical samples for absorbance and fluorescence measurements were filtered into 40-mL pre-combusted amber glass VOC vials and stored in the dark at 4 °C until analysis.

Water Sample Analyses

Disinfection By-Products in Finished Water

DBP analyses were performed on finished-water samples at Umpqua Research Laboratories (ORELAP Certification ID# OR100031) in Myrtle Creek, Oregon. Analyses included four THMs (chloroform, CHCl_3 ; bromoform, CHBr_3 ; bromodichloromethane, CHCl_2Br ; and dibromochloromethane, CHClBr_2) and five HAAs (monochloroacetic acid, MCAA; dichloroacetic acid, DCAA; trichloroacetic acid, TCAA; bromoacetic acid, BrAA; and dibromoacetic acid, Br_2AA) following the same methods used for DWTP compliance monitoring—EPA method 524.2 for THMs (U.S. Environmental Protection Agency, 1992) and method 6251B for HAAs (American Public Health Association, 2003).

Dissolved Organic Carbon (DOC) Analysis

DOC samples were analyzed at Test America using high-temperature combustion, standard method 5310B. Quality assurance split samples were analyzed at the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, using a persulfate oxidation method described by Brenton and Arnett (1993). Filtrate for DOC samples was collected into pre-combusted amber glass bottles: 125-mL for NWQL analyses and 250-mL for Test America analyses (for QA comparison of these labs, see Appendix [table 2.1](#)).

Absorbance and Fluorescence Measurements and Data Corrections

Absorbance spectra and fluorescence matrices were measured simultaneously on filtered water samples at room temperature (21 °C) in an acid-cleaned 1-cm quartz cuvette (Starna 3-Q-10) within 5 days of collection at the USGS in Portland, Oregon, using a benchtop spectrofluorometer equipped with a charge-coupled device (CCD) (Aqualog, Horiba Instruments, New Jersey) according to the method described in Hansen and others (2018). Briefly, absorbance and fluorescence measurements were performed using a double-grating monochromometer, a 150-W Xenon arc lamp with a 5-nm bandpass, and a 1-s integration time at wavelengths ranging from 250 to 450 nm. Emission spectra were collected with a CCD at approximately 3.2 nm intervals at wavelengths ranging from 300 to 600 nm.

Spectral corrections included instrument-specific excitation and emission corrections, baseline correction, and normalization to the daily water Raman peak area (Murphy, 2011) obtained by measuring organic-free water. Concentration-related inner-filter effects were corrected as described by Gu and Kenny (2009). Fluorescence is expressed in Raman-normalized intensity units (RU), and absorbance is reported in absorbance units (AU) obtained directly from the instrument.

Data processing was performed using MATLAB (version R2015b), including removal of Rayleigh scatter lines, vectorization of fluorescence data, and linear interpolation to 1-nm wavelength increments to calculate the commonly reported peaks and indices (Coble, 2007; Hudson and others, 2007; Stedmon and Bro, 2008). Final data were graphed into contour plots and surface maps for visual inspection.

The long-term laboratory method detection limits (LT-MDLs) for absorbance varies by wavelength, from 0.01 AU at 240 nm (A_{240}) to 0.004 AU at 600 nm (A_{600}), whereas fluorescence LT-MDLs vary by excitation / emission pairs, ranging from 0.004 RU throughout much of the EEM spectra to 0.1 RU in the region of peak B (ex 275 nm, em 304 nm) (Hansen and others, 2018). As a result, and because of the relatively low levels of DOC in much of the McKenzie River Basin, many of these values were below detection, and is discussed below.

Land Cover and Vegetation Class Data

Each of the 15 watershed sites within the McKenzie River Basin were delineated using USGS StreamStats program (U.S. Geological Survey, 2012), which uses topographic information to determine basin areas. In urban areas, basins were refined with hand delineation to correct for complex stormwater drainage. Land cover for each basin was calculated using the 2011 National Land Cover Data (NLCD; Homer and others, 2015). Land cover and vegetation class statistics were computed for each site's watershed using the final delineated watershed polygons and the NLCD 2011 land cover raster data

(October 10, 2014, edition; downloaded January 26, 2018). In ArcMap, a ModelBuilder model was created to clip the NLCD raster by each watershed and merge all of the raster attribute tables together. Watershed values (sum of areas, in square meters, and percentages) for each land cover type and vegetation class were calculated using MicrosoftTM Excel.

Statistical Analyses

The final dataset included 158 water samples from 16 tributary and main stem sites and 11 samples of finished drinking water. Fluorescence EEMs were decomposed using parallel factor analysis (PARAFAC) to identify representative components in the dataset to describe the different types of DOM present. Multivariate and regression statistics were used to identify surrogates for DBP precursors such as DOC concentration, fluorescence peaks, and (or) PARAFAC model components, and then to identify land cover types or vegetation classes associated with these sources of DOM.

Parallel Factor Analysis

PARAFAC was used to decompose the fluorescence signatures from corrected EEMs into unique components that contain information about the chemical characteristics of the DOM pool (Bro, 1997). PARAFAC is a multi-way analysis that resolves excitation / emission spectra into orthogonal fluorophore groups (components) and determines loadings for each component proportional to their fluorescence intensity. Component percentages (for example, Pct_C1, Pct_C2, Pct_C3, etc.) were calculated by dividing each component loading by the sum of the total loadings to reveal qualitative differences between samples (Andersson and Bro, 2000).

Procedures established by Stedmon and Bro (2008) were used to develop a PARAFAC model for the McKenzie River samples using the N-way toolbox, version 6.1 (Bro, 1997; Andersson and Bro, 2000), and the drEEM toolbox, version 0.1.0 (Murphy and others, 2013) with commercial software, MATLAB (version R2015.b). The model included a nonnegative constraint to help alleviate issues with higher relative instrument noise in samples having low fluorescence. Additionally, the data were normalized to the unit variance to alleviate collinearity. The PARAFAC model was validated using a combination of outlier identification, residual analysis, spectral analysis, replication by split-half analysis, and visual inspection of the components (Stedmon and Bro, 2008; Murphy and others, 2013).

Multivariate Statistical Analyses

Spearman rank correlations were generated using PRIMER-E statistical software package (Clarke and Gorley, 2006). Random Forest analyses were performed (R Core Team, 2013) to test which variables (DOC, UVA_{254} , fluorescence peaks, and PARAFAC model components) in raw water

were most important in predicting concentrations of HAA5s and THM4s in 11 paired samples of raw source water and finished water. PARAFAC model components included individual components (C1, C2, C3, etc.) and two summed groups (C1+C2+C3 and C4+C5) to test the respective importance of recalcitrant (humic-like) DOM (C1+C2+C3) versus more labile (fresh-like) carbon (C4+C5) in predicting DBP occurrence in treated drinking water.

Results and Discussion

Seasonal Patterns in Dissolved Organic Carbon and Disinfection By-Product Concentrations

The highest average DOC concentrations (all sites) occurred during the October 2012 and September 2013 storms, both “first flush” event type of storms (storms 1 and 7; [fig. 9](#); [table 3](#)). Another storm in May 2013, sampled during a relatively low-flow period, produced a relatively high DOC concentration (13 mg/L DOC) in one sample collected at the 52nd Street stormwater outfall ([tables 4, 5](#)).

Concentrations of DBPs in treated drinking water generally tracked the DOC concentrations in raw water, with the highest concentrations occurring during the October, November, and December 2012 storm events ([fig. 10](#)). HAAs were also elevated during the February 2014 storm (but not THMs), when the DOC was 2.1 mg/L ([fig. 10A](#)). Over the past 20 years, based on quarterly compliance monitoring by EWEB ([fig. 4](#); Oregon Health Authority, 2020), the lowest concentrations of DBPs in treated drinking water have occurred during the months of January, when dilution is often large, and September, which is typically a base flow period when inputs from lower-basin tributaries is minimal and the dominant source of water is groundwater (Gannett and others 2003; Jefferson and others, 2004), discharge from Clear Lake and Trail Bridge Reservoir in the McKenzie River headwaters, and water releases from Cougar Reservoir and Blue River Lake.

Spatiotemporal Patterns in Dissolved Organic Carbon Concentrations

DOC concentrations ranged from 0.4 mg/L in the upper McKenzie River at Frissell Bridge (the forested reference site) to 16 mg/L in the 52nd Street stormwater outfall ([fig. 11](#)). DOC concentrations in the main stem averaged 1.5 mg/L (ranged from 0.4 to 3 mg/L) and generally increased downstream due to inputs from tributaries with higher concentrations of DOC including Blue River and South Fork McKenzie River, Quartz, Gate, Haagen, Camp, and Cedar

Creeks. The three highest DOC concentrations (10–16 mg/L) were observed at the 52nd Street stormwater outfall ([fig. 11](#); [table 4](#)), but, due to its low volume, the outfall did not increase DOC concentrations in the main stem McKenzie River appreciably during this study.

Average DOC concentrations increased 70 percent from Frissell Bridge to the EWEB water treatment plant intake ([table 4](#)). Nearly all of this increase occurred in the reach upstream of Vida, owing to tributary inputs including Quartz Creek, which drains industrial private forestland containing numerous plots of clear-cuts ([fig. 12](#)), Blue River, and the South Fork McKenzie River. These data generally point to the middle basin as an important contributor of DOC in the McKenzie River, and the local land use patterns suggests Quartz Creek be evaluated further for its contributions of organic carbon and DBP precursors, possibly from soil erosion after timber harvesting, especially in light of the recent wildfire.

DOC concentrations in the lower main stem from Vida to the EWEB intake did not change greatly. Despite the inputs of organic carbon from tributaries downstream of Vida, average DOC concentrations were just 2.7 percent higher, on average, at Hendricks Park, and about 2 percent lower downstream at the EWEB intake ([table 4](#)). Although seemingly paradoxical, high DOC concentrations in runoff may be partly counteracted or even diluted by inputs of low-DOC rainwater coming from impervious surfaces in developed parts of the lower basin during heavy precipitation events.

Disinfection By-Products in Finished Drinking Water

None of the samples collected for this study, or for the quarterly compliance monitoring by EWEB, exceeded EPA Maximum Contaminant Levels (MCLs) of 0.06 mg/L for total HAAs (HAA5) or 0.08 mg/L for total THMs (THM4) ([fig. 10](#)). Concentrations of bromodichloromethane (CHBrCl₂), however, ranged from 0.0007 to 0.012 mg/L (Carpenter, 2022), exceeding the MCL goal of 0 mg/L in all 11 samples of finished water.

Concentrations of DBPs in finished water averaged 0.025 mg/L for THMs and 0.031 mg/L for HAAs during the 11 storm events; maximum values were about 0.040 mg/L for both classes of DBPs ([fig. 10B](#)). The two highest THM4 and HAA5 concentrations occurred during a series of unusually large storms with peak flows of 20,000–26,000 ft³/s at Hayden Bridge ([table 3](#)), along with high turbidity, up to 40–45 FNU. However, those conditions are rare. Flows have been that high only twice between 2014 and 2019 (U.S. Geological Survey streamgage 14162500; U.S. Geological Survey, 2021a; https://waterdata.usgs.gov/nwis/uv/?site_no=14162500).

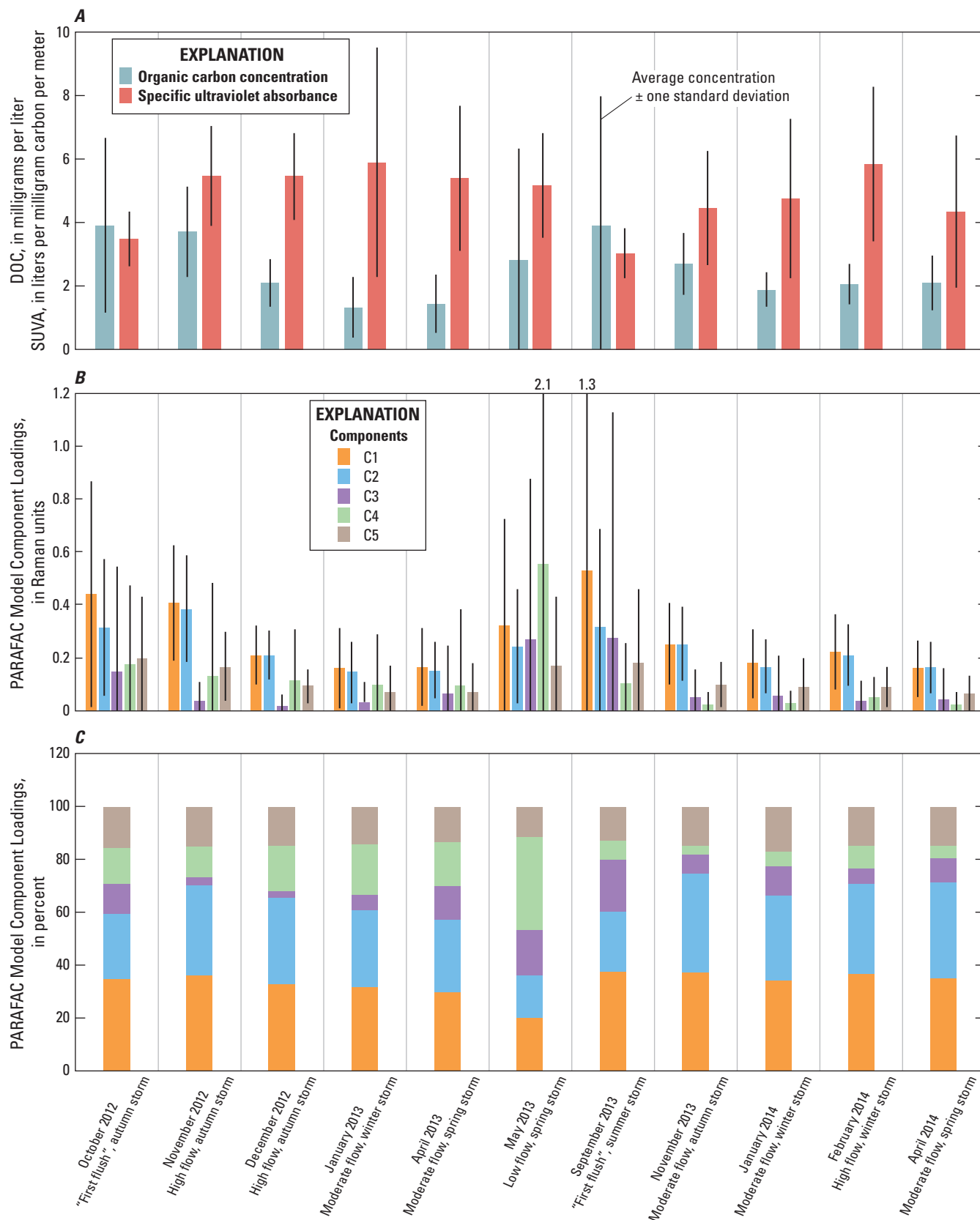


Figure 9. (A) Dissolved organic carbon (DOC) concentrations and specific ultraviolet absorbance (SUVA_{254}) and (B,C) parallel factor analysis (PARAFAC) model component loadings and percentages for all sites sampled during each storm event, McKenzie River, Oregon. X-axis dates are in month/year. mg/L, milligram per liter; \pm , plus or minus.

Table 4. Site and group average and standard deviation values for selected optical properties in the McKenzie River, tributaries, raw, and finished (treated) drinking water, 2012–14.

[Average values \pm standard deviation shown for each site or site group for all sampling dates. C1-C5 show parallel factor analysis (PARAFAC) model component loadings. Peaks A, C, M, D, and B refer to fluorescence within specific literature based ex-em regions. UVA₂₅₄ is the ultraviolet absorbance at 254 nanometers. SUVA₂₅₄, HIX, FI, BI, and β : α are defined in table 1. **Abbreviation and symbol:** AVG, average; DOC, dissolved organic carbon; STDEV, standard deviation; —, not applicable]

	DOC		UVA ₂₅₄		Peak A		Peak C		Peak M	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Sites, listed in general downstream order										
McKenzie River at Frissell Bridge	0.9	0.34	0.03	0.02	0.10	0.04	0.06	0.03	0.05	0.02
South Fork McKenzie River above Cougar Reservoir	2.2	0.84	0.08	0.03	0.31	0.12	0.20	0.08	0.13	0.06
South Fork McKenzie River near Rainbow	1.1	0.28	0.04	0.01	0.14	0.03	0.09	0.02	0.06	0.01
Blue River at McKenzie Highway Bridge	1.5	0.50	0.05	0.02	0.19	0.06	0.12	0.04	0.08	0.03
Quartz Creek at mouth near Finn Rock	3.1	0.97	0.14	0.05	0.45	0.16	0.29	0.11	0.20	0.09
McKenzie River near Vida	1.6	0.68	0.06	0.03	0.21	0.10	0.13	0.07	0.09	0.04
Gate Creek at Vida	2.4	1.44	0.11	0.06	0.35	0.21	0.22	0.14	0.15	0.11
Haagen Creek at McKenzie River	3.0	1.16	0.14	0.07	0.43	0.19	0.27	0.12	0.18	0.09
Haagen Creek at Deerhorn Road	3.3	1.91	0.16	0.08	0.48	0.30	0.30	0.20	0.21	0.14
McKenzie River at Hendricks Park	1.6	0.65	0.07	0.04	0.21	0.10	0.13	0.06	0.10	0.04
Unnamed tributary to Walterville Canal	2.7	1.34	0.16	0.07	0.60	0.23	0.36	0.14	0.28	0.11
Camp Creek at Camp Creek Road Bridge	3.7	1.53	0.28	0.05	0.68	0.24	0.41	0.15	0.30	0.11
Cedar Creek at Springfield	2.6	1.11	0.21	0.13	0.57	0.27	0.33	0.15	0.28	0.14
52 nd St. stormwater outfall at Highway 126	6.1	4.40	0.21	0.07	1.59	1.31	0.75	0.58	0.89	0.77
McKenzie River above Hayden Bridge	1.6	0.66	0.07	0.04	0.22	0.11	0.13	0.07	0.10	0.05
Finished water from Hayden Bridge DWTP	0.8	0.24	0.01	0.00	0.05	0.01	0.03	0.01	0.03	0.01
Site groups										
Reference: McKenzie River at Frissell Bridge	0.9	0.34	0.03	0.02	0.10	0.04	0.06	0.03	0.05	0.02
Reference: South Fork McKenzie River above Cougar Reservoir	2.2	0.84	0.08	0.03	0.31	0.12	0.20	0.08	0.13	0.06
Blue River and South Fork McKenzie near Rainbow (Reservoir outflows)	1.3	0.39	0.05	0.02	0.17	0.05	0.11	0.03	0.07	0.02
All McKenzie River mainstem sites	1.4	0.58	0.06	0.03	0.19	0.09	0.12	0.06	0.08	0.04
Three middle basin tributaries (Quartz, Gate, Haagen Creeks [lower only])	2.8	1.19	0.13	0.06	0.41	0.19	0.26	0.12	0.18	0.09
Forested tributaries (lower Haagen only, not at Deerhorn)	2.2	0.87	0.09	0.04	0.31	0.13	0.20	0.09	0.14	0.06
McKenzie River at Hendricks Park	1.6	0.65	0.07	0.04	0.21	0.10	0.13	0.06	0.10	0.04
Lower basin tributaries and 52 nd St. outfall	3.8	2.10	0.22	0.08	0.86	0.51	0.46	0.26	0.43	0.28
Watershed samples (no finished water samples)	2.5	1.19	0.12	0.05	0.44	0.23	0.25	0.13	0.21	0.12
McKenzie River above Hayden Bridge (source water)	1.6	0.66	0.07	0.04	0.22	0.11	0.13	0.07	0.10	0.05
Finished water from Hayden Bridge DWTP	0.8	0.24	0.01	0.00	0.05	0.01	0.03	0.01	0.03	0.01
Percentage changes between key mainstem sites										
Frissell to Vida	68	—	104	—	102	—	99	—	100	—
Vida to Hendricks Park	2.7	—	11.9	—	3.8	—	3.0	—	5.5	—
Hendricks Park to Hayden Bridge	−2	—	12	—	1	—	−0.4	—	1	—
Frissell to Hayden Bridge	70	—	156	—	112	—	104	—	113	—
Percentage changes between source and finished water										
Hayden Bridge raw vs finished (percent change)	−48	—	−86	—	−78	—	−77	—	−70	—

Table 4. Site and group average and standard deviation values for selected optical properties in the McKenzie River, tributaries, raw, and finished (treated) drinking water, 2012–14. —Continued

[Average values +/- standard deviation shown for each site or site group for all sampling dates. C1-C5 show parallel factor analysis (PARAFAC) model component loadings. Peaks A, C, M, D, and B refer to fluorescence within specific literature based ex-em regions. UVA₂₅₄ is the ultraviolet absorbance at 254 nanometers. SUVA₂₅₄, HIX, FI, BI, and $\beta:\alpha$ are defined in table 1. **Abbreviation and symbol:** AVG, average; DOC, dissolved organic carbon; STDEV, standard deviation; —, not applicable]

	Peak D		Peak B		Peak T		Peak N		fDOM	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Sites, listed in general downstream order										
McKenzie River at Frissell Bridge	0.03	0.01	0.03	0.03	0.03	0.01	0.03	0.01	0.05	0.02
South Fork McKenzie River above Cougar Reservoir	0.09	0.04	0.01	0.05	0.06	0.04	0.08	0.04	0.16	0.06
South Fork McKenzie River near Rainbow	0.04	0.01	0.01	0.02	0.03	0.01	0.04	0.01	0.07	0.02
Blue River at McKenzie Highway Bridge	0.06	0.02	0.00	0.01	0.04	0.01	0.05	0.02	0.09	0.03
Quartz Creek at mouth near Finn Rock	0.14	0.04	0.00	0.04	0.09	0.06	0.13	0.06	0.23	0.08
McKenzie River near Vida	0.06	0.03	0.01	0.02	0.05	0.03	0.06	0.03	0.10	0.05
Gate Creek at Vida	0.10	0.06	0.00	0.02	0.08	0.05	0.10	0.07	0.17	0.10
Haagen Creek at Mckenzie River	0.13	0.06	0.01	0.06	0.11	0.06	0.13	0.07	0.22	0.10
Haagen Creek at Deerhorn Road	0.15	0.09	–0.01	0.04	0.11	0.08	0.14	0.10	0.24	0.15
McKenzie River at Hendricks Park	0.06	0.03	0.02	0.03	0.06	0.02	0.07	0.03	0.11	0.05
Unnamed tributary to Walterville Canal	0.14	0.06	0.08	0.04	0.18	0.08	0.22	0.08	0.26	0.11
Camp Creek at Camp Creek Road Bridge	0.18	0.06	0.05	0.07	0.19	0.07	0.22	0.08	0.32	0.11
Cedar Creek at Springfield	0.13	0.06	0.06	0.08	0.19	0.09	0.23	0.14	0.24	0.12
52 nd St. stormwater outfall at Highway 126	0.25	0.15	1.03	1.40	0.79	0.53	0.86	0.65	0.48	0.31
McKenzie River above Hayden Bridge	0.06	0.03	0.01	0.02	0.05	0.03	0.07	0.03	0.10	0.06
Finished water from Hayden Bridge DWTP	0.01	0.00	0.01	0.01	0.01	0.01	0.02	0.00	0.02	0.00
Site groups										
Reference: McKenzie River at Frissell Bridge	0.03	0.01	0.03	0.03	0.03	0.01	0.03	0.01	0.05	0.02
Reference: South Fork McKenzie River above Cougar Reservoir	0.09	0.04	0.01	0.05	0.06	0.04	0.08	0.04	0.16	0.06
Blue River and South Fork McKenzie near Rainbow (Reservoir outflows)	0.05	0.02	0.01	0.02	0.04	0.01	0.05	0.01	0.08	0.03
All McKenzie River mainstem sites	0.05	0.03	0.02	0.02	0.05	0.02	0.06	0.03	0.09	0.05
Three middle basin tributaries (Quartz, Gate, Haagen Creeks [lower only])	0.12	0.05	0.00	0.04	0.09	0.06	0.12	0.07	0.20	0.09
Forested tributaries (lower Haagen only, not at Deerhorn)	0.09	0.04	0.01	0.03	0.07	0.04	0.09	0.04	0.15	0.07
McKenzie River at Hendricks Park	0.06	0.03	0.02	0.03	0.06	0.02	0.07	0.03	0.11	0.05
Lower basin tributaries and 52 nd St. outfall	0.18	0.08	0.30	0.40	0.34	0.19	0.38	0.24	0.33	0.16
Watershed samples (no finished water samples)	0.11	0.05	0.09	0.13	0.14	0.08	0.16	0.10	0.19	0.09
McKenzie River above Hayden Bridge (source water)	0.06	0.03	0.01	0.02	0.05	0.03	0.07	0.03	0.10	0.06
Finished water from Hayden Bridge DWTP	0.01	0.00	0.01	0.01	0.01	0.01	0.02	0.00	0.02	0.00
Percentage changes between key mainstem sites										
Frissell to Vida	100	—	–54	—	95	—	111	—	101	—
Vida to Hendricks Park	2.2	—	69.3	—	9.4	—	6.2	—	2.9	—
Hendricks Park to Hayden Bridge	–3	—	–46	—	–7	—	–0.5	—	–2	—
Frissell to Hayden Bridge	99	—	–58	—	100	—	123	—	102	—
Percentage changes between source and finished water										
Hayden Bridge raw vs finished (percent change)	–88	—	–31	—	–79	—	–76	—	–83	—

Table 4. Site and group average and standard deviation values for selected optical properties in the McKenzie River, tributaries, raw, and finished (treated) drinking water, 2012–14. —Continued

[Average values +/- standard deviation shown for each site or site group for all sampling dates. C1-C5 show parallel factor analysis (PARAFAC) model component loadings. Peaks A, C, M, D, and B refer to fluorescence within specific literature based ex-em regions. UVA₂₅₄ is the ultraviolet absorbance at 254 nanometers. SUVA₂₅₄, HIX, FI, BI, and $\beta:\alpha$ are defined in table 1. **Abbreviation and symbol:** AVG, average; DOC, dissolved organic carbon; STDEV, standard deviation; —, not applicable]

	SUVA ₂₅₄		HIX		FI		$\beta:\alpha$	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Sites, listed in general downstream order								
McKenzie River at Frissell Bridge	3.31	1.20	0.87	0.07	1.62	0.09	0.53	0.03
South Fork McKenzie River above Cougar Reservoir	3.90	0.56	0.90	0.03	1.60	0.07	0.50	0.01
South Fork McKenzie River near Rainbow	3.54	0.60	0.89	0.03	1.63	0.08	0.54	0.01
Blue River at McKenzie Highway Bridge	3.43	0.72	0.90	0.03	1.66	0.09	0.54	0.02
Quartz Creek at mouth near Finn Rock	4.53	0.62	0.89	0.02	1.62	0.06	0.51	0.01
McKenzie River near Vida	3.67	0.77	0.88	0.03	1.64	0.08	0.52	0.05
Gate Creek at Vida	4.60	0.89	0.88	0.03	1.63	0.07	0.52	0.02
Haagen Creek at McKenzie River	4.80	1.09	0.87	0.02	1.64	0.10	0.50	0.01
Haagen Creek at Deerhorn Road	5.17	1.03	0.88	0.02	1.61	0.08	0.50	0.01
McKenzie River at Hendricks Park	4.03	0.89	0.87	0.03	1.64	0.09	0.53	0.02
Unnamed tributary to Walterville Canal	6.38	1.58	0.85	0.02	1.68	0.06	0.59	0.03
Camp Creek at Camp Creek Road Bridge	8.62	2.65	0.83	0.03	1.64	0.08	0.55	0.04
Cedar Creek at Springfield	8.08	3.65	0.82	0.02	1.66	0.07	0.61	0.03
52 nd St. stormwater outfall at Highway 126	4.20	1.40	0.76	0.06	1.63	0.08	0.66	0.04
McKenzie River above Hayden Bridge	4.54	1.16	0.87	0.03	1.63	0.07	0.53	0.01
Finished water from Hayden Bridge DWTP	1.35	0.45	0.87	0.05	1.94	0.27	0.53	0.03
Site groups								
Reference: McKenzie River at Frissell Bridge	3.31	1.20	0.87	0.07	1.62	0.09	0.53	0.03
Reference: South Fork McKenzie River above Cougar Reservoir	3.90	0.56	0.90	0.03	1.60	0.07	0.50	0.01
Blue River and South Fork McKenzie near Rainbow (Reservoir outflows)	3.48	0.66	0.89	0.03	1.64	0.09	0.54	0.02
All McKenzie River mainstem sites	3.89	1.00	0.87	0.04	1.63	0.08	0.53	0.03
Three middle basin tributaries (Quartz, Gate, Haagen Creeks [lower only])	4.64	0.87	0.88	0.03	1.63	0.08	0.51	0.01
Forested tributaries (lower Haagen only, not at Deerhorn)	4.13	0.75	0.89	0.03	1.63	0.08	0.52	0.01
McKenzie River at Hendricks Park	4.03	0.89	0.87	0.03	1.64	0.09	0.53	0.02
Lower basin tributaries and 52nd St. outfall	6.82	2.32	0.81	0.04	1.65	0.08	0.60	0.04
Watershed samples (no finished water samples)	4.85	1.25	0.86	0.03	1.63	0.08	0.54	0.02
McKenzie River above Hayden Bridge (source water)	4.54	1.16	0.87	0.03	1.63	0.07	0.53	0.01
Finished water from Hayden Bridge DWTP	1.35	0.45	0.87	0.05	1.94	0.27	0.53	0.03
Percentage changes between key mainstem sites								
Frissell to Vida	11	—	0.5	—	1	—	-1	—
Vida to Hendricks Park	9.7	—	-1.1	—	0.0	—	1.1	—
Hendricks Park to Hayden Bridge	13	—	0.2	—	-0.4	—	1	—
Frissell to Hayden Bridge	37	—	-0.4	—	1	—	2	—
Percentage changes between source and finished water								
Hayden Bridge raw vs finished (percent change)	-70	—	0.01	—	19	—	-2	—

Table 5. Site and group average and standard deviation for parallel factor analysis (PARAFAC) model loadings and percentages.

[Average values +/- standard deviation shown for each site or site group for all sampling dates. C1-C5 show PARAFAC model component loadings. PARAFAC component fluorescence given in Raman Units and as a percentage. **Abbreviation:** DWTP, drinking water treatment plant]

	C1		C2		C3		C4		C5	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Sites, listed in general downstream order										
McKenzie River at Frissell Bridge	0.07	0.03	0.07	0.03	0.00	0.00	0.03	0.03	0.02	0.01
South Fork McKenzie River above Cougar Reservoir	0.20	0.09	0.21	0.08	0.00	0.00	0.03	0.05	0.06	0.03
South Fork McKenzie River near Rainbow	0.10	0.02	0.09	0.03	0.01	0.01	0.02	0.02	0.03	0.01
Blue River at McKenzie Highway Bridge	0.13	0.04	0.12	0.05	0.01	0.01	0.01	0.01	0.04	0.02
Quartz Creek at mouth near Finn Rock	0.30	0.14	0.30	0.09	0.01	0.01	0.03	0.04	0.10	0.05
McKenzie River near Vida	0.14	0.07	0.14	0.07	0.00	0.00	0.02	0.02	0.05	0.03
Gate Creek at Vida	0.24	0.17	0.22	0.12	0.01	0.01	0.02	0.02	0.08	0.06
Haagen Creek at McKenzie River	0.28	0.14	0.29	0.13	0.01	0.01	0.04	0.05	0.11	0.05
Haagen Creek at Deerhorn Road	0.31	0.22	0.33	0.19	0.01	0.01	0.03	0.04	0.11	0.08
McKenzie River at Hendricks Park	0.14	0.07	0.14	0.07	0.01	0.01	0.03	0.02	0.05	0.03
Unnamed tributary to Walterville Canal	0.40	0.16	0.34	0.14	0.07	0.03	0.11	0.06	0.17	0.07
Camp Creek at Camp Creek Road Bridge	0.45	0.18	0.42	0.13	0.03	0.02	0.12	0.05	0.19	0.06
Cedar Creek at Springfield	0.37	0.18	0.31	0.15	0.13	0.18	0.11	0.04	0.18	0.08
52 nd St. stormwater outfall at Highway 126	0.97	0.89	0.56	0.32	0.89	0.89	1.08	1.40	0.53	0.28
McKenzie River above Hayden Bridge	0.14	0.08	0.14	0.08	0.01	0.01	0.03	0.02	0.05	0.03
Finished water from Hayden Bridge DWTP	0.04	0.01	0.02	0.00	0.01	0.00	0.01	0.01	0.01	0.01
Site groups										
Reference: McKenzie River at Frissell Bridge	0.07	0.03	0.07	0.03	0.00	0.00	0.03	0.03	0.02	0.01
Reference: South Fork McKenzie River above Cougar Reservoir	0.20	0.09	0.21	0.08	0.00	0.00	0.03	0.05	0.06	0.03
Blue River and South Fork McKenzie near Rainbow (Reservoir outflows)	0.11	0.03	0.11	0.04	0.01	0.01	0.01	0.01	0.03	0.01
All McKenzie River mainstem sites	0.12	0.06	0.12	0.06	0.01	0.00	0.03	0.02	0.04	0.02
Three middle basin tributaries (Quartz, Gate, Haagen Creeks [lower only])	0.28	0.15	0.27	0.11	0.01	0.01	0.03	0.04	0.09	0.05
Forested tributaries (lower Haagen only, not at Deerhorn)	0.21	0.10	0.21	0.08	0.01	0.01	0.02	0.03	0.07	0.04
McKenzie River at Hendricks Park	0.14	0.07	0.14	0.07	0.01	0.01	0.03	0.02	0.05	0.03
Lower basin tributaries and 52nd St. outfall	0.55	0.35	0.41	0.19	0.28	0.28	0.36	0.39	0.27	0.12
Watershed samples (no finished water samples)	0.28	0.16	0.24	0.11	0.08	0.08	0.11	0.13	0.12	0.06
McKenzie River above Hayden Bridge (source water)	0.14	0.08	0.14	0.08	0.01	0.01	0.03	0.02	0.05	0.03
Finished water from Hayden Bridge DWTP	0.04	0.01	0.02	0.00	0.01	0.00	0.01	0.01	0.01	0.01
Percentage changes between key mainstem sites										
Frissell to Vida	99	—	102	—	287	—	-22	—	128	—
Vida to Hendricks Park	3.6	—	3.2	—	90.4	—	42.6	—	4.9	—
Hendricks Park to Hayden Bridge	1	—	-3	—	41.2	—	-13	—	-1	—
Frissell to Hayden Bridge	109	—	102	—	941	—	-4	—	136	—
Percentage changes between source and finished water										
Hayden Bridge raw vs finished (percent change)	-70	—	-89	—	-11	—	-65	—	-85	—

Table 5. Site and group average and standard deviation for parallel factor analysis (PARAFAC) model loadings and percentages. — Continued

[Average values +/- standard deviation shown for each site or site group for all sampling dates. C1-C5 show PARAFAC model component loadings. PARAFAC component fluorescence given in Raman Units and as a percentage. **Abbreviation:** DWTP, drinking water treatment plant]

	Pct_C1		Pct_C2		Pct_C3		Pct_C4		Pct_C5	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Sites, listed in general downstream order										
McKenzie River at Frissell Bridge	36.9	6.4	36.9	8.3	0.8	1.1	13.8	17.3	11.6	3.4
South Fork McKenzie River above Cougar Reservoir	40.3	1.6	43.5	4.4	0.4	0.9	3.3	5.1	12.4	1.4
South Fork McKenzie River near Rainbow	39.8	2.9	36.3	3.6	4.4	3.1	7.5	6.7	12.1	1.6
Blue River at McKenzie Highway Bridge	42.0	1.6	40.2	4.3	2.4	2.8	2.7	3.4	12.7	1.9
Quartz Creek at mouth near Finn Rock	40.9	2.1	42.9	5.5	0.9	1.7	2.8	3.6	12.5	1.6
McKenzie River near Vida	38.2	2.7	38.6	5.0	1.8	2.2	6.5	5.6	14.8	5.9
Gate Creek at Vida	40.1	3.6	40.1	4.4	2.0	1.8	4.5	4.9	13.4	1.4
Haagen Creek at Mckenzie River	39.0	1.7	40.4	6.4	1.1	1.7	5.1	5.5	14.4	1.4
Haagen Creek at Deerhorn Road	38.5	3.0	43.1	3.9	1.0	1.5	3.5	4.2	13.8	0.9
McKenzie River at Hendricks Park	37.1	3.0	37.2	5.8	2.9	2.5	8.9	8.2	13.9	2.2
Unnamed tributary to Walterville Canal	36.7	2.4	31.0	1.9	7.0	2.6	10.1	2.9	15.1	1.0
Camp Creek at Camp Creek Road Bridge	36.3	2.9	34.9	2.4	2.8	1.5	10.6	4.6	15.4	0.9
Cedar Creek at Springfield	33.2	2.7	28.7	6.1	10.9	8.9	10.6	3.9	16.5	0.6
52 nd St. stormwater outfall at Highway 126	24.3	6.2	16.0	5.0	20.5	8.0	24.1	15.6	15.0	3.5
McKenzie River above Hayden Bridge	38.2	2.4	36.3	5.1	4.1	2.6	7.5	6.5	13.9	1.5
Finished water from Hayden Bridge DWTP	50.0	5.7	18.1	3.3	13.0	3.8	10.1	7.8	8.8	4.4
Site groups										
Reference: McKenzie River at Frissell Bridge	36.9	6.4	36.9	8.3	0.8	1.1	13.8	17.3	11.6	3.4
Reference: South Fork McKenzie River above Cougar Reservoir	40.3	1.6	43.5	4.4	0.4	0.9	3.3	5.1	12.4	1.4
Blue River and South Fork McKenzie near Rainbow (Reservoir outflows)	40.9	2.3	38.2	3.9	3.4	3.0	5.1	5.1	12.4	1.7
All McKenzie River mainstem sites	37.6	3.6	37.2	6.1	2.4	2.1	9.2	9.4	13.5	3.2
Three middle basin tributaries (Quartz, Gate, Haagen Creeks [lower only])	40.0	2.5	41.1	5.5	1.3	1.7	4.1	4.6	13.4	1.5
Forested tributaries (lower Haagen only, not at Deerhorn)	40.3	2.3	40.6	4.8	1.9	2.0	4.3	4.9	12.9	1.5
McKenzie River at Hendricks Park	37.1	3.0	37.2	5.8	2.9	2.5	8.9	8.2	13.9	2.2
Lower basin tributaries and 52 nd St. outfall	32.6	3.6	27.7	3.8	10.3	5.2	13.9	6.8	15.5	1.5
Watershed samples (no finished water samples)	37.4	3.0	36.4	4.8	4.2	2.9	8.1	6.5	13.8	1.9
McKenzie River above Hayden Bridge (source water)	38.2	2.4	36.3	5.1	4.1	2.6	7.5	6.5	13.9	1.5
Finished water from Hayden Bridge DWTP	50.0	5.7	18.1	3.3	13.0	3.8	10.1	7.8	8.8	4.4
Percentage changes between key mainstem sites										
Frissell to Vida	4	—	5	—	122	—	-53	—	28	—
Vida to Hendricks Park	-2.9	—	-3.7	—	60.0	—	36.5	—	-6.5	—
Hendricks Park to Hayden Bridge	3	—	-2	—	42	—	-16	—	0	—
Frissell to Hayden Bridge	4	—	-2	—	405	—	-46	—	20	—
Percentage changes between source and finished water										
Hayden Bridge raw vs finished (percent change)	31	—	-50	—	217	—	34	—	-37	—

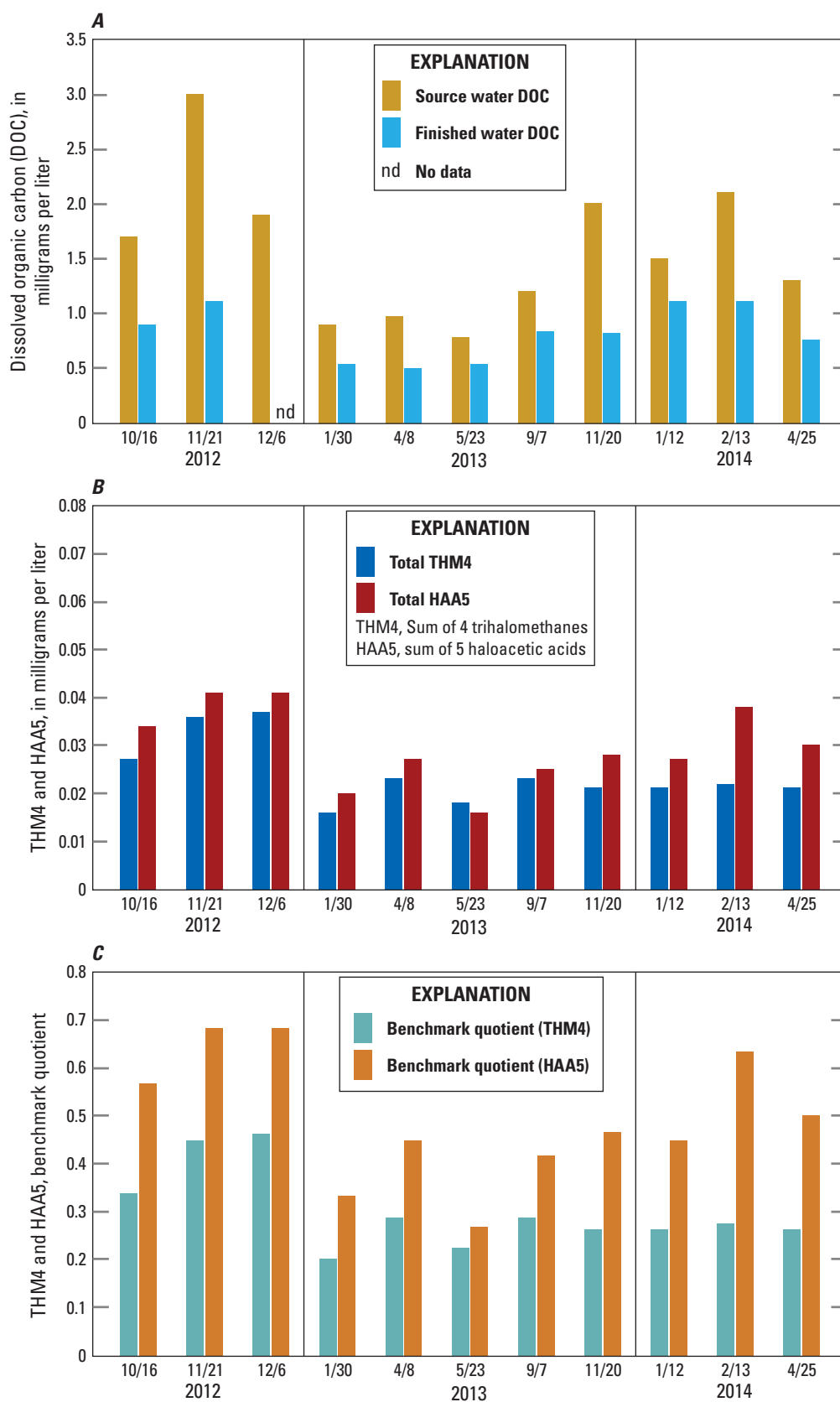


Figure 10. Concentrations of (A) dissolved organic carbon (DOC) in source and finished water of the Eugene Water & Electric Board (EWEB) drinking water treatment plant, (B) disinfection by-products in finished water, and (C) resulting benchmark quotients, McKenzie River, Oregon.

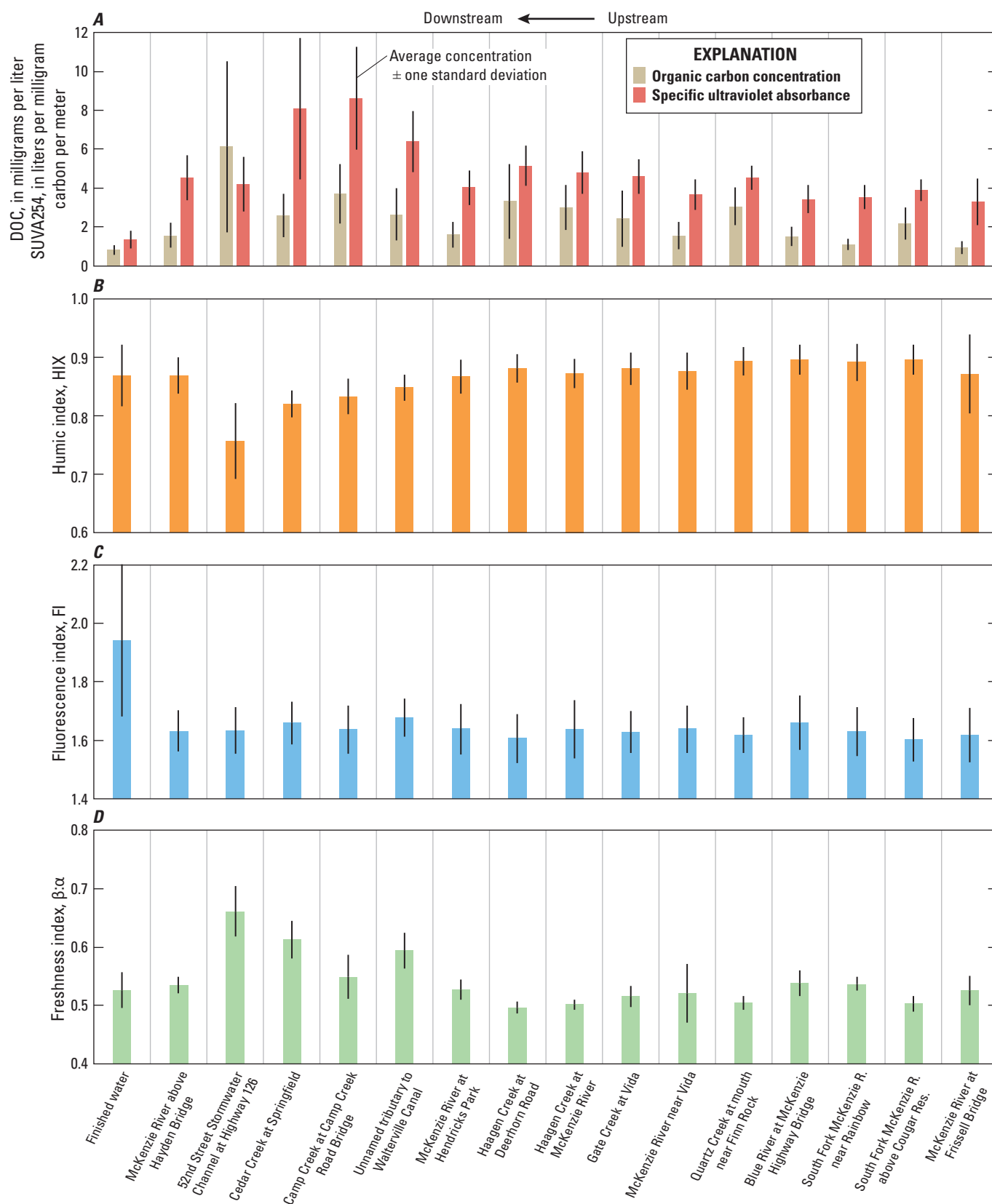


Figure 11. Graphs showing (A) concentrations of dissolved organic carbon (DOC) and specific ultraviolet absorbance (SUVA₂₅₄), (B) humification index (HIX), (C) fluorescence index (FI), and (D) freshness index ($\beta:\alpha$) values in the McKenzie River, tributaries, raw, and finished (treated) drinking water, Oregon, 2012–14.

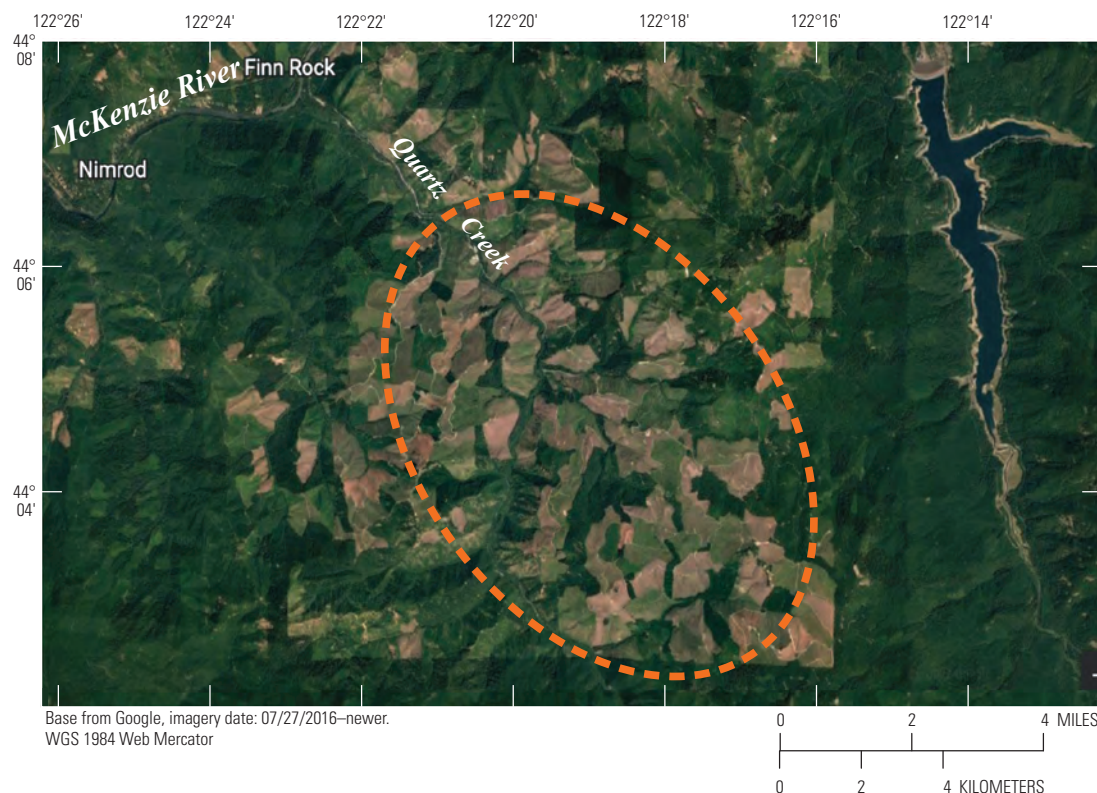


Figure 12. Aerial image of the Quartz Creek Basin in the middle McKenzie River Basin southeast of Nimrod, Oregon, in various states of harvest and regrowth (red dotted line) prior to 2020 wildfires. Image taken from Google Earth, 2021.

The two highest concentrations of DBPs in finished water occurred during back-to-back storms in November and December 2012 (fig. 10). The November storm produced approximately 50 percent higher DOC concentrations compared with December's storm, yet DBP concentrations were similar for both THMs and HAAs (fig. 10). Higher stream-flow in December ($> 26,000 \text{ ft}^3/\text{s}$) may have caused further dilution of the DOC concentrations but mobilized DOC with greater potential for DBP formation. The DOC and DBP concentrations, especially THM4, were lower in subsequent storms, in January through September 2013 until a storm in February 2014 produced some elevated HAA concentrations, but not THMs (fig. 10).

Compared with samples collected for this study, the routine compliance samples resulted in slightly higher DBP concentrations, up to 0.046 mg/L THM4 and 0.047 mg/L HAA5 in December 2012; corresponding Benchmark Quotient Values (BQ) and ratio of the measured concentrations to the EPA MCL were 0.58 and 0.78, respectively, for THM4 and HAA5 for these compliance samples. The higher BQ for HAAs places greater emphasis on the importance of identifying the sources of DOC that form these compounds. Although SUVA_{254} was higher during this December 2012 period (fig. 9), it was not significantly correlated with any DBPs (see correlation results below).

In this study, THM4 and HAA5 concentrations in finished water were 68 and 33 percent higher, respectively, than those reported in a 2007–08 study, likely because source-water DOC concentrations were twice as high, averaging 1.6 mg/L in this study compared with 0.8 mg/L in 2007–08 (Kraus and others, 2010). We attribute the higher DOC and DBP concentrations in this study to the current focus on sampling storms, as the highest DOC concentrations tend to occur during storm runoff.

The maximum DBP concentrations of $0.04\text{--}0.05 \text{ mg/L}$ for THM4 and HAA5 were comparable to those found in the nearby Clackamas River (Carpenter and others, 2013), but the average concentration for HAA5 was about 40 percent higher in the McKenzie River: 0.031 mg/L during this study compared with 0.022 mg/L in the 2010–2011 Clackamas River study. This finding is relevant because the EPA MCL for HAA5 (0.06 mg/L) is lower than the MCL for THM4 (0.08 mg/L). Therefore, maximum BQs were higher for HAAs ($\text{BQ}_{\text{HAA5}} = 0.68$) than THMs ($\text{BQ}_{\text{THM4}} = 0.46$) (fig. 10); on average, BQ_{HAA5} was 0.5 and BQ_{THM4} was 0.3.

Finished water THM4 and HAA5 concentrations increased on September 30, 2013; however, DOC or optical data were unavailable. Toward the end of the study in February 2014, the same storm that produced high flows over $26,000 \text{ ft}^3/\text{s}$ at Hayden Bridge resulted in elevated BQ_{HAA5}

(BQ = 0.63), but THM4 remained low (BQ < 0.3) (fig. 10), demonstrating the varied and dynamic nature of the occurrence of these two classes of DBPs.

Five Components Identified in the Parallel Factor Analysis (PARAFAC) Model

Parallel Factor Analysis (PARAFAC) identified a 5-component model representing five distinct organic matter fluorophores: Components C1–C5 (fig. 13). Comparing these 5 components with those identified by Kraus and others (2010) and Carpenter and others (2013)—all from Cascade Range rivers—suggests that components C1, C2, and C3 represent DOM associated with microbially processed and therefore more-humified carbon that is likely soil derived (fig. 13). Components C4 and C5 represent “fresher,” more recently produced and less processed DOM, derived from plant litter, including polyphenolic plant compounds, leaves and other freshly decomposed organic matter, or algae and cyanobacteria from the reservoirs and periphytic benthic algae in the main stem, and DOM mobilized during storms from exposed reservoir sediments (McKnight and others, 2001; Stedmon and others, 2003; Coble, 2007; Hudson and others, 2007; Stedmon and Bro, 2008; Cory and others, 2010).

Components C1 and C2 were present in all water samples, and all five components were present at each site at least during one high flow event during the study. PARAFAC models were constructed using EEMs from watershed, source, and finished water samples. Based on the comparison of PARAFAC models for each type of water sample, it was concluded suitable to use a single PARAFAC model including all types of samples (figs. 13, 14). Model output resulted in a good fit (90 percent or greater) between the measured and modeled EEMs (data not shown).

DOM composition can be discerned by examining the percent contribution of PARAFAC model components. The percent contribution of the component loadings for McKenzie River at the EWEB intake were nearly identical to the watershed averages—approximately 37 percent C1, 36 percent C2, 14 percent C5, 8 percent C4, and 4 percent C3—with some variation by site (table 4) and storm event (fig. 9). Although this carbon is likely dominated by natural sources of DOM leaching out of forest soils, human activities such as road construction and timber harvesting that cause erosion (Swanston and Swanson, 1976) may contribute organic leachates that reach surface waters from overland or subsurface pathways. And some of this may leach down into deep soil layers (Lee and Lajtha 2016).

PARAFAC model components C1 and C2 were highly correlated to DOC concentration ($\rho = 0.93$, $p < 0.001$; table 6) and DBP concentrations ($\rho = 0.94$, $p < 0.001$; fig. 15; table 8). C1 was highly correlated with C2, C3, and C5; peaks A, C, M, N, and D, and fDOM; whereas C2 was highly correlated with

peaks A, C, M, N, D, fDOM, and C5 (table 6). The loadings of C1 and C2 increased about 100 percent in the upper McKenzie River from Frissell Bridge to Vida, with a 10 percent further increase in C1, and no increase in C2 downstream at the EWEB intake (table 4). This longitudinal pattern indicates that the major DOM sources of C1 and C2 are in the middle-basin tributaries, upstream from the most developed portion of the basin, or that low DOM rainfall runoff from the developed areas dilutes some of the DOM pool in the river by the time it reaches the EWEB intake. This latter dilution hypothesis is in line with trends seen in the DOC concentration data.

Component C3, which was a “new” component identified in the present study compared to the findings from Kraus and others (2010) (fig. 13), is similar to C1 and C2 in that it represents humic-like DOM derived from terrestrial sources. C3 contributed less than 5 percent of the total fluorescent DOM pool at all sites except the 52nd Street stormwater outfall where it represented about 20 percent on average (fig. 14; table 4). This outfall was not sampled during the previous 2007–08 study, which may explain its absence in the original PARAFAC model.

Other sites with a relatively high contribution of C3 to total fluorescence included Cedar and Camp Creeks, and the unnamed tributary to Walterville Canal. C3 was notably higher during the October 2012 and September 2013 “first flush” events, and during the May 2013 low-flow spring storm, but only at these lower-basin tributary and outfall sites, suggesting that this DOM source material may be attributed to floodplain soils in agricultural and otherwise developed areas downstream from Hendricks Park. C3 was most highly correlated with peaks A, M, N, and T (table 6).

The fluorescence response of C4 (table 5) was highly correlated to peak B ($\rho = 1.00$; table 6), which occurs in the region of EEMs (fig. 2) that is typically associated with fresh-like DOM likely derived from fresh litter leachates, including polyphenolic plant compounds, and (or) from algae and cyanobacteria (see references listed in table 5). Across all sites and dates, C4, similar to C3, had the highest model loadings at tributary sites in the lower basin, especially the 52nd Street stormwater outfall (fig. 14; Carpenter 2022). C3 and C4 were not as highly correlated with DOC concentration as C1, C2, and C5 (table 6), and may therefore represent a lower risk for producing DBPs.

The fluorescence response of C5 (table 5) occurs in the region of EEMs (fig. 2) typically associated with fresh-like DOM, and was highly correlated with peaks M, N, and T ($\rho = 0.94$ – 0.97 , table 6). C5 was lowest in the upper-basin sites, higher in the middle-basin tributaries (Quartz, Gate, and Haagen Creeks), and most abundant in the lower-basin tributaries (fig. 14). Of all the carbon indices, the Freshness Index ($\beta:\alpha$) had the highest correlations with the percentage of C5, considering all watershed samples (Pct_C5; $\rho = 0.39$, $p < 0.001$, table 7) suggesting that C5 represents organic matter that was recently produced.



Figure 13. Five parallel factor analysis (PARAFAC) model components identified in the PARAFAC model for the McKenzie River Basin, Oregon.

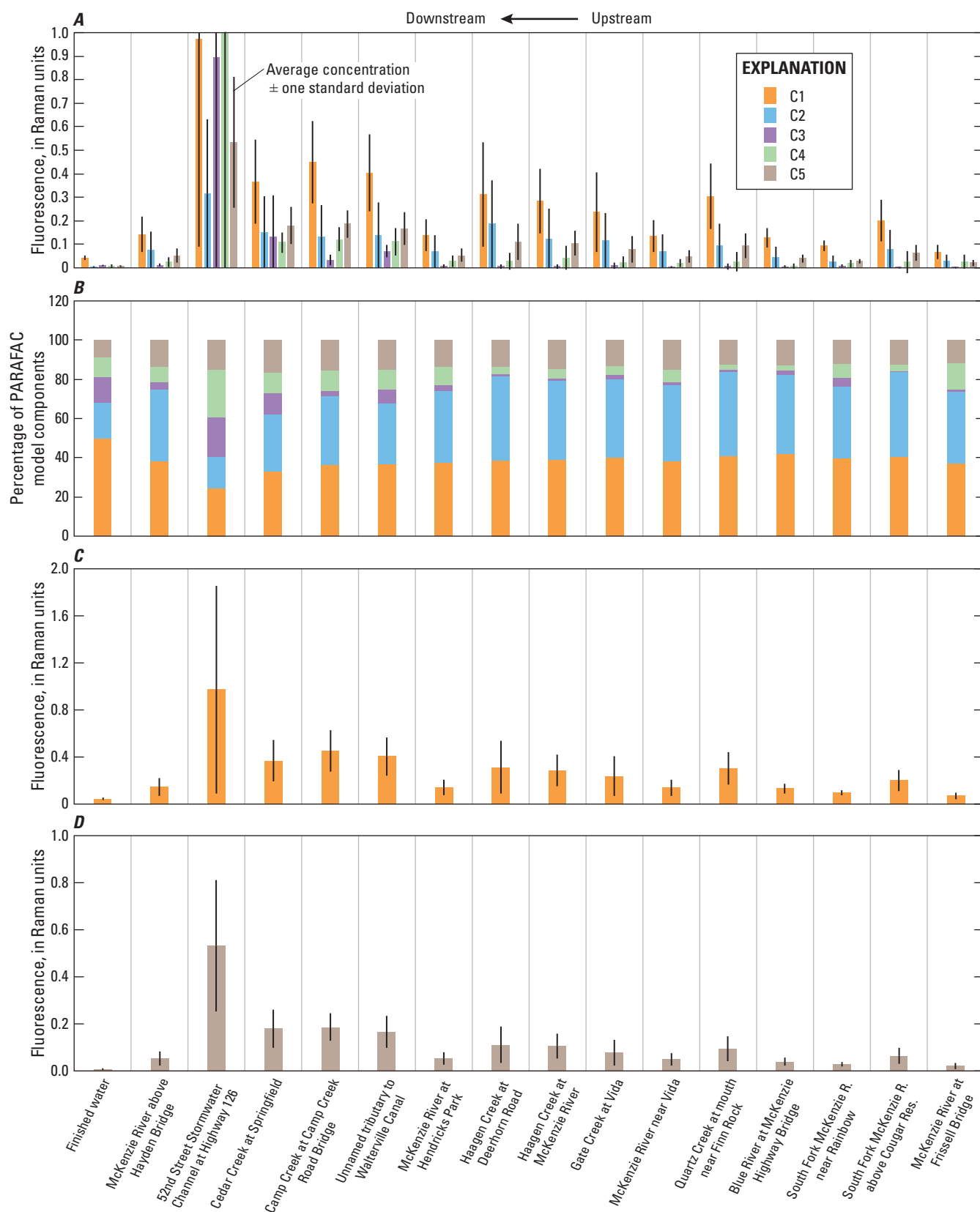


Figure 14. Graphs showing the (A) parallel factor analysis (PARAFAC) model component loadings, (B) percentage of PARAFAC model component loadings, and (C, D) and loading of components C1 and C5 in the McKenzie River Basin, Oregon, 2012–14.

Table 6. Spearman rank correlations (rho values) showing relationships among dissolved organic carbon concentrations, peaks, and other optical properties for all watershed samples (excludes finished water samples) (n=150).

[See Abbreviations and Acronyms (p. vii–viii) and table 1 for variable definitions. Locations of the various peaks are shown in figure 2. Spearman rank correlations (rho values), with p value significance indicated by asterisks: * $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$]

Variable	DOC	UVA ₂₅₄	Peak A	Peak C	Peak M	Peak D	Peak B	Peak T	Peak N	fDOM	C1	C2	C3	C4	C5
DOC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
UVA ₂₅₄	0.73***	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Peak A	0.93***	0.65***	—	—	—	—	—	—	—	—	—	—	—	—	—
Peak C	0.95***	0.73***	0.99***	—	—	—	—	—	—	—	—	—	—	—	—
Peak M	0.91***	0.58***	0.99***	0.97***	—	—	—	—	—	—	—	—	—	—	—
Peak D	0.95***	0.84***	0.92***	0.97***	0.88***	—	—	—	—	—	—	—	—	—	—
Peak B	0.56***	0.25*	0.53***	0.46***	0.55***	0.39***	—	—	—	—	—	—	—	—	—
Peak T	0.83***	0.52***	0.85***	0.81***	0.86***	0.73***	0.86***	—	—	—	—	—	—	—	—
Peak N	0.88***	0.54***	0.97***	0.93***	0.98***	0.83***	0.67***	0.93***	—	—	—	—	—	—	—
fDOM	0.96***	0.81***	0.95***	0.98***	0.91***	1***	0.42***	0.77***	0.87***	—	—	—	—	—	—
C1	0.93***	0.65***	0.99***	0.99***	0.99***	0.93***	0.46***	0.80***	0.95***	0.95***	—	—	—	—	—
C2	0.94***	0.86***	0.91***	0.96***	0.86***	1***	0.38***	0.72***	0.82***	0.99***	0.91***	—	—	—	—
C3	0.76***	0.34***	0.91***	0.83***	0.94***	0.67***	0.65***	0.86***	0.96***	0.73***	0.87***	0.66***	—	—	—
C4	0.59***	0.31***	0.54***	0.49***	0.56***	0.42***	1.00***	0.88***	0.68***	0.45***	0.48***	0.42***	0.64***	—	—
C5	0.89***	0.64***	0.94***	0.92***	0.94***	0.86***	0.65***	0.94***	0.97***	0.89***	0.91***	0.85***	0.87***	0.67***	—

Table 7. Spearman rank correlations (rho values) showing relationships among qualitative carbon indicators—specific ultraviolet absorbance at 254 nanometers (SUVA₂₅₄), dissolved organic carbon (DOC) normalized peaks, carbon indices, and percentage of parallel factor analysis (PARAFAC) components for all watershed samples (excludes finished water samples) (n=150).

[See the **Abbreviations and Acronyms** (p. viii) and **table 1** for definitions of variables. Spearman rank correlations (rho values), with p value significance indicated by asterisks: * $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$. —, not applicable]

Variable	SUVA ₂₅₄	Peak A / DOC	Peak C / DOC	Peak M / DOC	Peak D / DOC	Peak B / DOC	Peak T / DOC	HIX	FI	β : α	Pct_C1	Pct_C2	Pct_C3	Pct_C4	Pct_C5
SUVA ₂₅₄	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Peak A / DOC	0.03	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Peak C / DOC	0.08	0.99***	—	—	—	—	—	—	—	—	—	—	—	—	—
Peak M / DOC	-0.02	0.99***	0.97***	—	—	—	—	—	—	—	—	—	—	—	—
Peak D / DOC	0.17*	0.92***	0.97***	0.88***	—	—	—	—	—	—	—	—	—	—	—
Peak B / DOC	-0.11	0.53***	0.46***	0.55***	0.39***	—	—	—	—	—	—	—	—	—	—
Peak T / DOC	-0.04	0.85***	0.81***	0.86***	0.73***	0.86***	—	—	—	—	—	—	—	—	—
HIX	-0.27**	-0.38***	-0.36***	-0.39***	-0.32***	-0.58***	-0.63***	—	—	—	—	—	—	—	—
FI	-0.12	0.14	0.15	0.13	0.12	0.08	0.15	-0.01	—	—	—	—	—	—	—
β : α	0.24**	0.36***	0.3***	0.38***	0.21**	0.41***	0.52***	-0.66***	0.08	—	—	—	—	—	—
Pct_C1	-0.17**	-0.35***	-0.28***	-0.37***	0.21**	-0.6***	-0.62***	0.8***	0.01	-0.72***	—	—	—	—	—
Pct_C2	-0.01	-0.52***	-0.48***	-0.55***	-0.37***	-0.54***	-0.69***	0.81***	-0.31***	-0.76***	0.78***	—	—	—	—
Pct_C3	-0.04	0.59***	0.51***	0.62***	0.38***	0.4***	0.62***	-0.44***	0.19***	0.77***	-0.62***	-0.76***	—	—	—
Pct_C4	0.06	0.25**	0.21**	0.27***	0.15	0.59***	0.53***	-0.85***	0.16	0.47***	-0.82***	-0.78***	0.31***	—	—
Pct_C5	0.27***	0.09	0.13	0.08	0.19***	-0.11	0.08	-0.34***	-0.03	0.39***	-0.16***	-0.22**	0.17***	-0.10	—

Similar to C1 and C2, C5 was highly correlated with concentrations of HAA5 and THM4 (table 8; fig. 15). In fact, C5 had the highest correlations with both THM4 and HAA5 in finished drinking water, suggesting that fresh carbon sources may be important DBP precursors even when contributing a smaller portion of the carbon load compared with C1–C3. These results suggest that land management practices that minimize inputs of fresh organic matter into surface waters might be helpful for reducing DBP concentrations in finished drinking water.

There was a slight increase in the percentage of C5 (Pct_C5) in the McKenzie River near Vida due partly from input of Quartz Creek (fig. 14). C5 was lower in the two sites downstream from the reservoirs—South Fork McKenzie and Blue Rivers—relative to Quartz Creek and the upper South Fork McKenzie River, suggesting that freshly decomposed

vegetation from these upstream areas is the most likely source of this carbon and DBP precursors, despite prior identification of contributions of C5 from algae and cyanobacteria, which would be expected from cyanobacteria blooms in these reservoirs.

Finished water DBP concentrations were highly correlated with PARAFAC components C1, C2, and C5 (table 8), which were reduced by 84–88 percent during treatment, demonstrating high removal efficiency of humic-like DOM by coagulation and (or) disinfection at the EWEB treatment plant. Half (50 percent) of the DOC in finished drinking water—the portion that was not removed or converted during treatment—was composed of C1; percentages for the other components were 18 percent C2, 13 percent C3, 10 percent C4, and 9 percent C5 (table 4). However, the carbon remaining

Table 8. Spearman rank correlations (rho values) between disinfection by-product concentrations in finished (treated) drinking water from the Hayden Bridge Drinking Water Treatment Plant and raw source water carbon indicators.

[Eleven pairs of raw and finished water samples were collected, see text for description. See **Abbreviations and Acronyms** (p. vii–viii) and table 1 for variable definitions. Locations of the various peaks are shown in figure 2. Spearman rank correlations (rho values), with *p* value significance indicated by asterisks: **p*<0.05, ***p*<0.01, and ****p*<0.001. **Abbreviation:** DBPs, disinfection by-products]

Variable	Disinfection by-products in finished drinking water					
	CHCl ₃	THM4	MCAA	DCAA	TCAA	HAA5
Rho values among finished water DBPs						
THM4	0.96***	—	—	—	—	—
MCAA	0.56	0.60	—	—	—	—
DCAA	0.53	0.56	0.14	—	—	—
TCAA	0.78**	0.78**	0.29	0.70	—	—
HAA5	0.82**	0.83**	0.49	0.82**	0.94***	—
Rho values between raw water carbon indicators and finished water DBPs						
DOC	0.78**	0.72*	0.17	0.62	0.92***	0.84**
UVA ₂₅₄	0.70*	0.69*	0.05	0.63	0.88***	0.78**
Peak A	0.74*	0.71*	0.05	0.62	0.89***	0.78**
Peak C	0.76	0.74*	0.09	0.62	0.90***	0.79**
Peak M	0.78**	0.75*	0.14	0.64*	0.91***	0.82**
Peak D	0.77**	0.73*	0.09	0.62	0.89***	0.79**
Peak B	0.11	0.26	0.66*	0.01	0.13	0.08
Peak T	0.76*	0.77**	0.23	0.63*	0.89***	0.83**
Peak N	0.76*	0.75*	0.14	0.57	0.90***	0.79**
fDOM	0.76*	0.72*	0.08	0.61	0.90***	0.79**
SUVA ₂₅₄	0.17	0.21	−0.11	0.29	0.38	0.28
HIX	0.20	0.25	0.50	0.21	0.06	0.23
FI	0.18	0.22	0.12	−0.76*	0.34	0.52
β:α	−0.63	−0.62	−0.24	−0.37	−0.67*	−0.61
C1	0.77**	0.75**	0.12	0.62	0.91***	0.80**
C2	0.75**	0.71**	0.06	0.64*	0.89***	0.79**
C3	−0.39	−0.34	−0.25	−0.18	−0.38	−0.37
C4	0.47	0.58	0.69*	0.26	0.21	0.38
C5	0.80**	0.77**	0.21	0.64*	0.91***	0.84**

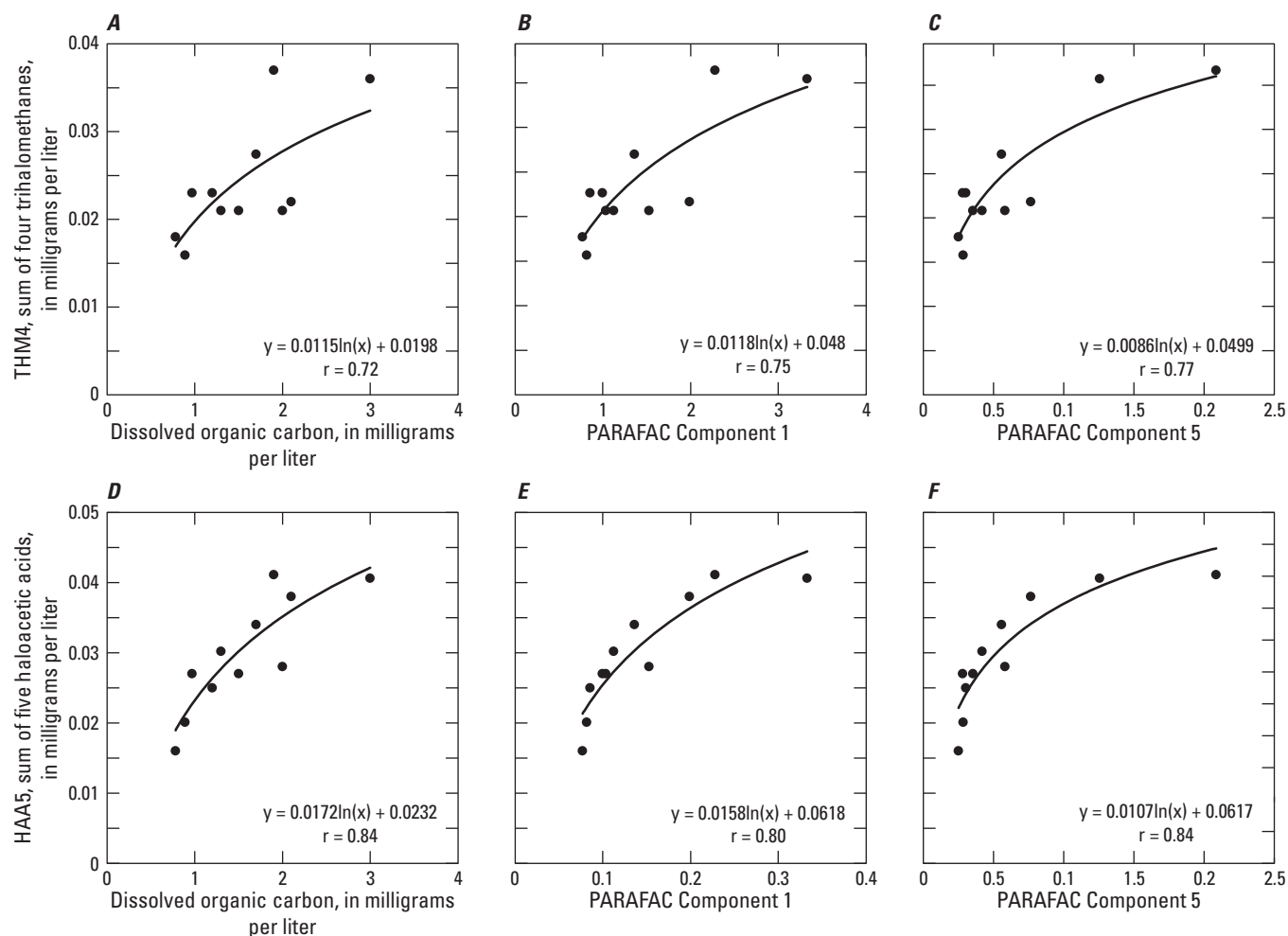


Figure 15. Plots showing relationships between dissolved organic carbon (DOC) concentration and parallel factor analysis (PARAFAC) model component loadings C1 and C5 in raw water from the McKenzie River above Hayden Bridge, Oregon, and (A, B, C) trihalomethanes (THM4) and (D, E, F) haloacetic acids (HAA5) in finished drinking water.

in these finished water samples is the net result of coagulation, disinfection, and other treatment processes and reactions that cannot easily be disentangled.

Dissolved Organic Matter Optical Properties

Absorbance and fluorescence measurements and their associated calculated indices provide information about the concentration and composition of the DOM pool, including DBP precursors, in transport to the EWEB intake during storms (tables 1, 4; Carpenter, 2022). High dilution rates in the McKenzie River resulted in many of the individual fluorescence ex/em values being low (<0.1 Raman units), possibly pushing the limits of analytical detection at times. Fluorescence LT-MDLs, or long-term method detection limits, established by Hansen and others (2018), vary by excitation / emission pairs, ranging from 0.004 RU throughout much of the EEM spectra to 0.1 RU in the region of peak B (ex 275 nm / em 304 nm). Caution should be used when interpreting

results near the LT-MDL. For example, nearly 88 percent of results for peak B fall below its LT-MDL. Fluorescence at peak B (ex 275/em 304) is an indication of fresh-like DOM likely derived from source material such as algae, polyphenolic plant compounds, and leaf litter leachate, which could be a useful indicator. Though most of the values were below the LT-MDL, peak B was highest (up to 5.3 RU) in the samples collected from the 52nd Street stormwater outfall site, indicating the presence of a higher amount of fresh DOM, which is consistent with low humic index (HIX) values at this location.

Similarly, nearly 90 percent of the HIX values, which are calculated from a range of fluorescence wavelengths (see table 1), included at least one emission result below the LT-MDL, which reduces the utility of this index to some degree. The Fluorescence Index (FI) and Freshness Index ($\beta:\alpha$) (table 1) were somewhat less affected by low fluorescence, making them potentially more reliable indicators, but

~50 percent of the values for these indices included at least one emission result below the LT-MDL, which presents some limitations.

Values for UVA_{254} in the upper McKenzie River averaged 0.03 at Frissell Bridge and increased downstream: 0.06 at Vida and 0.07 at Hayden Bridge, from the input of tributaries with higher UVA_{254} values (table 4). The UVA_{254} was most highly correlated with DOC, peak D, and PARAFAC component C2 ($\rho = 0.73\text{--}0.86$, $p < 0.001$) (table 6). Average SUVA_{254} values ranged from 1.3 to 8.6, with the highest values in Camp and Cedar Creeks, with respective averages of 8.0 and 8.6 L/mg-m (fig. 11). Although higher SUVA_{254} values are associated with higher aromatic, high molecular weight compounds, it should be noted that SUVA_{254} values exceeding six are likely biased high from enhanced absorbance by iron (Poulin and others, 2014) or colloids, a phenomenon previously reported for McKenzie River Basin tributaries (Kraus and others, 2010). The presence of these types of materials may indicate flushing of reduced iron, Fe (II), from soils, but this interference may preclude SUVA_{254} from being a useful indicator in the McKenzie River Basin. If desired, future studies could analyze for iron and apply a correction factor to some of the absorbance parameters according to Poulin and others (2014).

The humification index (HIX) is an indicator of the degree of humification of DOM in a sample, with higher amounts of soil-derived humic and fulvic acids increasing HIX values (Ohno, 2002). Here, average HIX values ranged from 0.76 to 0.90, with relatively constant HIX values in the main stem from Frissell Bridge downstream to EWEB's intake at Hayden Bridge (fig. 11). Despite inputs of water with relatively low HIX (the unnamed tributary to Walterville Canal, Camp and Cedar Creeks, and the 52nd Street stormwater outfall), the average HIX values in the McKenzie River at Hayden Bridge and Hendrix Park were the same (0.87; table 4). A similar pattern in other key parameters (for example, DOC concentration) suggests minimal effect on HIX from these lower-basin tributaries on the main stem. Fluorescence values less than the LT-MDL, as noted above, also may have limited the explanatory power of this index.

The Fluorescence Index (FI) values, commonly used to identify microbial sources within the DOM pool such as extracellular releases and leachate from bacteria and algae (table 1), ranged from about 1.6 to 1.9 at watershed sites (fig. 11). The average FI values increased in the main stem downstream from Blue and South Fork McKenzie Rivers, possibly from cyanobacteria decomposition products or periphytic algae, and leaf litter. The highest FI values occurred during a late summer "first flush" storm in September 2013, with the highest values (about 1.8) occurring in samples from Blue River, Haagen Creek, and the McKenzie River at Hendricks Park. Samples collected during moderate and high flow events, when dilution would be greatest, had the lowest FI values, generally less than 1.6, which as discussed above, were based on weak fluorescence signals (< 0.1 RU) that may approach limits of instrument detection and reliability.

Nevertheless, this trend in FI and other indices is consistent with the interpretation that first flush events deliver DOM characterized by higher FI values indicative of fresher, less processed DOM, including microbially-derived DOM as well as fresh plant and algal material, while later and higher flow events transported DOM with higher humic content in the river (Hood and others, 2006; Hansen and others 2016). Note that although we report the FI of finished water samples (range 1.6–2.5; fig. 11; Carpenter, 2022), as mentioned above, coagulation and chlorination alter the optical signature of DOM; thus, interpretation of optical indices for finished water is complex and challenging (Beggs and others, 2009).

The Freshness Index ($\beta:\alpha$) is another indicator of recently produced, fresh DOM, including carbon leached from the decomposition of terrestrial and aquatic plant biomass (Parlanti and others, 2000; Wilson and Xenopoulos, 2009). The average site values for $\beta:\alpha$ ranged from 0.5 to 0.7, with 9 of the highest 13 values from the 52nd Street stormwater outfall site (table 4; fig. 11). The highest DOC concentrations, averaging over 6 mg/L, and maximum DOC of 16 mg/L (Carpenter, 2022), also occurred at this outfall site indicating that fresh organic matter leaches DOC that enters surface waters via this outfall during storms. The low HIX values at this site also point to fresh carbon as the dominant source of DOM, not humified carbon more indicative of sites in the upper forested watershed. Other sites with relatively high $\beta:\alpha$ values included the unnamed tributary to Walterville Canal and Cedar Creek (fig. 11), where anthropogenic activities including crop production may be contributing DOM. Elevated $\beta:\alpha$ values occurred in Blue River and the South Fork McKenzie River possibly owing to freshly fixed autotrophic carbon exported from Blue River Lake and Cougar Reservoir, respectively. Monitoring by EWEB downstream from both reservoirs shows blooms of cyanobacteria during summer (*Dolichospermum*, *Gloeotrichia*, and others), which are one source of DOM; other sources including downstream periphyton also contribute fresh DOM resulting in higher $\beta:\alpha$ values at these sites.

Although most sites were sampled once per storm, the 52nd Street stormwater outfall site was sampled twice, about 24 hours apart, during a May 2013 storm (table 3.1). This provided a unique opportunity to see how DOM concentration and composition changed from a point early in a spring storm to a later point in time, after considerably more rainfall. Despite much higher streamflows (estimated from nearby Camp Creek, which increased 6–7 fold between the time of the two sample collections), most concentration-related optical measurements decreased 1–3 fold by the following day. The greatest decline was seen in DOC, peaks B and T, and C4, suggesting DOM quantity dissipated with continued rainfall. The second sample, despite much greater streamflow, exhibited shifts in many of the quality-related optical indices during this storm event, from fresher DOM to more humified DOM in the second sample. Particularly, SUVA_{254} and Pct_C2 nearly doubled from 2.4 to 4.56 and from 7.6 to 12.7, respectively, in this 24-hour period. This would indicate that DOM from fresh

source materials (algae, decomposing litter in surface soils, for example) had mobilized early in the storm and then attenuated as rainfall continued.

Comparison of Carbon Concentrations and Quality with Prior 2007–08 Study

While it may be useful to compare quantitative and (or) qualitative DOM results obtained here with those in 2007–08 (Kraus and others, 2010), data collection for this 2012–14 study targeted storms, sampled a greater number of storms, and captured higher flow events. Thus, any comparison between studies must be done cautiously because the conditions affecting hydrology and water quality were different. For example, DOC concentrations in this study (for the four main stem McKenzie River sites sampled for both studies) averaged 95 percent higher than the earlier study. DOC concentrations in Blue and South Fork McKenzie Rivers averaged about 60–70 percent higher, and Camp Creek was 80 percent higher, during the current study. The average THM4 concentration in finished water was 68 percent higher, and HAA5 concentration 33 percent higher, compared with the earlier study. These higher DOC concentrations provide greater opportunity for identifying sources of DOM that contribute to DBP formation during periods of greatest concern. But despite these differences in DOC concentration, the quality of the carbon was similar to that characterized in the earlier Kraus and others (2010) and Carpenter and others (2013) studies (see bottom of [table 5](#)). The primary sources of DOM contributing to DBPs are derived from soils and plant materials (components C1 and C2) and fresh-like DOM associated with component C5, which were most highly correlated with concentrations of DBPs ([table 8](#)).

Watershed Sources of Organic Carbon Contributing Disinfection By-Product Precursors

Streams draining the lower McKenzie River Basin (downstream from Hendricks Park) had the highest average concentrations of DOC (3.8 mg/L; [table 4](#)), and other carbon indicators. While this could point to these lower basin tributaries as important source areas the loads of carbon from these tributaries may not be substantial relative to the much larger streamflows in the main stem McKenzie River. For example, flows in Cedar Creek, one of the larger tributaries in the lower basin, averaged 42 ft³/s during the first half of the water year in 2013, compared with about 6,000 ft³/s for the main stem at Hayden Bridge; Cedar Creek contributed just 0.6 percent of the flow at Hayden Bridge, on average.

The middle basin tributaries—Quartz, Haagen, and Gate Creeks ([fig. 1](#))—had DOC concentrations averaging 2.8 mg/L, or three times higher than the main stem McKenzie River at Frissell Bridge. These basins are steeper, and their higher elevations create greater potential for orographic rainfall

and subsequent runoff compared with the smaller basins in the lowlands. Much of the lands within these watersheds are managed for timber production, which could increase DOC concentrations downstream. Quartz Creek ([fig. 16](#); Talberth and Koehn, 2015) had an average DOC concentration of 3.1 mg/L and a maximum of 4.4 mg/L ([table 4](#)). Elevated DOC combined with greater flows from these middle-basin streams make these watersheds potentially important in shaping the McKenzie River water quality downstream. The loads of DOC from these tributaries might explain much of the increase in DOC observed at Vida. Input of DOC from these middle-basin watersheds appear to be even more important than the lower-basin tributaries that have higher DOC concentrations because of their low flows relative to the main stem.

Most of the carbon increases observed in the McKenzie River—including DOC concentrations and PARAFAC components C1, C2, and C5—occurred between the upstream reference site at Frissell Bridge and Vida ([fig. 17](#); [table 4](#)). DOC concentrations increased an average of 71 percent (range 30–120 percent), and PARAFAC components C1, C2, and C5—which were highly correlated with DBPs in finished water—increased, on average, 109 to 136 percent (range 20–250 percent) in this reach. This portion of the river includes inputs from Quartz Creek (and several smaller unsampled tributaries), Blue River, and the South Fork of the McKenzie River, including discharges from the two large reservoirs. Together these reservoirs contributed 8–37 percent of the DOC loads at Vida, with the highest contributions (28, 29, and 37 percent) occurring during the November 2013 and January 2014 storms (loads shown in Carpenter, 2022). This leaves two-thirds to over 90 percent of the DOC loads in the McKenzie River at Vida to other sources, including these middle-basin tributaries.

Several land cover and vegetation classes were correlated with DOC concentration and various optical indicators of DOM ([table 9](#)). Developed lands, in all classes of



Figure 16. Photograph showing clear cut harvested units in the Quartz Creek, Oregon, watershed prior to the 2020 wildfires. Photograph by Doug Nelson, Center for Sustainable Economy.

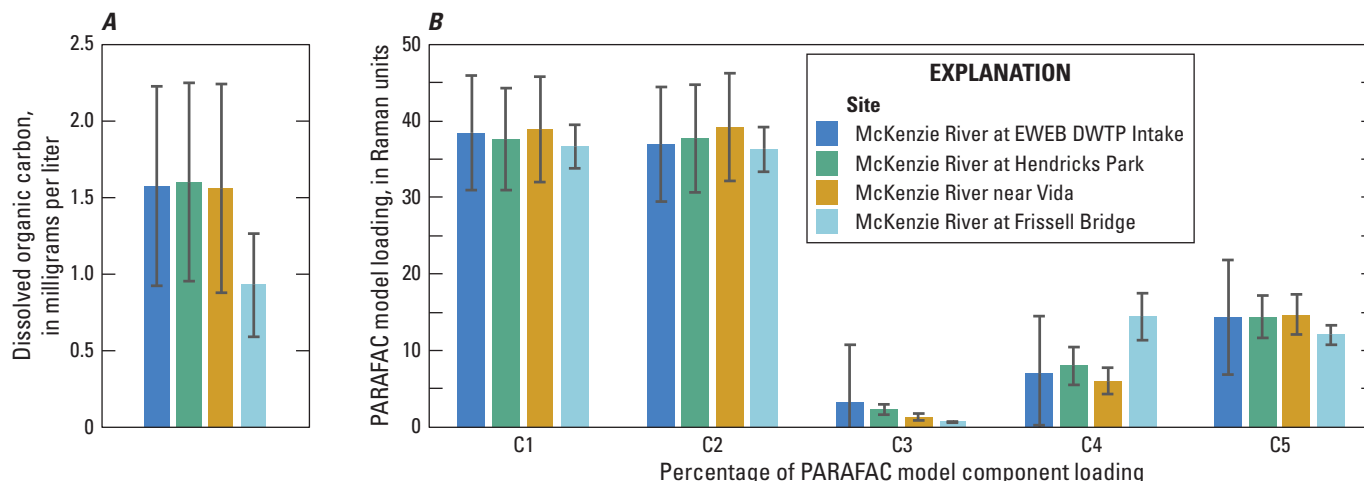


Figure 17. (A) Main stem concentrations of dissolved organic carbon (DOC) and (B) percentage of parallel factor analysis (PARAFAC) component loadings, McKenzie River, Oregon. EWEB DWTP, Eugene Water & Electric Board drinking water treatment plant.

intensity—low, medium, and high, and developed open space—were positively correlated with DOC, UVA_{254} , and numerous fluorescence peaks. While all the PARAFAC components were significantly ($p < 0.001$) positively correlated with the 3 classes of developed lands, component C1, 3, 4, and 5 had highly significant rho values ($p < 0.001$; table 9). These results suggest that the developed lands in the McKenzie River Basin are important sources of DOC, which was, again, highly correlated with DBPs in finished drinking water. Therefore, reductions in the generation and movement of fresher forms of organic matter, through targeted Best Management Practices, restoration of riparian habitats, or other strategies may reduce the transport of DBP precursors from developed lands into the McKenzie River.

Evergreen forest coverage was significantly negatively correlated with DOC ($p < 0.001$) and most other optical indicators of DOM, whereas mixed forest was positively correlated with DOC, fDOM, and several peaks ($p < 0.001$; table 9). This latter finding suggests deciduous leaf fall (fig. 18) contributes to the building of organic matter content in soils that yields DOC and, to some unknown extent, DBP precursors. These results suggest that the coniferous forests leach less DOC than mixed deciduous forests, which in the McKenzie River Basin includes big leaf maple, red alder, cottonwood, and other species. Evergreen forests were negatively correlated with the loading of all 5 PARAFAC model components, whereas mixed forest was positive and significantly correlated with components C2 and C5 (rho values = 0.41 and 0.32, respectively; $p < 0.001$; table 9). These apparent connections between the different forest types and ages could be confirmed with a more detailed study of vegetation types and carbon export that includes loading of DBP precursors from representative vegetation classes. The forest type and condition may also influence carbon dynamics, as a study by Hood and others (2006) suggested that old growth forests exported more DOC compared with previously logged watersheds due to removal of organic matter and burning of slash.

Predicting Disinfection By-Products in Finished Drinking Water

With more attention on disinfection by-products (DBPs) and growing concerns about the health effects of DBPs on humans and potential future changes in the regulatory standards, at least for haloacetic acids (U.S. Environmental Protection Agency, 2016), there is much interest in identifying surrogates in source water to predict DBPs in finished drinking water. In this study, DOC concentrations, optical measurements, calculated optical indices, and modeled PARAFAC components were screened for this purpose using Spearman rank correlations (table 8). Optical measurements had the highest correlations, in general, with the HAAs (table 8). Many of the positive, significant correlations between optical properties and DBPs were higher for the primary component of each type of regulated THM and HAA, namely chloroform ($CHCl_3$) and trichloroacetic acid (TCAA), respectively, compared with the aggregated THM4 or HAA5 compound classes (table 8).

Concentrations of HAAs in finished water were positively and significantly correlated with several source water carbon indicators, including DOC concentration, PARAFAC components C1, C2, and C5, UVA_{254} , and peaks T, M, D, and C (all $p < 0.01$). Rho values for correlations between these optical properties and TCAA were even higher (table 8). TCAA was the dominant HAA in finished drinking water making up 48–63 percent of HAA5 during this study (Carpenter, 2022). The highest correlations with HAA5 and THM4 came from DOC concentration and PARAFAC components C1 and C5 (fig. 15), the latter being one of the two fresher carbon components. The Freshness Index ($\beta:\alpha$), an indicator of recently produced organic matter, was significantly correlated ($p < 0.05$) with TCAA concentrations in finished water, suggesting that fresh forms of carbon, including algae and cyanobacteria, may be important contributors of TCAA precursors in particular.

Table 9. Spearman rank correlations between land cover categories and average optical property values indicative of DOM amount and quality for each of 15 sites.

[See **Abbreviations and Acronyms** (p. vii–viii), and **table 1** for definition of variables. Locations of the various peaks are shown in **figure 2**. Spearman rank correlations (rho values), with p value significance indicated by asterisks: * $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$ between each site and the average value for each of the carbon indicators]

Carbon indicators	Barren land	Cultivated crops	Deciduous forest	Developed, high intensity	Developed, low intensity	Developed, medium intensity	Developed, open space	Evergreen forest	Hay/pasture	Herbaceous	Mixed forest	Shrub/scrub	Woody wetlands
DOC	-0.28***	0.04	0.14	0.52***	0.52***	0.52***	0.44***	-0.49***	0.09	0.15	0.37***	0.03	0.27***
UVA ₂₅₄	-0.43***	0.18*	0.19*	0.29***	0.34***	0.31***	0.31***	-0.54***	0.25**	0.31***	0.51***	0.17*	0.36***
Peak A	-0.22**	0.1	0.04	0.62***	0.64***	0.62***	0.57***	-0.55***	0.17*	-0.01	0.27***	-0.14	0.38***
Peak C	-0.27***	0.13	0.08	0.56***	0.58***	0.57***	0.51***	-0.56***	0.19*	0.05	0.31***	-0.08	0.35***
Peak M	-0.17*	0.08	0.02	0.64***	0.65***	0.65***	0.59***	-0.53***	0.14	-0.06	0.24	-0.18*	0.38***
Peak D	-0.36***	0.14	0.15	0.47***	0.5***	0.48***	0.42***	-0.56***	0.2*	0.19*	0.41***	0.04	0.31***
Peak B	-0.01	-0.01	-0.05	0.58***	0.58***	0.58***	0.53***	-0.36***	0.04	-0.17*	0.09	-0.24**	0.29***
Peak T	-0.13	0.06	-0.01	0.76***	0.77***	0.77***	0.71***	-0.58***	0.14	-0.14	0.22	-0.26**	0.44***
Peak N	-0.14	0.07	0	0.72***	0.73***	0.72***	0.68***	-0.55***	0.14	-0.12	0.22	-0.24**	0.43***
FDOM	-0.33***	0.16	0.12	0.52***	0.54***	0.52***	0.47***	-0.58***	0.22**	0.13	0.37***	-0.01	0.34***
C1	-0.22**	0.11	0.05	0.57***	0.58***	0.57***	0.52***	-0.53***	0.17*	0	0.27	-0.12	0.35***
C2	-0.37	0.17*	0.15	0.48***	0.50***	0.48***	0.42***	-0.59***	0.23**	0.18*	0.41***	0.04	0.32***
C3	-0.04	0	-0.05	0.69***	0.70***	0.7***	0.65***	-0.44***	0.06	-0.20*	0.12	-0.29***	0.40***
C4	-0.03	0	-0.04	0.59***	0.59***	0.59***	0.54***	-0.38***	0.06	-0.15	0.12	-0.22**	0.31***
C5	-0.2	0.11	0.03	0.77***	0.79***	0.77***	0.72***	-0.64***	0.19*	-0.09	0.28***	-0.23**	0.49***
SUVA ₂₅₄	-0.34***	0.27***	0.12	-0.09	-0.01	-0.06	0.03	-0.32***	0.31***	0.25**	0.32***	0.15	0.29***
FI	-0.05	0.16	-0.01	0.07	0.03	0.01	0.03	-0.1	0.16	-0.09	-0.05	-0.09	0.07
HIX	0.02	-0.12	0.01	-0.61***	-0.66***	-0.63***	-0.66***	0.54***	-0.20*	0.16	-0.22	0.25**	-0.52***
FRI	-0.08	0.31***	-0.2	0.66***	0.74***	0.68***	0.75***	-0.6***	0.39***	-0.41	-0.04	-0.54***	0.66***
Pet_C1	-0.06	-0.07	0.02	-0.71***	-0.74***	-0.72***	-0.76***	0.53***	-0.14	0.22**	-0.18***	0.32***	-0.55***
Pet_C2	-0.03	-0.20*	0.14	-0.69***	-0.74***	-0.71***	-0.75***	0.56***	-0.28***	0.36***	-0.03	0.47***	-0.58***
Pet_C3	-0.09	0.15	-0.1	0.73***	0.79***	0.75***	0.79***	-0.54***	0.22**	-0.32***	0.06	-0.46***	0.63***
Pet_C4	0.16	0.07	-0.11	0.50***	0.52***	0.51***	0.52***	-0.36***	0.13	-0.25**	0.02	-0.29***	0.33***
Pet_C5	-0.13	0.18*	0.13	0.13	0.18***	0.15	0.21***	-0.3***	0.20***	0.03	0.23**	-0.02	0.30***

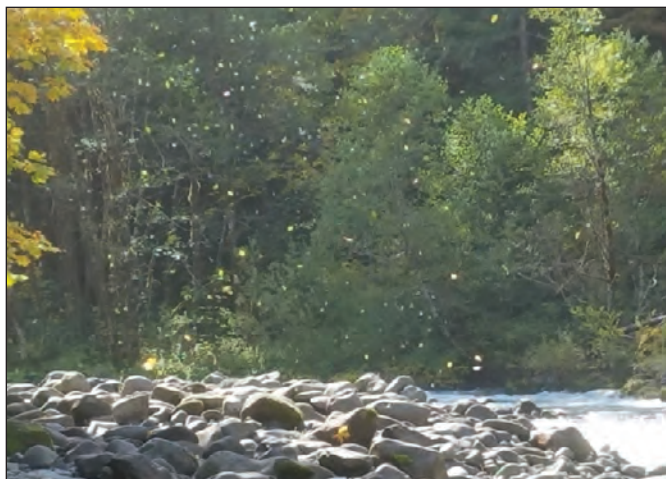


Figure 18. Photograph showing abundant leaf fall in the upper South Fork McKenzie River Basin, Oregon, September 2017. Photograph by Kurt Carpenter, U.S. Geological Survey.

Although predictors of THMs and HAAs were similar, the correlation between THM4 and HAA5 in finished water was only 0.83 ($p < 0.01$); this correlation supports previous studies that found that the fraction of the DOM pool that forms THMs and HAAs are distinct, though they may overlap (Kraus and others, 2010, 2011). Therefore, these classes of disinfection compounds are best considered independently for the purposes of watershed management and water treatment purposes.

The best single predictor of THM4 in finished water was peak T and PARAFAC component C5 (both $\rho = 0.77$, $p < 0.01$); PARAFAC components C1 and C2, DOC concentration, fDOM, peaks N, D, M, C, and A, and UVA_{254} were also statistically significant ($p < 0.05$). Like HAAs, higher ρ values were found for the dominant THM (chloroform, CHCl_3), which had significant positive correlations with DOC, PARAFAC components C5 and C1, and peaks M and D ($p < 0.001$).

Combinations of fluorescence peaks and indices were simultaneously evaluated for predicting HAA5 and THM4 concentrations (separately) in finished drinking water. Random forest analysis identified a subset of 8 variables explaining 62.5 percent of the variation in HAA5 concentrations; these include PARAFAC component C1 and its associated fluorescence peaks (A, C, and M), and PARAFAC component C5 and its associated peaks (T and N). A second model including just C1, C2, and C5 explained 60 percent of the variation in HAA5, in descending order of importance: C1, C5, C2. For THM4, carbon components C4 + C5, and C1 and associated peaks T, A, and N, explained about 33 percent of the variation in THM4 concentrations in finished water, only about half as much variation explained compared with the model for HAAs.

Taken together, and because of their higher loadings at nearly all sites, these analyses suggest that both soil-derived DOM (especially C1 and C2) and fresher DOM (especially

C5) (table 8) are the principal sources of precursor compounds that form HAAs and THMs in treated drinking water from the EWEB water treatment plant.

Early Detection of Disinfection By-Product Precursors and Prediction of Disinfection By-Products in Treated Drinking Water

Fluorescence and absorbance spectral properties and PARAFAC model loadings can be diagnostic of DOM quantity and quality, and predictors of DBP formation during water treatment (Kraus and others, 2010; Carpenter and others, 2013; Hansen and others, 2018). Identifying the primary sources of this reactive carbon is critical for DBP management. A better understanding of how land cover and vegetation classes in watersheds affect carbon exports to rivers, in combination with real-time monitoring of fDOM, will allow DWTP operators to anticipate and forecast rises in DOC and associated DBP precursors over time.

Early warning and prediction of DBPs can be achieved, in part, through monitoring of fDOM (fig. 2), which had a high correlation with DOC concentration in this study ($r^2 = 0.91$; fig. 19). A 2007–08 study by Kraus and others (2010) and another in the nearby Clackamas River (Carpenter and others, 2013) also found very high correlations ($r^2 > 0.9$) between fDOM and DOC. Custom in situ fDOM sensors, such as those deployed in the Clackamas River study, or those currently deployed in the McKenzie River by EWEB and USGS, can provide continuous real-time data on the carbon concentrations in source water to inform water treatment.

In this McKenzie River study, laboratory-derived fDOM was more highly correlated with DOC and PARAFAC components than was UVA_{254} (fig. 19), suggesting fluorescence is a better indicator or predictor of DOC concentration in this system than absorbance. These results are consistent with Kraus and others (2010) in finding fDOM highly correlated with DBP formation potentials for THMs and HAAs ($r^2 = 0.95$ and 0.91, respectively); absorbance is more prone to interference from high concentrations of dissolved iron or colloids. Therefore, the use of fDOM in future studies, outlined below, can provide an efficient, reliable indicator of DOC over long and short time scales.

Data Quality Assurance

Quality assurance (QA) samples included field blanks and field replicate samples; these data are shown in table 1.1. Small quantities of DOC were detected in five of six blank samples at concentrations up to 0.33 mg/L (average was 0.2 mg/L). These concentrations were all less than the lowest DOC concentration found during the study (0.38 mg/L at Frissell Bridge). Replicate samples for DOC ($n = 11$) had RPDs ranging from 0 to 7.4 percent; median was 2.1 percent

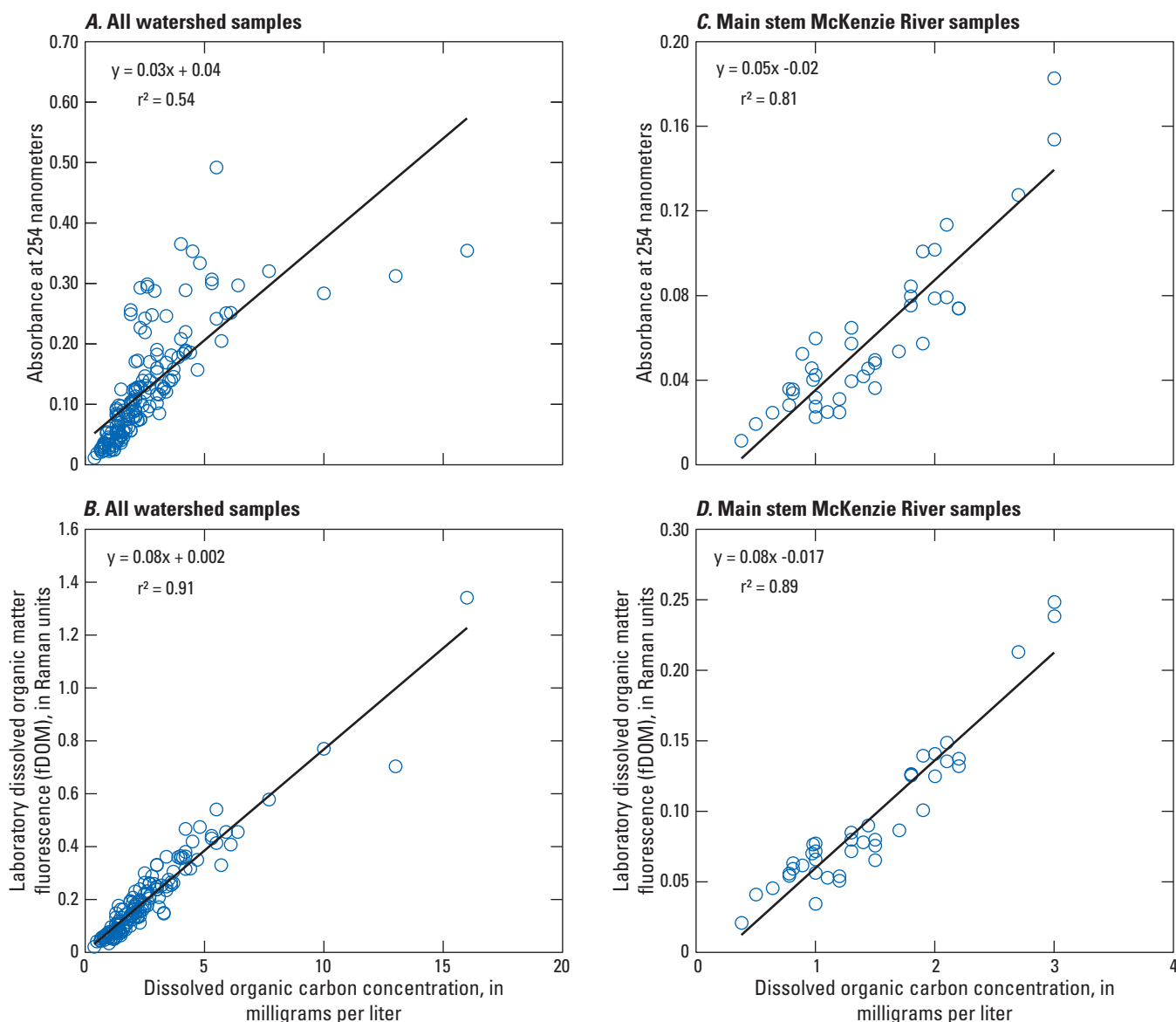


Figure 19. Relationship between concentrations of dissolved organic carbon (DOC) and laboratory measurement of UVA_{254} and fluorescent dissolved organic matter (fDOM) for (A,B) all watershed samples and (C,D) main stem only McKenzie River, Oregon, samples.

(table 1.1). These data suggest variations in DOC have negligible effects on data interpretations. Analysis of replicate split samples ($n = 23$) submitted to the USGS NWQL and Test America (TA) Laboratories produced an r^2 of 0.99, and RPDs ranged from 2 to 21 percent (average 11 percent), indicating a slight-to-moderate negative bias for the TA laboratory compared with the USGS NWQL (table 2.1).

Some replicate samples had relatively high RPDs for fluorescence variables including peak B (RPD up to 343 percent; median 20 percent), peak T (RPD up to 22 percent; median was 8.3 percent), Humic Index (RPD up to 45 percent; median

11.8 percent), and PARAFAC component C5 (RPD up to 34 percent; median 11 percent) (table 1.1). Much of this variation is due to the frequent occurrence of low fluorescence values, less than 0.1 Raman units. As discussed above, all three indices (HIX, FI, and $\beta:\alpha$) and peak B had a large proportion of sample values based on emissions that may approach limits of instrument detection. Due to the greater variations in these fluorescence peaks and metrics, greater care should be exercised when making comparisons or interpretations between stations and samples for these parameters and metrics.

Future Studies

Future studies on the loading of DOC and particulate organic carbon (POC) from different parts of the McKenzie River Basin would identify areas that yield the highest DBP precursors to guide future restoration and monitoring programs. Although this and previous studies on DOM quantity and quality have provided useful information on the sources of DOM for the McKenzie River Basin, the relative contributions (loads) from the different tributaries are still not known because streamflow data were not concurrently collected. And the 2020 Holiday Farm Fire (FEMA, 2020) burned a large swath of the basin, which has affected water quality in several watersheds. Though flows are continuously monitored in the main stem, flows from most tributaries, particularly in the middle portion of the watershed, were not monitored until recently. The Gate Creek USGS gaging station (USGS streamgage 14163000; U.S. Geological Survey, 2021b; https://waterdata.usgs.gov/or/nwis/uv?site_no=14163000), including streamflow and water quality sonde, was reactivated in December 2020 following the Holiday Farm Fire. This new station provides a unique opportunity to evaluate the post-fire response in a mid-sized tributary draining a basin that was completely encircled by the fire perimeter.

The steep topography and moderate basin sizes of the middle-basin tributaries suggest that the DOC loads could be even more substantial than the lower basin tributaries given their higher streamflow. Separating the effect of Quartz or Gate Creeks, versus Blue River Lake and Cougar Reservoir, is not, however, possible with the distribution of sites sampled for the current study but could be quantified with the current network of water quality monitors and post-fire data collection currently underway by EWEB and USGS. Quantifying the loads of DOC would greatly advance our understanding of sources of organic carbon that contribute to forming DBPs in EWEB's treated drinking water.

Future studies could also examine the effects of precipitation quantity and intensity and temperature on organic matter decomposition rates and DOC fluxes from flushing of forest soils using lysimeters placed in different locations and depths in the soil profile. These data could help watershed managers better understand flow paths in different settings and how climate change might impact carbon cycling and identify these influences on water quality in the McKenzie River at EWEB's source water intake.

Concentrations of DOC were significantly and positively correlated ($p < 0.001$) with water temperature (fig. 20), suggesting that anticipated increases in air and water temperature from climate change could increase DOC concentrations in source water and perhaps also increase DBP precursors. The McKenzie River with its streamflow dominated by cold groundwater may, however, be buffered to some degree from warming although receding glaciers and reduced snowpack during drought could, if occurring for prolonged periods, be impacted negatively by higher air temperatures.

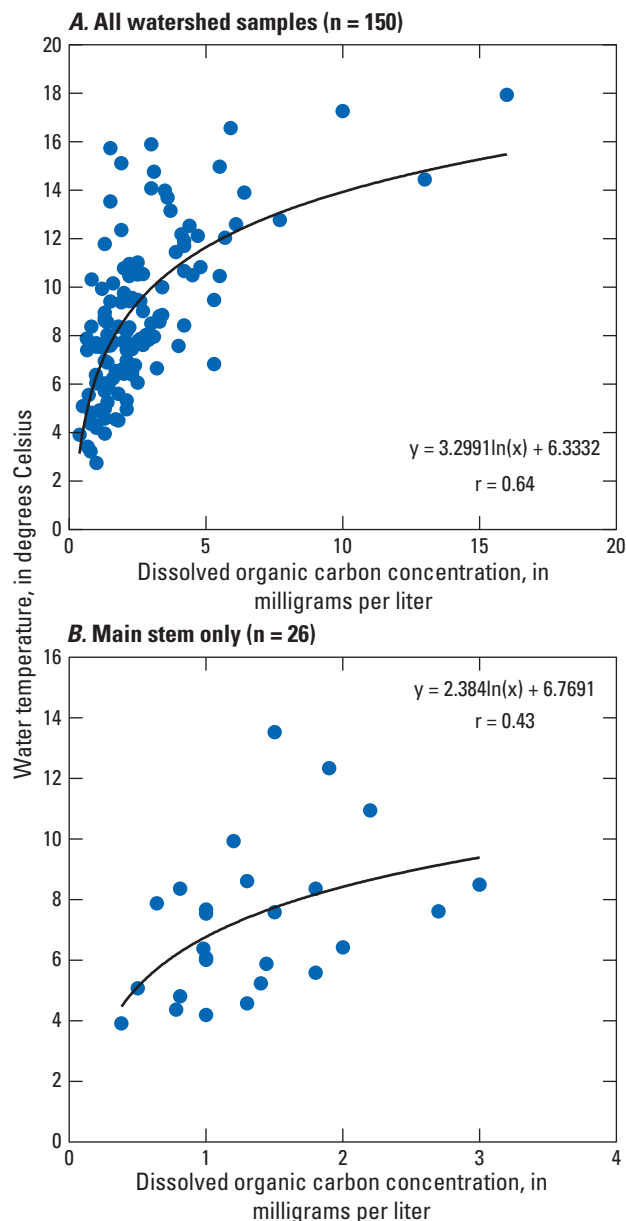


Figure 20. Relationship between dissolved organic carbon (DOC) and water temperature for (A) all watershed samples and (B) main stem McKenzie River samples, Oregon, 2012–14.

As part of this bulk statistical analysis, the THM and HAA concentrations, their sums and components in finished water, were examined for positive relationships with the quality of the raw source water at the EWEB water treatment plant. But because treatment removes part of the DOM pool by coagulation—simultaneous or prior to chlorination—and coagulation can vary temporally in its effectiveness at removing DOC, the actual carbon reacting with the chlorine is not the same as that in source water (that is, some DOC was removed by coagulation). Therefore, any conclusions about the effects of treatment should be made with care and verified using jar tests or other methods.

Future studies could include laboratory-based DBP formation potential (FP) measurements (Kraus and others, 2010; Carpenter and others, 2013) to more specifically identify watershed sources of DOM contributing DBP precursors (particularly DOM associated with PAFARAC components C1, C2, and C5). These sources could include, for example, terrestrial, soil-derived DOM from litter layers and deeper, more humified horizons, and fresh-like DOM originating from sources including attached benthic algae (periphyton), benthic and planktonic cyanobacteria, including harmful algal blooms in the two large reservoirs, deciduous leaves, fir needles, moss, and other types of “fresher” organic matter.

Experimental jar tests using different coagulation treatments (see Carpenter and others, 2013) could be conducted to examine potential treatment options for the enhanced removal of PARAFAC components C1, C2, and C5, which were most highly correlated with DOC and DBP concentrations. In this study, a comparison between PARAFAC components in source and finished water suggests DOM associated with C1 was removed less efficiently during treatment compared with other DOM fractions, thus, evaluating enhanced treatment options for their removal, such as biofilters or other coagulants, might be a strategy to lower DBP concentrations in finished water.

Future studies could examine the role of particulate organic carbon—materials such as soil particles, algae, cyanobacteria and partially decomposed leaves and other plant materials commonly observed in the McKenzie River in transport at the intake—in forming DBPs (Carpenter and others 2013). Studies could include laboratory-based measurements of DBP FP on filtered and unfiltered samples, with additions of alum and powdered activated carbon, like those conducted for the Clackamas River study (Carpenter and others, 2013), or testing of other novel biological treatments to remove DBP precursors. Some of these, including biological treatment, is currently being piloted at the EWEB treatment plant.

The use of fluorescence sensors such as fDOM to monitor the concentration and composition of raw water supplies may be improved for detection of specific DBP precursors geared to provide continuous and real-time data to treatment plant operators. Although fDOM currently is measured continuously at five locations in the McKenzie River Basin, adding a site on the McKenzie River upstream of Quartz Creek, or in Quartz Creek directly, could determine the relative impact of this tributary on main stem water quality, particularly post-fire. Commercially available optical sensors that measure more than one ex/em pair (for example, Carpenter and others, 2013) could also provide an opportunity to identify changes in DOM concentration and composition, to capture various events and watershed processes over time.

Finally, the continuous and real-time data currently being collected in the McKenzie River Basin, which, at the time of this study included five water quality monitoring stations in addition to several streamflow gages, can be used to understand how water quality changes as it traverses the watershed down to the EWEB intake. Two of these stations are located downstream from Blue River Lake and Cougar Reservoir,

which, along with the downstream main stem stations at Vida, Walterville, and Hayden Bridge, provide key information on stream conditions to inform drinking water treatment. In response to the Holiday Farm Fire, additional monitoring stations were installed in the McKenzie River at Walterville (USGS streamgage 14163900; U.S. Geological Survey, 2021c; https://waterdata.usgs.gov/nwis/uv/?site_no=14163900) and Gate Creek (USGS streamgage 14163900; U.S. Geological Survey, 2021b; https://waterdata.usgs.gov/or/nwis/uv?site_no=14163000), with another station upstream on the McKenzie River below Trail Bridge Reservoir, (USGS streamgage 14158850; U.S. Geological Survey, 2021d; https://waterdata.usgs.gov/or/nwis/uv?site_no=14158850), a relatively undisturbed “reference” site upstream from the influence of the recent fires.

Post-fire monitoring by EWEB has shown that one of the responses to wildfire is enrichment with nutrients such as nitrate, with the highest concentrations in tributaries such as Gate Creek. Nutrient enrichment is one of the primary causes of harmful algal blooms, and proliferations of potentially toxin-producing benthic cyanobacteria were found during EWEB and USGS post-fire reconnaissance monitoring in 2021. A new profiling system in Blue River Lake (USGS site 441022122193200) currently provides seasonal continuous water quality data in near real-time to dam operators and downstream water users including EWEB. This monitor tracks water quality including fDOM, turbidity, and algal and cyanobacterial pigments, and when deployed during the spring refilling period, can allow early detection of a developing bloom, which has become a near-annual event. Future enhanced integration and analyses of these continuous monitoring data with machine learning and other advanced tools such as remote sensing could expand our understanding of river conditions—the influences of reservoirs, snowpack, and other factors—to predict water quality conditions for the mutual benefit of people and aquatic life.

Conclusions

This study aimed to characterize and quantify the specific forms of organic carbon in the McKenzie River that reacts to produce DBPs in treated drinking water. Storm periods were targeted for sampling since runoff from the surrounding landscape tends to produce the highest DOC concentrations. The average DOC concentration in the McKenzie River was relatively low, 1.5 mg/L, with some higher concentrations up to about 3 mg/L from tributary inflows. Lower-basin tributaries had the highest concentrations of DOC (up to 16 mg/L), but with relatively low flows, the highest loads of DOC likely came from the higher flow middle-basin tributaries, such as Quartz and Gate Creeks, where private forestland is concentrated. On average, McKenzie River DOC concentrations increased 68 percent between Frissell Bridge and Vida, due

to these tributary inputs plus inflows from streams connected to Blue River Lake and Cougar Reservoir, two other potential sources of DOC in the basin.

Fluorescence characterization of the DOC revealed soil-derived, more degraded and humic-like organic matter as the dominant type of organic carbon in the river, with “fresher” DOC derived from terrestrial and aquatic plants including algae and cyanobacteria being secondary components. Several fluorescence indicators: peaks A, C, M, N, and T, were identified as having high correlations with DBPs in treated drinking water and could be important to track in the aftermath of the 2020 Holiday Farm fire. We found higher DOC concentrations and other carbon indicators in watersheds with higher amounts of deciduous trees, compared with conifers, so the loss of coniferous forest during extensive wildfires may increase carbon and nutrient export from burned watersheds into the main stem, depending on the revegetation of deciduous tree species.

The high level of human activities in the middle and lower portion of the basin have resulted in substantial loss of native forests, which contributed to some enrichment with organic carbon. But thanks, in part, to robust streamflow much of the time, the McKenzie remains a high-quality source of drinking water. Despite our targeting of storms during worst-case conditions, including events with elevated turbidity and carbon concentrations, all samples of treated (finished) drinking water met EPA standards for DBPs during our study. Concentrations of DBPs in EWEB’s finished drinking water were positively correlated with DOC concentrations in raw source water, as expected, and fDOM was an excellent proxy for DOC concentrations in raw source water at EWEB’s water intake. Today, continuous in situ fDOM monitoring is conducted at several locations along the McKenzie River in real time to assist EWEB’s water treatment operations, to inform sampling programs, and to track post-fire recovery and restoration. Current and future monitoring by EWEB, USGS, academia, and others will continue to document changes and assess impacts from the recent Holiday Farm fire on aquatic communities and human health over time.

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Appendix 1. Quality Assurance Results for Dissolved Organic Carbon and Optical Properties of Dissolved Organic Matter from the McKenzie River Basin, Oregon, 2012–14

Table 1.1. Quality assurance results for dissolved organic carbon and optical properties of dissolved organic matter from the McKenzie River Basin, Oregon, 2012–14.

[Table 1.1 is an Excel file that can be accessed at <https://doi.org/10.3133/sir20225010>.]

Appendix 2. Quality Assurance Comparisons for Dissolved Organic Carbon Split Samples Analyzed at the U.S. Geological Survey National Water Quality Laboratory and Test America Laboratories

Table 2.1. Quality assurance comparisons for dissolved organic carbon split samples analyzed at the U.S. Geological Survey National Water Quality Laboratory (NWQL) and Test America (TA) Laboratories.

[Date: Format is month/day/year. Abbreviations: DOC, dissolved organic carbon; RPD, relative percent difference between split samples]

Site name	Date	DOC (TA)	DOC (NWQL)	RPD
52nd St. stormwater outfall at HWY 126	10/15/2012	10.00	11.06	10
Camp Creek at Camp Creek Road Bridge	10/16/2012	6.40	7.29	13
Gate Creek at Vida	10/16/2012	6.10	7.06	15
52nd St. stormwater outfall at HWY 126	11/19/2012	5.70	6.63	15
Cedar Creek at Springfield	11/20/2012	5.50	6.56	18
Haagen Creek at McKenzie River	11/20/2012	5.30	6.52	21
Unnamed tributary to Walterville Canal	10/16/2012	5.50	6.09	10
Camp Creek at Camp Creek Road Bridge	11/19/2012	4.80	5.92	21
Camp Creek at Camp Creek Road Bridge	11/20/2012	4.50	5.03	11
Quartz Creek at mouth near Finn Road	10/15/2012	4.40	4.90	11
Haagen Creek at McKenzie River	10/15/2012	3.70	4.45	18
Quartz Creek at mouth near Finn Road	11/20/2012	4.20	4.43	5
Cedar Creek at Springfield	10/15/2012	3.00	3.40	13
McKenzie River at Hendricks Park	11/20/2012	3.00	3.36	11
Gate Creek at Vida	11/20/2012	3.00	3.26	8
McKenzie River near Vida	11/20/2012	2.70	2.82	4
McKenzie River near Vida	10/16/2012	2.20	2.13	3
Blue River at McKenzie Hwy Bridge	11/20/2012	2.00	2.03	2
McKenzie River at Hendricks Park	10/16/2012	1.90	1.74	9
McKenzie River above Hayden Bridge	10/16/2012	1.70	1.58	7
Blue River at McKenzie Hwy Bridge	10/16/2012	1.50	1.47	2
South Fork McKenzie River near Rainbow	11/20/2012	1.40	1.32	6
South Fork McKenzie River near Rainbow	10/16/2012	0.82	0.91	11

Appendix 3. Changes in Dissolved Organic Carbon Concentration and Optical Properties of Dissolved Organic Matter in the 52nd Street Stormwater Outfall During One Storm, May 21–22, 2013

Table 3.1. Changes in dissolved organic carbon concentration and optical properties of dissolved organic matter in the 52nd Street stormwater outfall during one storm, May 21–22, 2013.

[Abbreviations: DOC, dissolved organic carbon; UVA_{254} , absorbance at 254 nanometers; $SUVA_{254}$, specific ultraviolet absorbance at 254 nanometers; C1, C2, etc., PARAFAC model Components; PCT_C1, percentage of each PARAFAC model components.]

Date Time Sample ID	First sample	Second sample	Change factor
	May 21, 2013	May 22, 2013	
	16:45 MK92	16:05 MK95	
DOC	13.00	3.90	3.3
UVA_{254}	0.31	0.18	1.8
Peak A	2.74	1.28	2.1
Peak C	1.16	0.54	2.1
Peak M	1.54	0.66	2.3
Peak D	0.36	0.19	1.9
Peak B	5.29	0.92	5.7
Peak T	2.11	0.74	2.9
Peak N	1.75	0.74	2.4
FDOM	0.69	0.36	1.9
C1	1.49	0.64	2.3
C2	0.80	0.43	1.8
C3	2.04	0.86	2.4
C4	5.29	0.99	5.3
C5	0.89	0.48	1.9
$SUVA_{254}$	2.40	4.56	0.5
FI	1.66	1.68	1.0
HIX	0.66	0.74	0.9
$\beta:\alpha$	0.68	0.71	0.9
Pct_C1	14.14	18.73	0.8
Pct_C2	7.57	12.74	0.6
Pct_C3	19.45	25.20	0.8
Pct_C4	50.36	29.18	1.7
Pct_C5	8.48	14.15	0.6
Peak A/DOC	0.21	0.33	0.6
Peak C/DOC	0.09	0.14	0.6
Peak M/DOC	0.12	0.17	0.7
Peak D/DOC	0.03	0.05	0.6
Peak B/DOC	0.41	0.24	1.7
Peak T/DOC	0.16	0.19	0.9
Peak N/DOC	0.13	0.19	0.7
Peak C: Peak T	0.55	0.74	0.7
Peak A: Peak T	1.30	1.74	0.7
Peak C: Peak A	0.42	0.42	1.0
Peak C: Peak M	0.75	0.82	0.9

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