Wildfire and Forest Harvesting Effects on Natural Organic Matter: Implications to Drinking Water Treatability

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Forested catchments are critical for water supply globally and provide ~60% of the water supplies for the world's 100 largest cities and 2/3 of all water supplies, including drinking water for ~180 million people in the U.S. In Alberta, Canada, approximately 2/3 of the population's drinking water comes from the eastern slopes of the Rocky Mountains. Ironically, the high quality and quantity water from these forested regions makes these supplies particularly vulnerable to the deleterious impacts of climate change and associated landscape disturbances. Wildfire has the potential to be the most catastrophic of these disturbances. It can produce significant changes in the quantity, timing, and quality of water originating in these settings. Notably, it also may necessitate significant increases in costly drinking water treatment infrastructure, operations and maintenance.

Aquatic natural organic matter (NOM) is typically evaluated by measurement of dissolved organic carbon (DOC) and is one key water quality parameter that drives the design of drinking water treatment infrastructure. Changes in the amount and quality of DOC can increase the need for and cost of water treatment infrastructure because of increased chemical coagulant dosing requirements and the potential for formation of several currently regulated disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs). They can also result in increased membrane fouling and microbial regrowth in the distribution system. While many proxy indicators (DOC, UV_{254}, specific UV absorbance [SUVA], fluorescence index [FI], fluorescence excitation-emission matrices [FEEMs], other NOM fractions, etc.) have been suggested for inferring drinking water treatability implications of changes in NOM, clear guidance regarding the most informative proxy indicators and the reliability of their connectivity to drinking water treatability assessment is still lacking.

The overall goal of this research was to compare and improve upon available strategies for characterizing challenges and threats to drinking water treatability arising from wildfire and forest harvesting disturbance-associated changes in DOC. Potential increases in regulated DBP formation potential (i.e., DBP-FP) were focused upon because infrastructure and operations implications; relative potential implications of these disturbances to membrane fouling and microbial regrowth in distributions systems were also evaluated. Of course, other

impacts such as those on coagulant demand are equally important, though more site- or treatment configuration-specific. While it is generally believed that coagulant demand during drinking water treatment may increase after severe disturbance as a result of elevated and increasingly variable turbidity and/or changes in source water DOC, the implications of wildfire to membrane fouling and microbial regrowth potential in distributions systems have not been reported to date. Similarly, forest harvesting impacts on DBP-FPs have not been reported and elevated DBP-FPs resulting from wildfire have been suggested, but only recently demonstrated at the watershed-scale with consideration of hydro-climatic variability. Despite these critically foundational, but nascent linkages, clear guidance regarding optimal approaches for informing drinking water treatability in response to landscape disturbance-associated changes in source water quality is currently unavailable. Thus, to advance the broad goal of informing strategies for characterizing challenges and threats to drinking water treatability arising from potential wildfire- and forest harvesting-associated changes in NOM, five phases of research were conducted.

In Phase 1, the most common methods of NOM characterization and their relationship to drinking water treatability (including limitations) were reviewed, particularly as related to the formation of regulated carbonaceous DBPs. These methods include DOC, UV_{254}, and SUVA metrics, as well as resin fractionation, liquid chromatography-organic carbon detection (LC-OCD), fluorescence excitation-emission matrices, and other techniques. The review demonstrated that no universal proxy indicators for NOM reactivity with oxidants such as chlorine have been identified to date, thereby underscoring the need to advance approaches for evaluating NOM reactivity in a manner that links different source watershed settings and disturbance impacts to treatability challenges.

In Phase 2, a comprehensive DOC characterization investigation was conducted throughout the treatment process at a conventional water treatment plant (WTP) with aerobic biofiltration. This work is among the first studies in which NOM removal during conventional treatment and biofiltration has been evaluated concurrently using several metrics of NOM concentration and character—this enabled direct confirmation of which of these parameters might be the most useful as proxy indicators for drinking water treatability when characterizing changes in source water quality. Samples were collected from the WTP intake and at different treatment stages (post-sedimentation, post-ozonation, and GAC biofilter effluents) at the Mannheim WTP, in Kitchener, Ontario. As would be expected, the coagulation/flocculation/sedimentation process (after which post-clarification samples were obtained) efficiently removed aromatic compounds (UV_{254}, hydrophobic organic carbon as measured by resin fractionation [HPO %], and the humic substances [HS] fraction as measured by liquid chromatography with organic carbon detection [LC-OCD]) and THM- and HAA-FPs. Further removal of these compounds was observed during biofiltration, highlighting that aromatic compounds (removed by chemical pre-treatment) were the main contributors to the THMs, though some smaller DOC fractions (removed by biofiltration with GAC) also played a role in the formation of THMs. Changes in post-treatment THM- and HAA-FP were generally comparable—this was expected given that they share common precursors. Higher molecular weight fractions contributed more to the formation of HAAs than THMs. Overall, metrics indicative of aromatic compounds were shown to be good proxy indicators of DOC reactivity and formation of regulated DBPs. These quantitative results were consistent with the qualitative results obtained using fluorescence excitation-emission matrices [FEEMs]. Utilization of LC-OCD had the additional advantage of detecting changes in medium to low molecular weight (LMW) fractions of DOC (e.g. building blocks and LMW neutrals) throughout treatment.

In Phase 3, changes in DOC concentration and character, and their relationships to regulated DBP-FPs (THM-FPs and HAA-FPs), were comprehensively characterized using multiple NOM characterization techniques during a two-year period following severe wildfire in the eastern slopes of the Rocky Mountains in south-western Alberta. Several NOM fractions also were characterized by LC-OCD during the latter of those years. This work was conducted as part of an ongoing (>9 years, at the time) watershed-scale study of wildfire and post-fire salvage logging impacts on hydrology, water quality, and aquatic ecology (i.e., the Southern Rockies Watershed Project). In that work, samples collected from multiple unburned (reference), burned, and post-fire salvage logged watersheds during dominant regional streamflow regimes (baseflow, snowmelt freshet, and stormflow) demonstrated that DOC

concentration and hydrophobicity increased after wildfire and even more so after post-fire salvage-logging, especially during high discharge events in headwater streams. These changes in aquatic DOC in streams draining disturbed watersheds were concurrent with increases in THM- and HAA-FPs. Contributing to, and building on that investigation, the work presented herein is the first to report that the mass of HS, biopolymers, and building blocks fractions of DOC also increased significantly in streams draining wildfire and post-fire salvage logged watersheds, thereby suggesting that these disturbances may have significant implications for carbonaceous DBP-FP, coagulant demand, and membrane fouling. In contrast, the mass of the LMW neutrals fraction of DOC, which contributes to microbial regrowth in the distribution system, was not significantly different in streams impacted by either wildfire or post-fire salvage logging. This work was also the first to comprehensively demonstrate wildfire-associated changes in DOC character (by measuring HPO %, UV_{254}, SUVA, FI, and FEEMs) and related DBP-FPs, at the watershed-scale and over multiple flow regimes. The disturbance impacts indicated by all of these quantitative, DOC-associated metrics were all statistically significant, except for FI. Qualitative FEEM results were consistent with these significant shifts. Notably, despite the continued development and promotion of various proxy indicators, UV_{254} offered the most precise linear correlation with THM-FP, with a coefficient of determination (R^2) of 0.6 (in contrast to values of 0.47, 0.42, and 0.39 for DOC, SUVA, and HPO %). Thus, changes in the proxy indicators were related to changes in THM-FP; however, they could not adequately explain response variability, thereby demonstrating the need to 1) better understand relationships between disturbance-associated changes in DOC and their implications to DOC reactivity and 2) advance modeling approaches for describing these relationships. While the mass of various DOC fractions obtained using LC-OCD and HAA-FPs was not analyzed in this manner because of the limited size of the data sets, similar relationships were suggested. Overall, these data suggest that severe wildfire may lead to significant DOC-associated drinking water treatability challenges and that post-fire salvage logging may further exacerbate them—notably, UV_{254} is unequivocally the best available tool for monitoring these potential impacts at present.

THM-FP is generally understood to be linearly correlated with aromatic NOM as measured by UV_{254} and/or SUVA. In Phase 4, simple strategies for enhancing the prediction of THM-FPs using NOM-associated proxy indicators were investigated. Specifically, the relationship between NOM aromaticity (HPO %, HS, UV_{254}, and SUVA) and THM-FP was examined. Then, HPO and HS were re-analyzed after weighting by mass (DOC concentration)—this appreciably enhanced their prediction performance. This improvement was especially evident for HS, for which the coefficients of determination (R^2) increased from 0.10 and 0.26, to 0.85 and 0.88 (Phase 2 and 3 data, respectively). Thus, data processing and reporting are critical to anticipating NOM reactivity; absolute quantities have superior prediction performance. Notably, regardless of these improvements, the relationships between DBP-FP and NOM proxy indicators can be quite variable spatially and temporally, and frequently site specific. More work is required to link source water quality to DBP-FP and drinking water treatability more broadly.

In Phase 5, changes in DOC concentration and character and their relationships to regulated DBP-FPs were comprehensively characterized using multiple NOM characterization techniques in the two years during and immediately after forest harvesting in the eastern slopes of the Rocky Mountains in south-western Alberta. Several NOM fractions also were characterized by LC-OCD to inform the relative potential for membrane fouling and microbial regrowth in distribution systems. Like Phase 3, this work was conducted as part of the ongoing SRWP in which two watersheds that served as unburned-reference watersheds in Phase 3 were studied. They were fully calibrated for climate, streamflow, and water quality for 11 years [2004-2014]). Three sub-watersheds within one watershed were harvested using clear-cut with patch retention, strip-shelterwood cut, and partial cut. All possible best management practices (BMPs) were followed to minimize disturbance impacts on water quality. Samples were collected during the dominant regional streamflow regimes. Notably, no substantial impacts of forest harvesting on water quality and treatability were observed during the harvest and first post-harvest years. Thus, this work suggests that forest harvesting with careful implementation of BMPs for erosion control may mitigate the potentially catastrophic impacts of wildfire on drinking water treatability without significantly compromising it.

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Chapter 1

Introduction

1.1 Research Motivation

Forested catchments are critical sources of drinking water globally. In U.S, they provide approximately 2/3 of all freshwater supplies and are the drinking water source for 180 million people (Stein and Butler, 2004). Similarly, ~2/3 of Canadians get their drinking water from surface water that predominately originates in forested areas (Natural Resources Canada, 2015). Ironically, the high quality and quantity of snowmelt-associated water from forested regions makes these supplies particularly vulnerable to impacts of climate change, which creates favorable conditions for catastrophic natural disturbances such wildfire and insect outbreaks (Dale et al., 2001; Emelko et al., 2011; Kaufmann et al., 2008; Logan and Powell, 2009). Anthropogenic disturbances such as agriculture, sewage pollution, recreational use, grazing, and logging can further compromise high quality water supplies. While natural and anthropogenic land disturbances have the potential to produce significant changes in the quantity, timing, and quality of water originating in these settings, they also may necessitate significant increases in costly drinking water treatment infrastructure, operations and maintenance (Emelko et al., 2011).

Dissolved organic carbon (DOC) is a particularly critical water quality parameter that is typically present at low concentrations in forested watersheds and increases (and/or changes in character) as a result of land disturbance (O'Donnell et al., 2010; Emelko et al., 2011). Increased levels of DOC can negatively impact drinking water treatability and may necessitate the use of more complicated and costly water treatment processes (Emelko et al., 2011); they can also often result in increased chemical coagulant dosing requirements (White et al., 1997; Edzwald and Tobiason, 1999; Melia et al., 1999; Hohner et al., 2016). Hydrophobic natural organic matter (NOM) is a reactive precursor of currently regulated disinfection by-products (DBPs) (Singer, 1999; Kitis et al., 2002). Hydrophilic NOM is more difficult to remove by conventional water treatment (Jacangelo et al., 1995; Kitis et al., 2002; Chow et al., 2004) and may be responsible for forming non-regulated DBPs of emerging health concern (Liang and Singer, 2003; Ates et al., 2007; Chen and Westerhoff, 2010). Other treatability challenges associated with increased DOC levels and changes in its characteristics (e.g., relative proportion of hydrophilic and hydrophobic fractions) include increased potential of bacterial regrowth in the distribution system (van der Kooij, 1992; Escobar et al., 2001; van der Kooij and van der Wielen, 2014); increased chemical disinfectant dosing requirements (Amy et al., 1987; Babcock and Singer, 1979); adverse impacts on taste, odor, and color (Amy et al., 1987; Jacangelo et al., 1995); membrane fouling (Lee et al., 2004; Kwon et al., 2005; Lee et al., 2006; Amy, 2008; Brinkman and Hozalski, 2015; Rahman et al., 2014; Yamamura et al., 2014); and increased potential for heavy metal complexation (Frimmel, 1998; Wu et al., 2004; Waples et al., 2005).

Reactions of different groups of aquatic organic matter with chlorine and other drinking water disinfectants (chloramines, chlorine dioxide, and ozone) result in the formation of various classes of DBPs. To date, 600 to 700 DBPs have been identified (Richardson et al., 2002; Krasner et al., 2006); many of which—but not all—are considered to be cytotoxic, genotoxic or carcinogenic in laboratory animals (Singer, 1999; Plewa et al., 2002). Formation of DBPs depends on the amount and composition of NOM, as well as the disinfectant type and disinfection conditions (Krasner et al., 2006; Krasner, 2009). To limit the public health risks of DBPs, the United States Environmental Protection Agency (USEPA) has regulated trihalomethanes (THMs) and five haloacetic acids (HAA_5). Maximum Contaminant Levels (MCL) of these compounds are 80 μg/L and 60 μg/L, respectively (USEPA, 2012). The corresponding levels in Canada are 100 μg/L and 80 μg/L, respectively (Health Canada, 2017). Studies suggest that some non-regulated DBPs are of greater health concern than the regulated ones (Krasner, 2009). Accordingly, proper characterization of NOM before and throughout the treatment process is critical to identifying promising measurements/proxies for regulated and emerging DBP formation, as well as other treatability challenges. NOM characterization also may be a useful tool for communities to better 1) weigh the impacts of land use/management on drinking water supplies and treatability and 2) respond to land use/management-associated changes in source water quality and mitigate their impacts.

Various techniques and metrics have been developed to characterize bulk and fractionated forms of NOM (Leenheer and Croué, 2003; Croué, 2004), which is a vast collection of ill-known organic compounds with diverse characteristics (Larsen et al., 2010; Deb and Shukla, 2011). Significant experimental efforts have focused on establishing relationships between NOM and DBP formation potential (DBPFP) and identifying DBP precursors; however, many findings are site specific and inconsistent due to the spatial and temporal variability of NOM (Edzwald et al., 1985; Collins et al., 1986; Reckhow and Singer, 1990; Reckhow et al., 1990; Singer, 1999; Bolto et al., 2002; Kitis et al., 2002; Goslan et al., 2004; Ates et al., 2007; Bougeard et al., 2010). Moreover, many, if not most of these efforts have focused on raw (untreated) water. Thus, in depth investigations of the reactivity of NOM fractions that cannot be easily removed during drinking water treatment (recalcitrant/refractory hydrophilic fractions) are still required.

1.2 Research Objectives

The overall goal of this research was to compare and improve upon available strategies for characterizing challenges and threats to drinking water treatability (formation of regulated DBPs) arising from changes in DOC from wildfire and forest harvesting landscape disturbances.

Specific research objectives developed to address this goal were to:

1) Review and evaluate the most common methods of NOM characterization and their relationship to drinking water treatability, particularly as related to the formation of regulated DBPs.;
2) Comprehensively evaluate NOM concentration and character through the drinking water treatment process;
3) Identify the NOM concentration and/or characterization metrics that show the greatest promise as proxy indicators for assessing THM-FP through drinking treatment plants;
4) Identify the NOM concentration and/or characterization metrics that show the greatest promise as proxy indicators for drinking water treatability (THM-FP) in source watersheds after three key types of landscape disturbances relevant to forested watersheds; specifically:
    a. severe wildfire,
    b. post-fire salvage logging, and
    c. contemporary forest harvesting.
5) Evaluate data processing strategies to enhance THM-FP predictions using NOM metrics.

1.3 General Research Approach

To achieve the broad goal of informing strategies for characterizing challenges and threats to drinking water treatability arising from potential wildfire- and forest harvesting-associated changes in NOM, five phases of research were conducted. Figure 1-1 and the descriptions below elaborate on these research phases.

In the first phase (Phase 1), the most common methods of NOM characterization and their relationship to drinking water treatability (including limitations) were critically reviewed, particularly as related to the formation of regulated carbonaceous DBPs. The goal of this phase was to compare different NOM associated metrics with regard to their efficiency in describing threats to drinking water treatability, particularly formation of regulated DBPs.

In Phase 2, DOC character throughout the treatment process was comprehensively evaluated at a drinking water treatment plant (WTP). This work is among the first studies in which NOM removal during conventional treatment and biofiltration has been evaluated concurrently using several metrics of NOM concentration and character. The unique contribution of this work is that 1) several NOM characterization metrics were evaluated concurrently and 2) several key steps comprising conventional treatment as well as biofiltration were evaluated. This enabled direct confirmation of which metrics are the most useful proxy indicators for 1) drinking water treatability (THM-FP) in response to changes in source water quality and 2) treatment process performance in removing these precursors. Samples were collected from the WTP intake, post-sedimentation, post-ozonation, and GAC biofilter effluent points at the Mannheim WTP, in the Kitchener, Ontario, Canada. NOM was evaluated using conventional approaches such as DOC concentration, ultraviolet absorbance at 254 nm (UV_{254}) and specific ultraviolet absorbance (SUVA), and characterization methods such as resin- (XAD) based fractionation, liquid chromatography-organic carbon detection (LC-OCD), and fluorescence spectroscopy excitation emission matrix (FEEM). Regulated DBP-FPs (THM- and HAA-FPs) were investigated because THM and HAA formation can lead to penalties and/or service disruptions. While DBP yield (i.e., DBP concentration normalized by DOC concentration) has been used to describe relative DOC reactivity in forming DBPs across different water sources (Summers et al., 1996), it was not utilized herein because those types of spatial comparisons were not a focus of this investigation.

In Phase 3, changes in DOC character and its relationship to regulated DBP-FPs (THM- and HAA-FPs) following severe wildfire and post-fire salvage logging in the eastern slopes of the Rocky Mountains in south-western Alberta were comprehensively evaluated. This work contributed to an ongoing (>9 years at the time) larger watershed-scale study of wildfire and post-fire salvage logging impacts on hydrology, water quality, aquatic ecology, and drinking water treatability that was conducted over multiple flow regimes, and in a manner that accounts for hydro-climatic variability. The NOM characterization techniques utilized here were the same as those in Phase 2, thereby linking the results obtained from the two experimental phases.

In Phase 4, data processing strategies for enhancing THM-FP predictions based on relatively simple source water DOC characterization (i.e., NOM proxy indicators from Phases 2 and 3) were evaluated. Linear regression was used and the relationships between THM-FP and the hydrophobicity measured by resin fractionation, humic fraction measured by LC-OCD, UV_{254}, and SUVA were examined. Linear regression is commonly used to describe the relationships between DOC, its fractions, and the formation of regulated DBPs— these approaches are widely utilized because these precursor materials are generally understood to be directly proportional to the by-products they form (Edzwald et al., 1985; Reckhow and Singer, 1990; Singer, 1999; Goslan et al., 2004; Ates et al., 2007; Wassink et al., 2011); thus, its application is not new. The novel contribution of this work was the comparative examination of two common approaches for reporting fractionation data for THM-FP prediction. The reporting of relative fractions of DOC (as percentages) and absolute quantities (mass-based concentration) was compared and recommendations for future reporting were provided.

In Phase 5, changes in DOC character and its relationship to regulated DBP-FPs (THM-FPs and HAA-FPs) were characterized following forest harvesting. Like Phase 3, this work was conducted as part of the ongoing SRWP in which two SRWP watersheds that served as unburned-reference watersheds in Phase 3 were studied. They were fully calibrated for climate, streamflow, and water quality for 11 years [2004-2014]). Three sub-watersheds (within one watershed) were harvested in 2015, using: clear-cutting with patch retention, strip-shelterwood cutting, and partial cutting. The harvesting work was conducted to ensure that all best management practices (BMPs) were followed to minimize disturbance impacts on water quality. This nested, paired watershed design (BACI; before/after, control/impact) enabled explicit separation of harvesting impacts on hydrology and water quality from background variability produced by seasonal or climatic variation (Loftis et al., 2001); however, that analysis is part of a longer term study that is outside of the scope of the present investigation. Here, only a preliminary assessment of the immediate aspects of forest harvesting on DOC and associated drinking water treatability implications was conducted. The NOM characterization/fractionation techniques utilized in this phase were the same as those in Phases 2 and 3 to enable linkages between the results obtained from the three experimental phases. The strategies developed as part of phase 4 were implemented here as well.

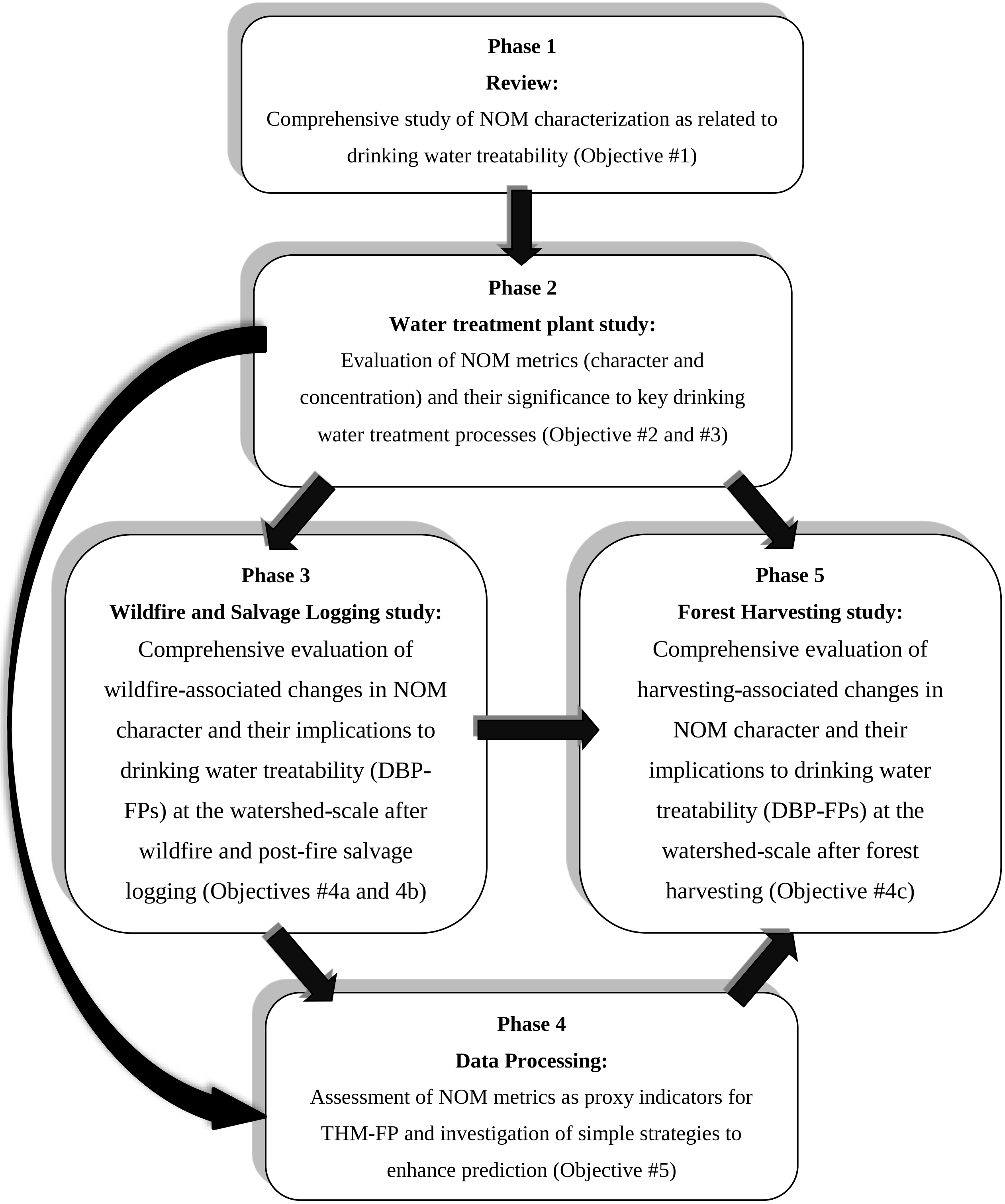


Figure 1-1. Research approach and associated objectives.

1.4 Thesis Organization

This Thesis consists of seven chapters. The review (Chapter 2) and results chapters (3-6) have been prepared in a paper format; however, they have not been submitted to co-authors for commentary.

In Chapter 2, the background science, relevant to the research objectives, was summarized (Phase 1). The existing literature regarding NOM source, variability, reactivity, and associated drinking water treatability challenges is discussed. The most common NOM fractionation and characterization techniques, and their relationships to the formation of regulated carbonaceous DBPs, are comprehensively and critically reviewed. Known DBPs and their potential health effects are also discussed.

In Chapter 3, the results from experiments conducted at the Mannheim drinking water treatment plant (Phase 2) are summarized (Phase 2). The quantity and character of NOM fractions are analyzed and evaluated before and after each treatment process. The removal and transformation of the characterized fractions are discussed in connection with the roles and function of different treatment processes. Several metrics of NOM character and concentration are then compared as proxy indicators for drinking water treatability.

In Chapter 4, wildfire-associated changes in NOM character and their associated implications to drinking water treatability (DBP-FPs) are comprehensively evaluated at the watershed-scale after wildfire and post-fire salvage logging (Phase 3).

In Chapter 5, the results from Phases 2 and 3 of the research are used to assessment several NOM metrics as proxy indicators for THM-FP and simple strategies to enhance prediction of THM-FP (based solely on the quantitative data) are investigated. Specifically, common reporting practices that specify either relative fractions of DOC (as percentages) or absolute quantities (mass-based concentration) are compared (Phase 4).

In Chapter 6, contemporary forest harvesting-associated changes in NOM character their associated implications to drinking water treatability (DBP-FPs) are evaluated at the watershed-scale during the harvest and first post-harvest years (Phase 5).

Finally, the conclusions of this research and recommendations for future research are presented in Chapter 7.

Chapter 2

Analysis and Characterization of Aquatic Natural Organic Matter and Its Implications for Drinking Water Treatment

2.1 Overview

Natural Organic Matter (NOM) is ubiquitous and plays an important role in all aquatic environments. It is also a key driver of drinking water treatment that significantly contributes to infrastructure needs, design, and operations (Emelko et al., 2011; MWH, 2012). The amount, chemical characteristics, and reactivity of NOM from different sources can vary widely depending on their origin. Temperature, pH, hydrology, and biogeochemical processes of carbon cycling are amongst the factors that impact NOM characteristics and levels. This dependency makes NOM vulnerable to changes in the environment. Given increases in the rate of natural and anthropogenic disturbances in the environment, the investigation of NOM and its structure and reactivity in water is of paramount importance. Dissolved Organic Carbon (DOC) is the main (operationally-defined) metric used in the water industry to describe aquatic NOM concentration; however, it does not provide information regarding the chemical characteristics and reactivity of NOM. Thus, different methods have been developed to quantitatively and qualitatively characterize NOM structure and fractions; of course, these methods have limitations. Here, the most common methods of aqueous NOM characterization and reactivity assessment are reviewed in the context of their known and/or believed connectivity to drinking water treatability. Their limitations are also discussed and key knowledge gaps and operational needs are highlighted. This review underscores the lack of a "one size fits all" approach to evaluating aquatic natural organic matter and the need to continue to develop specific methods that inform its implications to and reactivity during drinking water treatment.

2.2 Introduction: Natural Organic Matter

Natural organic matter (NOM) is a complex blend of organic compounds that vary in molecular size, mass, polarity, aromaticity, and chemical composition (Leenheer and Croué, 2003; Deb and Shukla, 2011). It is described as a mixture of organic compounds that arise in natural waters from allochthonous or autochthonous sources. While allochthonous NOM originates from the decomposition of soil organic matter and plants, autochthonous NOM results from photosynthetic and biological activities of bacteria, macrophytes, and algae (Thurman, 1985; Aiken and Cotsaris, 1995). Total organic carbon (TOC) and NOM are synonymous when measured TOC does not include any synthetic sources of carbon (e.g., pesticides, chlorinated organic compounds, etc.). TOC concentrations in natural waters can vary considerably; ranging from 0.1 mg/L (in some groundwaters) to 200 mg/L (in some swamps) (MWH, 2012). TOC in drinking water sources is frequently >70%, and often >90% dissolved organic carbon (DOC), with concentrations in the range of 0.5 mg/L to 60 mg/L (Thurman, 1985). NOM levels and characteristics vary spatially and temporally and can be altered by landscape disturbances (urbanization, agriculture, natural resource extraction, wildfires, etc.), which can impact carbon availability, transport, and fate (Schiff et al., 1990; Wu et al., 2004), thereby potentially affecting ecosystem productivity and health (Williams et al., 2010; Beggs and Summers, 2011; Emelko et al., 2011; Smith et al., 2011; Yamashita et al., 2011). The concentration and character of aquatic NOM is also critical to drinking water treatment because it affects 1) taste, odor, and color (Leenheer and Croué, 2003); 2) potentially toxic disinfection by-product formation (Babcock and Singer, 1979; Singer, 1999; Kitis et al., 2002; Liang and Singer, 2003; Ates et al., 2007; Chen and Westerhoff, 2010); 3) chemical coagulation (White et al., 1997; Edzwald and Tobiason, 1999; O'Melia et al., 1999; Sharp et al., 2006; Yan et al., 2008); 4) membrane fouling (Lee et al., 2006; Amy, 2007; Brinkman and Hozalski, 2011; Rahman et al., 2014; Yamamura et al., 2014); 5) oxidant demand during disinfection (Owen et al., 1993; Fabris et al., 2008); 6) bacterial regrowth in distribution systems (Rittmann and Snoeyink, 1984; van der Kooij, 1992; LeChevallier et al., 1996; Kaplan et al., 2005; van der Kooij and van der Wielen, 2014); and 7) heavy metal complexation (Frimmel, 1998; Wu et al., 2004; Waples et al., 2005; Deonarine and Hsu-Kim, 2009). Notably, climate change is intensifying biogeochemical cycling of carbon, resulting in increased exports of terrestrial carbon to aquatic systems (Tranvik and Jansson, 2002)—it is also intensifying the occurrence of natural landscape disturbances such as wildfires (Westerling et al., 2006), which may increase aquatic NOM concentrations (Mast and Clow, 2008; Emelko et al., 2011).

A wide range of techniques have been utilized to characterize aquatic NOM; however, no one approach is universally and singularly useful for all applications because 1) NOM is diverse and largely undefined in composition and 2) the analytical techniques used to characterize NOM often describe different attributes of carbon. Moreover, the need to characterize specific types of NOM reactivity and contributions to chemical coagulant demand, DBP-FP, oxidant demand, membrane fouling, etc. is unique to the drinking water industry and may not be most efficiently informed by attributes such as structural composition. Nonetheless, NOM can be characterized using a variety of techniques that ultimately focus on certain aspects of structure.

The past several decades of drinking water treatment research have underscored the critical importance of NOM and its relationship to water treatability. This has been accompanied by extremely rapid expansion in the use and development of NOM characterization techniques, leading to a wide range of approaches used, reported results, and conclusions; sometimes, with contradictory outcomes. Here, emerging NOM characterization techniques and those that are more widely used in the water industry are organized according to the specific aspects of NOM structure to which they correspond. These categories of NOM characterization include size, polarity, and other structural attributes (i.e., aspects of structure not represented in the other categories, such as aromaticity, fluorescence, and other spectral characteristics that may capture multiple aspects of structure). The purpose of this review is to 1) summarize currently available NOM characterization techniques, 2) organize these techniques according to the fundamental information they provide, and 3) discuss the limitations of these for informing drinking water treatability and treatment performance.

2.3 NOM Characterization

NOM characterization has been studied extensively in water science and engineering because of its utility in carbon source identification (Schiff et al., 1990; McKnight et al., 1994; 2001; Aiken and Cotsaris, 1995; Coble, 1996; McKnight et al., 2001a; Liang et al., 2008) and prediction of NOM reactivity, which is context dependent. For example, NOM reactivity can be described to better understand aquatic ecosystem health and trophic status (Dunalska, 2011) or to inform drinking water treatability challenges such as disinfection by-product (DBP) formation potential (Singer et al., 1981; Collins et al., 1986; Amy et al., 1987; Reckhow and Singer, 1990; Newcombe et al., 1997; Liang and Singer, 2003; Goslan et al., 2004; Kitis et al., 2002; Soh et al., 2008; Wassink et al., 2011; Awad et al., 2016), chemical coagulant demand (Chow et al., 2004; Sharp et al., 2006; Yan et al., 2008; Hohner et al., 2016), distribution system regrowth potential (Kaplan et al., 2005; van der Kooij and van der Wielen, 2014) and membrane fouling (Amy, 2008; Rahman et al., 2014; Yamamura et al., 2014). Thus, while the general goal of NOM characterization is to gain comprehensive insight into its composition and reactivity, the most informative combination of metrics and analytical procedures can vary substantially depending on the intended inference space.

Various techniques and metrics have been developed to characterize NOM based on different features of its structure such as size, polarity, other structural aspects, and biodegradability. NOM has been characterized in bulk and fractionated forms. Low dissolved organic carbon (DOC) concentrations in bulk water samples are the main barrier to effectively characterizing NOM. Thus, a number of techniques have been developed to fractionate and concentrate NOM, isolate its constituent compounds, and simplify their identification (Leenheer and Croué, 2003; Abbt-Braun, 2004). The analysis of “bulk water samples” typically describes NOM characterization procedures in which NOM structural constituents are not modified during the analyses—these can be especially informative during drinking water treatability assessments because they are representative of actual treatment conditions. Also, several of these analyses are relatively rapid, inexpensive, and still informative. The choice of appropriate NOM characterization method(s) depends on the application and objectives of the analysis. Equipment availability and time are other determining factors. Common and emerging NOM characterization methods can be categorized by the characteristics of NOM on which they are based (structural or reactivity) and analytical approaches utilized for evaluating them, as presented in Figure 1, summarized in Table 1, and discussed in detail below.

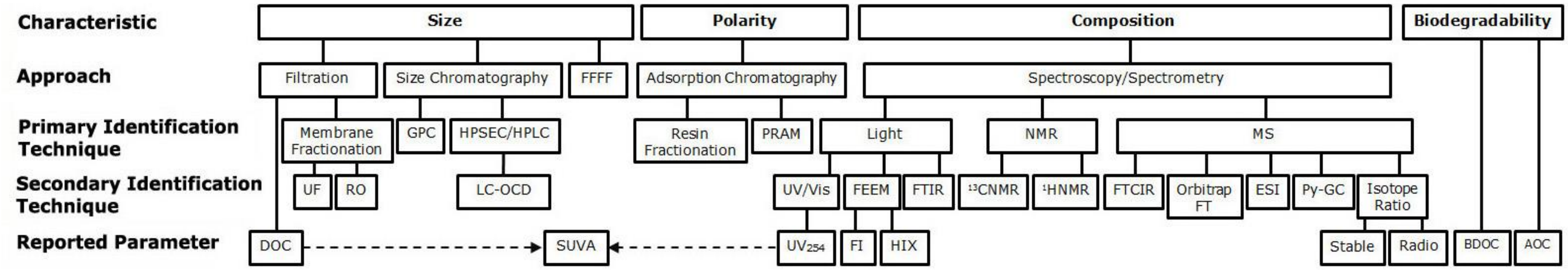


Figure 2-1. Dissolved NOM characterization methods organized by the characteristics of NOM upon which they are based (structural or reactivity) and analytical approaches utilized.

Table 2-1. Summary of NOM characterization methods.

Character	Characterization Method			Description	Advantages	Disadvantages	Reference
Size	Filtration	TOC/DOC		Total organic carbon/dissolved organic carbon (filtered through 0.45 µm filter)	Simple; online-application of TOC; integral to water treatment	Only bulk information; sensitive to pH, operational definition	Singer et al., 1981; Thurman, 1985; Reckhow and Singer, 1990; Edzwald, 1993; Wassink et al., 2011; Shams et al., 2014 and 2015
		Membrane	UF	Fractionates NOM based on molecular size (weight) by filtration under pressure	Fractionate large volumes of water; do not alter SUVA; determine the composition and reactivity of a broad range of NOM	Sensitive to pH, membrane, ionic strength; broad nominal cutoffs; membrane-solute interactions	Gjessing, 1970; Gjessing, 1973; Aiken et al., 1984; Amy et al., 1987; Laine et al., 1989; Newcombe et al., 1997; Assemi et al., 2004; Goslan et al., 2004; Lamsal et al., 2012; Revchuk and Suffet, 2014
			RO		Fractionate large volumes of water; do not alter SUVA; determine the composition and reactivity of a broad range of NOM	Concentrates all solutes, rather than only NOM	Maurice et al., 2002; Song et al., 2009
	Size Exclusion Chromatography	GPC		Fractionates NOM based on molecular size. Separation is performed in columns by elution of the sample through porous beads of a soft gel (Sephadex)	No preparation; no chemical alterations	Long, poor separation; sensitive to pH; interaction of humic acid with gel	Gjessing, 1973; Becher et al., 1985; Amy et al., 1987; Hongve et al., 1996
		HPLC)/HPSEC /LC-OCD		The modified form of SEC with rigid silica or polymer based stationary phase replacing the soft gel beads of GPC. The solvent is pumped through the column and the column effluent passes through a detector. An organic carbon and/or UV detector can follow the column to detect eluted species	Fast; no preparation; provides a good diagram of NOM fractions and characterization that can replace the operational distinction between humic and fulvic acids; informative for water treatment over a wide range of molecular weight fractions	Interaction of analyte with stationary phase; limitation in full separation of all individual peaks challenging calibration; no precise determination of molecular weight	Fukano et al., 1978; Becher et al., 1985; Huber and Frimmel, 1992a,b; Huber et al., 1994; Hongve et al., 1996; Bolto et al., 1999; Croué, 2004; Ates et al., 2007; Wu et al., 2007a; Huber et al., 2011; Wagner et al., 2016;; Wu et al., 2007a; Soh et al., 2008; Baghoth et al., 2009; Wassink et al., 2011; Rahman et al., 2014 and 2016; Azzeh et al., 2015; Pharand et al., 2015; Shams et al., 2014

Table 2-1: Summary of NOM characterization methods (con't).

Character	Characterization Method				Description	Advantages	Disadvantages	Reference
Size	**FFF**				Fractionates NOM based on the difference in the mobility of molecules of different sizes	Does not need a stationary phase	Molecular weight cut off of the membranes (not low enough); adsorptive interaction between sample and membrane; need of appropriate calibration standards	Giddings et al., 1976; Beckett et al., 1987; Giddings et al., 1987; Newcombe et al., 1997; Pelekani et l., 1999
Polarity	**Adsorption Chromatography**	**Resin Fractionation**			Separates hydrophobic and hydrophilic fractions (operationally-defined)of NOM by having them adsorbed to Amberlite® XAD resins	Accepted by IHSS as standard method of separating humic and fulvic acids; very helpful for coagulation application; provides information on reactivity	Operational definition of parameters; time consuming; complex; sensitive to pH; contamination potential from resin	Leenheer, 1981; Thurman and Malcolm 1981; Leenheer and Noyes, 1984; Collins et al., 1986; Aiken et al., 1992; Malcolm and MacCarthy, 1992; Town and Powell, 1993; Bolto et al., 1999; Krasner et al., 1996; Kitis et al., 2002; Marhaba et al., 2003; Liang and Singer, 2003; Chow et al., 2004; Croué, 2004; Goslan et al., 2004; Soh et al., 2008; Shams et al., 2014 and 2015
		PRAM			Separates NOM fractions based on polarity by having them adsorbed to solid phase extraction cartridges with different polarities	Fast; simple; needs small volumes of samples; does not chemically alter samples	Unable to produce mass balance	Rosario-Ortiz et al., 2004; Rosario-Ortiz et al., 2007a,b; Philibert et al., 2012
Other Structural Attributes	**Spectroscopy**	**Light**	**UV/Vis**	**UV $_{254}$**	Measurement of compounds that absorb UV light at 254 nm; provides an indication of aromaticity	Fast; simple; on-line application; integral to coagulation; very helpful for reactivity application	Only information on aromatic compounds; sensitive to pH and ionic strength	Singer et al., 1981; Edzwald et al., 1985; Ates et al., 2007Wassink et al., 2011; Awad et al., 2016; Shams et al., 2014 and 2015
				SUVA	SUVA = UV$_{254}$/DOC SUVA >4: hydrophobic, humic with high MW. SUVA <2: non humic, low MW, hydrophilic 2<SUVA<4: mixture of hydrophobic and hydrophilic	Fast; simple; very helpful in coagulation application; useful (but not consistently) for reactivity application	Sensitive to pH and ionic strength; less reliably informative NOM reactivity	Edzwald and Van Benschoten, 1990; Reckhow et al. 1990; Edzwald and Tobiason 1999; Kitis et al. 2001; Weishaar et al., 2003; Goslan et al., 2004; Ates et al., 2007; Bougeard et al., 2010; Li et al., 2014; Hua et al., 2015

Table 2-1: Summary of NOM characterization methods (con't).

Character	Characterization Method				Description	Advantages	Disadvantages	Reference
Other Structural Attributes	**Spectroscopy**	**Light**	**Fluorescence**	**FEEM**	Identifies groups of NOM, by irradiating fluorescence to the sample at different wavelengths and analyzing the spectrum of the emitted radiation at different wavelengths. Three major groups: humic and fulvic like, microbial by-product, and protein like	Fast; simple; sensitive; on-line application; potential for quantitative interpretation	Quantitatively not universally established yet; sensitive to pH; challenging calibration	Senesi et al., 1989; Coble et al., 1993; Hofstraat and Latuhihin, 1994; Coble, 1996; Baker, 2001; McKnight et al., 2001b; Chen et al., 2003a,b; Holbrook et al., 2006; Spencer et al., 2007; Wu et al., 2007b; Peiris et al., 2010; Pifer andFairey 2014; Pifer et al., 2014; Peleato and Andrews, 2015; Korak et al., 2015; Peleato et al., 2017
				(FI)	Reveals information about the source by exciting the molecules at 370 nm and analyzing the ration of emission intensity at 450 nm to emission intensity at 500 nm	Fast; simple; no preparation; useful information on aromaticity	Sensitive to hydrology regime; limited to existence of certain wavelengths	McKnight et al., 2001b; Brooks and Lemon, 2007; Cory et al., 2010; Johnson et al., 2011; Rodríguez et al., 2014; Shams et al., 2014 and 2015; Korak et al., 2015; Hohner et al., 2016
				(HIX)	Measures proportion of humified to non-humified fractions of NOM by dividing the emission intensity at large wavelengths (ex. 390) by emission intensity at short wavelengths (ex. 355) (at excitation of 254 nm)	Fast; simple; no preparation; useful information on the aromatic nature of NOM	Sensitive to DOC concentrations; not recommended for DOC < 3	Zsolnay et al., 1999; Kalbitz et al., 2000; Ohno, 2002
			Infrared	**FTIR**	Identifies functional groups of NOM, by irradiating IR to the sample and analyzing the absorbance spectrum of the sample	Capable of analyzing both liquid and solid phase samples	Mainly qualitative analysis; difficult data interpretation; spectral overlapping; intensive sample preparation	Leenheer et al., 1987; Bloom and Leenheer, 1989; Ricca and Severini, 1993; Chen et al., 2002
		NMR	**^{13}CNMR and ^{1}HNMR**		Identifies structural elements (carbon atoms) and functional groups of NOM based on carbon bonded to H, C, N and P	Valuable information especially when ^{1}H NMR and ^{13}C NMR are used together	Difficult data interpretation; spectral overlapping; quantitative limitations; overestimation of aliphatic fractions; intensive sample preparation	Leenheer et al., 1987; Ricca and Severini, 1993; Westerhoff et al., 1999;Poirier et al., 2000;González-Vila et al., 2001; Templier et al., 2005

Table 2-1: Summary of NOM characterization methods (con't).

Character	Characterization Method				Description	Advantages	Disadvantages	Reference
Other Structural Attributes	Spectrometry	Mass Spectrometry (MS)	ESI		Use of electrospray ionization in MS	Introduces liquid samples into MS; enables coupling MS with HPLC (LC-MS)	Difficult data interpretation; need of appropriate calibration standards	Brown and Rice, 2000; Klaus et al., 2000; Leenheer et al., 2001
			FTICR		Use of ion cyclotron resonance in MS for separating ions from each other in addition to use of fourier transform analysis for quantification	Ultra-high resolutions; promising results at a molecular level		Reemtsma et al., 2008; Reemtsma, 2009; Kunenkov et al., 2009; Herzsprung et al., 2014; Cao et al., 2015; Lu et al., 2015; Herzsprung et al., 2015; Li et al., 2016; Hertkorn et al., 2016; Li et al., 2016
			Orbitrap FT		Use of Orbitrap^{TM} technology (trapping in an electric field) in MS in addition to use of fourier transform analysis for quantification	Smaller; less expensive; higher trapping capacity compared to other MS techniques		Makarov, 2000; Urai et al., 2014
			Py-GC-MS		Uses heat and degrades complex molecules into smaller ones that are volatile and can be introduced into gas chromatography	Enables identification of natural biopolymers; less expensive comparing to other MS techniques	Difficult data interpretation; need of appropriate calibration standards; overestimation of aliphatic fractions; limitations on transferring all higher-molecular weight fractions from the pyrolysis unit to the GC	Saiz-Jimenez, 1994; Poirier et al., 2000; González-Vila et al., 2001; Croué, 2004; Templier et al., 2005; Parsi et al., 2007
			Isotope Ratio	$\delta^{13}C$ and ^{14}C	δ^{13} = ratio of stable carbon isotopes, reveals information on the origin of carbon compounds based on their relative weight ^{14}C = radioactive carbon isotope, reveals information on age of carbon compounds	Very useful information; high sensitivity at low levels	Complicated; time consuming; undesirable interactions with inorganic carbon species; ^{14}C is sensitive to residence time	Williams et al., 1969; Hedges et al., 1986; Williams and Druffel, 1987; Murphy et al., 1989a,b; Schiff et al., 1990; Bauer et al., 1991; Kendall and Caldwell, 1998; Raymond and Bauer, 2001; Gandhi et al., 2004; Mayorga et al., 2005; De Troyer et al., 2010; Jian et al., 2010; Bridgeman et al., 2014

Table 2-1: Summary of NOM characterization methods (Cont'd).

Character	Characterization Method	Description	Advantages	Disadvantages	Reference
Biodegradability	**BDOC**	The fraction of DOC that can be metabolized by heterotrophic microorganisms	Useful information for drinking water treatment and distribution	Operational definition; can be time consuming; can over/under estimate if not used in complimentary with AOC	Servais et al., 1987; Lucena et al., 1991; Frias et al., 1995; Volk and LeChevallier, 2000; Escobar and Randall, 2001; Zappia et al., 2008; Yapsakli and Çeçen, 2009
	AOC	The fraction of DOC that can be used by specific bacteria and converted to cell mass	Able to detect very low concentrations; useful information for drinking water treatment and distribution	Very sensitive to the environment contamination; time consuming; laborious; can over/under estimate if not used in complimentary with BDOC	Van der Kooij et al., 1982; Huck, 19990; Frias et al., 1995; Escobar and Randall, 2001; Kang et al., 2006

2.3.1 Size-based Characterization

2.3.1.1 Filtration

2.3.1.1.1 Dissolved Organic Carbon

DOC is the soluble fraction of TOC and the most common parameter used for describing aquatic NOM. It is operationally-defined as the organic carbon that can be filtered through a 0.45μm nominal porosity membrane filter (Thurman, 1985). Though sensitive to pH, measurement of TOC/DOC is simple and fast, and TOC analysis is possible in real time. Although it is not a common practice in the drinking water industry; online TOC analysis has been proposed for monitoring direct potable reuse process performance. DOC analysis is integral to water treatment because DOC concentration often correlates directly with the formation of regulated DBPs whose presence signals potential health concerns (Singer et al., 1981; Reckhow and Singer, 1990; Wassink et al., 2011; Shams et al., 2014 and 2015) and chemical coagulant demand (Edzwald, 1993). However, these relationships tend to be site specific and breakdown when samples are collected from different sources (Reckhow and Singer, 1990), possibly as a result of different hydro-climatic conditions and sources contributing to DOC. An important limitation of TOC/DOC analysis is that it is limited to NOM quantity and does not inform NOM quality or structure. Although most studies have focused on the dissolved fraction of organic matter, the importance of monitoring suspended sediment associated particulate organic carbon (POC) in addition to DOC, as a potential source of increased reactivity (i.e., THM-FP) resulting from high discharge during storm events has been recently demonstrated (Jung et al., 2014); however, methods for assessing particulate NOM and their potential application to treatability are beyond the scope of this review.

2.3.1.1.2 Membrane Fractionation

Membrane fractionation methods enable characterization of molecules on the basis of molecular size/weight, by filtration under pressure and have demonstrated that NOM consists of a complex mixture of organic matter molecules of variable size and weight (Gjessing, 1970; Aiken, 1984; Collins et al., 1986; Liu et al., 2007; Lamsal et al., 2012; Green et al., 2015). Reverse osmosis membrane technology has been used to isolate and concentrate NOM from large volumes of water, but it also concentrates several other solutes as well (Maurice et al. 2002; Song et al, 2009); accordingly, ultrafiltration (UF) is more commonly used because although it excludes a smaller size range of molecules.

Ultrafiltration (UF)

Ultrafiltration has been widely used to isolate NOM based on molecular size cutoffs (Collins et al., 1986; Amy et al., 1987; Laine et al., 1989; Lamsal et al., 2012). An important advantage of these approaches is that large volumes of water can be fractionated without requiring alteration of the chemical properties of NOM (e.g., by acidification) during processing (Goslan et al., 2004). High molecular weight fractions obtained by UF have been reported as highly colored with high carbohydrate content and high specific ultraviolet absorbance (SUVA-discussed below), while low molecular weight fractions have typically been lower in color, with long aliphatic carbon chains (Newcombe et al., 1997; Wei et al., 2008).

Laine et al. (1989) reported that membrane composition can affect NOM fractionation by UF and concluded that membrane hydrophilicity results in better NOM fractionation. Membrane-solute interactions and operational conditions also affect NOM fractionation by membranes. Adherence of macromolecules to the walls of membrane pores affects membrane permeability and thus separation efficiency. Concentration polarization caused by deposition of macromolecules, can restrict flow and adversely impact isolation (Amy et al., 1987). Other factors including pH, pressure, ionic strength, membrane uniformity, pore size, and calibration standards can also affect the molecular weight distributions of NOM fractions obtained by UF (Aiken, 1984; Amy et al., 1987; Leenheer and Croué, 2003). A particular concern associated with this method is that NOM charge and structure may affect fraction isolation and rejection (Assemi et al., 2004; Revchuk and Suffet, 2014); therefore, UF fractionation and subsequent molecular weight estimation should be conducted carefully (Aiken, 1984; Assemi et al., 2004).

UF fractionation of NOM has been compared to other methods such as chromatographic separation. In one comparison, UF fractionation and gel permeation chromatography (GPC) yielded similar outcomes for NOM size and molecular weight (Gjessing, 1973). By contrast, other comparisons of NOM characterization by UF and GPC did not yield consistent outcomes.

Specifically, molecular weights obtained using GPC were higher than those obtained with UF for the same source water. It was further shown that these differences were attributable to sensitivity to changes in pH; thus, it was concluded that UF is more reliable for NOM fractionation than GPC (Amy et al., 1987). Although neither of these methods was particularly precise in determining absolute molecular size, they were adequate for monitoring organic carbon in source waters and removal its fractions during water treatment (Amy et al., 1987).

Higher molecular weight fractions obtained using UF fractionation have been found to be more reactive in forming THMs (Amy et al., 1987) and also more prone to removal by conventional treatment as well as direct filtration (Collins et al., 1986), relative to lower molecular weight fractions. In contrast, a study by Goslan et al. (2004) showed that fractions with low molecular weight were reactive and contributed to formation of regulated DBPs (Goslan et al., 2004), while Kitis et al (2002) did not find any significant relationships between fractions obtained from UF separation and formation of regulated DBPs (Kitis et al., 2002). These contradictory results suggest that molecular size may not be the best metric for the prediction of DBP formation.

2.3.1.2 Size Exclusion Chromatography

Size Exclusion Chromatography (SEC) involves NOM fractionation based on molecular size. It also can be used as to measure the molecular size of NOM fractions collected by other fractionation techniques (Croué, 2004; Baghoth et al., 2009). NOM fractionation by SEC involves passing the mobile phase (eluent and sample) through a column packed with porous beads (stationary phase). The fractions with smaller molecular size penetrate the stationary phase, while larger molecules move rapidly and have a shorter retention time in the column (Gjessing and Lee, 1967; Leenheer and Croué, 2003; Croué, 2004).

2.3.1.2.1 Gel Permeation Chromatography (GPC)

SEC was first performed with soft gel forming polymers (such as Sephadex) as the stationary phase, resulting in gel permeation chromatography (GPC) (Gjessing, 1973; Amy et al, 1987). This process is very time consuming because soft gels perform poorly at high pressure and flow rates (Hongve et al., 1996). The main disadvantage of this method is poor separation

(Becher et al., 1985) caused by factors such as electrostatic and adsorption interactions between the gel and the humic acids, which interfere with size exclusion separation (Amy et al., 1987). Electrostatic interactions tend to occur in solutions with low ionic strength, while adsorption interactions occur at lower pH; thus, using a basic buffer eluent with a high ionic strength is recommended to diminish these unwanted interactions (Amy et al., 1987).

2.3.1.2.2 High Performance Size Exclusion Chromatography (HPSEC)/High Pressure Liquid Chromatography (HPLC)

To improve the performance of SEC and overcome the disadvantages of using GPC, SEC was modified for use with rigid gels (silica- or polymer-based) instead of soft ones (Wu et al., 2007a; Soh et al., 2008). Rigid beads can work at higher pressure and achieve better performance. Thus, the modified technique is called high pressure liquid chromatography (HPLC) or high performance size exclusion chromatography (HPSEC) (Fukano et al., 1978; Hongve et al., 1996). HPLC requires less analytical time than GPC and the resulting chromatograms have higher resolution (Becher et al., 1985). HPLC makes it possible to fractionate NOM into humic substances, biopolymers, building blocks, low molecular weight organic acids and neutrals and hydrophobic organic carbon fractions (Huber et al., 2011). Combining HPLC with multiple detectors (UV, FEEM, DOC, and DON) and advanced characterization tools (e.g. electrospray-MS, pyrolysis GC-MS) has been critical in the advancement of NOM characterization (Leenheer and Croué, 2003; Wagner et al., 2016). The main advantage of liquid chromatography is its capacity for revealing information on a large range of compounds from low to high molecular weights. Therefore, its application is beneficial in understanding the removal and reactivity of medium to low molecular weight compounds that cannot be described by other methods that only identify aromaticity (such as resin fractionation and UV_{254}) (Shams et al., 2015). HPLC has been used in conjunction with on-line detectors such as UV, DOC and fluorescence excitation emission matrix (FEEM) analyzers (Huber and Frimmel, 1992 a,b; Huber et al, 1994; Bolto et al., 1999, Croué, 2004; Wu et al., 2007a; Soh et al., 2008; Baghoth et al., 2009; Wassink et al., 2011; Rahman et al., 2014 and 2016; Azzeh et al., 2015; Pharand et al., 2015; Shams et al., 2014 and 2015). Although UV analyzers are more commonly used in this context, the addition of an organic carbon detector (OCD) to HPLC (called LC-OCD) can provide more information regarding the amount and composition of NOM (Huber and Frimmel, 1992a,b; Wu et al., 2007a). The technique has been refined by adding an organic nitrogen detector (OND) and output of a humic substances (HS) diagram where aromaticity (defined as UV_{254}/DOC) of the HS fraction is plotted against its nominal average molecular weight (Huber et al., 2011). The separation of various types of humic substances on the HS diagram suggests qualitative information about NOM origin (Huber et al., 2011); however, this capacity may be limited because LC-OCD cannot achieve full separation of all individual peaks associated with NOM fractions (Huber et al., 2011), thereby precluding proper calibration and adequate characterization/quantification of some types of NOM. Positive correlations between HS fraction (obtained by LC-OCD) and other aromaticity metrics (UV_{254}, SUVA, and HPO) have been reported which confirms that although these metrics have different operational definitions, there is an overlap between the compounds that they describe (Shams et al., 2017). HPLC cannot precisely determine absolute molecular weight and works best for finding the relative proportions of organic fractions with different molecular sizes (Ates et al., 2007) whose peaks do not overlap.

2.3.1.3 Flow Field-Flow Fractionation (FFFF)

Flow field-flow fractionation (FFFF) separates NOM based on differences in the mobility of molecules of different sizes. It has been used to measure the molecular size of NOM in different water sources (Rosario-Ortiz et al., 2007b; Moon et al., 2006; Pifer and Fairey, 2012) and NOM fractions collected using other fractionation techniques (Newcombe et al., 1997; Assemi et al., 2004). NOM fractionation is achieved by injecting a sample into a thin channel while an external flow field perpendicular to the channel is introduced, applying a physical force to the sample and bending and shifting its flow to separate molecules based on their size/mobility. The fractions move toward an accumulation wall (semi-permeable or cellulose acetate membrane) for ultimate separation. Smaller sized molecules move faster than larger ones, which therefore have shorter retention times in the channel (Giddings et al., 1976; Beckett et al., 1987). NOM fractionation and molecular size determination by FFFF and SEC yield similar outcomes (Pelekani et al., 1999; Rosario-Ortiz, 2007b); in contrast, FFFF and UF fractionation have yielded different outcomes (Newcombe et al., 1997; Assemi et al., 2004).

2.3.2 Polarity-based Characterization

2.3.2.1 Adsorption Chromatography

2.3.2.1.1 Resin Fractionation

Resin fractionation has been widely used for carbon fractionation. Ion exchange resins separate hydrophobic and hydrophilic fractions of NOM by adsorption at specific pH conditions (Leenheer, 1981; Thurman and Malcolm, 1981). Resin composition and surface area govern adsorption capacity (Cheng, 1977). The fractions separated by XAD resins are operationally-defined such that the hydrophobic acid fraction is the portion of DOC that adsorbs on a column of XAD-8 resin at pH 2 and is eluted at pH 13 (Leenheer, 1981; Aiken et al. 1992). This fraction is also defined as fulvic acid (Thurman and Malcolm, 1981) and can contain aliphatic carboxylic acids of 5-9 carbons, one- and two-ring aromatic carboxylic acids, one- and two-ring phenols, and aquatic humic substances. The hydrophilic acid fraction is the portion of the DOC contained in the XAD-8 resin effluent at pH 2 that sorbs on a column of XAD-4 resin that is eluted at pH 13. This fraction can contain poly-functional organic and aliphatic acids with five or fewer carbon atoms (Aiken et al. 1992; Malcolm and MacCarthy 1992). Resin fractionation typically uses Amberlite® XAD-8 and XAD-4 resins in series to adsorb aromatic hydrophobic and non-humic hydrophilic fractions, respectively. The terms and definitions assigned to the fractions have varied somewhat between studies. The method developed by Thurman and Malcolm (1981) has been used by the International Humic Substances Society (IHSS) as a standard method to distinguish between fulvic and humic acids (Senesi et al., 1989) relies upon operational definitions that involve adsorption on XAD-8 at pH 2, desorption at pH 13, and precipitation at pH 1 (Thurman and Malcolm, 1981). More recently, the addition of a third resin has been proposed to further separate the hydrophilic fraction of NOM (Bolto et al., 1999; Marhaba et al., 2003). Although resin fractionation has been broadly applied, its major drawbacks are that it is time consuming and complicated. A “rapid” resin fractionation method that involves mini-columns has been proposed (Chow et al., 2004) in which NOM is isolated into four fractions: 1) very hydrophobic acids (VHA); 2) slightly hydrophobic acids (SHA); 3) hydrophilic charged acids (CHA) that were separated on Supelite DAX-8, Amberlite XAD-4, and Amberlite IRA-958, respectively; and 4) hydrophilic neutrals (NEU) which did not adsorb to the aforementioned resins (Bolto et al., 1999).

Operational conditions used during resin fractionation can affect the results, making comparisons between studies difficult. For example, the extreme pH conditions used during resin fractionation can alter the chemical properties of the NOM fractions; accordingly, further characterization of the fractions is not necessarily representative of the original sample. Irreversible adsorption to the resins, contamination from resin bleeding, size-exclusion effects, and poor recovery are further challenges associated with the operational specifics of resin fractionation techniques (Town and Powell, 1993). Despite these challenges, resin fractionation has been quite informative in some applications such as drinking water coagulation, where it has been consistently demonstrated that hydrophobic fractions drive coagulant demand and are easier to remove than hydrophilic fractions (Collins et al., 1986; Kitis et al., 2002; Liang and Singer, 2003; Chow et al., 2004; Sharp et al., 2006; Soh et al., 2008). It has been less consistently informative elsewhere, such as assessment of NOM reactivity with oxidants (e.g. chlorine). While many studies have suggested that humic/hydrophobic fractions of NOM are more reactive with chlorine and major contributors to the formation of regulated DBPs in natural waters (Collins et al., 1986; Kitis et al., 2002; Liang and Singer, 2003; Soh et al., 2008; Shams et al., 2014 and 2015), hydrophilic compounds are also reactive (Krasner et al.,1996) and have been show to act as major precursors of regulated DBPs (Collins et al., 1986; Bolto et al., 2002; Kwon et al., 2005) and DBPs of emerging health concern (Chen and Westerhoff, 2010). This inconsistency underscores that although resin fractionation is an informative method, it is likely inadequate (when used alone) for drawing general conclusions on the reactivity of hydrophobic/hydrophilic fractions of different source waters during drinking water treatment.

2.3.2.1.2 Polarity Rapid Assessment Method

The polarity rapid assessment method (PRAM) involves analyzing the quantity of NOM that can be adsorbed onto a parallel series of solid phase extraction (SPE) cartridges with different polarities that include: non-polar (C18, C8, and C2), polar (CN, diol and silica) and anionic exchangers (NH2, SAX). NOM breakthrough is expressed as DOC and/or UV_{254} (Rosorio-Ortiz et al., 2004; 2007a). A retention coefficient ($RC = 1- \frac{C_{max}}{C_0}$, where C_o is the initial DOC or UV_{254} and C_{max} is the maximum DOC or UV_{254} after passage through each cartridge) describes the fraction of NOM that is adsorbed onto each of the cartridge (Rosorio-Ortiz et al., 2007a). The analysis is rapid relative to techniques such as resin fractionation because no sample pretreatment is required and passage of the small sample volume through an SPE cartridge takes approximately 10 minutes.

PRAM does not involve matrix adjustment; therefore, NOM is not modified during analysis (Rosorio-Ortiz et al., 2004). As would be expected, when matrix pH or ionic strength is modified, NOM configuration is modified, resulting in considerably different results compared to those obtained at ambient conditions (Rosario-Ortiz et al., 2007a). Polarity adsorption is relatively stable at DOC concentrations up to 10 mg/L when other matrix conditions are constant. Retention increases at higher DOC concentrations (e.g., ~27 mg/L); therefore, sample dilution is recommended prior to analysis when high levels (>10 mg/L) of DOC are present (Rosario-Ortiz et al., 2007a). A significant limitation of this method is that the adsorbed fractions overlap somewhat between the SPE cartridges, so that it is not quantitative and mass balance cannot be assessed. Moreover, adsorbed NOM fractions cannot be collected for further structural characterization (Rosario-Ortiz et al., 2007a). Not surprisingly, the hydrophobic fraction of PRAM (operationally-defined as the fraction adsorbed to C18 sorbent at natural pH) has not correlated well with hydrophobic fractions obtained with XAD resin fractionation at acidic conditions; even when PRAM analysis was conducted at similar conditions (pH<3), only weak correlations between the methods were found (Philibert et al., 2012). Also, characterizing NDMA precursors by resin fractionation and PRAM did not produce similar results and showed higher selectivity of PRAM (Laio et al., 2015). These contrasts underscore that most operationally-defined protocols are typically defined either by correlation with parameters of interest (e.g., coagulant dose, DBP formation potential, etc.) or by availability of analytical tools, sometimes both. Accordingly, care must be taken when interpreting their significance and relationship to carbon character, origin, and reactivity.

2.3.3 Other Structural Attributes

2.3.3.1 Spectroscopy/Spectrometry

Different compounds have unique absorption or emission spectra when exposed to radiative energy (e.g., light, magnetic radiation, UV etc.), thereby enabling spectroscopy-based characterization. Fluorescence- and UV-based spectroscopic methods are the most common of these types of NOM characterization methods (Abbt-Braun et al., 2004; Croué, 2004). In contrast, mass spectrometry (MS) involves the use of unique mass-to-charge ratio spectra and the abundance of gas-phase ions upon ionization to identify the amount and type of compounds present in NOM. MS has been used in combination with other characterization techniques such as liquid/gas chromatography (González-Vila et al., 2001; Templier et al., 2005) to provide detailed information on NOM structure and reactivity.

2.3.3.1.1 Ultraviolet Visible (UV/Vis) and Specific Ultraviolet Absorbance (SUVA)

Organic compounds absorb light over a wide range of wavelengths in the UV region. For instance, aromatic compounds absorb UV at 254 nm (UV_{254}) (Edzwald et al., 1985). UV_{254} is considered an excellent predictor of the formation potential of regulated DBPs (i.e., THMs and haloacetic acids [HAAs]) (Singer et al., 1981; Edzwald et al., 1985; Wassink et al., 2011; Awad et al., 2016; Shams et al., 2017). In general, it has been a better predictor of DBP formation potential than TOC (Reckhow et al., 1990), though this correlation does not necessarily hold for all water matrices, such as those with low SUVA (defined below), suggesting that fractions of NOM that do not absorb UV_{254} (non-aromatic/hydrophilic) also play a role in DBP formation (Ates et al., 2007). UV_{254} has found widespread use in the drinking water industry because it can be measured online and in real time.

Specific ultraviolet absorbance (SUVA) is defined as the measured UV_{254} divided by the DOC (with units of L/mg.m); it was first used to describe chemical coagulation performance in removing relatively hydrophobic fractions of NOM during drinking water treatment (Edzwald and Van Benschoten, 1990; Edzwald and Tobiason, 1999). It also has been strongly correlated with aromaticity as determined by ^{13}C NMR for isolates from a variety of aquatic environments (Weishaar et al., 2003). Accordingly, it is useful for estimating dissolved aromatic carbon content in aquatic systems. The utility of SUVA as a THM-FP predictor has been widely investigated and has resulted in good, precise correlations in some cases (Reckhow et al. 1990; Kitis et al. 2001), but not in others (Goslan et al., 2004; Bougeard et al., 2010; Hua et al., 2015). The lack of consistently precise correlation has been especially observed in low aromaticity waters (SUVA < 2) (Ates et al., 2007; Li et al., 2014), as would be expected given that high aromaticity water contains more precursor material. A wide range of reactivity of water samples with similar SUVA values also has been reported, underscoring that not all reactive materials significantly absorb UV at 254 nm and not all aromatic materials are reactive (Weishaar et al., 2003; Ates et al., 2007). So, while SUVA is useful for generally characterizing NOM, it is less reliable in predicting NOM reactivity.

2.3.3.1.2 Fluorescence Spectroscopy

While only a small fraction of aromatic species actually emit light making them detectable by fluorescence spectroscopy (Lapen and Seitz, 1982), the potential for relatively inexpensive, real time analysis has led to extensive investigation of its use for characterizing aqueous NOM. Several environmental factors such as solution temperature, composition, concentration, pH, and salinity affect fluorescence signal characteristics (Green et al., 1992; Mobed et al., 1996; Carstea, 2012). As scattering (i.e. Rayleigh, Raman) of incident light can affect fluorescence signals (particularly in turbid waters), it is critical that fluorescence responses are appropriately corrected (Mobed et al., 1996; Ohno, 2002; Carstea, 2012).

Strong and consistent relationships have been reported between the fluorescence properties, molecular weight, and composition of NOM (Croué et al. 2000). Thus, fluorescence spectroscopy has been widely applied for NOM characterization. Fluorescence-based methods are particularly sensitive to proteins (tryptophan, tyrosine, and phenylalanine) and humic substances (humic and fulvic acids) (Coble, 1996; McKnight et al., 2001b; Chen et al., 2003b). Fluorescence signals are typically recorded as a 1) fluorescence emission spectrum, 2) fluorescence excitation spectrum (representing the dependence of emission intensity, measured at a single emission wavelength, upon the excitation wavelengths), 3) synchronous fluorescence spectrum, 4) total synchronous fluorescence spectrum, or 5) excitation–emission spectrum (Carstea, 2012). In most cases, complex multi-component mixtures like those found in environmental systems cannot be described well using conventional fluorescence methods. As a result, synchronous fluorescence spectroscopy, total synchronous fluorescence spectroscopy, and excitation-emission matrices (Coble, 1996, Hudson et al., 2007; Barker et al., 2009) have emerged for rapid DOM characterization by fluorescence analysis (Carstea, 2012); of these, excitation-emission matrices are the most commonly utilized. These techniques are discussed in greater detail below.

Fluorescence Excitation Emission Matrix (FEEM)

Fluorescence Excitation Emission Matrix (FEEM) approaches involve the collection of repeated emission scans collected at numerous excitation wavelengths to yield fluorescence contour maps (Coble, 1996). Fluorescence intensity maxima are identified excitation/emission wavelength pairs. As EEMs utilize fluorescence, humic- and protein-like peaks are the two main components studied (Wu et al., 2007b; Zhang et al., 2008; Baghoth et al., 2009). Specific focus on tryptophan-like, fulvic-like, coumarin-like, and particulate matter has also been reported (Senesi et al., 1989; Chen et al., 2003a,b; Liu et al., 2007; Spencer et al., 2007 Peiris et al., 2010; Wassink et al., 2011).

Strong correlations between humic/fulvic-like fluorescence intensity, DOC, and molecular size of NOM have been reported (Liu et al., 2007; Wu et al., 2007b; Wassink et al., 2011). FEEM also has been used online in a 3-D form to provide qualitative information about NOM structure (Wu et al., 2007b). It is important to note that fluorescence spectra include instrumental bias (Hofstraat and Latuhihin, 1994) that can result in systematic errors that preclude inter-laboratory comparisons if the biases are not removed through proper calibration and application of correction factors to both excitation and emission spectra (Coble et al., 1993)—this is particularly important with EEMs relative to conventional fluorescence spectroscopy because a large number of data are often reduced to the wavelength coordinates and fluoresce intensity of observable peaks (Coble et al., 1996; Holbrook et al., 2006).

Fluorescence regional integration and peak picking have been applied to qualitatively interpret the data (Chen et al., 2003b). However, methods for quantitative interpretation of these data have not yet been fully established and do not yield consistent or validated results. It is believed that application and continued refinement of multivariate data decomposition/analysis methods such as principal component analysis (PCA) and parallel factor analysis (PARAFAC) will ultimately overcome this inadequacy (Hiriart-Baer et al.; 2008; Peiris et al., 2010; Pifer and Fairey, 2014; Pifer et al., 2014; Korak et al., 2015; Peleato and Andrews, 2015; Peleato et al., 2017). It is believed that because these apprroaches make use of the entire EEM they will provide better description of complex fluorophore moieties (Holbrook et al., 2006). Nonetheless, all EEM analyses are reliant upon spatial variations of fluorescence intensity; inaccurate quantification of fluorescence intensity or location within the matrix may result in significant error. Accordingly, proper instrument calibration and removal of instrument bias is critical for inter-laboratory comparison (Holbrook et al., 2006). Moreover, strategies for method validation and mass-based interpretation are currently lacking.

Fluorescence Index (FI) and Humification Index (HIX)

While EEMs capture large amounts of fluorescence data, fluorescence (FI) and humification (HIX) indices summarize key aspects of such data and are predominantly associated with NOM aromaticity (McKnight et al., 2001b; Kalbitz et al., 2000; Zsolnay et al., 1999; Ohno, 2002). FI is computed in the fulvic acid-influenced region of EEMs as the ratio of emission intensity at 450 nm to that at 500 nm obtained at an excitation of 370 nm (McKnight et al., 2001b, Larsen et al., 2010). Instrument bias associated with this technique can be successfully corrected (Cory et al., 2010). The FI has been suggested for characterizing the bioavailability and sources of aqueous NOM and correlates well with aromaticity (McKnight et al., 2001b; Rodríguez et al., 2014). FI values in the range of 1.3-1.8 have been reported for river water (Brooks and Lemon, 2007). Microbially-derived NOM is associated with higher FI (e.g., ~1.9), while terrestrially-derived NOM has lower FI (~1.4) (McKnight et al., 2001b). If FI is to be used in hydrologic investigations, care should be taken in characterizing source water seasonal patterns because fluorescence characteristics can vary both spatially and temporally (Johnson et al., 2011; Hohner et al., 2016). Moreover, the application of this metric may not be relevant for all source waters such as those in which florescence at the associated wavelengths is very low or non-existent (Shams et al., 2014). Notably, high quality source waters such as those originating in healthy forested watersheds are frequently among those that are at highest risk for disturbance-associated water quality and treatability deterioration, and therefore for which such metrics would be desirable, but are unfortunately less informative.

HIX is a measure of NOM aromaticity defined as the ratio of the emission intensity at large wavelengths to emission intensity at short wavelengths (Ohno, 2002); its use is more commonly associated with soil rather than aqueous NOM characterization. When first proposed, it involved fixing the excitation wavelength at 254 nm and defining the large and short emission wavelengths as 435-480 nm and 300-345 nm, respectively (Zsolnay et al., 1999). Different emission wavelengths have also been used (Kalbitz et al., 2000; Ohno, 2002). HIX results generally correlate with UV_{254}, but their accuracy can be limited for samples with DOC concentrations lower than 3 mg/L (Kalbitz et al., 2000); thus, like FI, it would have limited utility for high quality source waters.

2.3.3.1.3 Fourier Transform Infra-Red (FTIR)

Fourier transform infra-red (FTIR) spectroscopy detects molecular vibrations associated with atomic bonds after exposure to infra-red light; the absorption spectrum provides information regarding inorganic and organic functional groups within NOM (Leenheer et al., 1987; Ricca and Severini, 1993; Chen et al., 2002; Chen et al., 2003b; Croué, 2004; Kim and Yu, 2007; Her et al., 2008; Zhang et al., 2009; Yang et al., 2013; Zhou et al., 2014). FTIR is capable of analyzing both liquid and solid phase samples but the preparation is intensive (Leenheer et al., 1987; Chen et al., 2002). The other main drawback of this technique is the difficulty in quantitatively interpreting spectra with overlapping bands from different NOM fractions (Bloom and Leenheer, 1989; Chen et al., 2002).

2.3.3.1.4 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) provides information about the number and distribution of carbon atoms based on unique responses in re-emitted electromagnetic radiation when samples are placed in a magnetic field (Leenheer et al., 1987). ^{13}C-NMR and ^{1}H-NMR are the most common NMR types used in NOM characterization, providing information about functional groups present in its structure (Leenheer et al., 1987; Ricca and Severini, 1993; Westerhoff et al., 1999; Chen et al., 2002; Chen et al., 2003b; Croué, 2004; Templier et al., 2005; Kim and Yu, 2007; Li et al., 2014; Nwosu and Cook, 2015; Li et al., 2016; Ikeya and Watanbe, 2016; Hertkornet al., 2016). In one investigation, changes in humic substances at various points in a water treatment plant were similar when characterized by ^{1}H-NMR and FTIR (Kim and Yu, 2007). Similar results for relative abundance of aromatic fractions in water samples from a wetland also were reported when assessed by ^{13}C-NMR, FTIR, and UV spectroscopic methods (Chen et al., 2002), though it also has been suggested that SUVA may be better than ^{13}C-NMR in indicating the reactivity of aromatic NOM (Westerhoff et al., 1999). NMR techniques are not commonly applied to characterize aqueous NOM because of intensive sample preparation requirements (Chen et al., 2003b) and limited practical utility. Quantitative interpretation of NMR data is limited by the complex nature of NOM that causes overlaps in the spectra of different fractions (Westerhoff et al., 1999; Chen et al., 2002). It has been reported that ^{13}C-NMR overestimates aliphatic NOM fractions, while underestimating aromatic fractions (Poirier et al., 2000; González-Vila et al., 2001; Templier et al., 2005).

2.3.3.1.5 Mass Spectrometry (MS)

Mass spectrometry (MS) involves ionizing chemical compounds and measuring the abundance of gas-phase ions as a function of the mass-to-charge ratio. It is used to determine the elemental or isotopic signatures and other aspects of chemical structure. MS has been combined with other characterization techniques such as gas/liquid chromatography (González-Vila et al., 2001; Templier et al., 2005), FTCIR (Brown and Rice 2000; Reemtsma et al., 2008; Reemtsma, 2009; Kunenkov et al., 2009; Herzsprung et al., 2014; Cao et al., 2015; Lu et al., 2015; Herzsprung et al., 2015; Hertkorn et al., 2016; Li et al., 2016), and pyrolysis (Poirier et al., 2000; Croué, 2004; Templier et al., 2005; Parsi et al., 2007) to provide more detailed information regarding NOM structure and reactivity. Electrospray ionization (ESI-MS) is an advancement that enables the introduction of liquid samples in MS (thereby precluding the need for derivatization of NOM) and enables coupling mass spectrometers with high performance liquid chromatography (Leenheer et al., 2001; Leenheer and Croué, 2003).

Fourier Transform Ion Cyclotron Resonance (FTICR) MS provides an ultra-high resolution signal. In combination with ESI it should have sufficient accuracy to allow molecular formula calculation, though further development in NOM enrichment and chromatographic separation is required and tools for data analysis and comparison must be improved (Reemtsma et al., 2008; Reemtsma, 2009; Lu et al., 2015). Orbitrap Fourier transform-mass spectrometry (Orbitrap FT-MS) involves trapping ions in an electric field, thereby resulting in a mass spectrometer that is smaller, less expensive, and with greater ion trapping capacity than FTCIR, which only uses a magnetic field (Makarov, 2000; Urai et al., 2014). It should be underscored that a key drawback to all of these methods is the lack of well-defined reference compounds that are needed to calibrate these techniques (Leenheer and Croué, 2003; Reemtsma, 2009). Overall, and likely due to some of these limitations, potential linkages between these methods and drinking water treatability or treatment performance assessment have not been widely investigated relative to many of the other analyses described above.

Pyrolysis (PY)

Most NOM is too large for analysis by standard GC/MS. Pyrolysis gas chromatography and mass spectroscopy (Py-GC-MS) overcomes this limitation by using anoxic heat to break NOM into smaller, lower-molecular weight fragments that are volatile and can be introduced into gas chromatography (Croué, 2004; Templier et al., 2005). Non-discriminating pyrolysis minimizes transfer losses of large-molecular fragments (Parsi et al., 2007). Pyrolysis-GC-MS enables identification of NOM building blocks such as polysaccharides, proteins, lignin, and aromatic and polyhydroxyaromatic compounds, as well as biopolymers (Leenheer and Croué, 2003; Croué, 2004). Characterization of humic fractions and biopolymers by Py-GC-MS has correlated with ^{13}C-NMR (González-Vila et al., 2001; Leenheer and Croué, 2003); however, both methods overestimate aliphatic fractions (Poirier et al., 2000; González-Vila et al., 2001). Pyrolysis also is sensitive to matrix effects (thereby relying on the use of reference compounds) and can result in side reactions that form new compounds (Saiz-Jimenez, 1994).

Isotope Ratio Mass Spectrometry

Changes in isotope abundance at natural levels are relatively minute, so measured isotope ratios are expressed relative to a contemporaneously measured isotope ratio of a standard of known isotopic composition (e.g., Vienna Pee Dee Belemnite in the case of ^{13}C). To facilitate manageability of results, “delta notation” was adopted such that $\delta^{13}C = 1000 * [(^{13}C/^{12}C \text{ sample}) / (^{13}C/^{12}C \text{ standard}) -1]$; the results are referred to as per mil values (‰). If the isotopic ratio of the sample is higher than that of the standard then δ will be positive (enriched); for an isotopic ratio lower than that of the standard δ will be negative (depleted) (Kendall and Caldwell, 1998). The difference in stable isotope ratios ($\delta^{13}C$) can provide useful information regarding NOM sources.

While the stable isotopic ratio is a good tracer of carbon sources, the radioactive carbon isotope (^{14}C) can be used to assess carbon age and turnover times. For example, it has been successfully used to estimate the age of groundwater where inorganic carbon interactions do not interfere with the method (Murphy et al., 1989b; Schiff et al., 1990; Kendall and Caldwell, 1998). It has been observed that the age of groundwater is typically older than that of surface water, which confirms extensive cycling of groundwater DOC (Schiff et al., 1990). In contrast, the age of the radiocarbon in rivers is often reported as relatively young because of microbial activity and associated utilization of older, terrestrial carbon (Raymond and Bauer, 2001; Mayorga et al., 2005). As would be expected, the utility of this approach for water age dating can be limited when waters of very different ages blend (Kendall and Caldwell, 1998).

Stable (^{12}C and ^{13}C) and radio- (^{14}C) isotopes of carbon have been used to investigate the origin, transport, and fate of DOC in marine environments (Williams et al., 1969; Williams and Druffel, 1987; Bauer et al., 1991), streams and rivers (Hedges et al., 1986; Murphy et al., 1989a; Schiff et al., 1990; Raymond and Bauer, 2001; Gandhi et al., 2004; Mayorga et al., 2005), groundwater (Murphy et al., 1989b; Schiff et al., 1990), wetlands (Schiff et al., 1990), and lakes (Schiff et al., 1990; Jiang et al., 2010). This method has also been recently applied to investigate the effects of different processes on DOC character during drinking water treatment to demonstrate that new sources of organic carbon are added during treatment and that treated water is isotopically lighter and younger in ^{14}C-DOC age than untreated water (Bridgeman et al., 2014). Isotopic carbon analysis is facilitated by using organic carbon analyzers coupled to mass spectrometers (De Troyer et al., 2010). These techniques are faster and less complicated compared to traditional methods that utilize off-line DOC oxidation followed by isotope ratio mass spectrometry (IRMS) (Raymond and Bauer, 2001; Gandhi et al., 2004).

2.3.4 Biodegradability-based Characterization

2.3.4.1 Biodegradable Organic Carbon (BDOC)

Biodegradable organic matter (BOM) is the fraction of NOM that can be mineralized by heterotrophic bacteria. Neutral hydrophilic fractions of NOM are the main components of BOM (Soh et al., 2008). BDOC is the biodegradable fraction of DOC that is used to evaluate the biological stability of drinking water distribution systems, the potential to form disinfection by-products, and reduction in chlorine demand (Volk and LeChevallier, 2000; Escobar and Randall, 2001). It is operationally-defined by several methods and is measured as the difference in DOC concentration before and after an incubation period in batch- or bioreactor-based methods (Joret and Levy 1986; Servais et al., 1987; Huck, 1990; Lucena et al., 1991; Frias et al., 1995). These methods should be contrasted with others focused on the analysis of biodegradable fractions of particulate organic carbon alone or in combination with DOC (Jung et al., 2014). A comparison of conventional (developed by Servais et al., 1987) and rapid BDOC (developed by Lucena et al. 1991) analysis in different water sources showed that conventional methods could achieve more reliable and robust results, closer to the spiked values in ground and surface waters (Zappia et al., 2008). The limiting factors of the rapid method were identified to be: biofilm conditioning, oxygen limitation, and soluble microbial product (Zappia et al., 2008).

2.3.4.2 Assimilable Organic Carbon (AOC)

AOC is the fraction of DOC that is assimilated into microbial cell mass (Van der Kooij et al., 1982). The growth of *Pseudomonas fluorescens* strain P17 (AOC-P17) and *Spirillum* sp. strain NOX in water is assessed in batch reactors. A conversion factor is typically used to convert the microbial biomass to a carbon concentration. AOC is a parameter that is used in the assessment of heterotrophic bacterial growth in drinking water disribution systems, though it typically comprises a small portion of DOC (Van der Kooij et al., 1982; Huck, 1990; Kang et al., 2006) that can hardly be removed during conventional treatment (Kang et al., 2006). It is advised to use AOC and BDOC as complementary metrics as measuring only one may lead to over/under-estimation of bio stability or bacterial regrowth (Escobar and Randall, 2001).

2.4 Research Gaps and Needs

To identify different NOM/DOC fractions and evaluate their reactivity, various types of DOC characterization and fractionation techniques have been introduced and developed over the past 50 years. These methods have enabled the development of site specific correlations between DOC fractions and their reactivity with oxidants (e.g. chlorine) and coagulant demand. LMW fractions have been associated with microbial regrowth in the distribution system (Escobar et al., 2000; van der Kooij and van der Wielen, 2014) and more recently, biopolymer fractions have been linked with membrane fouling (Rahman et al., 2014; Yamamura et al., 2014). Nonetheless, comprehensive isolation and identification of DOC fractions has not been achievable and the complex mixture of NOM and its spatial and temporal variability has precluded the identification of universal proxy indicators for predicting NOM reactivity in forming compounds such as THMs. This is in part because the results and inferences associated with fractionation techniques are affected by operational conditions (e.g., acidification, pH) and thus, are often inconsistent with or difficult to interpret in combination with those obtained at different operational conditions or using different techniques. Compositional characterization methods also are generally complicated and expensive; moreover, many have limitations related to calibration. As a result, no universal precursors for NOM reactivity with oxidants (e.g., chlorine) have been identified, making it difficult to compare NOM reactivity between watersheds, or even seasonally within a given watershed. Logically, it is unlikely that a single, directly-measured universal precursor for DBP-FP will ever be identified based on structural characteristics of NOM. As a result, data obtained from multiple NOM characterization methods must be combined and concurrently analyzed; this requires the use of appropriate multivariate analysis tools during exploratory data analysis to ensure that optimal predictive models that best extract information from available data are developed. While approaches such as principal components (Peiris et al., 2010; Peleato and Andrews, 2015) and parallel factor analysis (Korak et al., 2015; Peleato and Andrews, 2015; Peleato et al., 2017) have been applied to understanding FEEMs, there is a stark absence of multivariate analysis of broader NOM data. Given that several variables will likely be required to inform and develop universally predictive models for treatability metrics such as DBP-FP, the associated dispersion matrices will likely be too large to study and interpret, with too many pairwise correlations between variables that must be considered. Thus, more meaningful interpretation of the data requires them to be reduced—thoughtful selection of the best approaches (e.g., principal components analysis, factor analysis, etc.) is important, but beyond the scope of the present discussion. Regardless of the current absence of such models, the need to develop them is resoundingly clear; thus, there is also a corresponding need to further develop NOM characterization/fractionation techniques and include concurrent analyses using several different characterization/fractionation methods during field investigations of NOM character and reactivity.

Chapter 3

Comparative Assessment of NOM Surrogates for Evaluating the Potential for Disinfection By-product Formation, Distribution System Regrowth, and Membrane Fouling during Drinking Water Treatment

3.1 Overview

Control of the potential for 1) formation of regulated, disinfection by-products (DBPs), 2) membrane fouling, and 3) distribution system regrowth during drinking water treatment are all challenges and that are associated with source water natural organic matter (NOM), which is typically described by dissolved organic carbon (DOC) concentration and character. A comprehensive understanding of DOC character before and after each treatment step is important in developing resilient treatment strategies that can minimize treatment challenges—it is also important for assessing treatability needs in anticipation of or after landscape disturbances. Thus, this capacity is important for climate change adaptation, particularly in high quality, low DOC source watersheds. Here, several NOM characterization techniques were compared as proxy indicators for the removal of NOM attributes that contribute to the formation of regulated DBPs. NOM indicators of drinking water distribution system stability and membrane fouling also were evaluated. The relative potential for membrane fouling and distribution system regrowth was also examined. The unique contribution of this work is that 1) several NOM characterization metrics were evaluated concurrently and 2) several key steps comprising conventional treatment as well as biofiltration were evaluated. These included the plant intake and post-sedimentation, post-ozonation, and post-GAC biofiltration steps at a full-scale drinking water treatment plant. DOC, UV_{254}, SUVA, hydrophobic fraction, and humic substances (HS) concentration (identified by liquid chromatography-organic carbon detection [LC-OCD]) correlated reasonably well with trihalomethane (THM) and haloacetic acid (HAA) formation potentials (FPs), whereas fluorescence index (FI) did not. The qualitative information about the humic/fulvic fractions indicated by fluorescence excitation emission matrices (FEEMs) was consistent with the aromaticity and hydrophobicity data. Thus, as would be expected, metrics indicating NOM aromaticity and hydrophobicity were all reasonably precise predictors of DOC reactivity and formation of regulated DBPs—UV_{254} demonstrated the best predictive capacity. Chemical pre-treatment (coagulation, flocculation, sedimentation) was critical for reducing both THM- and HAA-FPs as well as biopolymer, which can contribute to membrane fouling. Biofiltration also demonstrated the capacity to remove DBP precursors, biopolymers, and building blocks, as well as low molecular weight (LMW) neutrals in particular, whose presence favors bacterial regrowth and biofilm formation in drinking water distribution systems (Escobar et al., 2000; van der Kooij and van der Wielen, 2014). This work underscores the continued need to further 1) develop relatively rapid and inexpensive approaches for assessing NOM contributions to various types of drinking water treatment challenges and 2) make recommendations regarding the most practical and informative metrics for use in evaluating drinking water treatability implications of increasingly variable or deteriorated source water quality resulting from climate change-associated landscape disturbances.

3.2 Introduction

Dissolved organic carbon (DOC) is a key surrogate for natural organic matter (NOM) and is recognized as a critical water quality parameter that drives water treatment process design (MWH, 2012; Thurman, 1985). DOC concentrations and characteristics in water depend on watershed hydrological and biogeochemical processes, (Aiken and Cotsaris, 1995; Fabris et al., 2008; Krasner et al., 1996; Leenheer and Croué, 2003; Owen et al., 1995), and temperature (Leenheer and Croué, 2003). Accordingly, DOC levels and characteristics are subject to spatial and temporal changes (Pellerin et al., 2012; Spencer et al., 2008). Changes in DOC levels and characteristics may lead to challenges to water treatability such as 1) adverse impacts on taste, odor, and color (Leenheer and Croué, 2003); 2) membrane fouling (Amy, 2008; Brinkman and Hozalski, 2015; Lee et al., 2006); 3) increased potential for bacterial regrowth in distribution systems (Kaplan et al., 2005; van der Kooij and van der Wielen, 2014); 4) coagulation challenges (White et al., 1997; Edzwald and Tobiason, 1999; O'Melia et al., 1999; Yan et al., 2008; Hohner et al., 2016); 5) increased disinfectant dosing requirements (Owen et al., 1993; Fabris et al., 2008); 6) increased potential of heavy metals complexation (Frimmel, 1998; Wu et al., 2004; Waples et al., 2005; Deonarine and Hsu-Kim, 2009); and 6) increased DBP formation potential (DBP-FP) (Babcock and Singer, 1979; Singer, 1999; Kitis et al., 2002; Liang and Singer, 2003; Ates et al., 2007; Chen and Westerhoff, 2010). Each of these challenges is associated with certain fractions or characteristics of DOC. Thus, proper characterization of DOC before and throughout the treatment process is critical to better evaluation and development of appropriate, resilient treatment strategies. Enhanced coagulation and flocculation, followed by clarification (typically sedimentation) is the best available technology for DOC removal during drinking water treatment. Coagulation preferentially removes hydrophobic, aromatic DOC fractions with high molecular weight compared to aliphatic, hydrophilic fractions of low molecular weight (Collins et al., 1986; Kitis et al., 2002; Liang and Singer, 2003; Chow et al., 2004; Sharp et al., 2006; Soh et al., 2008). Post-coagulation adsorption with activated carbon has been suggested in situations where further removal of humic substances or lower molecular weight fractions of DOC that cannot be removed during chemical pre-treatment is required (Bond et al., 2011; Velten et al., 2011). Ozone can oxidize reactive organics to biodegradable compounds and therefore, application of ozonation prior to physico-chemical filtration is frequently suggested, with the additional recommendation of enabling biological filtration to enhance NOM removal—this is typically achieved by eliminating chlorination prior to filtration (Miltner et al., 1992; Chaiket et al., 2002; Bond et al., 2011). Biofiltration is thought to remove biodegradable fractions of DOC that are primarily of lower molecular weight (Liao et al., 2017; So et al., 2017); however, substantial removal of large molecular weight DOC fractions such as biopolymers by biofiltration also has been reported (Rahman et al., 2014; Azzeh et al., 2015; Pharand et al., 2015; So et al., 2017).

The fractions of DOC that are not removed during water treatment can potentially react with chlorine and other disinfectants (chloramines, chlorine dioxide, and ozone) to form different classes of DBPs. Many of identified DBPs are considered to be cytotoxic, genotoxic or carcinogenic in laboratory animals (Plewa et al., 2002; Woo et al., 2002; Plewa et al., 2004) and are potential public health risks if ingested, inhaled, or dermally absorbed during swimming and showering/bathing (Richardson et al, 2002; WHO, 2006). THMs and HAAs are the most prevalent DBPs and can represent a series of other chlorinated DBPs (WHO, 2006). Therefore, these two groups are regulated worldwide to control the risks of exposure to chlorinated DBPs in general (WHO, 2006; Health Canada, 2008; USEPA, 2012).

Accordingly, it is of critical importance to fully understand the changes of DOC levels and composition throughout treatment processes. This information will enable the identification of promising measurements/surrogates for DBP formation. NOM is a vast collection of ill-known organic compounds with diverse characteristics (Deb and Shukla, 2011) and various techniques and metrics have been developed to characterize its bulk and fractionated forms. Several investigations have focused on establishing relationships between DOC and DBP-FP and identifying DBP precursors. Most of these efforts have focused on raw (untreated) water; however, and the impacts of sequential individual treatment processes on the relationship have not been widely considered. Moreover, little effort has gone into comparing the information provided by different characterization techniques when describing the impacts of treatment on DOC composition at full-scale.

The primary focus of this study was to evaluate methods for characterizing DOC and its fractions through the treatment process that contribute to regulated, chlorinated DBP formations, membrane fouling, and bacterial regrowth in the distribution system. Several characterization methods were evaluated and compared based on their potential to predict the formation of regulated chlorinated DBPs (THMs and HAAs). Biopolymers were used as an indicator of membrane fouling (Rahman et al., 2014; Yamamura et al., 2014) and LMW neutrals were used to evaluate the relative potential for microbial regrowth in the distribution system (Escobar et al., 2000; van der Kooij and van der Wielen, 2014). The utility of several DOC metrics for predicting THM-FP was evaluated using linear regression, consistent with previous investigations (Edzwald et al., 1985; Reckhow and Singer, 1990; Singer, 1999; Goslan et al., 2004; Ates et al., 2007; Wassink et al., 2011). These approaches are widely utilized because these DBP precursor materials are generally understood to be directly proportional to the by-products they form.

3.3 Materials and Methods

3.3.1 Study Site and Sampling

Samples were collected from Mannheim WTP, which is supplied by the Grand River in Kitchener, Ontario, Canada. The historical measured DOC concentrations in the intake water of the treatment plant typically range from 5 to 7 mg/L. The average raw water characteristics of DOC-associated parameters during this study are listed in Table 3-1. The average turbidity and pH of the raw water were approximately 7.3 and 3 NTU, respectively. No bromide was detected in the raw water during the study.

The Mannheim WTP is a conventional drinking water treatment plant with a design capacity of 16 MGD and flow of 600 L/s. There, raw water is typically coagulated with 18 to 24 mg/L polyaluminum chloride, flocculated, and then settled for approximately 50 minutes in two settling tanks of 1850 m^3. Ozone is applied at 2 to 4.5 mg/L prior to biologically active granular activated carbon (GAC) filtration at hydraulic loading rates ranging from 7 to 10 m/h (corresponding to empty bed contact times [EBCTs] of 10 to14 min). The water is then disinfected with 40 mJ/cm^2 ultraviolet (UV) light and chlorine with a dose of 6-7 and 12-13 mg/L in summer and winter, respectively (to achieve a residual of approximately 1.0 mg/L). The treatment plant is divided into two parallel treatment trains (Train 1 and Train 2) (Figure 3-1). The samples for this study were collected at the WTP intake, Train 2 post sedimentation, Train 2 post-ozonation, and the filter 3 and 4 (F3 and F4) effluent sampling locations. Both filters were operated in a biologically active mode and contained 1.3 m of GAC over 0.3 m of 0.45-0.55 mm sand. The GAC was Filtrasorb 816 (coal based) with an effective size of 1.3–1.5 mm and uniformity coefficient of 1.4. The GAC in F4 was replaced with virgin GAC immediately prior to this study, while the media in F3 were essentially exhausted, as they had been in use for seven months prior to the study. Therefore, F4 was understood to have more adsorptive capacity than F3. Eight sampling events occurred over eight months starting in November 2014. The Mannheim WTP product water is a mixture of treated water from both trains; as such, it was not evaluated herein because performance in the two treatment trains can vary.

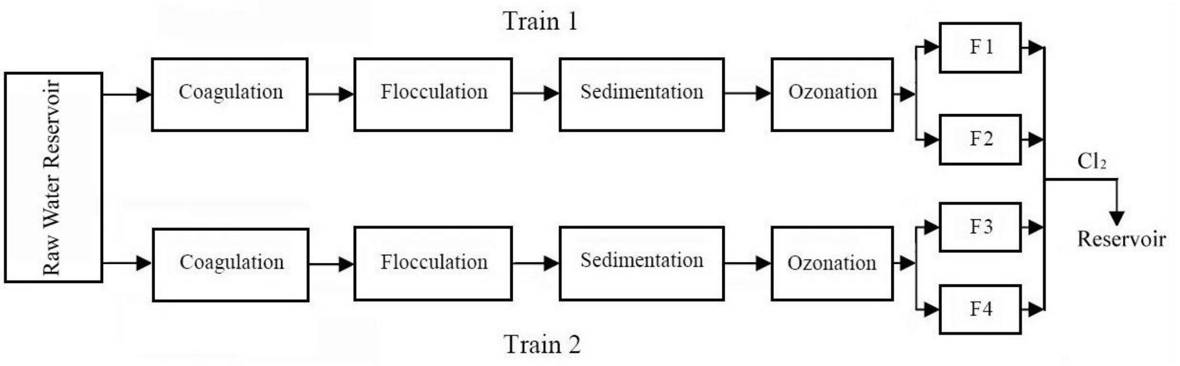


Figure 3-1. Mannheim Water Treatment Plant Schematic.

3.3.2 Analytical Methods

Several characterization techniques were employed to analyze and characterize DOC in its whole and fractionated forms. In brief, DOC concentrations were measured as per Standard Methods (Method 5310B; APHA et al., 2012) using a Shimadzu TOC-VCPH TOC analyzer. UV_{254} was analyzed using a Hewlett-Packard 8453 spectrophotometer with a 1 cm quartz cell (Method 5910 B; APHA et al., 2012). Specific ultraviolet absorbance (SUVA [L/mg.m]) was calculated as the measured UV_{254} (m^{-1}) divided by the DOC (mg/L) (Edzwald and Tobiason, 1999). Resin fractionation using Amberlite XAD-8® was utilized to isolate hydrophobic and hydrophilic fractions as described by Kitis et al. (2002). Liquid chromatography–organic carbon detection (LC-OCD) was used to characterize NOM fractions as defined by Huber et al. (2011). This technique employs a weak cation exchange column (250 mm × 20 mm, TSK HW 50S, 3000 theoretical plates) followed by a UV_{254} detector (UVD), an organic carbon detector (OCD), and an organic nitrogen detector (OND). ChromCALC, DOC-LABOR data processing software was used to quantify different NOM fractions (Huber et al., 2011). Fluorescence analyses were conducted using a Varian Cary Eclipse Spectrofluorometer. Fluorescence excitation-emission matrices (FEEM) were analyzed based on the method described by Peiris et al. (2010) and the data were interpreted based on a study by Chen et al. (2003). The excitation and emission ranges used were 200–400 and 300–600 nm, respectively. Fluorescence index (FI), defined as the ratio of emission intensity at the wavelength of 450 nm to that at 500 nm, both at the excitation of 370 nm (McKnight et al., 2001), was also calculated as a metric to characterize NOM. THM-FP was analyzed based on Standard Methods (Methods

5030B and 8260C; APHA et al., 2012) using GC/MS (Purge and Trap) on an Agilent Technologies 7890B -MS/5977A. HAA-FP and NDMA-FP were analyzed on a GC/MS/MS/CI Varian CP3800-MS/MS2000 (Saturn MS Ion Trap) analyzer. The method applied for HAA-FP analysis was USEPA Method 552.3 (USEPA, 2003). The analysis of NDMA-FP was conducted based on Standard Methods (Method 6410B; APHA et al., 2012) and an in-house method developed based on Blaise et al. (1994).

3.3.3 Statistical Analysis

Analysis of variance (ANOVA) was used to make inferences about the data. Predictions of THM-FP using NOM character were investigated using simple least squares linear regression. The significance and precision of the regression models were evaluated using customary approaches (i.e., *p* values obtained from ANOVA [Appendix A] and coefficients of determination [R^2], respectively). Diagnostic residual plots (Appendix B) were utilized to ensure that the assumptions of ANOVA were not violated.

3.4 Results and Discussion

3.4.1 Disinfection By-product Formation Potential

Trihalomethanes (THMs/THM_4) are the most abundant DBPs found in chlorinated drinking water. They were first detected and regulated in the United States (Bellar et al., 1974; NCI, 1976). Nine chloro- and bromo-HAAs are the second most prevalent category of DBPs in drinking water (Singer et al., 2002); five of these (HAA_5) are currently regulated (WHO, 2006; Health Canada, 2008; USEPA, 2012). To investigate the impacts of different treatment processes on formation of regulated DBPS, THM-FP and HAA-FP were analyzed at the intake and different stages of treatment as shown in Figure 3-2a and 3-2b, respectively.

3.4.1.1 THM-FP

THM-FP at the Mannheim WTP primarily consisted of chloroform. Bromoform was below detection limits during the study due to the lack of the precursors (bromide) in the water. The mean percentage of formation potentials of chloroform, bromodichloromethane (BDCM), and dibromochloromethane (DBCM) that compromised total THM-FP in the raw water throughout the eight-month study were 87±3%, 12±3%, and 1±1% (mean ± standard deviation), respectively. Despite variable THM-FP conditions in the source water, chemical pre-treatment (coagulation/flocculation/sedimentation) consistently demonstrated that it is the best available technology for removing THM-FP, even at less than optimal conditions (i.e., the pH was not low enough to achieve enhanced coagulation). The mean total THM-FP concentrations in the raw, settled, ozonated, and F3 and F4 effluent waters were 278±59, 139±34, 135±38, 110±26, and 97±26 µg/L, respectively (Figure 3-2a). The pH following coagulation was 7.1 on average and as such, less DOC removal would be expected than at lower pH conditions consistent with enhanced coagulation. It should be noted that enhanced coagulation is not practiced at the Mannheim WTP because it is not needed. Chemical pre-treatment (coagulation, flocculation, sedimentation) removed ~51±8% (mean ± standard deviation) of the THM-FP in the source water, making it the most important step for reducing THM-FP, as would be expected. This result was consistent with reports of effect removal of large molecular weight, aromatic compounds by these processes (Sharp et al., 2006; Soh et al., 2008). Biofiltration (F3 and F4) also removed THM-FP (~9±6 and ~14±12%, respectively (mean ± standard deviation). F4 showed slightly better THM-FP removal than F3, likely due to GAC replacement in the filter at the beginning of the study and its additional adsorptive capacity, which includes the ability to remove a wide range of DOC fractions, from medium size humics to lower molecular weight compounds (Bond et al., 2011; Velten et al., 2011). In contrast, ozonation did not contribute substantially to THM-FP removal (Table 3-1). Notably, biofiltration may have been able to remove more THM-FP if chemical pre-treatment had not been so effective at Mannheim—this is a possibility that merits broader consideration in the future.

3.4.1.2 HAA-FP

The potential formations of HAA_6 (monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA)) were measured over the second half of the sampling period. As both THMs and HAAs are carbonaceous DBPs, their formation potentials were significantly and closely correlated ($p = 10^{-8}$ and $R^2 = 0.84$) as would be expected for compounds with mutual precursors; similar correlations have been reported elsewhere

(Villanueva et al., 2003; Bougeard et al., 2010; Rocarro et al., 2014). Consistent with THM-FP and in all cases, the highest removal of HAA-FP was achieved after chemical pre-treatment. The mean total HAA-FP concentrations in the raw, settled, ozonated, and F3 and F4 effluent waters were 397±28, 153±36, 142±47, 101±26, and 95±17 µg/L, respectively (mean ± standard deviation) (Figure 3-2b). Chemical pre-treatment removed 61% of the HAA-FP and biofiltration by F4 and F3 removed approximately 12±11% and 10±7% of it (mean ± standard deviation), respectively. Ozonation did not effectively remove HAA-FP (mean removal of 3±7%). These results demonstrated that THM- and HAA-FP were comparably removed by the various treatment processes, as would be expected for compounds that share common precursors. However, higher removal of HAA-FP compared to THM-FP was observed during chemical pre-treatment (61±11% vs 51±8%), thereby indicating that higher molecular weight fractions had a more substantial contribution to formation of HAAs than THMs. Also, similar to the THM-FP findings, chlorinated HAA constituents were the dominant forms of HAA_6 and total HAA-FP, which consisted of 59% TCAA, 35% DCAA, 2% MCAA, and 3% BCAA. This was not surprising, considering the lack of bromide in the water (i.e., the formation of brominated HAAs was not observed). Notably, HAA-FP removals by F3 and F4 were more similar than THM-FP removals. This was likely attributable to GAC exhaustion in F4 during the second half of the experimental period during which HAA-FP was evaluated.

3.4.2 Dissolved Organic Carbon (DOC) Concentration

DOC is generally understood to positively correlate with the formation of regulated DBPs for a given source water (Singer et al., 1981; Reckhow and Singer, 1990). This prospect, along with the relative simplicity and speed of DOC analysis make it a favorable candidate for use as a proxy indicator for THM- and HAA-FPs. However, DOC only informs NOM quantity and does not describe the role of its structure in reactivity.

DOC levels at the intake of the Mannheim WTP generally varied between approximately 5 and 7 mg/L. Here, raw water DOC fluctuated between a minimum of 5.2 mg/L and a maximum of 6.1 mg/L. The mean DOC concentrations fin the raw, settled, ozonated, and F3 and F4 effluent waters were 5.7±0.4, 4.2±0.5, 4.1±0.5, 3.6±0.4, and 3.2±0.4 mg/L, respectively (mean

± standard deviation) (Figure 3-2c). Chemical pre-treatment consistently removed the most DOC, 27±5% on average—this was not surprising given that coagulation/flocculation/sedimentation is considered a best available technology for DOC removal during drinking water treatment, especially when operated in an enhanced coagulation mode (USEPA, 1998). Biofiltration in F3 and F4 also removed DOC and achieved average removals of 10±3 and 17±5% (mean ± standard deviation), respectively—these DOC reductions are consistent with those that have been previously reported by pilot- (Snider, 2011; Wong, 2015) and full-scale (Emelko et al., 2006) filtration at the Mannheim WTP. Insignificant (1±5% mean) removal of DOC was achieved by ozonation (Table 3-1). Ozone is not applied to directly remove NOM; however, its oxidation enhances biological DOC removal during subsequent biofiltration.

THM-FP and HAA-FP correlated reasonably well with DOC concentration—the observed coefficients of determination (R^2) were 0.85 and 0.81, respectively and the regressions were significant as per Table 3-2 (supported by Table A-1, Appendix A and Figure B-1, Appendix B). These results were consistent with those that have been reported previously (Singer et al., 1981; Reckhow and Singer, 1990; Wassink et al., 2011) for various source water matrices. The challenge in regular application of these relationships is that the models describing these correlations are extremely site specific (Reckhow and Singer, 1990).

3.4.3 DOC Character

DOC character through the treatment process was investigated using several metrics and characterization techniques. It has been reported that aromatic compounds, also recognized as hydrophobics, or humics, are the main precursors of THMs and HAAs (Collins et al. 1986; Singer, 1999; Liang and Singer, 2003). To investigate these specifically, several metrics were used because they inform DOC aromaticity (UV_{254} and SUVA), DOC hydrophobicity (resin fractionation), and the presence of humic substances (LC-OCD and fluorescence).

3.4.3.1 UV254 and SUVA

Aromatic organic compounds absorb UV at wavelength of 254 nm. Thus, UV_{254} has been recognized as a surrogate of aromaticity and is widely used due to its simplicity and capacity for real time analysis. Its application as a good surrogate for the formation of regulated DBPs has been widely demonstrated (Singer et al., 1981; Edzwald et al., 1985; Wassink et al., 2011; Awad et al., 2016). Its major drawback is that it cannot be reliably, quantitatively correlated to DBP-FP when major shifts in water quality occur.

Here, the mean UV_{254} levels in the raw, settled, ozonated, and filtered by F3 and F4 were 15, 4±1, 5±1, 4±1, and 3±1 m^{-1} (mean ± standard deviation), respectively (Figure 3-2d). Similar to DOC, the majority of UV_{254} absorbance reduction was achieved through chemical pre-treatment. However, while chemical pre-treatment removed 25±7% of DOC, 71±6% (mean ± standard deviation) of UV_{254} was removed. Thus, this result was consistent with the removal of THM- and HAA-FPs (Table 3-1) and confirmed that chemical pre-treatment selectively removes aromatic compounds as opposed to other DOC fractions. Biofiltration in F4 and F3 respectively removed an average of 7±5% and 3±4% of UV_{254} (mean ± standard deviation; Table 3-1; Figure 3-2d). This difference between the filters was consistent with the understanding that some adsorptive capacity remained in F4 when the study was initiated.

The fate of UV_{254} and DOC throughout the treatment train displayed a generally similar trend. This was confirmed by good precision in the regression ($R^2 = 0.81$) between these two parameters (Table 3-2). UV_{254} had excellent precision in the prediction of regulated DBPs (THM-FP and HAA-FP), with R^2 of 0.89 and 0.92, respectively (Table 3-2). These relationships confirmed that the majority of the regulated DBP precursors consisted of aromatic compounds, particularly for HAAs.

Changes in SUVA and its relationship to THM-FP and HAA-FP were also investigated. SUVA values in the raw water varied between 2.3 and 2.9 L/mg.m. The mean SUVAs for raw, settled, ozonated, and F3 and F4 filter effluent waters were 2.6±0.2, 1.0±0.2, 1.1±0.2, 1.1±0.2, and 1.0±0.2 L/mg.m, respectively (mean ± standard deviation) (Figure 3-2e). Accordingly, the raw water could always be described as a mixture of aquatic humics and other NOM, or a mixture of hydrophobic and hydrophilic NOM ($2 < SUVA < 4$), as defined by Edzwald and Tobiason (1999). Based on the same definition, the treated water in all cases of this study was composed of mostly non-humics or hydrophilic NOM ($SUVA < 2$). Thus, the majority of aromatic compounds were removed through treatment, primarily chemical pre-treatment. Good precision in predictions of THM-FP and HAA-FP using SUVA were observed (R^2 of 0.83 and 0.90, respectively; Table 3-2), showing that SUVA could be a somewhat reasonable predictor for DOC reactivity of DOC in forming regulated DBPs in the Mannheim matrix (Table 3-2). The utility of SUVA as a THM-FP predictor has been widely investigated and has resulted in good, precise correlations in some cases (Reckhow et al. 1990; Kitis et al. 2001), but not in others (Goslan et al., 2004; Bougeard et al., 2010; Hua et al., 2015). The lack of consistently precise correlation has been especially observed in low aromaticity waters (SUVA < 2) (Ates et al., 2007; Li et al., 2014).

3.4.3.2 Resin Fractionation

DOC fractionation by adsorption on ion exchange resins (resin fractionation) has been widely used to describe the humic nature and composition of NOM (Leenheer, 1981; Thurman and Malcolm, 1981). Although many fractionation methods exist, the International Humic Substances Society (IHSS) has recognized the method of Thurman and Malcolm (1981) as the standard method for separation of fulvic and humic acids. Here, hydrophobic and hydrophilic DOC fractions were isolated and analyzed. The raw water DOC was composed of a combination of hydrophobic and hydrophilic compounds; the minimum, maximum, and mean hydrophobic fractions (HPO) observed across the sampling events were 54, 59, and 57±1.5%, respectively. The percentage of HPO after chemical pre-treatment, ozonation, and biofiltration in F3 and F4 was 42±4.4, 41±4.8, 39±4.6, and 37±4.7% (mean ± standard deviation), respectively (Figure 3-2f; Table 3-1). The majority of HPO removal (~45%, considering that DOC concentration decreases with each treatment step) was achieved through chemical pre-treatment. Biofiltration in F3 and F4 also removed HPO and achieved mean HPO removals of 10±3 and 17±5% (mean ± standard deviation), respectively. Notably, it is difficult to conclude whether or not the full capacity of biofiltration in removing HPO was achieved herein because the chemical pre-treatment process was so effective at removing HPO. As with the previously discussed parameters, ozonation did not play a role in HPO removal (Table 3-1). These findings generally parallel the UV_{254} and SUVA findings, although the operational definitions of hydrophobicity and aromaticity in the resin fractionation and UV_{254} methods are not the same. Therefore, regardless of the chosen metric and definition, all of them validated the efficacy of chemical pre-treatment in removing aromatic compounds from the Grand River water matrix. The correlations between HPO, UV_{254} and SUVA were examined to better understand their interconnectivity (Table 3-2); as expected, they were all reasonably correlated with one another and the regressions were significant (Table 3-2), thereby underscoring that none of the more complicated metrics used to describe carbon character offered any meaningful advantages over UV_{254}. Thus, it would seem that the most important knowledge gaps related to NOM characterization and drinking water treatability are the current lack of universal models for predicting changes in DBP-FP and the inability to anticipate when and why source water quality changes to the point that new relationships between DBP-FP and NOM aromaticity (as indicated by UV_{254}) must be established.

3.4.3.3 LC-OCD

Unlike the metrics discussed above, liquid chromatography (LC) is a separation technique that can provide information on a wide range of NOM components, from aromatic (high molecular weight) to aliphatic (low molecular weight) compounds. Recent LC instrumentation developments have included the incorporation of organic carbon detection. Here, different NOM fractions as defined by Huber et al. (2011) were isolated and assessed at all sampling locations—this enabled assessment the potential for membrane fouling (if membranes were in place in the study system) by evaluation of the biopolymers fraction and bacterial regrowth in the distribution system by evaluation of the LMW neutrals fraction; in addition to DBP-FP, which correlates with the humic substances (HS) fraction.

The mean removal (of all sampling events) of humic substances (HS) by chemical pre-treatment, ozonation, and biofiltration in F3 and F4, was found to be 36±4, 1±5, 9±4, and 18±12% (mean ± standard deviation), respectively (Table 3-1 and Figure 3-3). This finding is similar to the results of mean removals of other aromaticity metrics, particularly HPO (Table 3-1). The removal of other DOC fractions, separated by LC-OCD, was also investigated (Figure 3-3). High molecular weight biopolymers were removed primarily by chemical pre-treatment (55±11%) and then to a lesser extent by F3 (8±7%) and F4 (6±5%) (mean ± standard deviation). Although the mean removal of biopolymers by biofiltration was low during the course of this study, it varied considerably over time. For instance, the mean removal of this fraction by F3 was 15±6% and 2±1% (mean ± standard deviation) during warmer months (May to July) and colder months (November to April), respectively. The maximum observed removal of biopolymers by F3 was 22% in June 2015, while the mean removal of this fraction by F3 was 11±3% and 2±2% (mean ± standard deviation) during warmer months (May to July) and colder months (November to April), respectively. This result was not surprising as it has been shown that seasonality is an important factor in performance of biofilters (Pharand et al., 2015; So et al., 2017). Removals of biopolymers during biofiltration with efficiencies of up to 31% have been previously reported (Rahman et al., 2014; Azzeh et al., 2015), and include one investigation conducted on the same source water for which biofiltration with a slightly different configuration (eight dual-media 1.6 m anthracite / 0.4 m sand biofilters) achieved maximum 35% removal of biopolymers (Pharand et al., 2015). Building blocks are defined as HS-like materials of lower molecular weight (Huber et al., 2011). A percentage of this fraction (8±19%) was oxidized and converted into low molecular weight neutrals (LMW neutrals) during ozonation (Figure 3-3). Biofiltration in F3 and F4 played a role in removing the building blocks fraction with 9±10 and 30±19% removals (mean ± standard deviation), respectively. LMW neutrals, which are composed of non-aromatic biodegradable molecules that contribute to microbial regrowth in the distribution system, were only removed during biofiltration. The mean removals achieved by F3 and F4 were 29±4 and 16±7% (mean ± standard deviation), respectively (Figure 3-3). The likely reason that F3 had a higher average removal was that this filter was biologically active from the beginning of this study, while the media in F4 were freshly replaced in November 2014. The observed increase in NOM removal in F4 through the study confirmed this argument; the average removal of LMW neutrals by F4 increased from 12±5% in the first few months of filter operation (November to March) to 20±6% in the remaining months of the study (April to July). Thus, the efficiency of adsorptive filters in the removal of humic substances, building blocks, and low molecular weight fractions was in agreement with findings of previous research (Velten et al., 2011). Furthermore, this work demonstrated that LC-OCD analysis was useful because it allowed concurrent investigation of aspects of NOM character other than aromaticity that can challenge drinking water treatability. The major drawback of LC-OCD, however was that it does not always achieve full separation of all individual peaks associated with NOM fractions (especially HS) (Huber et al., 2011); thus, conventional LC remains preferable in these cases.

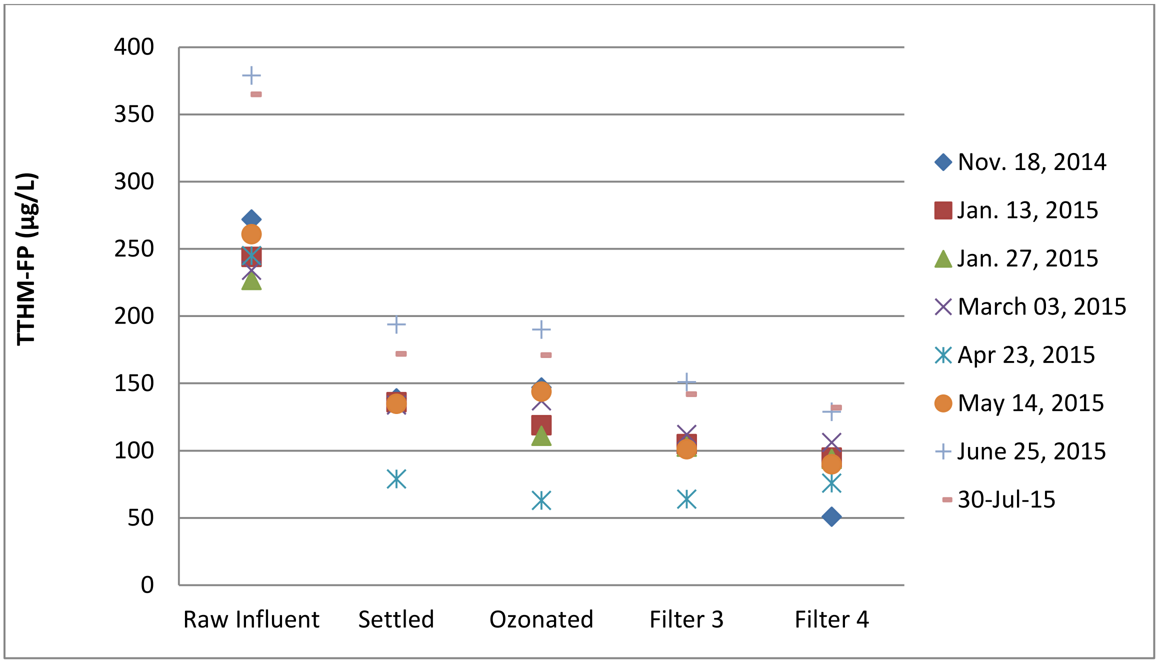
Correlations between the HS and BP fraction and regulated DBP formation potentials were examined. HS correlated with THM-FP and HAA-FP with R^2 of 0.84 and 0.78, respectively (Table 3-2), while the R^2 for correlations between BP and THM-FP and HAA-FP were 0.56 and 0.64, respectively. This showed that HS fraction of DOC was a reasonable surrogate for regulated DBP-FPs. However, based on the findings of this study, application of other aromaticity metrics, particularly UV_{254}, is more promising (Table 3-2) and more cost-effective. Positive correlations were also found between biopolymers (mg/L) and THM-FP and HAA-FP (R^2 of 0.51 and 0.62, respectively). Building blocks and LMW neutrals did not correlate well with regulated DBPs, as would be expected because regulated DBP_S are associated with the humic and larger MW fractions of DOC (Collins et al. 1986; Singer, 1999; Liang and Singer, 2003).

Table 3-1. Mean DOC-associated parameters in raw water and percentage removal through each treatment process (n = 8).

Parameter	Raw Water Mean	Average Removal (%)			
		Chemical pre-treatment	Ozonation	F3	F4
DOC (mg/L)	5.7±0.4	25±7	1±1	10±3	17±5
UV_{254} (m^{-1})	15±2	71±6	0±2	3±4	7±5
SUVA (L/mg.m)	2.6±0.2	61±6	-1±3	-2±5	0±7
HPO (%)	57±2	45±8	2±1	9±3	17±5
HS (mg/L)	3.7±0.4	36±4	1±5	9±4	18±12
THMFP (µg/L)	278±59	51±8	1±4	9±6	14±12
HAAFP (µg/L)	397±28	61±11	3±7	10±7	12±11

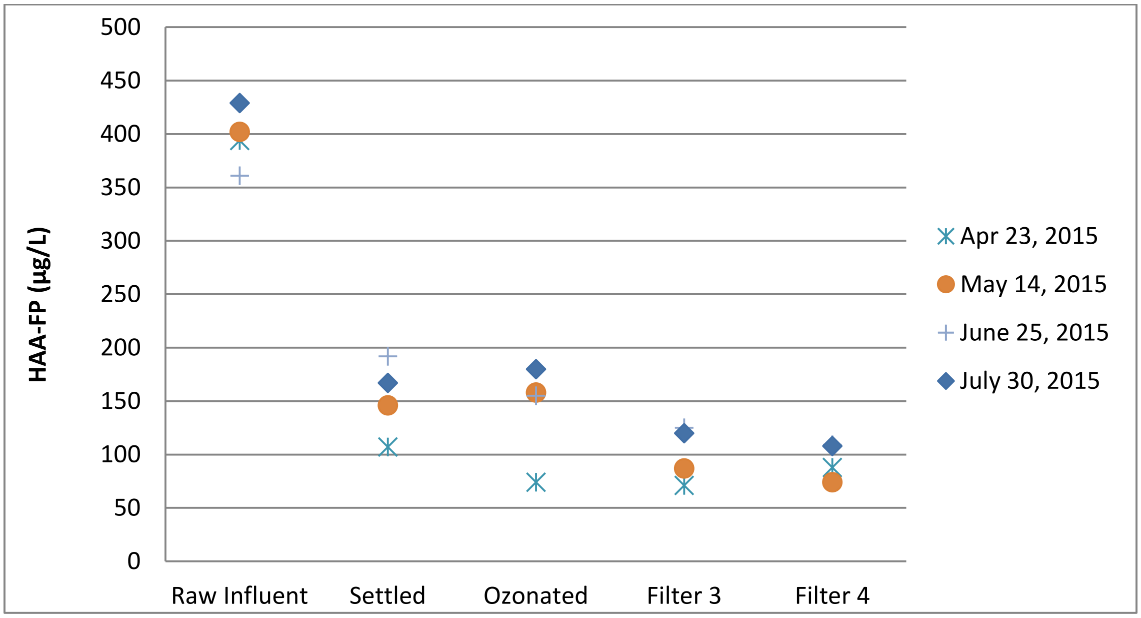
Table 3-2. Prediction precision (R^2) between different analyzed parameters (p value < 0.01) in all cases; n = 38 except for prediction of HAAFP where n = 19).

		THMFP (μg/L)	**HAAFP** (μg/L)	**DOC** (mg/L)	**UV$_{254}$** (m^{-1})	**SUVA** (L/mg.m)	**HPO** (%)
HAAFP (μg/L)	$\mathbf{R^2}$	0.84					
	***P*-value**	1×10^{-8}					
DOC (mg/L)	$\mathbf{R^2}$	0.85	0.81				
	***P* -value**	8×10^{-17}	6×10^{-8}				
UV$_{254}$ (m^{-1})	$\mathbf{R^2}$	0.89	0.92	0.81			
	***P* -value**	5×10^{-19}	2×10^{-11}	4×10^{-15}			
SUVA (L/mg.m)	$\mathbf{R^2}$	0.83	0.90	0.72	0.98		
	***P* -value**	6×10^{-16}	3×10^{-10}	6×10^{-12}	7×10^{-33}		
HPO (%)	$\mathbf{R^2}$	0.80	0.79	0.76	0.85	0.86	
	***P* -value**	1×10^{-14}	1×10^{-7}	2×10^{-13}	3×10^{-17}	9×10^{-18}	
HS (mg/L)	$\mathbf{R^2}$	0.84	0.78	0.81	0.81	0.76	0.81
	***P* -value**	5×10^{-17}	2×10^{-7}	3×10^{-15}	2×10^{-15}	3×10^{-13}	5×10^{-15}



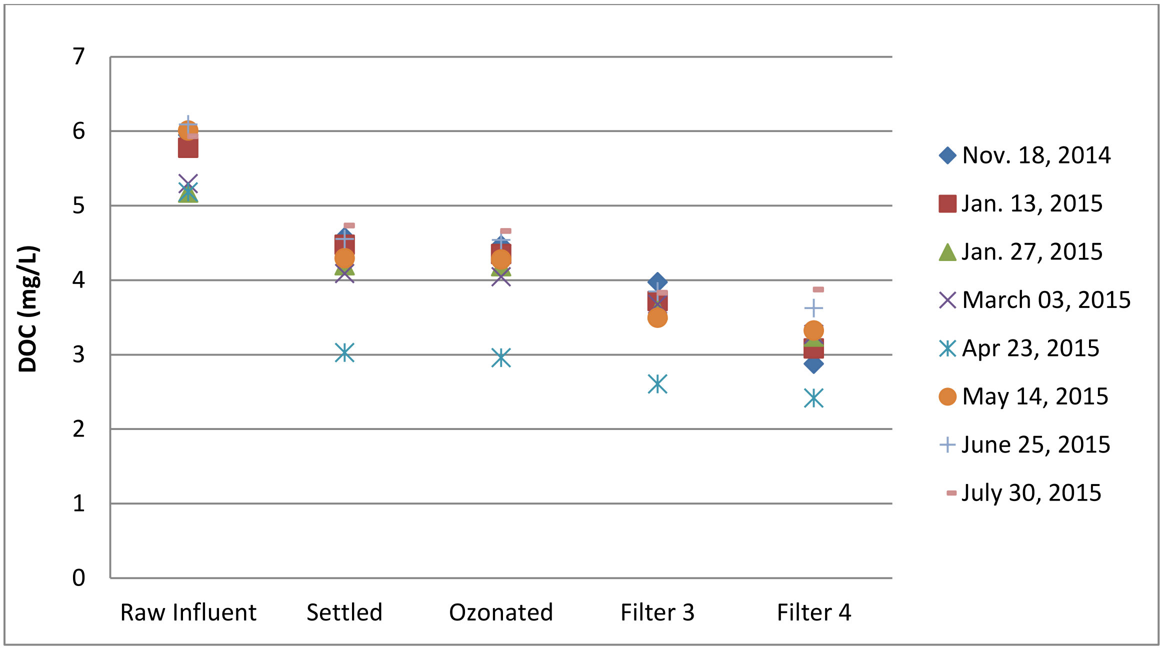
TTHM-FP (µg/L)
400
350
300
250
200
150
100
50
0
Raw Influent
Settled
Ozonated
Filter 3
Filter 4
Nov. 18, 2014
Jan. 13, 2015
Jan. 27, 2015
March 03, 2015
Apr 23, 2015
May 14, 2015
June 25, 2015
30-Jul-15

(a)



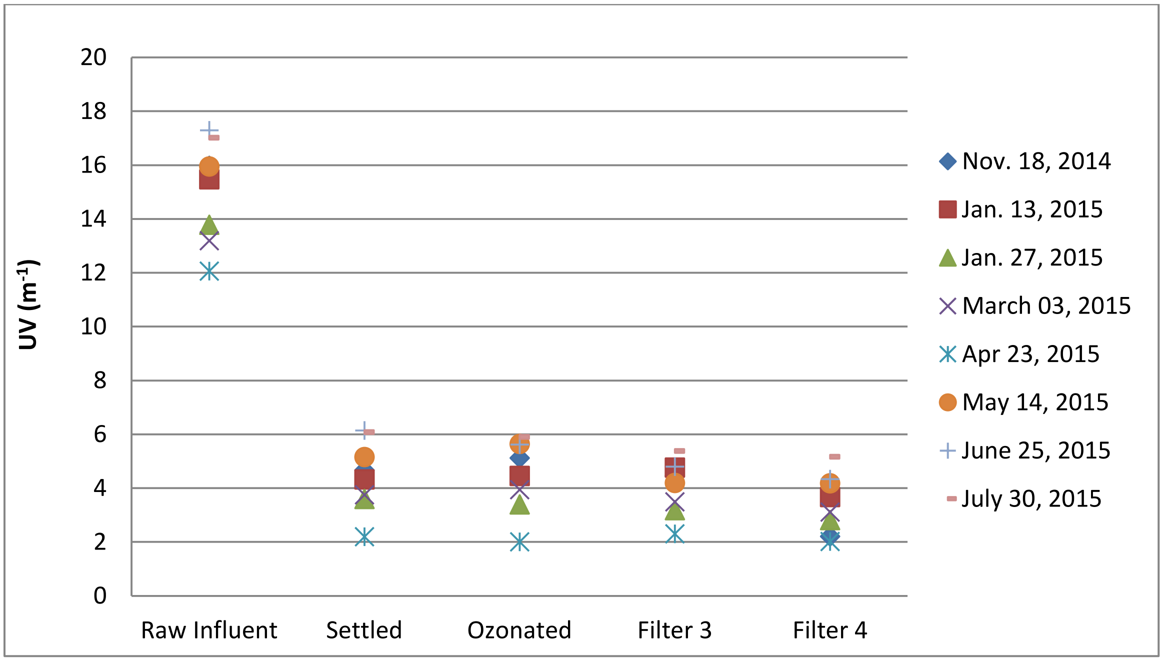
HAA-FP (µg/L)
500
450
400
350
300
250
200
150
100
50
0
Raw Influent
Settled
Ozonated
Filter 3
Filter 4
Apr 23, 2015
May 14, 2015
June 25, 2015
July 30, 2015

(b)



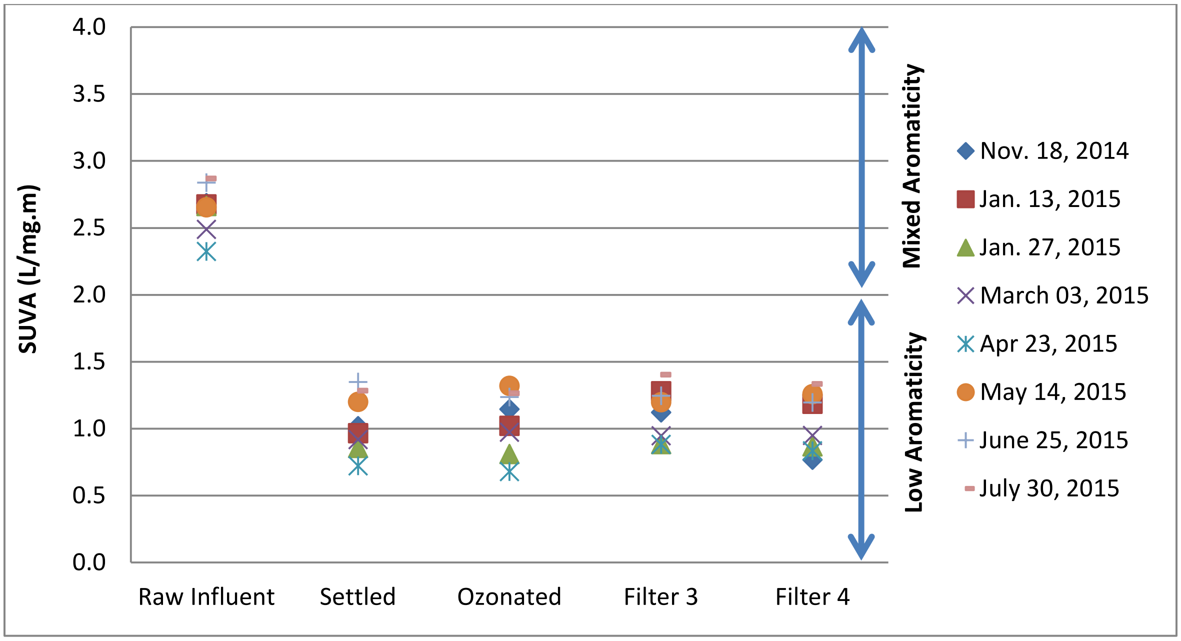
DOC (mg/L)
7
6
5
4
3
2
1
0
Raw Influent
Settled
Ozonated
Filter 3
Filter 4
Nov. 18, 2014
Jan. 13, 2015
Jan. 27, 2015
March 03, 2015
Apr 23, 2015
May 14, 2015
June 25, 2015
July 30, 2015

(c)



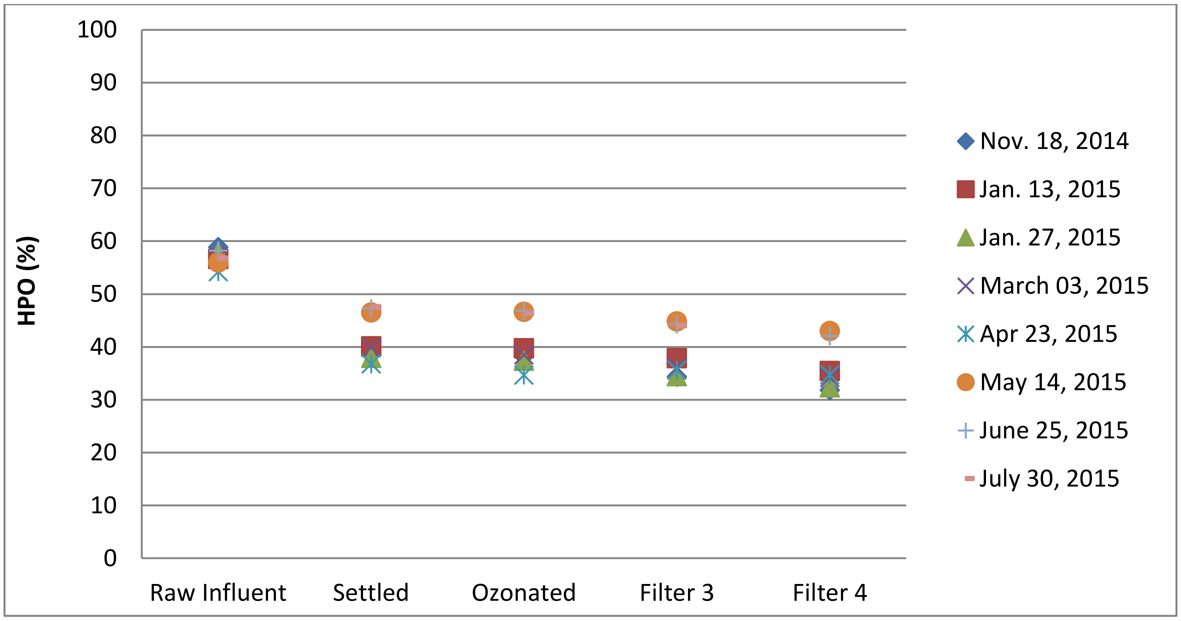
UV (m-1)
20
18
16
14
12
10
8
6
4
2
0
Raw Influent
Settled
Ozonated
Filter 3
Filter 4
Nov. 18, 2014
Jan. 13, 2015
Jan. 27, 2015
March 03, 2015
Apr 23, 2015
May 14, 2015
June 25, 2015
July 30, 2015

(d)



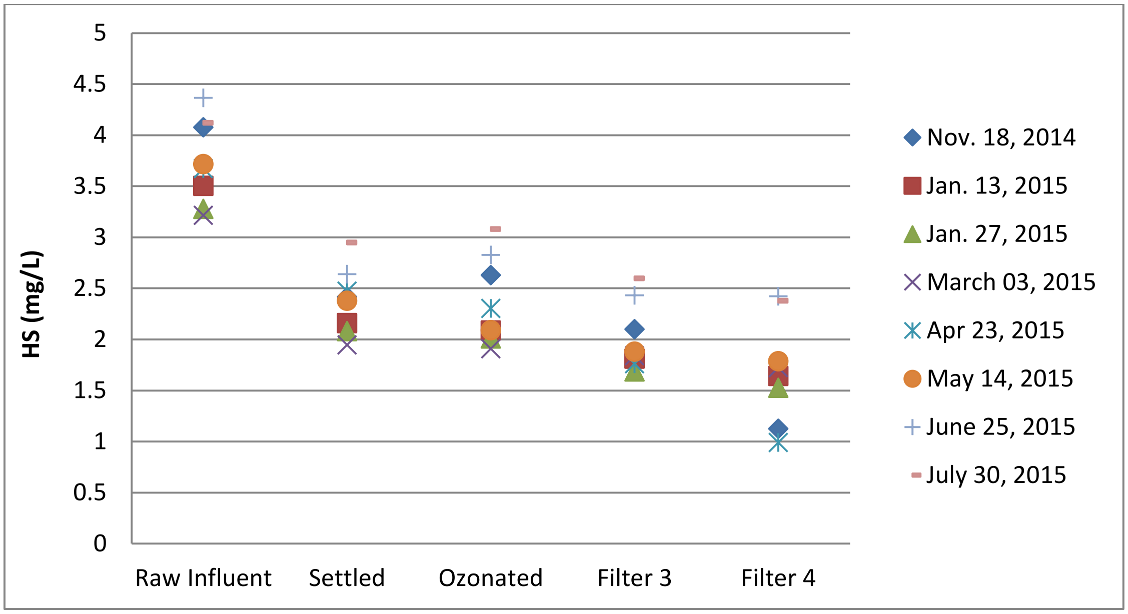
SUVA (L/mg.m)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Raw Influent
Settled
Ozonated
Filter 3
Filter 4
Mixed Aromaticity
Low Aromaticity
◆ Nov. 18, 2014
■ Jan. 13, 2015
▲ Jan. 27, 2015
× March 03, 2015
✳ Apr 23, 2015
● May 14, 2015
+ June 25, 2015
- July 30, 2015

(e)



HPO (%)
100
90
80
70
60
50
40
30
20
10
0
Raw Influent
Settled
Ozonated
Filter 3
Filter 4
◆ Nov. 18, 2014
■ Jan. 13, 2015
▲ Jan. 27, 2015
× March 03, 2015
✳ Apr 23, 2015
● May 14, 2015
+ June 25, 2015
- July 30, 2015

(f)



(g)

Figure 3-2. Amounts of (a) THM-FP, (b) HAA-FP, (c) DOC, (d) UV, (e) SUVA, (f) HPO, and (g) HS in raw water and after each treatment process during different sampling events.

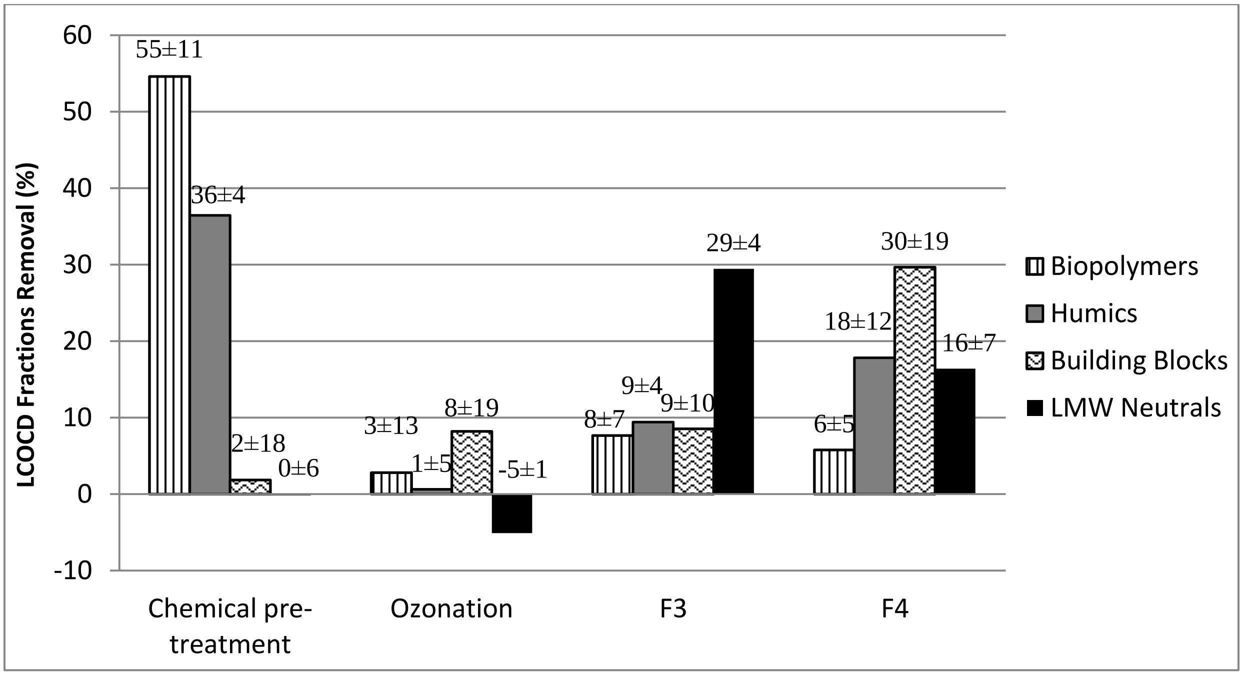


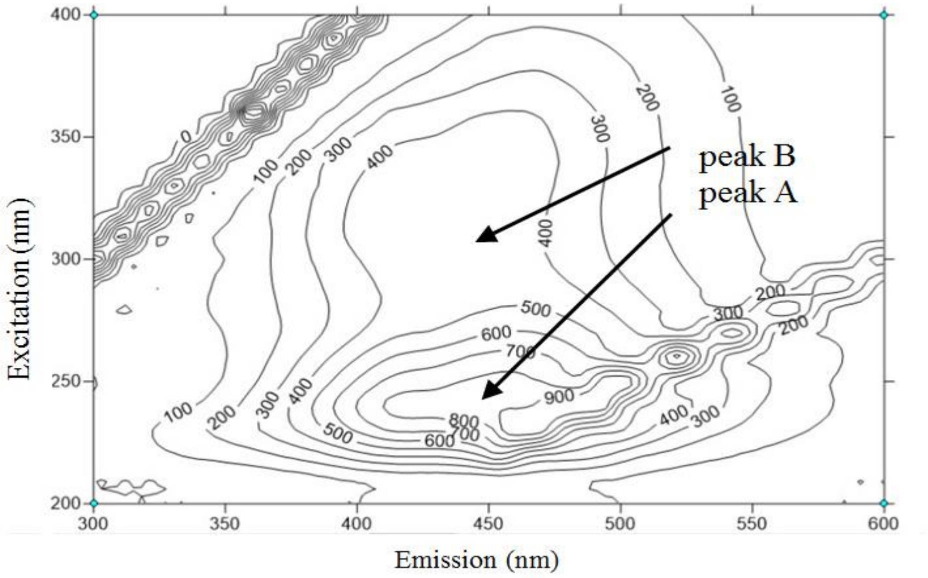
Figure 3-3. Mean (± standard deviation) removal of NOM fractions, separated by LC-OCD, after each treatment process for all sampling events.

3.4.3.4 Fluorescence

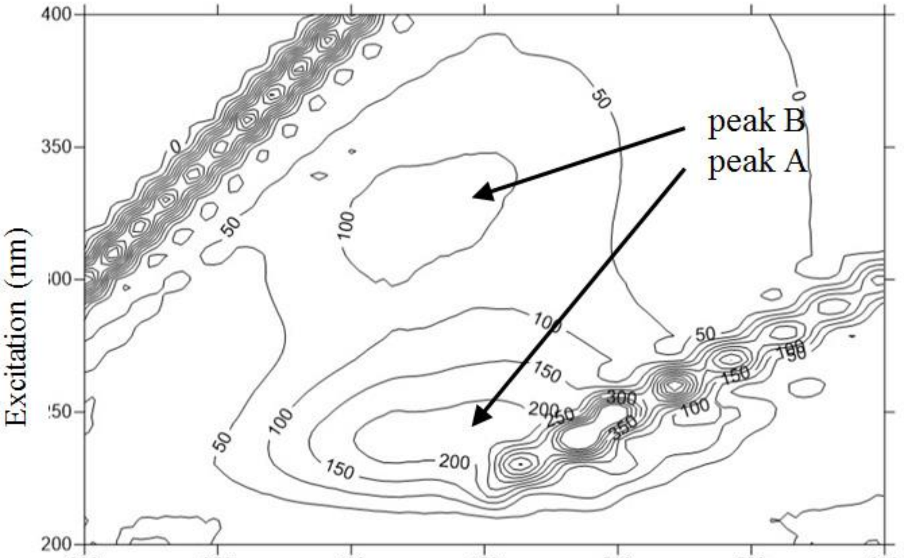
Application of fluorescence as a tool for NOM characterization has been commonly practiced in the past few decades and can reveal information on humic substances (humic and fulvic acids) and proteins (Coble, 1996; McKnight et al., 2001; Chen et al., 2003). The main benefits of this method are that it is fast, simple, and has the potential for use in real time. However, quantitative interpretations of the observations obtained using fluorescence are neither fully established nor reliable. Numerous statistical approaches are being investigated to overcome these limitations (Peiris et al., 2010; Peleato and Andrews, 2015; Peleato et al., 2017).

FEEM was employed here to investigate changes in humic DOC fractions. Intensity plots for representative raw, settled, ozonated, and F3 and F4 effluents are shown in Figure 3-4. Two main intensity peaks (A and B) representative of fulvic acid-like (Ex < 250 nm and Em > 350 nm) and humic acid-like (Ex > 280 nm and Em > 380 nm) compounds were identified (Chen et al., 2003). As shown for a representative sampling event (Figure 3-4), the intensity of the fulvic and humic acid-like compounds decreased after treatment, particularly following chemical pre-treatment. This finding, while non-quantitative, was in agreement with the trends observed for other humic-descriptive metrics (UV_{254}, SUVA, HPO, HS), and regulated DBP-FPs.

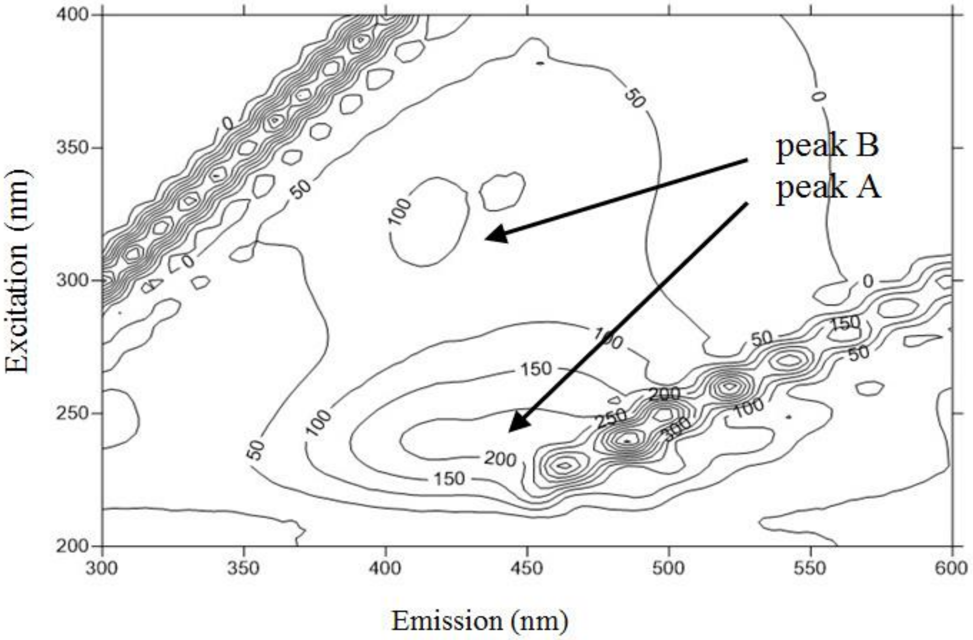
In an attempt to decode the large FEEM data sets with a simple quantitative metric, a fluorescence index (FI) has been defined (McKnight et al., 2001). It has been suggested that FI informs aromaticity and water origin (McKnight et al., 2001; Rodríguez et al., 2014). The mean FI of raw, settled, ozonated, and F3 and F4 filtered waters were 1.4, 1.7, 1.7, 1.8, and 1.7, respectively. Accordingly, the raw water was primarily composed of terrestrially derived fulvic acids (FI ≈ 1.4). Based on the same definition, the treated water observed herein had a similar composition to microbially derived fulvic acids (FI ≈ 1.9). This finding analysis suggests that the majority of terrestrial (aromatic) compounds were removed through the treatment (mainly by chemical pre-treatment) and was thus consistent with the conclusions drawn using the other metrics of NOM aromaticity discussed above. Notably, a key limitation associated with the use of the FI index is that it depends on the existence of florescence at the associated wavelengths and may not be relevant for all source waters (Shams et al., 2014).



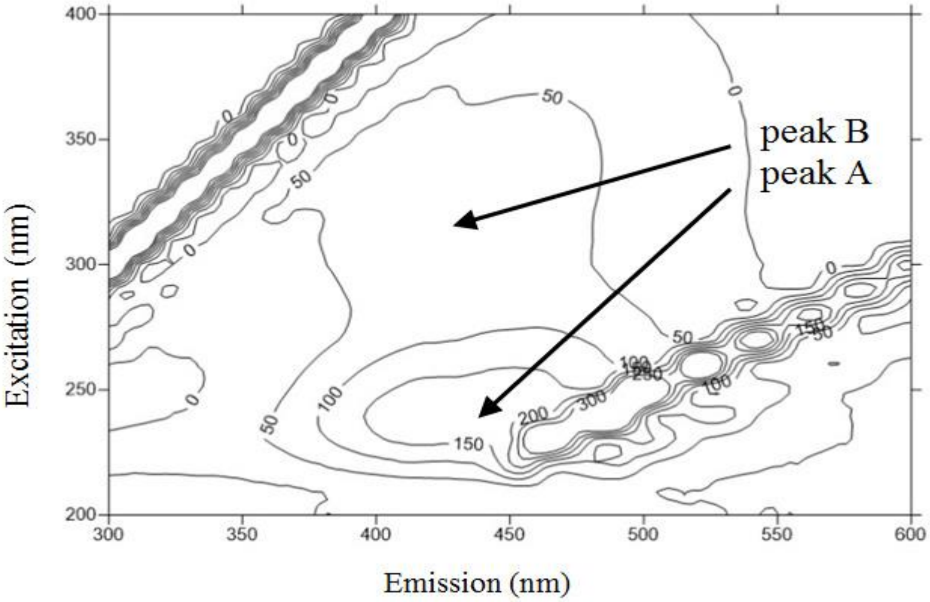
a) Raw



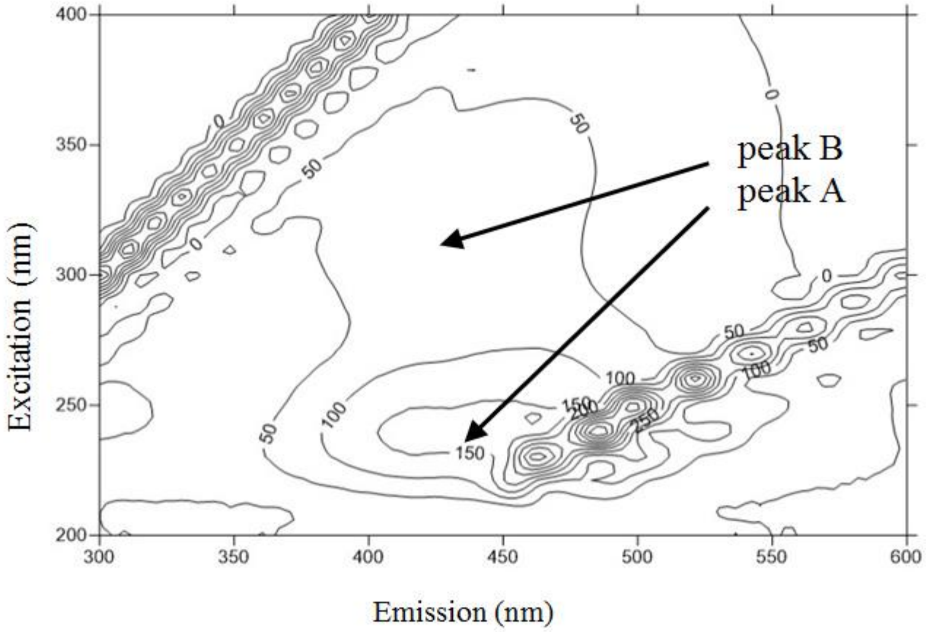
b) Settled



c) Ozonated



d) Filtered-F3



e) Filtered-F4

Figure 3-4. FEEM intensity plots for representative (a) raw, (b) settled, (c) ozonated, and (d) F3 and (e) F4 effluents.

3.5 Implications

Aromatic compounds are the primary precursors to THMs and HAAs, and therefore investigation of these DBPs would not be possible without their consideration. A number of methods/metrics have been developed to describe aromatic compounds, the most common of which are UV_{254} and SUVA, HPO (resin fractionation), and HS (liquid chromatography). These metrics correlate with each other and the formation of regulated DBPs; however, UV_{254} demonstrate the best prediction performance in predicting DBP-FPs. Application of UV_{254} to detect changes within large molecular weight aromatic compounds is recommended, especially considering its relative ease, speed, and low cost of the analysis as well as the potential to acquire on-line data in real time. While aromatics are the main reactive compounds that contribute to formation of regulated DBPs, some medium to small DOC fractions also play roles in the formation of THMs. In addition, DOC quantity and character changes throughout the treatment based on the mass and fractions that are removed by each treatment process. Liquid chromatography method enables the acquisition of this type of information. Additionally, this method enables investigation of the potential for other treatability challenges such as membrane fouling and bacterial regrowth in the distribution system by evaluation of the biopolymers and LMW neutrals fractions, respectively.

Chapter 4

An Assessment of Methods for Characterizing DOC Risks to Drinking Water Treatability after Wildfire and Post-fire Salvage Logging

4.1 Overview

Changes in dissolved organic carbon (DOC) concentration and character and their relationships to regulated DBP-FPs (THM-FPs and HAA-FPs) were comprehensively characterized using multiple natural organic matter (NOM) characterization techniques during two years following severe wildfire in the eastern slopes of the Rocky Mountains in south-western Alberta. Several NOM fractions were also characterized by liquid chromatography with organic carbon detection (LC-OCD) also were evaluated during the latter of those years. A lager study conducted at the same field site (and to which this work contributed) demonstrated that DOC concentration and hydrophobicity, and DBP-FPs increase after wildfire and even more so after post-fire salvage-logging, especially during high discharge events in headwater streams. Those increases were concurrent with increases in THM- and HAA-FPs. In contrast to and building on that investigation, the work presented herein is the first to report that the mass of humic substances (HS), biopolymers, and building blocks fractions of DOC also increased significantly in impacted streams as a result of wildfire (p = 0.18 and 0.14, respectively) and post-fire salvage logging (p = 10^{-4} and 5×10^{-3}, respectively), thereby suggesting that these disturbances may have significant implications for carbonaceous DBP-FP, coagulant demand, and membrane fouling. In contrast, the mass of the low molecular weight (LMW) neutrals fraction of DOC, which contributes to microbial regrowth in the distribution system, was not significantly different in streams impacted by either wildfire or post-fire salvage logging (p = 0.99 and 0.29, respectively), though it should be noted that this work does not speak to subsequent transformations of DOC that may occur during drinking water treatment. This work is also the first to comprehensively demonstrate wildfire-associated changes in DOC character (hydrophobic fraction as determined by resin fractionation [HPO %], UV_{254}, specific UV absorbance [SUVA], fluorescence index [FI], and fluorescence excitation-emission matrices

[FEEMs]) and their associated implications to DBP-FPs at the watershed-scale and over multiple flow regimes. Disturbance-associated impacts indicated by all of these quantitative DOC-associated metrics were statistically significant ($p < 0.01$), except for FI ($p = 0.16$ and 0.12 after wildfire and post-fire salvage logging, respectively). Qualitative FEEM results were consistent with these significant shifts. Notably, despite the continued development and promotion of various proxy indicators, UV_{254} offered the most precise prediction of THM-FP, with a coefficient of determination (R^2) of 0.6 (in contrast to values of 0.47, 0.42, and 0.39 for DOC, SUVA, and HPO %). Thus, changes in the proxy indicators were related to changes in THM-FP; however, they could not adequately explain the response variability, thereby demonstrating the need to 1) better understand relationships between disturbance-associated changes in DOC and their implications to DOC reactivity and 2) advance modeling approaches for describing these relationships. While the mass of various DOC fractions obtained using LC-OCD and HAA-FPs were not analyzed in this manner because of the limited sizes of the data sets, similar relationships were suggested. Overall, these data suggest that severe wildfire may lead to significant DOC-associated drinking water treatability challenges and that post-fire salvage logging may further exacerbate them—at present, UV_{254} is unequivocally the best available tool for monitoring these potential impacts.

4.2 Introduction

Forested catchments are major sources of drinking water. In the United States and Canada, approximately 2/3 of drinking water supplies originate in forested watersheds (Stein and Butler, 2004; Natural Resources Canada, 2015). Ironically, the high quality of water from healthy forested regions makes these supplies particularly vulnerable to the impacts of climate change. These attributes create favorable conditions for potentially catastrophic natural disturbances such as wildfire, insect outbreaks, and blowdown from hurricanes (Mast and Clow, 2008; Beggs and Summers, 2011; Emelko et al., 2011). Anthropogenic disturbances and land use such as agriculture and grazing, resource extraction, recreational activities, and sewage discharges can further compromise these high quality water supplies.

Dissolved organic carbon (DOC) is typically present at low concentrations in forested watersheds and may increase (and/or change in character) as a result of land disturbance (O'Donnell et al., 2010; Emelko et al., 2011; Hohner et al., 2016; Writer et al., 2017). Increased levels of DOC can negatively impact drinking water treatability and may necessitate the use of more complicated and costly water treatment processes (Emelko et al., 2011; Emelko et al., 2015; Hohner et al., 2016). The formation of disinfection by-products (DBPs) is one of the major treatability risks associated with changes in DOC. Reactions of different aspects of aquatic natural organic matter (NOM), for which DOC is a surrogate, with chlorine and other drinking water disinfectants result in the formation of various classes of DBPs. Thus, the formation of DBPs is directly influenced by the amount and composition of DOC, as well as the disinfectant type and dose, and treatment conditions such as temperature and contact time (Krasner et al., 2006; Krasner, 2009). To reduce consumer exposure to DBPs of health concern, THMs have been regulated universally where guidelines exist, and five haloacetic acids (HAA_5) have been regulated in U.S. and Canada (WHO, 2008; USEPA, 2012; Health Canada, 2017). Accordingly, an understanding of land disturbance impacts on source water quality and drinking water treatability (DBP-FP) is of critical importance to protecting public health through the provision of safe drinking water. This requires DOC characterization and identification of promising measurements/proxy indicators for DBP-FP, as well as other treatability challenges including coagulant demand, membrane fouling, and microbial regrowth potential in the distribution system.

A variety of approaches and metrics have been developed to characterize DOC based on different features of its structure. However, the complex mixture of compounds comprising DOC often makes each of the characterization techniques insufficient if used in isolation; applying multiple, independent methods is suggested to collect more comprehensive information (Abbt-Braun et al., 2004; Croué, 2004). Relationships between various metrics describing DOC concentration and/or character and DBP-FP have typically been highly site specific (Edzwald et al. 1985; Collins et al. 1986; Reckhow and Singer, 1990; Reckhow et al. 1990; Singer, 1999; Bolto et al., 2002; Kitis et al. 2002; Goslan et al., 2004; Ates et al., 2007; Bougeard et al., 2010). Although DOC concentration, DOC hydrophobicity, and DBP-FPs can significantly increase after severe wildfire (Emelko et al., 2015; Writer et al., 2017)—and even more so after post-fire salvage-logging—especially during high discharge events in headwater streams (Emelko et al., 2015), changes in NOM after severe wildfire have not been comprehensively characterized, particularly with respect to changes in DBP-FP. Moreover, relative wildfire- and post-fire salvage logging-associated implications to membrane fouling and microbial regrowth potential in the distributions system have never been reported.

This study focused on evaluating methods for characterizing changes of importance to water quality (DOC and its fractions) and the treatability risks understood to be associated with them (formation of regulated DBPs, membrane fouling potential, and potential for microbial regrowth in the distribution) after wildfire and post-fire salvage logging. A unique sampling program (temporal and spatial) from seven extensively instrumented watersheds (two unburned, three burned, and two post-fire salvage logged), designed and implemented by the Southern Rockies Watershed Project (SRWP) (Bladon et al., 2008; Silins et al., 2009), enabled this investigation over two years from multiple unburned (reference), burned, and post-fire salvage logged watersheds. Samples were collected during dominant regional streamflow regimes (baseflow, snowmelt freshet, and stormflow). The utility of several DOC metrics for predicting THM-FP was evaluated using linear regression, consistent with previous investigations (Edzwald et al., 1985; Reckhow and Singer, 1990; Singer, 1999; Goslan et al., 2004; Ates et al., 2007; Wassink et al., 2011). These approaches are widely utilized because these DBP precursor materials are generally understood to be directly proportional to the by-products they form. Here, THM- and HAA-FP prediction using five NOM characterization methods (DOC, UV254, specific UV absorbance [SUVA], percent hydrophobicity as determined by XAD resin fractionation, and fluorescence index [FI]) was evaluated using data from streams draining burned and post-fire salvage logged watersheds. This type of comparative assessment is currently lacking and critical for identifying the most useful techniques for evaluating disturbance impacts on water quality in drinking water source watersheds. The biopolymer and LMW neutral fractions obtained using LC-OCD were used to infer relative wildfire- and post-fire salvage logging-associated implications to membrane fouling and microbial regrowth potential in the distributions system. The HS fraction further informed relative changes in THM-FP and coagulant demand. Such information will contribute to developing source water protection strategies and weighing the impacts of land use/management on drinking water supplies to mitigate risks to treatability and public health. It should be noted that because of the relatively size of these data sets (20 sampling events), the relationships between these parameters and THM-FP were not modeled.

4.3 Materials and Methods

4.3.1 Study Site and Sampling

The 2003 Lost Creek Wildfire was one of the most severe forest fires experienced in the upper eastern slopes of Canadian Rocky Mountains (since 1930). It burned more than 21000 ha in Crowsnest Pass, south-western Alberta and disturbed the Oldman River basin, which is one of Alberta's major water supplies, by consuming the organic matter in nearly all the forest cover and floor of the burned area. Shortly after the fire (2004), three burned (South York, Lynx, and Drum Creeks) and two unburned (Star and North York Creeks) were established and instrumented by the Southern Rockies Watershed Project (SRWP). Later in 2005, two additional salvage logged sites (Lyons East and West Creeks) were added to the study (Figure 4-1). More information about the sites and details of the sampling program can be found in Bladon et al. (2008) and Silins et al. (2009). Comprehensive hydrometric and water quality data (since April 2004) from these watersheds demonstrated that DOC concentration and hydrophobicity, and THM- and HAA-FPs increase after wildfire and even more so after post-fire salvage-logging, especially during high discharge events in headwater streams (Emelko et al., 2015). To characterize the impacts of wildfire and salvage logging on DOC fractions and their relationship DBP-FPs, changes in dissolved organic carbon (DOC) concentration and character and their relationships to regulated DBP-FPs (THM-FPs and HAA-FPs) were comprehensively characterized using multiple natural organic matter (NOM) characterization techniques during two years (2013 and 2014) following severe wildfire in the eastern slopes of the Rocky Mountains in south-western Alberta. Several NOM fractions also were characterized by LC-OCD during the latter of those years. Samples collected from multiple unburned (reference), burned, and post-fire salvage logged watersheds during dominant regional streamflow regimes (baseflow, snowmelt freshet, and stormflow) as described elsewhere (Bladon et al., 2008; Silins et al., 2009).

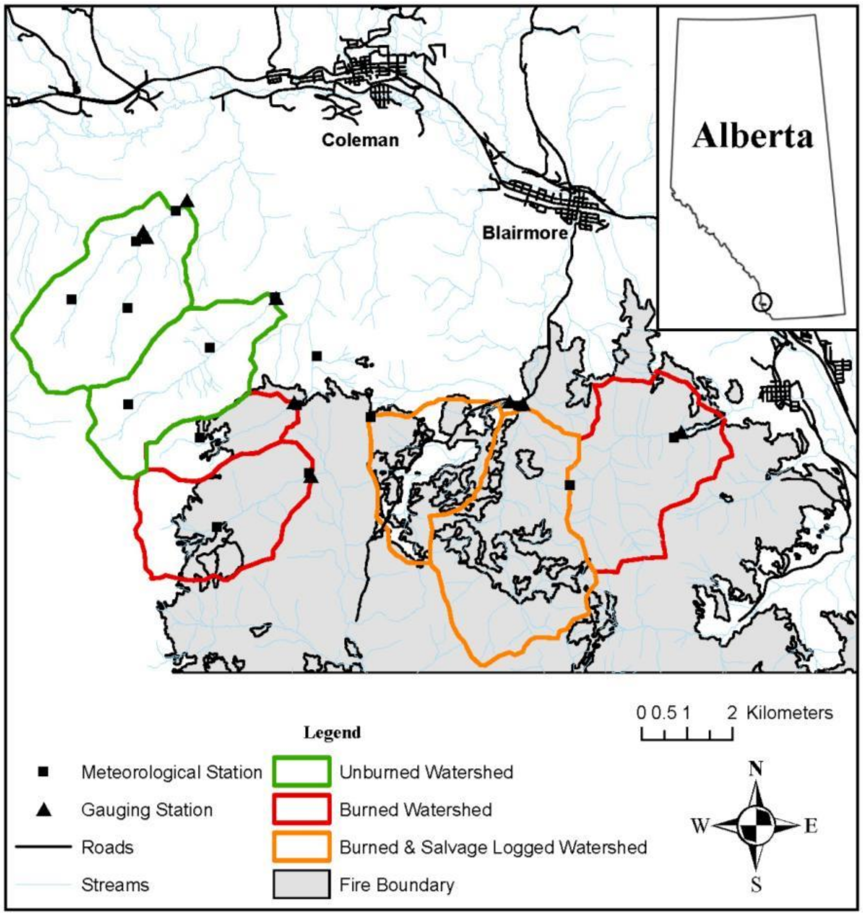


Figure 4-1. Map of the Southern Rockies Watershed Project research watersheds (from west to east: Star, North York, South York, Lynx, Lyons West, Lyons East, and Drum Creeks).

4.3.2 Analytical Methods

Several characterization techniques were employed to analyze and characterize DOC in its whole and fractionated forms. In brief, DOC concentrations were measured based on Standard Methods (Method 5310B; APHA et al., 2012) using a Shimadzu TOC-VCPH TOC analyzer. UV_{254} was analyzed using a Hewlett-Packard 8453 spectrophotometer with a 1 cm quartz cell (Method 5910 B; APHA et al., 2012). Specific ultraviolet absorbance (SUVA) was calculated as the measured UV_{254} divided by the DOC (L/mg.m) (Edzwald et al., 1985). Resin fractionation using Amberlite XAD-8® was utilized to isolate hydrophobic and hydrophilic fractions as described by Kitis et al. (2002). LC-OCD was used to characterize NOM as per the fractions defined by Huber et al. (2011); notably, this particular analysis was only conducted during one of the sampling years (2014). This technique employs a weak cation exchange column (250 mm × 20 mm, TSK HW 50S, 3000 theoretical plates) followed by a UV_{254} detector (UVD), an organic carbon detector (OCD), and an organic nitrogen detector (OND). ChromCALC, DOC-LABOR data processing software was used to quantify different NOM fractions (Huber et al., 2011). Fluorescence analyses were conducted using a Varian Cary Eclipse Spectrofluorometer. FEEMs were analyzed based on the method described by Peiris et al. (2010) and the data were interpreted based on a study by Chen et al. (2003). The excitation and emission ranges used were 200–400 and 300–600 nm, respectively. The FI, defined as the ratio of emission intensity at the wavelength of 450 to that at 500 nm, both at the excitation of 370 nm (McKnight et al., 2001b), was also calculated. THM-FP was assessed based on Standard Methods (Methods 5030B and 8260C; APHA et al., 2012) using GC/MS (purge and trap) on an Agilent Technologies 7890B -MS/5977A. HAA-FP and NDMA-FP were analyzed on a GC/MS/MS/CI Varian CP3800-MS/MS2000 (Saturn MS Ion Trap) analyzer. The method utilized for HAA-FP analysis was U.S. EPA Method 552.3 (USEPA, 2003). The analysis of NDMA-FP was conducted based on Standard Methods (Method 6410B; APHA et al., 2012) and as per Blaise et al. (1994).

4.3.3 Statistical Analysis

To evaluate the impacts of disturbance on water quality and treatability, a generalization of the standard linear model used in the general linear model (GLM) procedure in SAS/STAT® 9.2 was utilized to apply the method of least squares to fit general linear models to the data (SAS, 2008). Specifically, the MIXED procedure with REML was utilized. In brief, it fits a variety of mixed linear models to data and enables the use of these fitted models to make statistical inferences about the data—the method of restricted maximum likelihood (REML), also known as residual maximum likelihood was implemented to eliminate the effect of nuisance parameters. The generalization of the GLM procedure is that the data are permitted to exhibit correlation and non-constant variability. As described in detail in (SAS, 2008), the parameters of the mean model are referred to as fixed-effects parameters, and the parameters of the variance-covariance model are referred to as covariance parameters. The fixed-effects parameters are associated with known explanatory variables and can be either qualitative (as in the traditional analysis of variance) or quantitative (as in standard linear regression). However, the covariance parameters distinguish the mixed linear model from the standard linear model because they are needed in scenarios such as the one herein in which 1) the experimental units (sub-watersheds) on which the data (NOM and treatability metrics) are measured, can be grouped into clusters (groups of sub-watersheds impacted by a common type of disturbance), and the data from a common cluster are correlated (e.g., because of common hydrologic regimes) and 2) repeated measurements (NOM and treatability metrics) are collected on the same experimental unit (sub-watersheds), and these repeated measurements are correlated or exhibit variability that changes. Here, the repeated measures vary both spatially and temporally.

Analysis of variance (ANOVA) was used to make inferences about the data. Predictions of THM-FP using NOM character were investigated using simple least squares linear regression. The significance and precision of the regression models were evaluated using customary approaches (i.e., *p* values obtained from ANOVA [Appendix A] and coefficients of determination [R^2], respectively). Diagnostic residual plots (Appendix B) were utilized to ensure that the assumptions of ANOVA were not violated.

4.4 Results and Discussion

4.4.1 Disinfection By-product Formation Potential

A larger, previously reported study to which this work contributed demonstrated that THM- (Figure 4-2a) and HAA-FPs as well as DOC concentration (Figure 4-2b) and hydrophobicity increase after wildfire and even more so after post-fire salvage-logging, especially during high discharge events in headwater streams (Emelko et al., 2015). The detailed data, which also are presented herein, indicated that the elevated THM-FPs in streams draining the disturbed watersheds (regardless of flow regime) were significantly different from those in the unburned (reference) watersheds. Salvage logging was shown to significantly exacerbate the impacts of disturbance. The mean total THM-FP concentrations in steams draining unburned, burned, and post-fire salvage logged watersheds were 11, 22, and 70 µg/L in 2013 and 33, 81, and 218 µg/L in 2014, respectively. A significant increase of THM-FP in the disturbed watersheds was observed during the high streamflow conditions in 2014 ($p < 0.01$). This increase was likely associated with the catastrophic flooding that occurred in Alberta during June 2013—it caused extensive river bank erosion and discharge of sediments into the impacted streams and rivers including the Oldman River and resulted in increases in total suspended solids, total dissolved solids, and turbidity (Alberta Government, 2014; Noad, 2014). Regardless, the THM-FP primarily consisted of chloroform—no bromoform was detected during the study due to the lack of the precursors (bromide) in the study watersheds. The mean chloroform, bromodichloromethane (BDCM), and dibromochloromethane (DBCM) formation potentials comprising the total THM-FP throughout the two-year study were 93%, 6%, and 1%, respectively.

HAA-FPs were measured in October 2014. The mean total HAA-FP concentrations in streams draining unburned, burned, and post-fire salvage logged watersheds were 41, 174, and 218 µg/L, respectively. Similar to the THM-FP findings, brominated HAA constituents were not formed and total HAA-FP consisted of 70% trichloroacetic acid and 30% dichloroacetic acid. As would be expected for DBPs with mutual precursors, total HAA- and THM-FPs were significantly correlated ($p = 6\text{x}10^{-7}$, $R^2 = 0.99$). Similar correlations between THMs and HAAs have been previously reported (Villanueva et al., 2003; Rocarro et al., 2014). No NDMA-FP was expected or detected due to non-detectable levels of dissolved organic nitrogen and ammonia, and very low levels of nitrite in the watersheds. Nitrite at low concentrations (< 100 µg/L) has not been shown to be a contributor NDMA formation (Shah and Mitch, 2012). In contrast, organic nitrogen compounds that have been identified as NDMA precursors include: effluent organic matter (Mitch and Sedlak, 2004), pharmaceuticals and personal care products (Shen and Andrews, 2011), and certain pesticides and herbicides (Chen and Young, 2008). These compounds are often present in watersheds that are impacted by wastewater effluents (Shah and Mitch, 2012) —thus, these compounds would not be expected in the headwaters of the Rocky Mountain watersheds studied herein.

4.4.2 Dissolved Organic Carbon (DOC) Concentration

DOC is a critical water quality parameter that governs the choice and design of treatment processes and often correlates with the formation of regulated DBPs (Singer et al., 1981). The mean DOC concentrations during this study period were 1.0, 1.5, and 3.9 mg/L, in streams draining the unburned, burned, and post-fire salvage logged watersheds, respectively (Figure 4-2b). As indicated in Table 4-1 (supported by Table A-2, Appendix A and Figure B-2, Appendix B), the correlation between DOC and THM-FP over the study period was significant ($p = 2\text{x}10^{-10}$); however, changes in DOC only somewhat explained the variability in THM-FP ($R^2 = 0.47$). While investigation of the mechanisms that might explain why the relationships between DBP-FPs and proxy indicators such as DOC concentration are site specific and often change temporally is beyond the scope of this work, it is reasonable to expect that the catastrophic flood event of 2013 (Alberta Government, 2014; Noad, 2014) contributed to some of this variability. Good correlations between TOC and THM-FP for individual source waters have been reported previously (Singer et al., 1981; Reckhow and Singer, 1990); however, the correlations were not found to be precise when comparing water from different sources (Reckhow and Singer, 1990)—such differences likely also extend to flood events which may have introduced and/or removed different types or sources of NOM to/from the study watersheds.

4.4.3 DOC Character

To investigate the changes in DOC character resulting from wildfire and post-fire salvage logging, several metrics and characterization techniques were employed. Aromatic compounds, also known as humics or hydrophobics, are reported to be the main precursors of regulated carbonaceous DBPs (THMs and HAAs) (Collins et al. 1986; Reckhow and Singer 1990; Singer, 1999; Kitis et al., 2002). Accordingly, this study focused on the metrics that identify these fractions of DOC.

4.4.3.1 UV254 and SUVA

UV_{254} has been used as a surrogate for NOM aromaticity because aromatic organic compounds absorb UV light at 254 nm. UV_{254} has been widely utilized within the drinking water industry and elsewhere because it is simple and can be analyzed quickly or in real time. Consistent with the impacts of severe wildfire-associated disturbances on DOC concentrations that were discussed above, significantly elevated UV_{254} was observed especially during high discharge events in the wildfire-impacted headwater streams relative to those draining unburned (reference) watersheds ($p < 0.001$; Figure 4-2c)—post-fire salvage logging exacerbated those impacts ($p < 0.001$; Figure 4-2c). UV_{254} was an excellent predictor of THM-FP with reasonable precision in prediction (Table 4-1; $p = 2\times10^{-14}$, $R^2 = 0.60$). Notably, UV_{254} unequivocally offered the most precise prediction of THM-FP of all of the metrics of NOM character that were investigated. This observation is consistent with the widely reported literature in which the utility of UV_{254} in predicting regulated DBP-FPs has been historically demonstrated (Singer et al., 1981; Edzwald et al., 1985; Reckhow et al., 1990; Wassink et al., 2011; Awad et al., 2016).

Changes in SUVA resulting from wildfire-associated disturbances and their correlation with THM-FP also were investigated. The mean SUVA observed during this study increased with increasing watershed disturbance; from 1.8 L/mg.m in streams draining unburned watersheds to 2.6 and 3.0 L/mg.m in streams draining burned and post-fire salvage logged watersheds, respectively (Figure 4-2d). Accordingly, while the source water streams draining the unburned watersheds could be described as non-humic in nature (SUVA < 2), wildfire and salvage logging affected aquatic NOM structure and lead to a more humic blend (mixture of humics and other NOM) as defined by Edzwald and Tobiason (1999) in the disturbance-impacted streams. While SUVA correlated significantly with THM-FP, its prediction precision was low (Table 4-1; $p = 4x10^{-9}$, $R^2 = 0.42$), indicating that changes in SUVA were related to changes THM-FP; however, they could not adequately explain the response variability, thereby demonstrating the need to better understand relationships between disturbance-associated changes in SUVA and their implications to THM-FP. This result was also consistent with the reported literature in which contradictory conclusions have been reported regarding the utility of SUVA in explaining NOM reactivity and predicting THM formation. The utility of SUVA as a THM-FP predictor has been widely investigated and has resulted in good, precise correlations in some cases (Reckhow et al. 1990; Kitis et al. 2001), but not in others (Goslan et al., 2004; Bougeard et al., 2010; Hua et al., 2015). The lack of consistently precise correlation has been especially observed in low aromaticity waters (SUVA < 2) (Ates et al., 2007; Li et al., 2014).

4.4.3.2 Resin Fractionation

Ion exchange resin fractionation is one of the NOM characterization techniques that inform the humic nature and composition of NOM by isolating different fractions and adsorbing them onto the resins under specific pH conditions (Leenheer, 1981; Thurman and Malcolm, 1981). It should be noted that the fractions separated by resins are operationally-defined and vary between methods. The approach of Thurman and Malcolm (1981) is recognized by the International Humic Substances Society (IHSS) as the standard method for separating fulvic and humic acids. Here, the hydrophobic and hydrophilic fractions of DOC were isolated and analyzed. The mean hydrophobic (HPO%) fractions were 46%, 49%, and 60% of the DOC in the streams draining the unburned, burned, and post-fire salvage logged watersheds, respectively (Figure 4-2e). Significantly elevated HPO% was observed especially during high discharge events in the wildfire-impacted headwater streams relative to those draining unburned (reference) watersheds ($p < 0.001$; Figure 4-2e)—post-fire salvage logging exacerbated those impacts ($p < 0.001$; Figure 4-2e). Like SUVA, while HPO% correlated significantly with THM-FP, its prediction precision was low (Table 4-1; $p = 10^{-8}$, $R^2 = 0.39$), indicating that changes in HPO% were related to changes THM-FP; however, they could not adequately explain the response variability, thereby demonstrating the need to better understand relationships between disturbance-associated changes in NOM hydrophobicity (HPO%) and their implications to THM-FP.

Although the operational definitions of hydrophobicity in the applied method and aromaticity as defined by UV_{254} and SUVA are different, the implications to changes in THM-FP were generally consistent, regardless of the metrics used to describe NOM/DOC character. As would be expected, significant positive correlations between all of these metrics were observed; HPO was strongly correlated with UV_{254}, but much less so with SUVA (Table 4-1). Regardless, the data clearly demonstrated that UV_{254} was the most reliable predictor of changes in headwater THM-FPs that resulted from wildfire and salvage logging in the source watersheds.

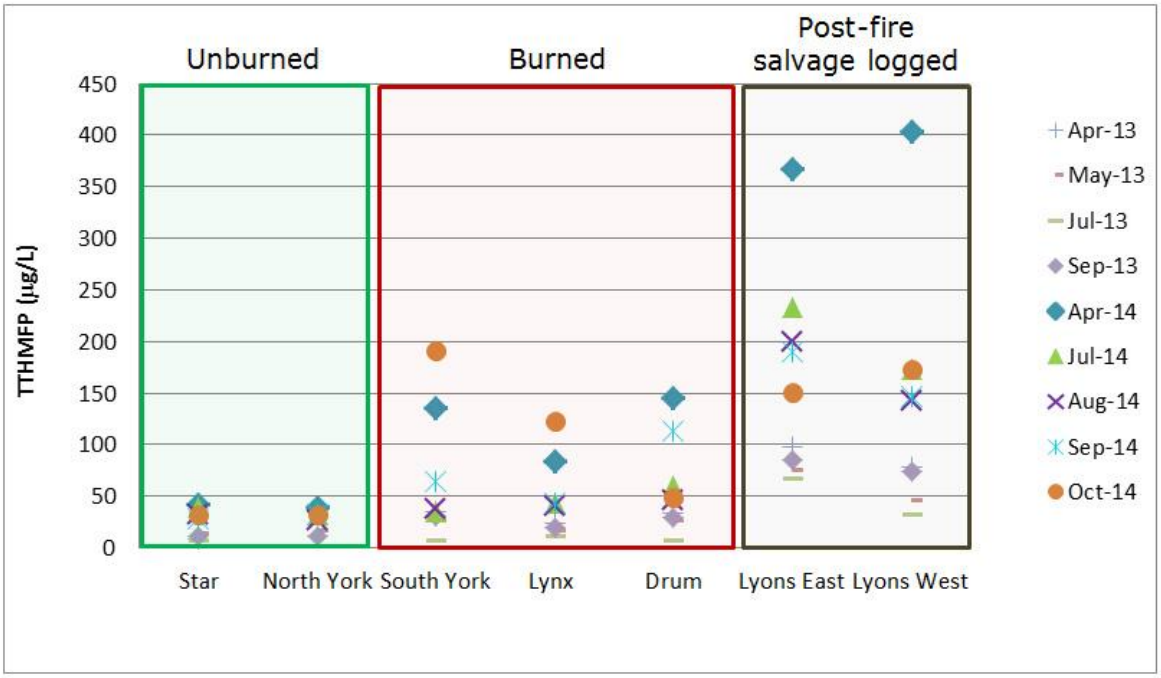
4.4.3.3 LC-OCD

LC-OCD (Huber et al., 2011) was employed in second half of this study (2014) to further evaluate the implications of wildfire and post-fire salvage logging to drinking water treatability; specifically, the relative potential for membrane fouling and microbial regrowth in the distribution system were evaluated. While specific treatability metrics that quantify those potentials are not currently available, the literature generally indicates that the biopolymer and LMW fractions of DOC are respectively associated with membrane fouling (Rahman et al., 2014; Yamamura et al., 2014) and microbial regrowth in the distribution system (Escobar et al., 2000; van der Kooij and van der Wielen, 2014). Thus, statistically significant increases in these parameters in streams draining disturbed watersheds relative to those draining unburned (reference) watersheds were interpreted as significant increases in the associated risks to drinking water treatability.

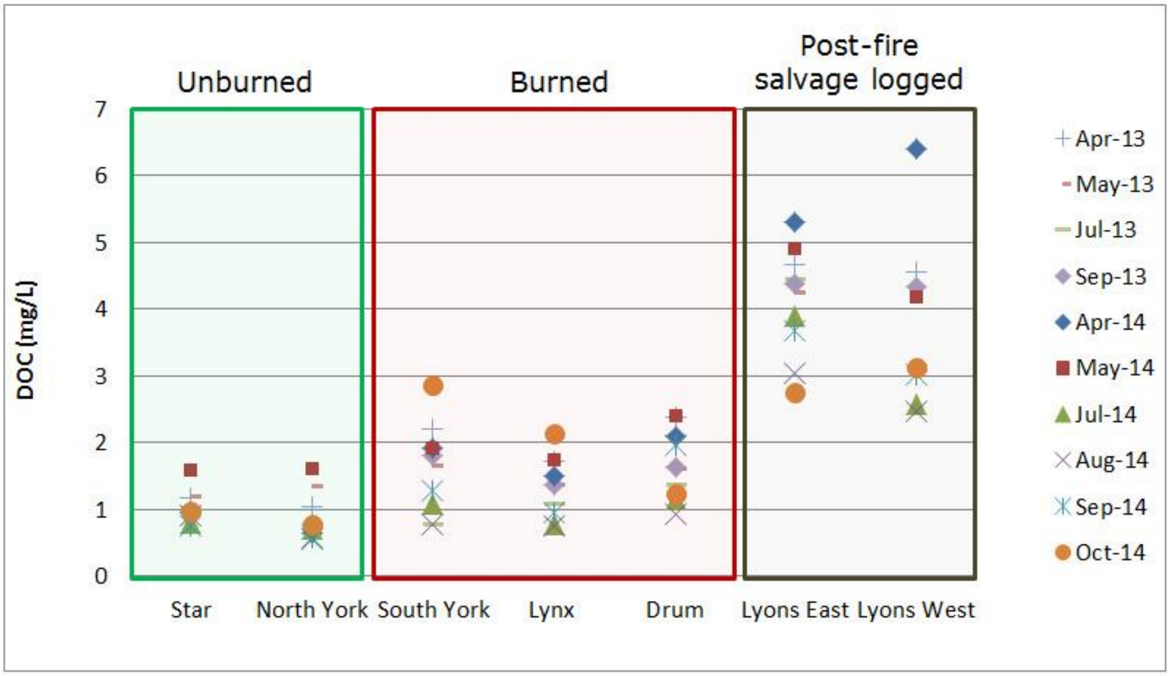
The work presented herein is the first to report that the amount of biopolymer fractions of DOC increased significantly as a result of wildfire ($p = 0.52$; Figure 4-3) and post-fire salvage logging ($p = 2\times10^{-3}$; Figure 4-3), suggesting that these disturbances may have significant implications for carbonaceous DBP-FP, coagulant demand, and membrane fouling. In contrast, the mass of the low molecular weight (LMW) neutrals fraction of DOC, which contributes to microbial regrowth in the distribution system, was not significantly different in streams impacted by either wildfire or post-fire salvage logging (p = 0.99 and 0.29, respectively). Notably, this work does not speak to subsequent transformations of DOC that may occur during drinking water treatment. The lack of disturbance-associated impacts on the LMW neutrals fraction of NOM that was observed herein must be considered in conjunction with the possibility of possible subsequent transformations of DOC that may occur during drinking water treatment, particularly if advanced oxidation processes (AOPs) such as ozonation are utilized. Such processes are known to increase concentrations of LMW fractions of DOC as a result of the oxidation of higher MW fractions (Chaiket et al., 2002; Bond et al., 2011). Thus, if such AOPs are utilized in absence of other processes that can remove LMW neutrals such as biological filtration (Liao et al., 2017; So et al., 2017), it is possible that significant challenges associated with increased oxidant demand and the potential for microbial regrowth in the distribution systems may ensue.

Table 4-1. Regression significance (*p* value) and prediction precision (R^2) between DOC, UV_{254}, SUVA, and hydrophobicity (HPO) ($p < 0.01$ in all cases; n = 64)

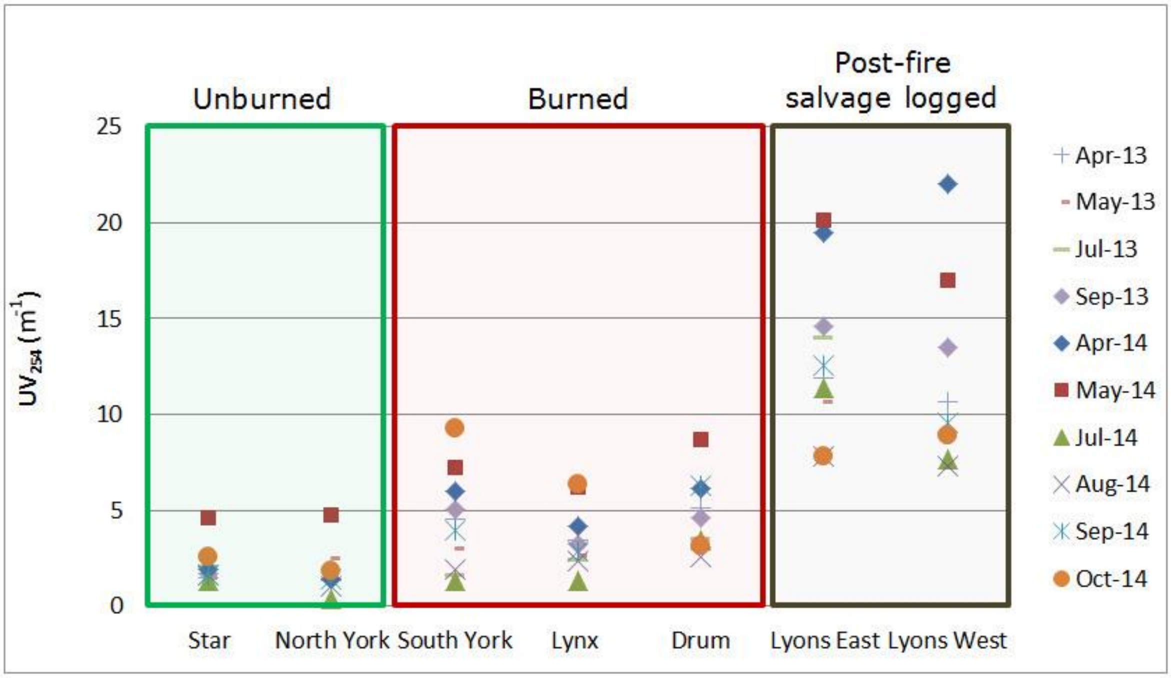
		THM-FP (µg/L)	**DOC** (mg/L)	**UV_{254}** (m^{-1})	**SUVA** (L/mg.m)
DOC (mg/L)	**R^2**	0.47			
	***p* value**	2×10^{-10}			
UV_{254} (m^{-1})	**R^2**	0.60	0.94		
	***p* value**	2×10^{-14}	9×10^{-41}		
SUVA (L/mg.m)	**R^2**	0.42	0.28	0.51	
	***p* value**	4×10^{-9}	4×10^{-6}	3×10^{-12}	
HPO (%)	**R^2**	0.39	0.81	0.79	0.38
	***p* value**	1×10^{-8}	2×10^{-24}	2×10^{-23}	3×10^{-8}


Unburned
Burned
Post-fire salvage logged
TTHMFP (µg/L)
450
400
350
300
250
200
150
100
50
0
Star
North York
South York
Lynx
Drum
Lyons East
Lyons West
Apr-13
May-13
Jul-13
Sep-13
Apr-14
Jul-14
Aug-14
Sep-14
Oct-14

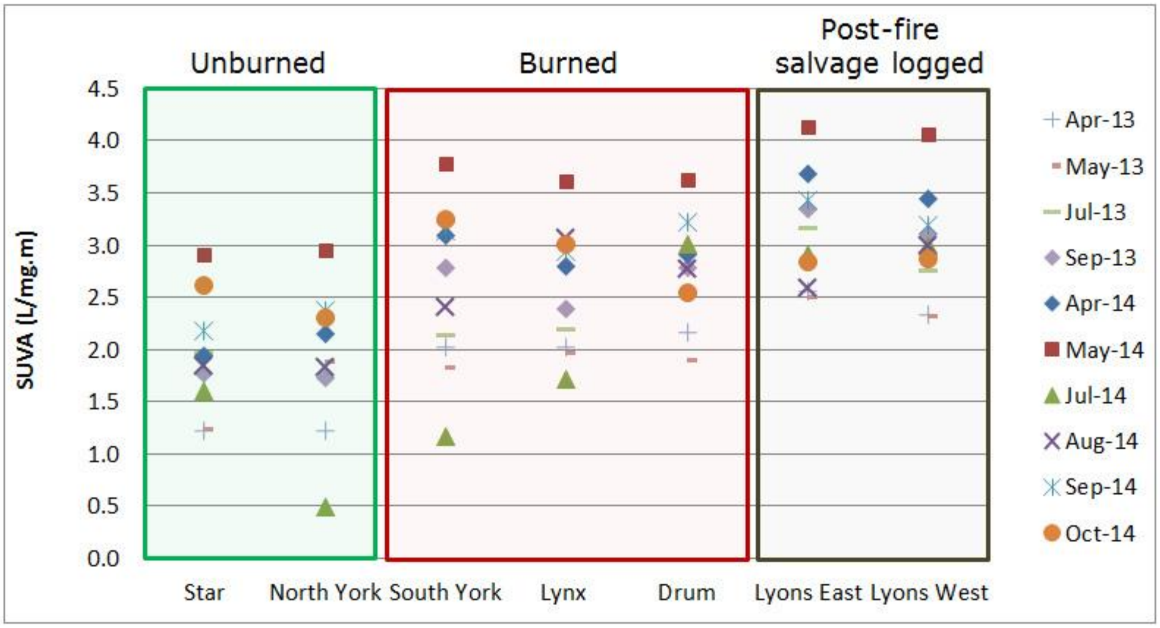
(a)


Unburned
Burned
Post-fire salvage logged
DOC (mg/L)
7
6
5
4
3
2
1
0
Star
North York
South York
Lynx
Drum
Lyons East
Lyons West
Apr-13
May-13
Jul-13
Sep-13
Apr-14
May-14
Jul-14
Aug-14
Sep-14
Oct-14

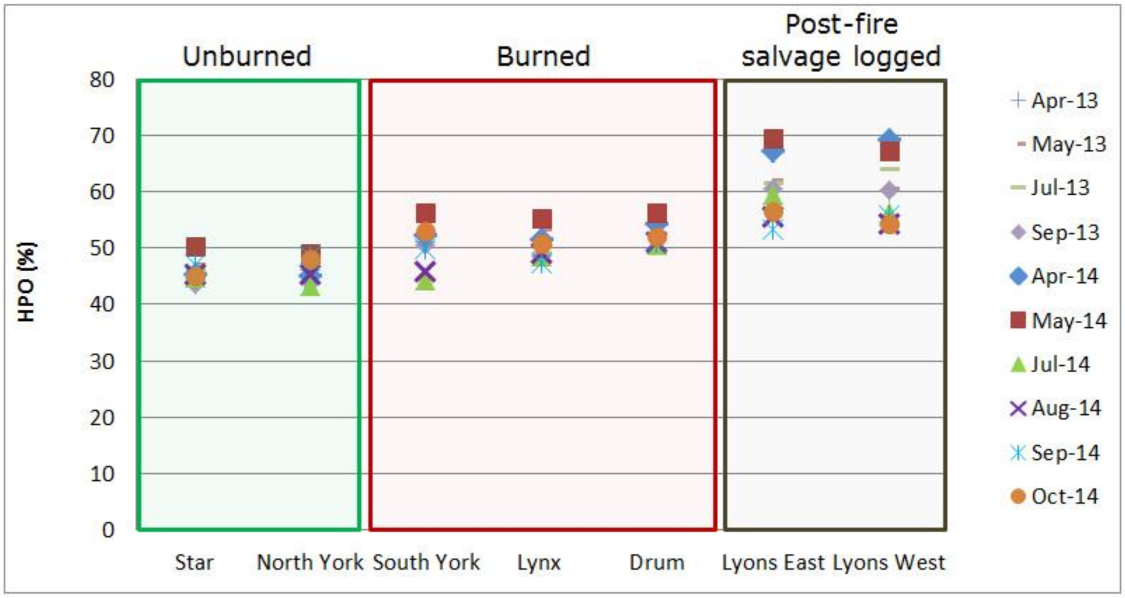
(b)


Unburned
Burned
Post-fire salvage logged
UV_{254} (m^{-1})
25
20
15
10
5
0
Star
North York
South York
Lynx
Drum
Lyons East
Lyons West
Apr-13
May-13
Jul-13
Sep-13
Apr-14
May-14
Jul-14
Aug-14
Sep-14
Oct-14

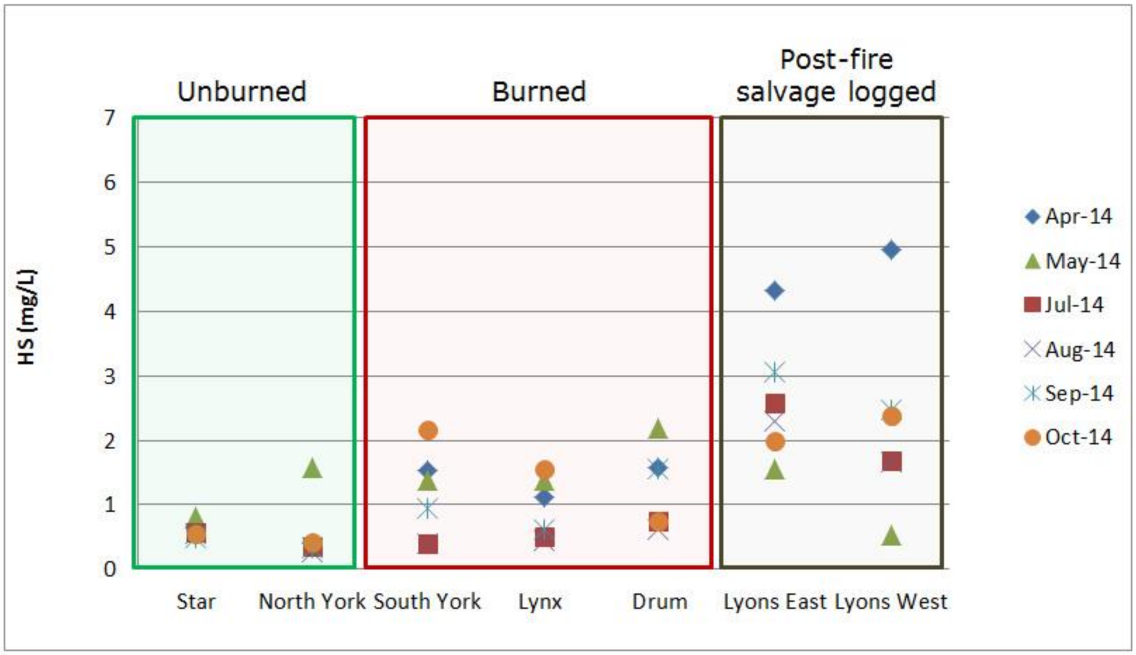
(c)


Unburned
Burned
Post-fire salvage logged
SUVA (L/mg.m)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Star
North York
South York
Lynx
Drum
Lyons East
Lyons West
Apr-13
May-13
Jul-13
Sep-13
Apr-14
May-14
Jul-14
Aug-14
Sep-14
Oct-14

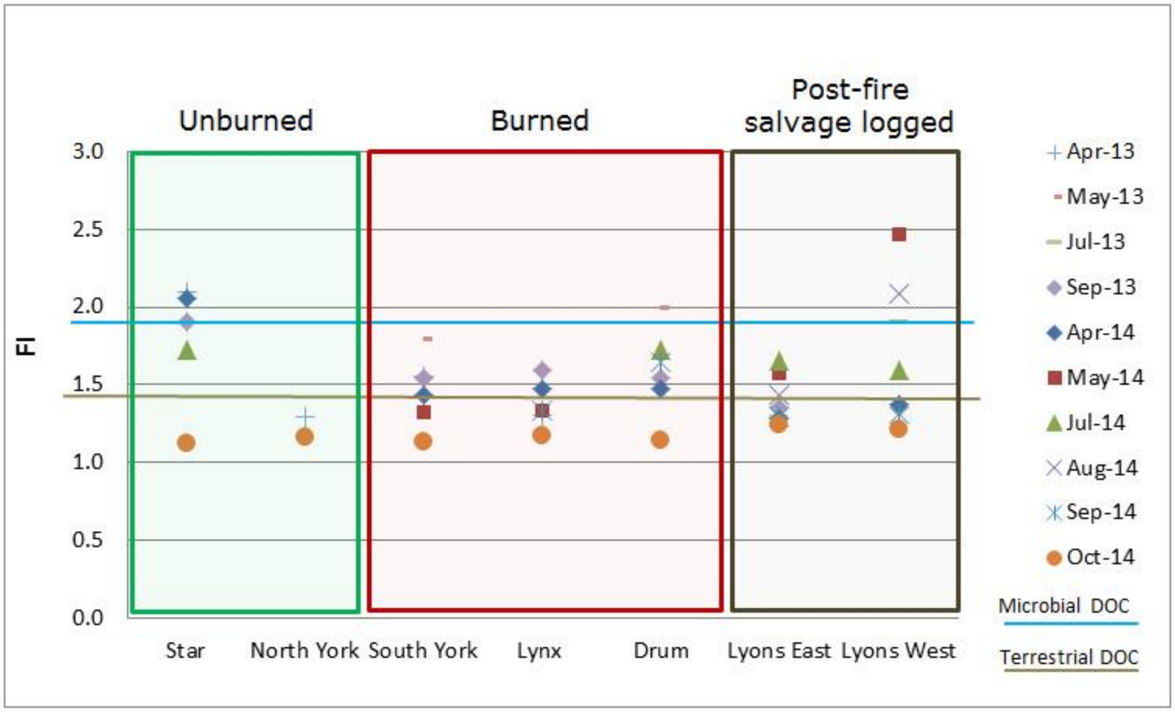
(d)


Unburned
Burned
Post-fire salvage logged
HPO (%)
80
70
60
50
40
30
20
10
0
Star
North York
South York
Lynx
Drum
Lyons East
Lyons West
Apr-13
May-13
Jul-13
Sep-13
Apr-14
May-14
Jul-14
Aug-14
Sep-14
Oct-14

(e)

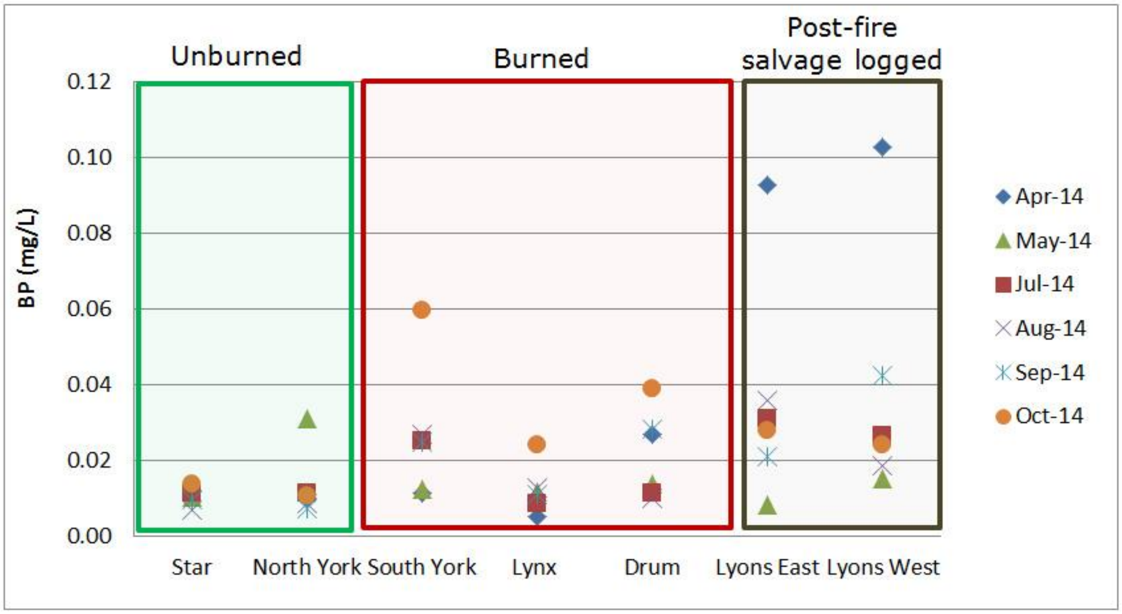

Unburned
Burned
Post-fire salvage logged
HS (mg/L)
7
6
5
4
3
2
1
0
Star
North York
South York
Lynx
Drum
Lyons East
Lyons West
Apr-14
May-14
Jul-14
Aug-14
Sep-14
Oct-14

(f)

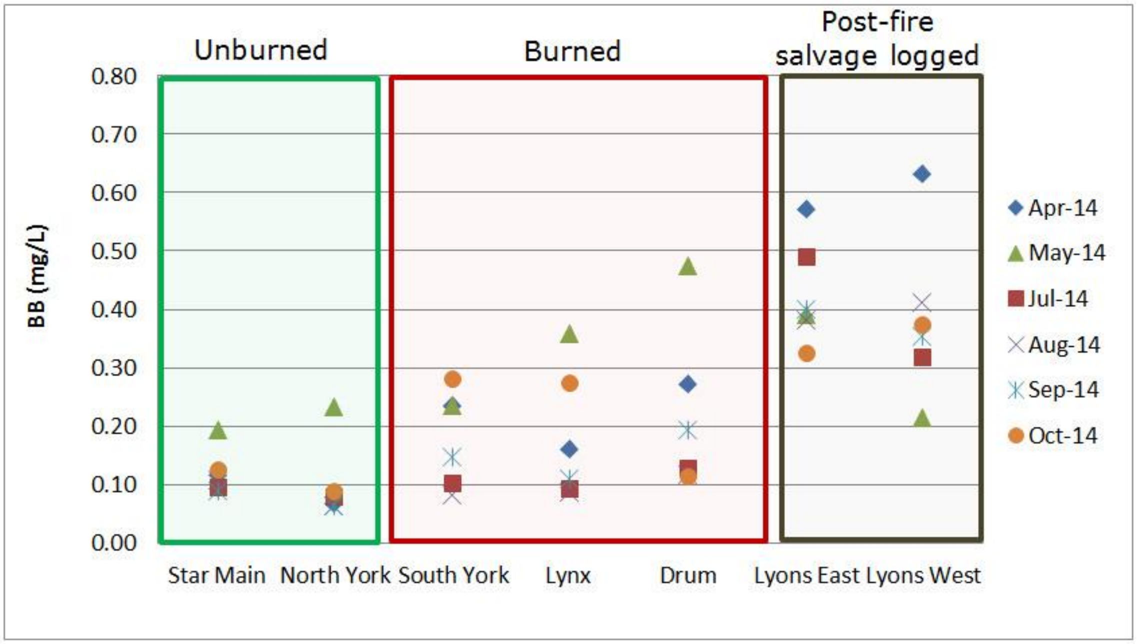


(g)

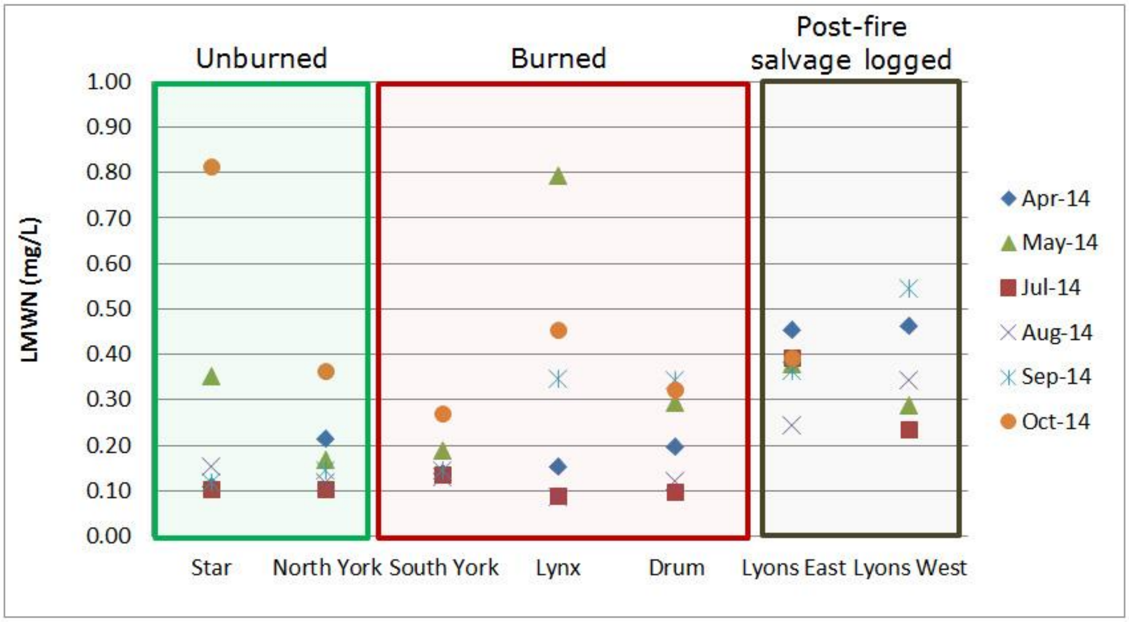
Figure 4-2. NOM character described by (a) THM-FP, (b) DOC, (c) UV, (d) SUVA, (e) HPO, (f) HS, and (g) FI in streams draining unburned, burned, and post-fire salvage logged watersheds.


Unburned
Burned
Post-fire salvage logged
BP (mg/L)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Star
North York
South York
Lynx
Drum
Lyons East
Lyons West
Apr-14
May-14
Jul-14
Aug-14
Sep-14
Oct-14

(a)


Unburned
Burned
Post-fire salvage logged
BB (mg/L)
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Star Main
North York
South York
Lynx
Drum
Lyons East
Lyons West
Apr-14
May-14
Jul-14
Aug-14
Sep-14
Oct-14

(b)



(c)

Figure 4-3. NOM character described by (a) biopolymers, (b) building blocks, and (c) LMW neutrals, fractions in streams draining unburned, burned, and post-fire salvage logged watersheds.

4.4.3.4 Fluorescence

Fluorescence has been widely used for NOM characterization due to its relative ease, low cost, and the potential for real time analysis. However, only a small fraction of the aromatic species actually emit light making them detectable by fluorescence spectroscopy (Lapen and Seitz, 1982). Different experimental and mathematical approaches have been introduced and continue being developed to overcome this method's shortcomings, which include a lack of standardized, reliable methods for generating quantitative results (Peiris et al., 2010; Korak et al., 2015; Peleato and Andrews, 2015; Peleato et al., 2017). Fluorescence-based methods are particularly sensitive to proteins and humic substances (humic and fulvic acids) (Coble, 1996; McKnight et al., 2001b; Chen et al., 2003b) and therefore may be meaningful for informing drinking water treatability risks associated with changes in source water quality.

FEEM intensity plots for representative unburned, burned, and post-fire salvage logged watersheds are shown in Figures 4-4a, 4b, and 4c, respectively. These figures indicate two main intensity peaks (A and B) representative of fulvic acid-like (Ex < 250 nm and Em > 350 nm) and humic acid-like (Ex > 280 nm and Em > 380 nm) compounds (Chen et al., 2003b). As shown for this sampling event (Figure 4-4), the intensity of the fulvic and humic acid-like compounds increased streams draining wildfire-impacted watersheds, and were further intensified in association with post-fire salvage logging. This finding, while non-quantitative, is in general agreement with the results discussed above for other humic-descriptive metrics (UV_{254}, SUVA, HPO), DOC concentration, and THM-FP.

The fluorescence index (FI) has been introduced to summarize key aspects of large data sets of FEEMs and is predominantly associated with NOM aromaticity. The FI is reported to correlate well with aromaticity with FI around 1.4 and 1.9 being representative of terrestrially derived fulvic acids and microbially derived fulvic acids, respectively (McKnight et al., 2001b; Rodríguez et al., 2014). This metric was investigated herein as a potential descriptor of source water treatability risks (THM-FP) after wildfire and salvage logging. Unfortunately, it did not meaningfully or reliably indicate impacts of land disturbance by wildfire and post-fire salvage logging on water quality and drinking water treatability. Its lack of relevance here is directly attributable to the lack of florescence at the associated wavelengths of importance (McKnight et al., 2001b), across a relatively large range of DOC concentrations (Table 4-2). Moreover, no significant trends in FI following wildfire or post-fire salvage logging were detected (Figure 4-2g; Table 4-2).

4.5 Implications for Drinking Water Treatability

Wildfire and salvage logging play important roles in changing the character of DOC and forming more reactive compounds (humics) that contribute to drinking water treatability risks (formation of regulated DBPs). Spatial and temporal variability in the watersheds can substantially affect DOC, its fractions, and reactivity. Therefore, the analysis of collective data sets from different locations or times should be conducted cautiously as they do not necessarily result in consistent and informative correlations. The analysis of DOC and UV_{254} were found to be useful in describing the changes in water quality and potential formation of regulated DBPs after wildfire and salvage logging. These analyses are relatively rapid, inexpensive, and informative. The operationally-defined hydrophobic fraction, as isolated by resin fractionation, can be a good indicator of the formation of regulated DBPs. However, the complexity and labour intensiveness of this method may limit its application and preclude it from being developed as a real-time technique in its present format. LC-OCD was particularly useful for informing treatability challenges that are not DBP-FP or coagulant demand-associated, including the potentials for membrane fouling and microbial regrowth in the distribution system; however, these relationships must still be further developed. DOC characterization by FEEM (especially changes in humic and fulvic acid-like substances) was qualitatively indicative of risks to drinking water treatability after land disturbances. Research to improve quantitative interpretation of this method is ongoing, but reliable quantitative analysis is as of yet unavailable; thus, its utility to the drinking water industry is presently limited. Ultimately, the choice of appropriate NOM characterization method(s) depends on the application and objectives of the analysis, equipment availability, and time.

Table 4-2. FI in streams draining unburned, burned, and post-fire salvage logged watersheds.

Date	Condition	Stream	Adjusted Wavelength Ext. 370		FI
			Emm. 450	Emm. 500	
Apr-13	Unburned	Star	21.12736893	10.10163116	2.09
	Unburned	North York	51.2986412	39.57427979	1.30
	Burned	South York	82.71910858	53.2678833	1.55
	Burned	Lynx	96.74668884	74.03311539	1.31
	Burned and Salvage logged	Drum	-50.35267639	-84.0299683	n.q*.
	Burned and Salvage logged	Lyons East	-196.4923706	-253.629303	n.q.
	Burned and Salvage logged	Lyons West	-37.15408325	-93.0406189	n.q.
May-13	Unburned	Star	-37.15408325	-93.0406189	n.q.
	Unburned	North York	21.74746704	5.10023499	4.26
	Burned	South York	44.35157013	24.6999054	1.80
	Burned	Lynx	-28.31297302	-40.80988312	n.q.
	Burned and Salvage logged	Drum	36.36485291	18.25868225	1.99
	Burned and Salvage logged	Lyons East	24.67346191	-12.19561768	n.q.
	Burned and Salvage logged	Lyons West	-29.02978516	-59.80400085	n.q.
Jul-13	Unburned	Star	7.81465149	-2.1060276	n.q.
	Unburned	North York	-	-	-
	Burned	South York	2.17144394	-6.50406265	n.q.
	Burned	Lynx	5.1031456	-3.93083572	n.q.
	Burned and Salvage logged	Drum	17.77527618	4.57972336	3.88
	Burned and Salvage logged	Lyons East	185.5371704	143.9020538	1.29
	Burned and Salvage logged	Lyons West	56.75753784	29.73249054	1.91
Sep-13	Unburned	Star	56.75753784	29.73249054	1.91
	Unburned	North York	-11.32582474	-19.26108551	n.q.
	Burned	South York	52.02320099	33.71346283	1.54
	Burned	Lynx	41.6676178	26.08548737	1.60
	Burned and Salvage logged	Drum	57.56787872	37.21660614	1.55
	Burned and Salvage logged	Lyons East	173.6407471	128.4358978	1.35
	Burned and Salvage logged	Lyons West	173.6407471	128.4358978	1.35
Apr-14	Unburned	Star	16.40093231	7.97731781	2.06
	Unburned	North York	-15.16821289	-20.98073959	n.q.
	Burned	South York	68.80652618	48.03305054	1.43
	Burned	Lynx	53.30444717	36.24378586	1.47
	Burned and Salvage logged	Drum	76.57413578	51.8984251	1.48
	Burned and Salvage logged	Lyons East	179.3233957	139.5700941	1.28
	Burned and Salvage logged	Lyons West	190.1952372	138.4262495	1.37

Date	Condition	Stream	Adjusted Wavelength Ext. 370		FI
			Emm. 450	Emm. 500	
May-14	Unburned	Star	-399.7931185	-417.4728546	n.q.
	Unburned	North York	0.864886285	-14.87950898	n.q.
	Burned	South York	76.03270245	57.34004974	1.33
	Burned	Lynx	81.03791714	60.63693619	1.34
	Burned and Salvage logged	Drum	-76.2499056	-95.40599824	n.q.
	Burned and Salvage logged	Lyons East	93.21375561	59.25078583	1.57
	Burned and Salvage logged	Lyons West	51.08024884	20.68382263	2.47
Jul-14	Unburned	Star	19.92752361	11.56298828	1.72
	Unburned	North York	4.09066486	-1.47730065	n.q.
	Burned	South York	-68.00599384	-73.23635483	n.q.
	Burned	Lynx	-6.49948597	-14.56195069	n.q.
	Burned and Salvage logged	Drum	30.61425305	17.71652603	1.73
	Burned and Salvage logged	Lyons East	67.33809185	40.77895736	1.65
	Burned and Salvage logged	Lyons West	49.87035656	31.37241745	1.59
Aug-14	Unburned	Star	-17.04513455	-25.18676377	n.q.
	Unburned	North York	-41.65909481	-46.29571152	n.q.
	Burned	South York	-25.18397045	-34.16797257	n.q.
	Burned	Lynx	-10.53387737	-18.83232117	n.q.
	Burned and Salvage logged	Drum	-26.93468762	-38.34539032	n.q.
	Burned and Salvage logged	Lyons East	91.38648319	63.89580917	1.43
	Burned and Salvage logged	Lyons West	41.64270115	20.00578689	2.08
Sep-14	Unburned	Star	-104.7947045	-114.2555485	n.q.
	Unburned	North York	-41.12949753	-49.08831215	n.q.
	Burned	South York	11.6810112	-2.885347365	n.q.
	Burned	Lynx	45.8753624	34.45617867	1.33
	Burned and Salvage logged	Drum	58.66978074	35.72951317	1.64
	Burned and Salvage logged	Lyons East	110.6998863	85.37017632	1.30
	Burned and Salvage logged	Lyons West	151.0780067	115.5058651	1.31
Oct-14	Unburned	Star	82.67550278	73.8305092	1.12
	Unburned	North York	69.96163178	60.42644884	1.16
	Burned	South York	189.7893524	167.0474091	1.14
	Burned	Lynx	160.0444565	136.1360245	1.18
	Burned and Salvage logged	Drum	98.4134903	86.23725511	1.14
	Burned and Salvage logged	Lyons East	206.1051559	166.2135391	1.24
	Burned and Salvage logged	Lyons West	211.7272034	175.0636749	1.21

* n.q. = not quantifiable

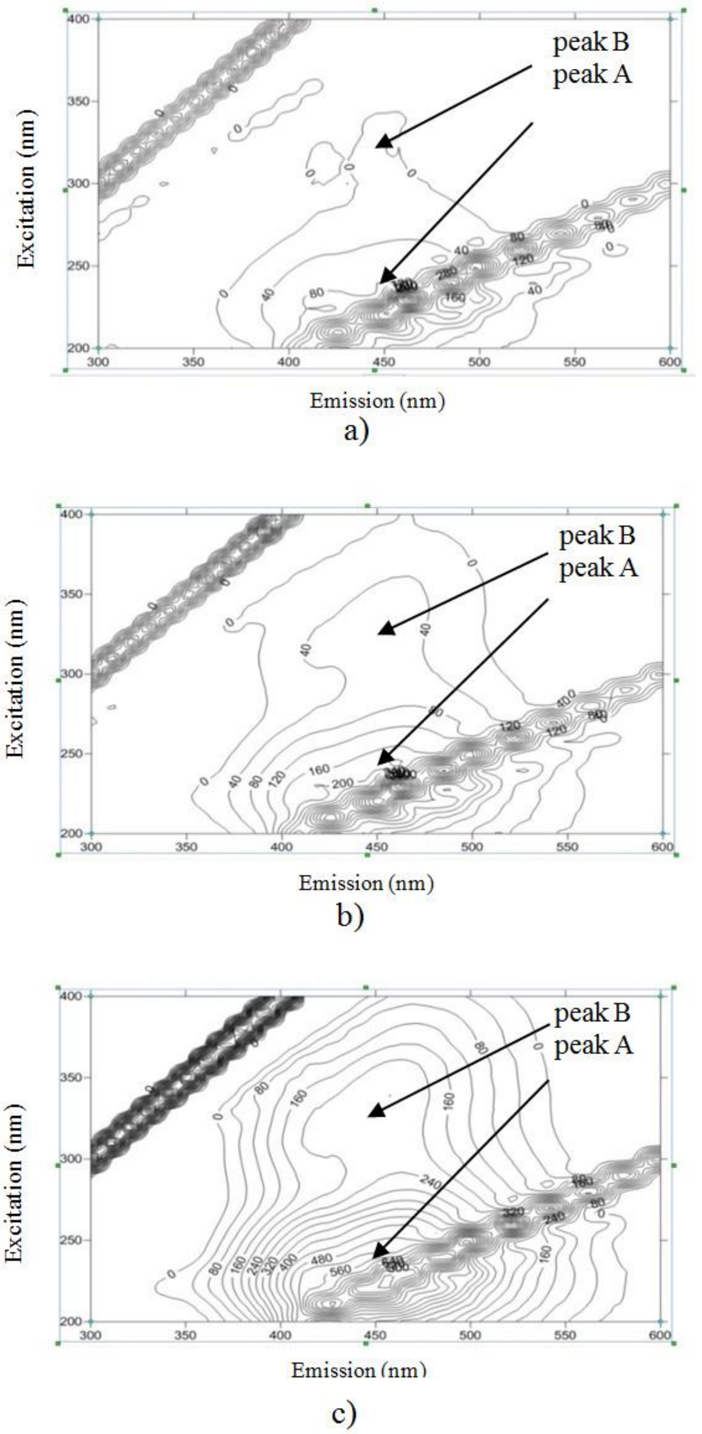


Figure 4-4. FEEM intensity plots for representative (a) unburned, (b) burned, and (c) post-fire salvage logged watersheds.

Chapter 5

Mass-Based Weighting of Surrogates for Organic Matter Enhances Prediction of Trihalomethane Formation Potential

5.1 Overview

A comprehensive understanding of dissolved organic carbon (DOC) character and identification of metrics that effectively and efficiently predict disinfection by-product (DBP) formation potential (DBP-FP) can help in developing strategies to control DBP precursors in source waters and minimize the formation of DBPs during drinking water treatment. Here, raw and treated waters from two diverse systems were comprehensively analyzed to investigate simple strategies for enhancing predictions of trihalomethane formation potential (THM-FP) as a function of DOC character. Raw water samples were collected from disturbed (wildfire-impacted) watersheds in the eastern slopes of the Rocky Mountains of south-western Alberta. Treated water was collected from different treatment stages at the Mannheim water treatment plant, in Kitchener, Ontario—the source water for this plant is the agriculturally-, municipally-impacted Grand River. Several DOC characterization metrics were compared and their direct relationship to THM-FP was examined. THM formation potential- (THM-FP), DOC-, and aromaticity-associated parameters including UV_{254}, SUVA, and hydrophobic (HPO) and humic substances (HS) fractions were evaluated. As expected, metrics indicative of aromatic compounds were good predictors of THM-FP in general; however, the prediction precision of HS and HPO fractions was enhanced (especially HS) when expressed as mass-based parameters (absolute quantities) as opposed to fractions or ratios of DOC (relative quantities). Thus, the use of a mass-based weighting approach for reporting NOM fractionation data is recommended for further exploration and use in discussing and evaluating NOM-related implications to drinking water treatability.

5.2 Introduction

Reactions of different types of aquatic organic matter with chlorine and other disinfectants (chloramines, chlorine dioxide, and ozone) result in the formation of various classes of DBPs (Richardson, 1998; Krasner et al., 2006), many of which are considered to be 1) cytotoxic, genotoxic or carcinogenic in laboratory animals (Plewa et al., 2002; Woo et al., 2002; Plewa et al., 2004) and 2) potential public health risks (Richardson et al, 2002; WHO, 2006). THMs and HAAs are regulated worldwide (WHO, 2006; Health Canada, 2008; USEPA, 2012) as the most prevalent DBPs whose removal is considered to be representative of the removal of other chlorinated DBPs (WHO, 2006), which may be of greater health significance, but typically are present at lower concentrations in treated drinking water (Richardson, 2011). Formation of DBPs depends on the amount and composition of NOM, as well as the disinfectant type and conditions (Krasner et al., 2006; Krasner, 2009). Increased levels of DBPs of regulatory concern are one of the most significant drinking water treatability challenges associated with source water changes in DOC associated with (natural and/or anthropogenic) landscape disturbance. Therefore, an understanding of the relationship between DOC character and DBP formation potential (DBP-FP) is critical to identifying and controlling DBP precursor concentrations in source waters and optimizing water treatment processes to minimize DBP formation.

Numerous studies have focused on establishing relationships between DOC character and the formation of regulated DBPs. The spatial and temporal variability of NOM often result in site-specific outcomes; however. Even when significant correlations are found they are not maintained at broader spatial or temporal scales (Edzwald et al. 1985; Collins et al. 1986; Reckhow and Singer, 1990; Reckhow et al. 1990; Singer, 1999; Bolto et al., 2002; Kitis et al. 2002; Goslan et al., 2004; Ates et al., 2007; Bougeard et al., 2010). Not surprisingly, no universal predictors for DBP-FP have been identified. Notably, most such investigations have focused on untreated or source water characterization of relationships between DBP-FP and NOM. In contrast, very few investigations have reported the effects of various treatment processes on concurrent changes in DOC character and concentration; of these, most have not comprehensively characterized changes in NOM by using multiple metrics concurrently. To make decisions regarding investments in either source water protection strategies or in-plant treatment infrastructure upgrades, drinking water utilities must understand both the source water DBP-FP implications of landscape disturbances and plant capacities to remove those DBP-FPs through the specific treatment processes—reliable and relatively inexpensive proxy indicators for anticipating/predicting regulated DBP-FPs are critical to enabling these decisions.

Aromatic compounds are known to be the main reactive fractions of DOC that contribute to the formation of regulated carbonaceous DBPs, including THMs (Singer, 1999; Kitis et al., 2002). The most common metrics that describe DOC aromaticity are UV_{254}, SUVA, hydrophobic (HPO) compounds, and humic substances (HS). All of these metrics are operationally-defined and differ from one another. The most common techniques for isolation and description of HPO and HS are resin fractionation (Leenheer, 1981; Thurman and Malcolm 1981; Leenheer and Noyes, 1984; Collins et al., 1986; Aiken et al., 1992; Malcolm and MacCarthy, 1992; Kitis et al., 2002; Chow et al., 2004) and liquid chromatography (Bolto et al., 1999; Croué, 2004; Baghoth et al., 2009; Huber et al., 2011), respectively. Notably, the units that have been used to report these fractions (as well as other operationally-defined fractions) are also varied; these fractions have been reported as both relative values (ratios and/or fractions of DOC) (Aiken et al., 1992; Malcolm and McCarthy, 1992; Carrol et al., 2000; Fan et al., 2001; Kitis et al., 2002; Croué, 2004; Goslan et al., 2004; Kim and Yu, 2005; Gray et al., 2007; Baghoth et al., 2009; González et al., 2013; Penru et al., 2013; Al Juboori et al., 2016; Urbanowska and Kabsch-Korbutowicz, 2016) and mass-based absolute values (Malcolm and McCarthy, 1992; Carrol et al., 2000; Lin et al., 2000; Marhaba et al., 2003; Chow et al., 2004; Kennedy et al., 2005; Liu et al., 2008; Harhoff et al., 2010; Jiang et al., 2011; Wassink et al., 2011; Lamsal et al., 2012; Jeong et al., 2013; González et al., 2013; Penru et al., 2013; Tian et al., 2013; Rahman et al., 2014; Han et al., 2015). While HPO typically is reported as a relative fraction of DOC, HS has been reported as both a relative and mass-based absolute quantity. The rationale for these reporting decisions has not been clearly explained, discussed, or compared.

The purpose of this study was to investigate the linear relationship between THM-FP and the aromatic fractions of DOC (which is generally understood to be a directly proportionality) to identify opportunities to improve their performance as THM-FP predictors (proxy indictors). THMs are formed because of chemical reactions between disinfectants and different constituents/fractions of DOC and THM concentrations are directly proportional to precursor concentrations. Accordingly, least squares linear regression analysis has been widely used to describe relationships between DBPs and potential proxy indicators such as DOC concentration (Edzwald et al., 1985; Reckhow and Singer, 1990; Singer, 1999; Goslan et al., 2004; Ates et al., 2007; Wassink et al., 2011). This method assumes that source data are normally distributed and independent, with linearity of the residuals and variables (Walpole et al., 2013). Here, HPO and HS were evaluated as relative (fractions) and absolute (mass-based concentration) quantities because both approaches to data reporting are commonly found in the literature, but specific guidance regarding optimal approaches for reporting these data is lacking. These data were then compared based on their potential to predict regulated THM-FPs. These relationships were also compared to those obtained using other metrics (UV_{254} and SUVA) of NOM aromaticity. Recognizing that it is unlikely that a single, directly-measured universal precursor for DBP-FP will ever be identified based exclusively on one descriptor of the structural characteristics of NOM, it is critical that the metrics that are utilized and reported as proxy indicators for DBP-FP describe as much of the response variability as possible (i.e., highest possible coefficient of determination [R^2]) because these will correspond to most precise predictions. Accordingly, the concurrent evaluation of multiple metrics of NOM character will 1) provide the most precise simple predictors of NOM reactivity and 2) enable the most efficient development of multivariate models for better predicting NOM reactivity. This type of comparative analysis is critical for identifying the most useful metrics for prediction of THMs and optimization of strategies to limit the drinking water treatment challenges associated with their formation.

5.3 Materials and Methods

5.3.1 Data

Two very different types of source water datasets were utilized in this investigation: high quality reference and wildfire-impacted raw/source water data from the Rocky Mountains (discussed in Chapter 3) and treated water originating in an agriculturally municipally impacted source watershed (Chapter 2). These datasets were selected to explore broadly relevant opportunities for improving THM prediction based solely on the quantitative data utilized. Specifically, common reporting practices of relative fractions of DOC (as percentages) and absolute quantities (mass-based concentration) were compared.

As previously reported (Shams et al., 2014), raw water was collected from disturbed (wildfire-impacted) watersheds in the eastern slopes of the Rocky Mountains of south-western Alberta. The samples were collected from streams draining burned, unburned, and post-fire salvage logged watersheds (Shams et al., 2014; Bladon et al., 2008; Silins et al., 2009) and reflected a full range of discharge conditions (baseflow, stormflow, and freshet) (Bladon et al., 2008; Silins et al., 2009). As it is commonly recognized that aquatic DOC concentrations and characteristics depend on watershed hydrological and biogeochemical processes, (Aiken and Cotsaris, 1995; Fabris et al., 2008; Krasner et al., 1996; Leenheer and Croué, 2003; Owen et al., 1995), and temperature (Leenheer and Croué, 2003), only a subset of the data collected during this thesis research were utilized. Specifically, the data collected from the reference, burned, and post-fire salvage logged catchments in 2014 were grouped and utilized in the present investigation. This was done to 1) ensure an adequate number and range of observed values, 2) focus the investigation on identifying opportunities for improving THM prediction based solely on the quantitative data utilized, and 3) exclude the need for analysis of other factors that contribute to spatial and temporal variability in DOC-associated proxies for THM-FP (Edzwald et al., 1985; Collins et al., 1986; Reckhow and Singer, 1990; Reckhow et al., 1990; Singer, 1999; Bolto et al., 2002; Kitis et al., 2002; Goslan et al., 2004; Ates et al., 2007; Bougeard et al., 2010; Pellerin et al., 2012; Spencer et al., 2008)—while this later topic is certainly important, it is well outside of the scope of the present investigation.

The treated water was collected from different treatment stages at the Mannheim Water Treatment Plant (WTP), in Kitchener, Ontario—the source water for this plant is the agriculturally-, municipally-impacted Grand River. Mannheim WTP is a conventional WTP that includes chemical pre-treatment (coagulation, flocculation, and sedimentation), ozonation, biological filtration, UV irradiation, and chloramination. More information on the intake water characteristic and the treatment processes at the Mannheim WTP can be found in Shams et al., (2015). The samples used herein were collected at the WTP intake, post-clarification, post-ozonation, and the effluents of two parallel filters. Eight sampling events were conducted over an eight-month period starting in November 2014.

5.3.2 Analytical Methods

The methods used to characterize NOM concentrations and reactivity and DBP-FP were previously reported (Shams et al., 2014 and 2015). In brief, THM-FP was analyzed based on Standard Methods (Methods 5030B and 8260C; APHA et al., 2012) using GC/MS (Purge and Trap) on an Agilent Technologies 7890B -MS/5977A. DOC concentrations were measured as per Standard Methods (Method 5310B; APHA et al., 2012) using a Shimadzu TOC-VCPH TOC analyzer. UV_{254} was analyzed using a Hewlett-Packard 8453 spectrophotometer with a 1 cm quartz cell (Method 5910 B; APHA et al., 2012). SUVA was calculated as the measured UV_{254} divided by the DOC (L/mg.m) (Edzwald and Van Benschoten, 1990). Resin fractionation using Amberlite XAD-8® was utilized to isolate hydrophobic and hydrophilic fractions as described by Kitis et al. (2002). Liquid chromatography–organic carbon detection (LC-OCD) was used to characterize humic substances (HS) fraction as defined by Huber et al. (2011). This technique employs a weak cation exchange column (250 mm × 20 mm, TSK HW 50S, 3000 theoretical plates) followed by a UV_{254} detector (UVD), an organic carbon detector (OCD), and an organic nitrogen detector (OND). ChromCALC, DOC-LABOR data processing software was used to quantify the fractions (Huber et al., 2011).

5.3.3 Statistical Analysis

Predictions of THM-FP using NOM character were investigated using simple least squares linear regression. The significance and precision of the regression models were evaluated using customary approaches (i.e., *p* values obtained from ANOVA [Appendix A] and coefficients of determination [R^2], respectively). Diagnostic residual plots (Appendix B) were utilized to ensure that the assumptions of ANOVA were not violated.

5.4 Results and Discussion

Correlations between THM-FP, DOC, and aromaticity metrics were investigated previously for the raw and treated water datasets used in herein (Shams et al., 2014 and 2015). In those previous studies, HS was reported and analyzed in a mass-based absolute quantity (concentration in mg/L) because it is the most commonly used unit reported for this metric. On the other hand, HPO is most commonly reported and analyzed as a fraction of DOC (%); thus, HPO was reported as a relative quantity (%). Here, the utility of these metrics as potential THM-FP proxy indicators was evaluated—both absolute and relative quantities (i.e. mass-based concentration vs fractions) were directly compared to identify opportunities for better prediction of THM-FP.

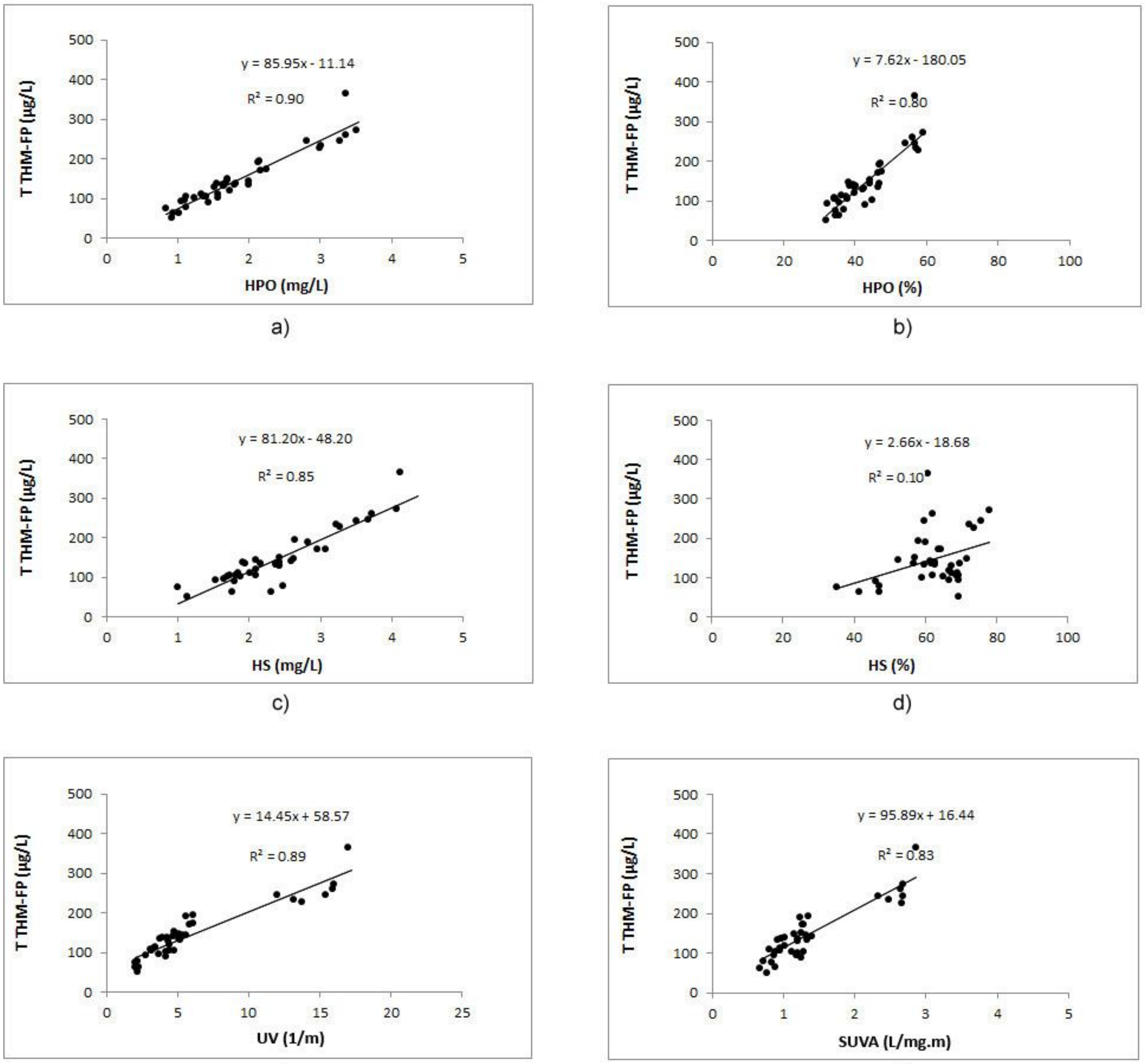
5.4.1 HPO Concentration vs HPO Fraction

Hydrophobic compounds are usually measured as relative quantities (fractions of DOC) and reported as a percentage (%). Reasonably good correlations between HPO and regulated DBPs have been reported (Collins et al., 1986; Kitis et al., 2002; Liang and Singer, 2003; Soh et al., 2008; Shams et al, 2014 and 2015). Here, HPO was calculated in both mass-based concentration (mg/L) and fraction (%) units and the associated prediction of THMFP was evaluated (Table 5-1; Figures 5-1 and 5-2) for the Mannheim WTP and Rocky Mountain datasets. Table 1 summarizes the coefficient of determination (R^2) for prediction of THM-FP using aromaticity metrics. The regression results for the Rocky Mountain watershed are presented in Figure 5-1 and the corresponding regression results for the Mannheim WTP are presented in Figure 5-2. As shown in the table and figures, THM-FP correlated well with HPO in general and regression was statistically significant ($p = 10^{-19}$ and $p = 10^{-2}$), thereby highlighting the utility of this metric as a potential proxy indicator for THM-FP in both source and treated waters, respectively. Notably, the model precision described by the R^2 improved substantially when HPO was analyzed as a mass-based parameter (mg/L); specifically it increased from 0.8 to 0.9 and from 0.83 to 0.89 for the Mannheim WTP and Rocky Mountain data sets respectively (Table 1; Figures 5-1 and 5-2). This improvement is likely because scaled data can increase measurement errors, thereby decreasing the statistical power of regression analyses. Scaling methods, also known as data normalization, are approaches in which data points are divided by a scaling factor to so that they can be compared to one another (van den Berg et al., 2006). Here, the DOC concentration in the hydrophobic fraction is the measured quantity—the relative fraction (%) that is hydrophobic (HPO %) is normalized by the measured

DOC concentration prior to fractionation. Thus, the relative fraction (%) of DOC that is hydrophobic (HPO %) is subject to additional measurement errors associated with DOC measurement. These can vary substantially and are especially relevant at low DOC concentrations, such as those that were regularly observed in the Rocky Mountain watersheds (Shams et al., 2017).

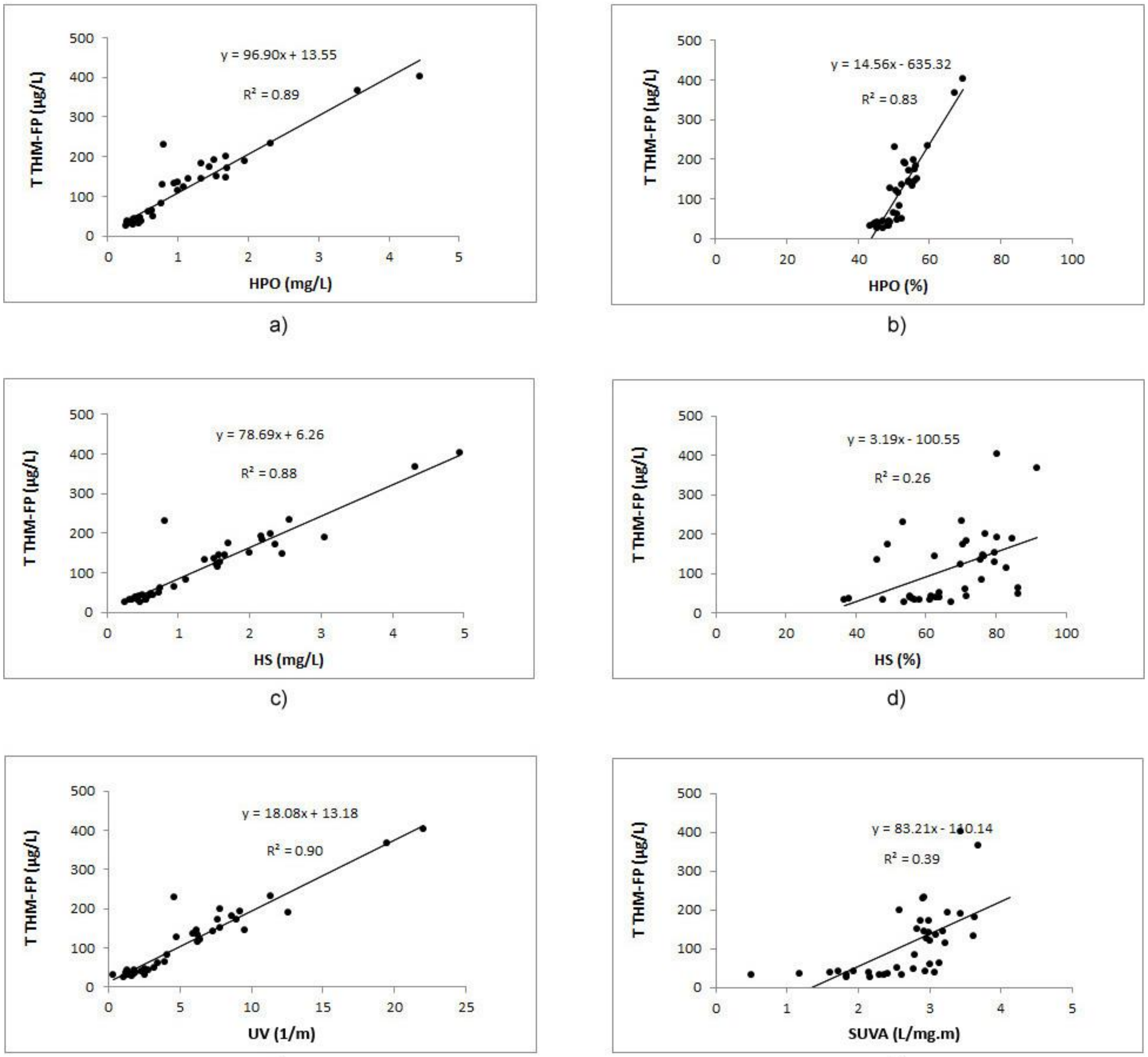
Table 5-1. Regression significance (*p* value) and prediction precision (R^2) between THM-FP and various metrics of NOM aromaticity.

		HPO (mg/L)	**HPO** (%)	**HS** (mg/L)	**HS** (%)	**UV_{254}** (m^{-1})	**SUVA** (L/mg.m)
Mannheim WTP (n = 38, p-value < 0.05)	**THM-FP** (µg/L)	0.90	0.80	0.85	0.10	0.89	0.83
Rocky Mountain 2014 (n = 38, p-value < 0.01)	**THM-FP** (µg/L)	0.89	0.83	0.88	0.26	0.90	0.39



a) b) c) d) e) f)

Figure 5-1. Linear regression between THM-FP and a) HPO (mg/L) , b) HPO (%), c) HS (mg/L), d) HS (%), UV (m^{-1}), and SUVA (L/mg.m) for the Mannheim WTP data set.



a) b) c) d) e) f)

Figure 5-2. Linear regression between THM-FP and a) HPO (mg/L) , b) HPO (%), c) HS (mg/L), d) HS (%), UV (m^{-1}), and SUVA (L/mg.m) Rocky Mountain data set.

5.4.2 HS Concentration vs HS Fraction

Humic substances are known as reactive compounds that are precursors for regulated DBPs (Collins et al. 1986; Reckhow et al., 1990; Singer, 1999; Liang and Singer, 2003). Correlations between HS and regulated DBPs have been reported (Wassink et al., 2011; Shams et al., 2014 and 2015). Here, the HS fractions obtained in samples from the Mannheim WTP and Rocky

Mountain watersheds also were analyzed in both mass-based concentration (mg/L) and fraction (%) units and the associated prediction of THM-FP were evaluated (Table 5-1; Figures 5-1 and 5-2). As shown in Table 5-1 and Figures 5-1 and 5-2 (supported by Table A-3, Appendix A and Figure B-3 and B-4, Appendix B), although regression was significant ($p = 5\times10^{-2}$ and $p = 7\times10^{-4}$), the correlations between THM-FP and HS when HS was measured as a fraction of DOC were very poor ($R^2 = 0.1$ and 0.26 for data obtained at the Mannheim WTP and Rocky Mountain watersheds, respectively). In contrast, when the absolute quantity of HS was not divided by DOC concentration and was used in the regression analysis as a mass-based concentration (mg/L), very precise, substantially improved correlations between it and THM-FP were identified; specifically, $R^2 = 0.85$ and 0.88 for the Mannheim WTP and Rocky Mountain watersheds, respectively. This result is consistent with the results observed for HPO and confirms the importance of data preprocessing and the advantage of using mass-based values for regression analysis.

5.4.3 UV_{254} vs SUVA

Although this work demonstrated mass-based weighting enhanced the utility of HPO and HS fractions of NOM as proxy indicators for THM-FP (Table 5-1, Figures 5-1 and 5-2), it is important to put those improvements in context relative to other common NOM aromaticity-based proxy indicators. UV_{254} is the most commonly used metric for describing NOM aromaticity. This analysis is relatively simple, fast, and inexpensive; it can also be done online. In addition, it has been shown to be a particularly good proxy indicator for the formation of regulated DBPs (Singer et al., 1981; Edzwald et al., 1985; Reckhow et al., 1990; Wassink et al., 2011; Awad et al., 2016; Shams et al., 2014 and 2015). However, UV_{254} has some important limitations, including inconsistencies at low and high concentrations due to low signal and saturation problems, respectively (Soovali et al., 2006).

The concept of specific UV absorbance (SUVA) was introduced by Edzwald and co-workers (Edzwald et al., 1985; Edzwald and Van Benschoten, 1990) as a way of scaling UV_{254} values (by dividing them by DOC) to analyze and compare the water aromaticity in different sources. The guidelines for use of SUVA in describing aromaticity/hydrophobicity were further modified and simplified comparison of NOM aromaticity between samples (Edzwald and Tobiason, 1999). The utility of SUVA as a THM-FP predictor has been widely investigated and has resulted in good, precise correlations in some cases (Reckhow et al. 1990; Kitis et al. 2001), but not in others (Goslan et al., 2004; Bougeard et al., 2010; Hua et al., 2015). The lack of consistently precise correlation has been especially observed in low aromaticity waters (SUVA < 2) (Ates et al., 2007; Li et al., 2014).

As shown in Table 5-1 and Figures 5-1 and 5-2, the relationship between UV_{254} and THM-FP was significant ($p = 5 \times 10^{-19}$ and 2×10^{-20}) and precise ($R^2 = 0.89$ and 0.9) for both the Mannheim WTP and Rocky Mountain watershed datasets, respectively. In contrast, while the relationship between SUVA and THM-FP was significant ($p = 6 \times 10^{-16}$ and 2×10^{-5}) for both the Mannheim WTP and Rocky Mountain watershed datasets, respectively, it was only precise for the Mannheim WTP dataset, but not for the Rocky Mountain watersheds ($R^2 = 0.39$). This difference is consistent with the reported literature discussed above (Goslan et al., 2004; Bougeard et al., 2010; Ates et al., 2007; Li et al., 2014; Hua et al., 2015) and is likely attributable at least in part to the relatively low DOC concentrations and SUVA values observed in the Rocky Mountain watersheds.

5.5 Summary

Overall and as expected, NOM metrics indicative of aromatic compounds were significant and reasonably precise predictors of THM-FP in general; however, the prediction precision of HPO and HS fractions (especially HS) was substantially enhanced when expressed as mass-based parameters (absolute quantities) as opposed to fractions or ratios of DOC (relative quantities). Thus, the use of a mass-based weighting approach for reporting NOM fractionation data is recommended for further exploration and use in discussing and evaluating NOM-related implications to drinking water treatability. Although it may not be the case for the specific data used herein, it should be be noted that despite these improvements, the relationships between DBP-FP and various NOM-associated proxy indicators can be quite variable spatially and temporally, and frequently site specific, thereby suggesting that other hydrological and/or biogeochemical factors may contribute to observed differences in these relationships.

Moreover, it is worth noting that despite the continued development and promotion of various proxy indicators for describing NOM reactivity, UV_{254} offered the best combination ease of use, and precision in prediction of THM-FP.

Chapter 6

Comprehensive Characterization of NOM Concentration and Character after Contemporary Forest Harvesting: Implications to Drinking Water Treatability

6.1 Overview

The value of natural storage and filtration of water by global forests has been estimated at $4.1 trillion (US)—this is in part because of the critical role that healthy forests play in the provision of high quality source waters for potable water production. Over the past 15 years, 7-fold increases in the size and severity of the largest wildfires have occurred in western Canada and globally, in part because of climate change. As a result, many utilities and governments are looking to forest harvesting as a source water protection tool for pre-emptive risk reduction. While forests are managed for many purposes, they are not widely managed for protection of drinking water supplies. Here, three sub-watersheds (within one watershed) were harvested in 2015, using: clear-cutting with patch retention, strip-shelterwood cutting, and partial cutting. All possible best management practices (BMPs) were followed to minimize disturbance impacts on water quality. Changes in DOC concentration and character and their relationships to regulated DBP-FPs (THM-FPs and HAA-FPs) were comprehensively characterized using multiple natural organic matter (NOM) characterization techniques during the two years during and immediately after forest harvesting in the eastern slopes of the Rocky Mountains in south-western Alberta. Several NOM fractions also were characterized by LC-OCD during the first year to inform the relative potential for membrane fouling and microbial regrowth in distribution systems. Samples were collected during the dominant regional streamflow regimes. Notably, no impacts of forest harvesting on water quality and treatability were observed during the harvest and first post-harvest years. Thus, this work suggests that forest harvesting with careful implementation of BMPs for erosion control may mitigate the potentially catastrophic impacts of wildfire on drinking water treatability without significantly compromising it.

6.2 Introduction

The value of natural storage and filtration of water by global forests has been estimated at $4.1 trillion (US) (Costanza et al, 1997). The drinking water for at least 58% of the largest urban communities in Canada (Stone et al, 2011) and 66% of American water supplies (Stein and Butler, 2004) originates in forested watersheds. Ironically, the high quality of water from healthy forested regions makes these supplies particularly vulnerable to deterioration, which is often associated with either natural or anthropogenic landscape disturbances. For example, wildfires release significant amounts of sediment (Kunze and Stednick, 2006; Silins et al, 2009), nutrients (Ranalli, 2004; Bladon et al, 2008; Aiken et al., 2011; Emelko and Sham, 2014), heavy metals (Kelly et al, 2006), and other contaminants (Kalabokidis, 2000; Crouch et al, 2006) to receiving waters. Forest harvesting can similarly deteriorate water quality (Stottlemyer and Troendle, 1992; Duncan, 1999; Ice and Stednick, 2004; Stednick, 2008). Variability in impact severity has been attributed to the range of harvesting practices and management intensity, as well as hydro-climatic and geological setting (Corner et al, 1996; Kreutzweiser and Capell, 2001; Ice and Stednick, 2004). While previous research provides some insights, it largely reflects impacts of historic forest management practices no longer used (Anderson and Lockaby, 2011). Recent work (Emelko et al, 2015a) and drinking water utility experience (Sham et al, 2013; Emelko and Sham, 2014) have demonstrated that global increases in wildfire threaten drinking water security by challenging water treatment processes beyond their capacity, necessitating potentially cost-prohibitive treatment changes to ensure provision of safe drinking water (Emelko et al, 2011; Sham et al, 2013; Bladon et al, 2014; Emelko et al, 2015a). These threats are particularly relevant for small systems (Emelko et al, 2011; Emelko et al, 2015a) and sediment-rich regions with gravel bed rivers—like western Canada—in which the storage and release of fine sediment and associated contaminants can lead to significant long-term drinking water treatment challenges (Emelko et al, 2015b). Notably, severe disturbance impacts on water may extend far downstream at larger basin scales (Stone et al, 2011; Allin et al, 2012; Stone et al, 2014; Emelko et al, 2015b).

Over the past 15 years, 7-fold increases in the size and severity of the largest wildfires have occurred in western Canada (Flannigan et al, 2009) and globally, in part because of climate change (Bladon et al, 2014; IPCC. 2014). As a result, forest harvesting is often utilized for pre-emptive risk reduction (Stephens et al, 2012; Rocca et al, 2014). While forests are managed for many purposes, they are not widely managed for protection of drinking water supplies. Water suppliers are increasingly interested in using fuel management for this purpose, however (Emelko and Sham, 2014). For example, recent catastrophic wildfire led to the Denver Water-U.S. Forest Service co-investment of >$49M to re-establish forest management strategies (thinning/fuel management) to mitigate future risks to water supplies; notably, these activities are partially funded by increased water rates (Sham et al., 2013). Forest harvesting is also the primary tool used to manage wildfire risks in Canada, but it also can impact water supplies (Gadgil, 1998).

Although the impacts of wildfire (Bladon et al, 2014) and forest harvesting (Binkley and Brown, 1993; Feller, 2005) on water (including water quality) have been well studied, little if any of that research has focused on impacts to drinking water treatability. At a minimum, these assessments involve evaluation of source water turbidity and dissolved organic carbon (DOC) concentrations because they are the main water quality drivers of treatment infrastructure and operational requirements/costs (MWH, 2005; Emelko et al., 2011). While increased solids/turbidity loads to treatment plants result in obvious removal needs, DOC has several less obvious implications. It is typically present at low concentrations in forested watersheds and increases and/or changes in character (e.g. aromaticity, hydrophilicity/hydrophobicity) as a result of landscape disturbance (O'Donnell et al, 2010; Aiken et al, 2011; Emelko and Sham, 2014; Emelko et al., 2015). Increases in DOC may necessitate the use of complicated and costly chemical pretreatment or increase chemical coagulant demand (MWH, 2005; Emelko et al., 2011; Hohner et al., 2016). Hydrophobic natural organic matter (NOM) is a reactive precursor of regulated disinfection by-products (DBPs) (Singer, 1999; Kitis et al. 2002). Hydrophilic NOM is more difficult to remove by conventional treatment (Kitis et al. 2002; Chow et al, 2004) and forms unregulated DBPs of emerging health concern (Liang and Singer, 2003; Ates et al, 2007; Chen and Westerhoff, 2010). Other treatability challenges associated with increased/changing DOC include increased risk of distribution system regrowth of bacteria (Kaplan et al, 1993); increased disinfectant demand (Amy et al, 1987; Jacangelo et al, 1995);

adverse taste, odor, and color (Amy et al, 1987; Jacangelo et al, 1995); membrane fouling (Lee et al., 2004; Kwon et al., 2005); and increased heavy metal complexation potential (Wu et al., 2004; Waples et al., 2005). Although DOC concentration, DOC hydrophobicity, and DBP-FPs can significantly increase after severe wildfire (Emelko et al., 2011; Writer et al., 2017)—and even more so after post-fire salvage-logging—especially during high discharge events in headwater streams (Emelko et al., 2015), changes in NOM after forest harvesting have not been characterized. Moreover, other harvesting-associated implications to drinking water treatability like relative implications to membrane fouling and microbial regrowth potential in distribution systems also have never been reported.

Here, changes in DOC concentration and character and their relationships to regulated DBP-FPs (THM-FPs and HAA-FPs) were comprehensively characterized using multiple natural organic matter (NOM) characterization techniques during two years (during and immediately after) forest harvesting in the eastern slopes of the Rocky Mountains in south-western Alberta. Several NOM fractions also were characterized by LC-OCD during the former of those years to inform the relative potential for membrane fouling and microbial regrowth in distribution systems. The utility of several DOC metrics for predicting THM-FP was evaluated using linear regression, consistent with previous investigations (Edzwald et al., 1985; Reckhow and Singer, 1990; Singer, 1999; Goslan et al., 2004; Ates et al., 2007; Wassink et al., 2011). These approaches are widely utilized because these DBP precursor materials are generally understood to be directly proportional to the by-products they form.

6.3 Materials and Methods

6.3.1 Study Site and Sampling

This work was conducted as part of the ongoing SRWP in which two watersheds that served as unburned-reference watersheds in Phase 3 were studied. They were fully calibrated for climate, streamflow, and water quality for 11 years [2004-2014]. Three sub-watersheds (within one watershed) were harvested in 2015, using: clear-cutting with patch retention, strip-shelterwood cutting, and partial cutting (Figure 6-1). All possible best management practices (BMPs) were followed to minimize disturbance impacts on water quality. This nested, paired watershed design (BACI; before/after, control/impact) enabled explicit separation of harvesting impacts on hydrology and water quality from background variability produced by seasonal or climatic variation. Here, samples were collected at 8 locations and included an undisturbed (reference) headwaters stream (North York Upper), three headwaters streams draining harvested watersheds (Star McLaren, Star East, and Star West), the confluence of headwaters streams draining harvested watersheds (Star Main), further downstream of this confluence just before it enters the Crowsnest River (Willow), and a downstream river upstream and downstream of harvesting (Crowsnest above and below Star)—these are detailed in Table 6-1. Like in Phase 3, all samples were collected during the dominant regional streamflow regimes (baseflow, snowmelt freshet, and stormflow). Notably, harvesting in these catchments was conducted with careful implementation of best management practices (BMPs) for erosion control to mitigate the potentially catastrophic impacts of wildfire on drinking water treatability without significantly compromising it.

Table 6-1. List and description of the Southern Rockies Watershed Project harvesting research watersheds.

Site Name	**Description**	**Treatment**
North York Upper	Headwaters reference	Reference
Star McLaren	Headwaters harvested	Partial Cut
Star East	Headwaters harvested	Strip Cut
Star West	Headwaters harvested	Clear Cut
Star Main	Headwaters confluence of harvested	Logged (multiple cut types)
Crowsnest Above Star	Downstream reference, upstream of harvesting	Reference
Crowsnest Below Star	Downstream of harvesting	Multiple Cut Types & Prescribed Burn
Willow	Downstream of harvesting	Multiple Cut Types & Prescribed Burn

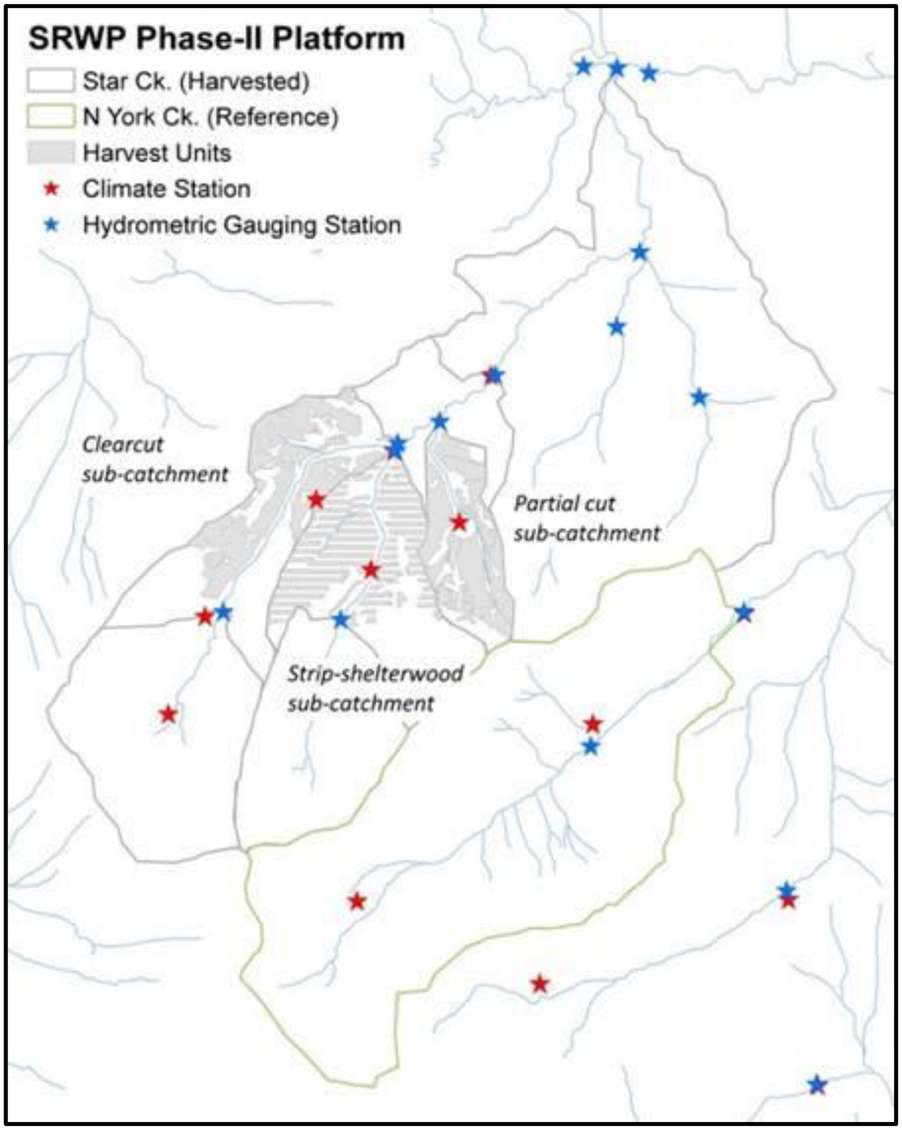


Figure 6-1. Map of the Southern Rockies Watershed Project harvesting research watersheds.

6.3.2 Analytical Methods

Several characterization techniques were employed to analyze and characterize DOC in its whole and fractionated forms. In brief, DOC concentrations were measured based on Standard Methods (Method 5310B; APHA et al., 2012) using a Shimadzu TOC-VCPH TOC analyzer. UV_{254} was analyzed using a Hewlett-Packard 8453 spectrophotometer with a 1 cm quartz cell (Method 5910 B; APHA et al., 2012). Specific ultraviolet absorbance (SUVA) was calculated as the measured UV_{254} divided by the DOC (mg/L·m) (Edzwald et al., 1985). Resin fractionation using Amberlite XAD-8® was utilized to isolate hydrophobic and hydrophilic fractions as described by Kitis et al. (2002). LC-OCD was used to characterize NOM as per the fractions defined by Huber et al. (2011); notably, this particular analysis was only conducted during one of the sampling years (2015). This technique employs a weak cation exchange column (250 mm × 20 mm, TSK HW 50S, 3000 theoretical plates) followed by a UV_{254} detector (UVD), an organic carbon detector (OCD), and an organic nitrogen detector (OND). ChromCALC, DOC-LABOR data processing software was used to quantify different NOM fractions (Huber et al., 2011). Fluorescence analyses were conducted using a Varian Cary Eclipse Spectrofluorometer. FEEMs were analyzed based on the method described by Peiris et al. (2010) and the data were interpreted based on a study by Chen et al. (2003). The excitation and emission ranges used were 200–400 and 300–600 nm, respectively. The FI, defined as the ratio of emission intensity at the wavelength of 450 to that at 500 nm, both at the excitation of 370 nm (McKnight et al., 2001), was also calculated. THM-FPs were assessed based on Standard Methods (Methods 5030B and 8260C; APHA et al., 2012) using GC/MS (purge and trap) on an Agilent Technologies 7890B -MS/5977A. HAA-FPs and NDMA-FP were analyzed on a GC/MS/MS/CI Varian CP3800-MS/MS2000 (Saturn MS Ion Trap) analyzer. The method utilized for HAA-FP analysis was U.S. EPA Method 552.3 (USEPA, 2003). The analysis of NDMA-FP was conducted based on Standard Methods (Method 6410B; APHA et al., 2012) and as per Blaise et al. (1994).

6.3.3 Statistical Analysis

To evaluate the impacts of harvesting on water quality and treatability, a generalization of the standard linear model used in the general linear model (GLM) procedure in SAS/STAT® 9.2

was utilized to apply the method of least squares to fit general linear models to the data (SAS, 2008). Specifically, the MIXED procedure with REML was utilized. In brief, it fits a variety of mixed linear models to data and enables the use of these fitted models to make statistical inferences about the data—the method of restricted maximum likelihood (REML), also known as residual maximum likelihood was implemented to eliminate the effect of nuisance parameters. The generalization of the GLM procedure is that the data are permitted to exhibit correlation and non-constant variability. As described in detail in (SAS, 2008), the parameters of the mean model are referred to as fixed-effects parameters, and the parameters of the variance-covariance model are referred to as covariance parameters. The fixed-effects parameters are associated with known explanatory variables and can be either qualitative (as in the traditional analysis of variance) or quantitative (as in standard linear regression). However, the covariance parameters distinguish the mixed linear model from the standard linear model because they are needed in scenarios such as the one herein in which 1) the experimental units (sub-watersheds) on which the data (NOM and treatability metrics) were measured, could be grouped into clusters (groups of sub-watersheds impacted by a harvesting, regardless of the approach), and the data from a common cluster were correlated (e.g., because of common hydrologic regimes), and 2) repeated measurements (NOM and treatability metrics) were collected on the same experimental unit (sub-watersheds), and these repeated measurements were correlated or exhibited variability that changed. Here, the spatial and temporal variations of repeated measures were not significant. It should be noted that differences in NOM-associated water quality parameters (THM- and HAA-FP, DOC, etc.) were only compared between grouped reference and grouped harvested (i.e., regardless of the specific harvesting approach) datasets because of the limited amount of data available after only one year post-harvest. Future investigations should include comparisons between the harvesting strategies implemented, as well as grouped and ungrouped comparisons to reference streams.

Predictions of THM-FP using NOM character were investigated using simple least squares linear regression. The significance and precision of the regression models were evaluated using customary approaches (i.e., *p* values obtained from ANOVA [Appendix A] and coefficients of determination [R^2], respectively). Diagnostic residual plots (Appendix B) were utilized to ensure that the assumptions of ANOVA were not violated.

6.4 Results and Discussion

No significant changes in THM- (Figure 6-2a) or HAA-FPs (Figure 6-2b) as a result of harvesting were detected (Table 6-2). As would be expected given that bromide has not been detected in the study watersheds, the THM-FP primarily consisted of chloroform (no bromoform was detected). The total THM-FP concentrations observed during this study did not vary much over the two-year investigation, regardless of hydrologic regime. Specifically, the mean concentrations at the North York Upper, Star McLaren, Star East, Star West, Star Main, Crowsnest above Star, Crowsnest below Star, and Willow sampling locations were 35±37, 46±6, 31±5, 30±8, 27±6, 42±10, 48±20, and 38±6 μg/L (mean ± standard deviation), respectively. Similar results were obtained with HAA-FPs, with mean (± standard deviation) concentrations of 59±76, 63±7, 39±12, 42±21, 44±24, 62±36, 87±73, and 54±19 μg/L, respectively. Also similar to the THM-FP findings, brominated HAA constituents were not formed and total HAA-FP consisted 67% trichloroacetic acid and 33% dichloroacetic acid. As would be expected for DBPs with mutual precursors, total HAA- and THM-FPs were significantly correlated (Table 6-3; $p = 10^{-22}$, $R^2 = 0.85$). Similar correlations between THMs and HAAs have been previously reported (Villanueva et al., 2003; Rocarro et al., 2014).

Similar to the DBP-FP observations, DOC concentrations observed during this study did not vary much over the two-year investigation (Table 6-2), regardless of hydrologic regime (Figure 6-2c). Specifically, the mean concentrations at the North York Upper, Star McLaren, Star East, Star West, Star Main, Crowsnest above Star, Crowsnest below Star, and Willow sampling locations were 1.1±0.6, 1.6±0.1, 1.2±0.3, 1.1±0.2, 1.0±0.1, 1.3±0.4, 1.3±0.3, 1.5±0.2 mg/L (mean ± standard deviation), respectively (Figure 6-2c). As indicated in Table 6-3 (supported by Table A-4, Appendix A and Figure B-5, Appendix B), the relationship between DOC and THM-FP over the study period was significant ($p = 5\text{x}10^{-15}$); however, changes in DOC only explained some of the variability in THM-FP ($R^2 = 0.70$)—the relationship between DOC and HAA-FP was similarly significant (Table 6-3; $p = 2\text{x}10^{-12}$, $R^2 = 0.62$). Significant correlations such as these between TOC and THM-FP for individual source waters have been reported previously (Singer et al., 1981; Reckhow and Singer, 1990); however, the precision in prediction typically declines when comparing water from different sources (Reckhow and Singer, 1990).

Aromatic compounds, also known as humics or hydrophobics, are the main precursors of regulated carbonaceous DBPs (THMs and HAAs) (Collins et al. 1986; Reckhow and Singer 1990; Singer, 1999; Kitis et al., 2002). Accordingly, these fractions of DOC were investigated. Notably, no changes in DOC character as a result of forest harvesting were observed (Table 6-2) at sampling locations, during either the period include the harvest and first post-harvest year—this observation applied to all of the metrics of DOC character that were investigated, including UV_{254} (Figure 6-2d), SUVA (Figure 6-2e), and hydrophobic organic carbon as measured by resin fractionation (HPO %) (Figure 6-2f). Given the low DOC concentrations that were observed throughout the investigation, it is not surprising that all of these parameters except for SUVA had significant, directly proportional relationships with THM-FP and HAA-FP; however, with only moderate or poor prediction precision, as detailed in Table 6-3. The best prediction performance ($R^2 = 0.80$ and 0.67 for THM- and HAA-FP, respectively; Table 6-3) was observed for HPO when it was expressed on a mass-weighted (mg/L) basis, as recommended in Chapter 5 of this thesis. The poorest predictor of both these DBP-FPs was SUVA ($R^2 = 0.03$ and 0.00 for THM- and HAA-FP, respectively; Table 6-3). This result was also consistent with the reported literature in which contradictory conclusions have been reported regarding the utility of SUVA in explaining NOM reactivity and predicting THM formation. The utility of SUVA as a THM-FP predictor has been widely investigated and has resulted in good, precise correlations in some cases (Reckhow et al. 1990; Kitis et al. 2001), but not in others (Goslan et al., 2004; Bougeard et al., 2010; Hua et al., 2015). The lack of consistently precise correlation has been especially observed in low aromaticity waters (SUVA < 2) (Ates et al., 2007; Li et al., 2014). As would be expected, significant positive correlations between all of these metrics except SUVA also were observed (Table 6-3).

LC-OCD (Huber et al., 2011) was employed during half of this study (2015) to better understand the implications forest harvesting to the relative potentials for membrane fouling and microbial regrowth in the distribution system. While specific treatability metrics that quantify those potentials are not currently available, the literature generally indicates that the biopolymer and LMW fractions of DOC are respectively associated with membrane fouling (Rahman et al., 2014; Yamamura et al., 2014) and microbial regrowth (Escobar et al., 2000; van der Kooij and van der Wielen, 2014) in the distribution system. Thus, statistically significant increases in these parameters in streams draining disturbed watersheds relative to those draining reference watersheds would have been interpreted as significant increases in the associated risks to drinking water treatability. Notably, no changes in these DOC fractions were observed (Table 6-2) at sampling locations, during either the harvest or first post-harvest years, regardless of harvesting approach—this observation applied to all of the DOC fractions that were investigated, including HS (Figure 6-2g), biopolymers (BP) (Figure 6-3a), building blocks (BB) (Figure 6-3b), and the low molecular weight (LMW) neutrals (Figure 6-3c). The relationships between the mass of various DOC fractions obtained using LC-OCD and the regulated DBP-FPs (THM-FP and HAA-FP) were not analyzed because of the limited sizes of the data sets.

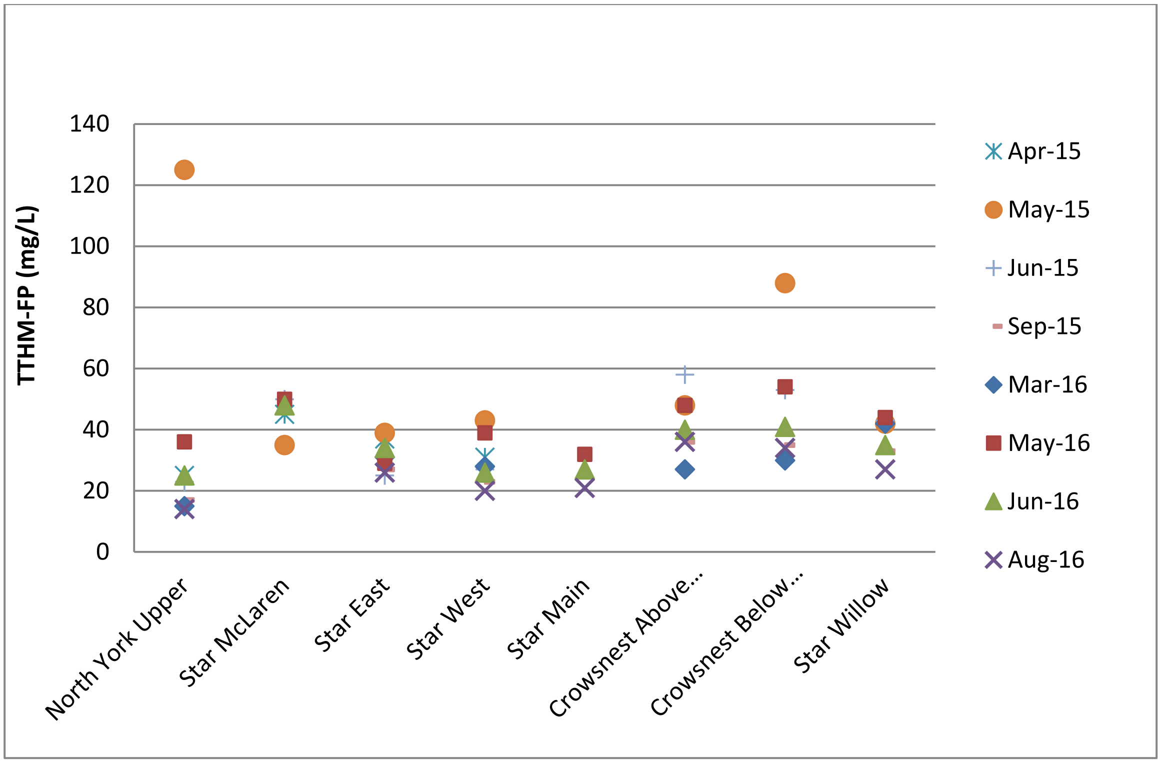
FEEM intensity plots for representative reference, partial cut, strip cut, clear cut, and multiple cut type watersheds are shown in Figures 6-4a, 4b, 4c, 4d, and 4e, respectively. As shown for this sampling event, no intensity peaks representative of fulvic acid-like (Ex < 250 nm and Em > 350 nm) and humic acid-like (Ex > 280 nm and Em > 380 nm), or other organic compounds (Chen et al., 2003b) were observed at either the upstream headwaters or downstream sampling locations. This lack of florescence intensity detection was consistent during either the harvest or first post-harvest years, regardless of harvesting approach. However, it was not surprising, considering the low concentrations and aromaticity of DOC throughout the investigation. Similarly, the fluorescence index (FI) at the associated wavelengths of importance (McKnight et al., 2001; Rodríguez et al., 2014) was non-detectable and did not describe impacts of forest harvesting on water quality.

Table 6-2. Significance of harvesting impacts (*p* value) on different NOM-associated parameters (comparison between reference and grouped harvested sites over the investigation period)

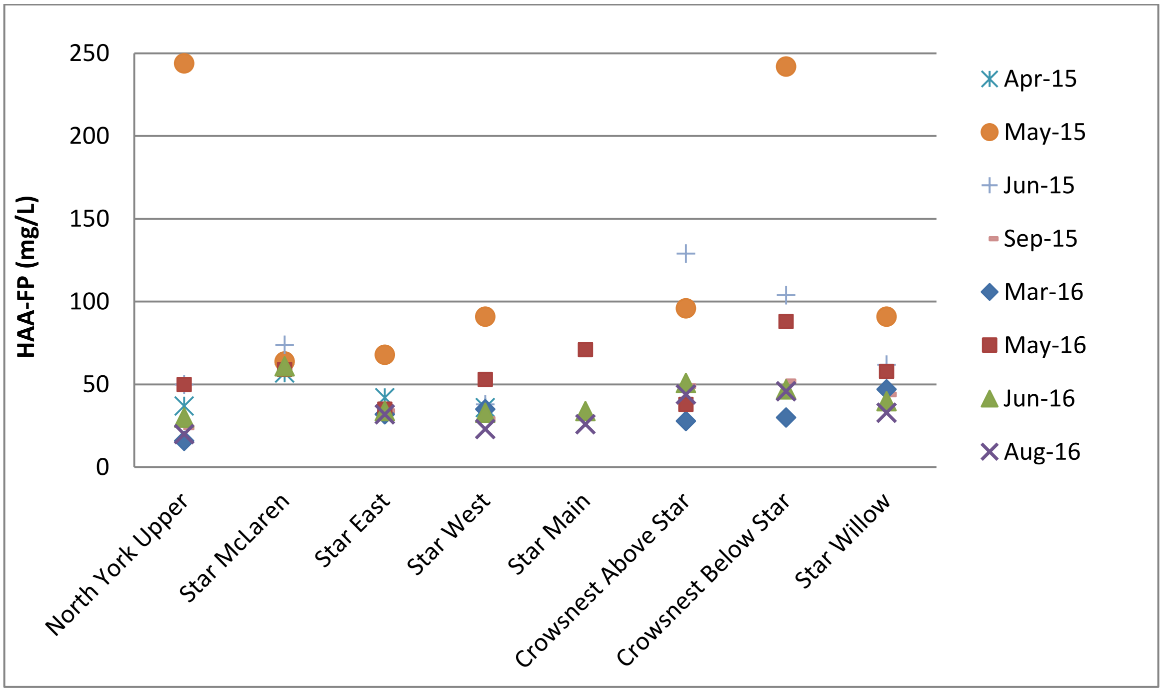
Parameter	**THM-FP** (µg/L)	**HAA-FP** (µg/L)	**DOC** (mg/L)	**UV_{254}** (m^{-1})	**SUVA** (L/mg.m)	**HPO** (%)	**HS** (mg/L)	**BP** (mg/L)	**BB** (mg/L)	**LMWN** (mg/L)
p value	0.87	0.73	0.36	0.49	0.62	0.77	0.67	0.29	0.83	0.41

Table 6-3. Regression significance (*p* value) and prediction precision (R^2) between DOC, UV_{254}, SUVA, and hydrophobicity (HPO) (n = 52)

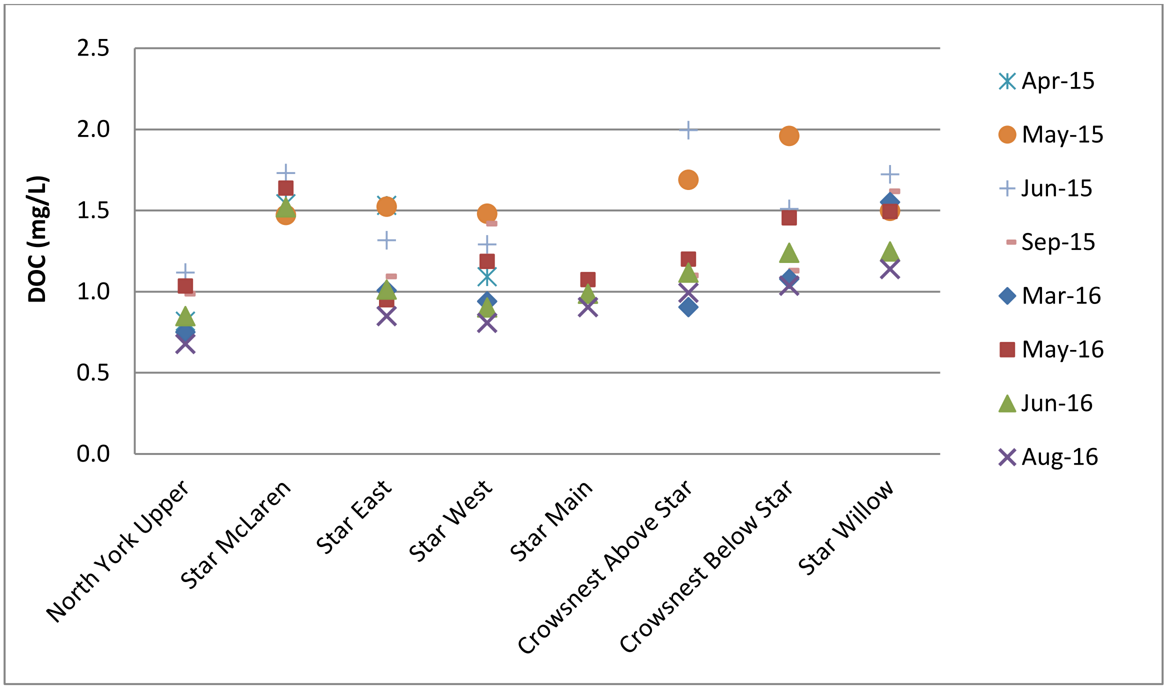
		HAA-FP (µg/L)	**THM-FP** (µg/L)	**DOC** (mg/L)	**UV_{254}** (m^{-1})	**SUVA** (L/mg.m)
THM-FP	**R^2**	0.85				
	***p* value**	1×10^{-22}				
DOC (mg/L)	**R^2**	0.62	0.70			
	***p* value**	2×10^{-12}	5×10^{-15}			
UV_{254} (m^{-1})	**R^2**	0.30	0.54	0.6		
	***p* value**	2×10^{-5}	2×10^{-10}	8×10^{-12}		
SUVA (L/mg.m)	**R^2**	0.00	0.03	0.01	0.44	
	***p* value**	0.92	1×10^{-1}	6×10^{-1}	4×10^{-8}	
HPO (%)	**R^2**	0.27	0.42	0.3	0.53	0.24
	***p* value**	4×10^{-5}	8×10^{-8}	1×10^{-5}	4×10^{-10}	1×10^{-4}
HPO (mg/L)	**R^2**	0.67	0.80	0.94	0.69	0.02
	***p* value**	4×10^{-14}	1×10^{-19}	9×10^{-33}	9×10^{-15}	2×10^{-1}


TTHM-FP (mg/L)
140
120
100
80
60
40
20
0
North York Upper
Star McLaren
Star East
Star West
Star Main
Crowsnest Above...
Crowsnest Below...
Star Willow
Apr-15
May-15
Jun-15
Sep-15
Mar-16
May-16
Jun-16
Aug-16

a)

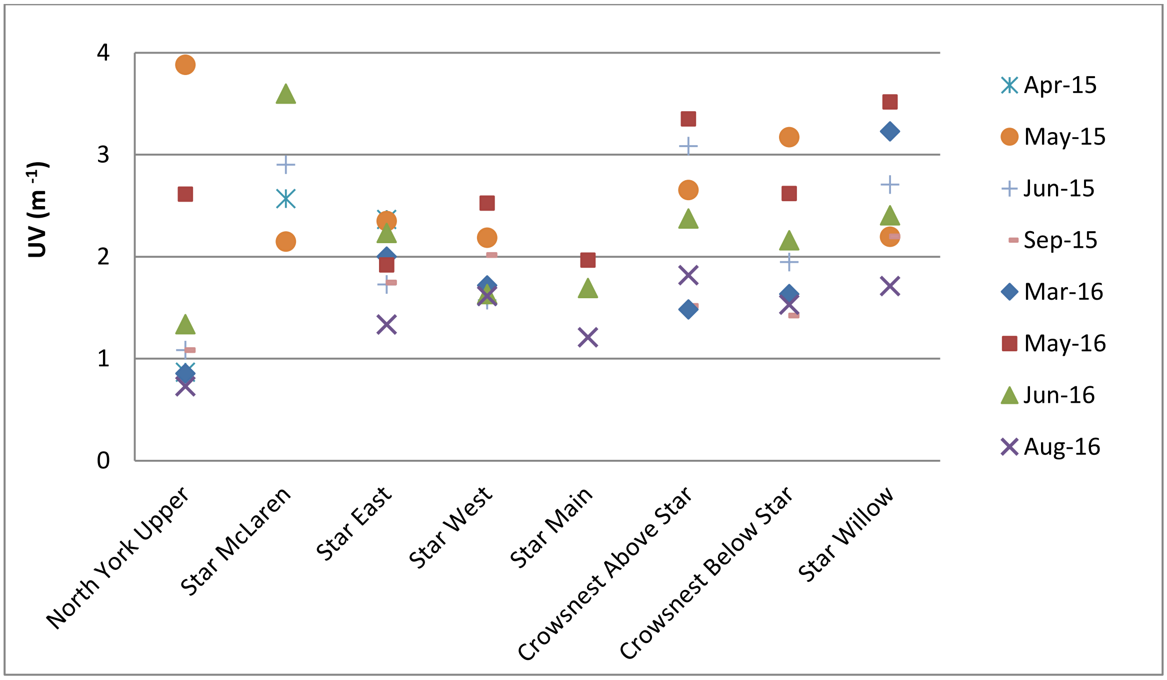

HAA-FP (mg/L)
250
200
150
100
50
0
North York Upper
Star McLaren
Star East
Star West
Star Main
Crowsnest Above Star
Crowsnest Below Star
Star Willow
Apr-15
May-15
Jun-15
Sep-15
Mar-16
May-16
Jun-16
Aug-16

b)



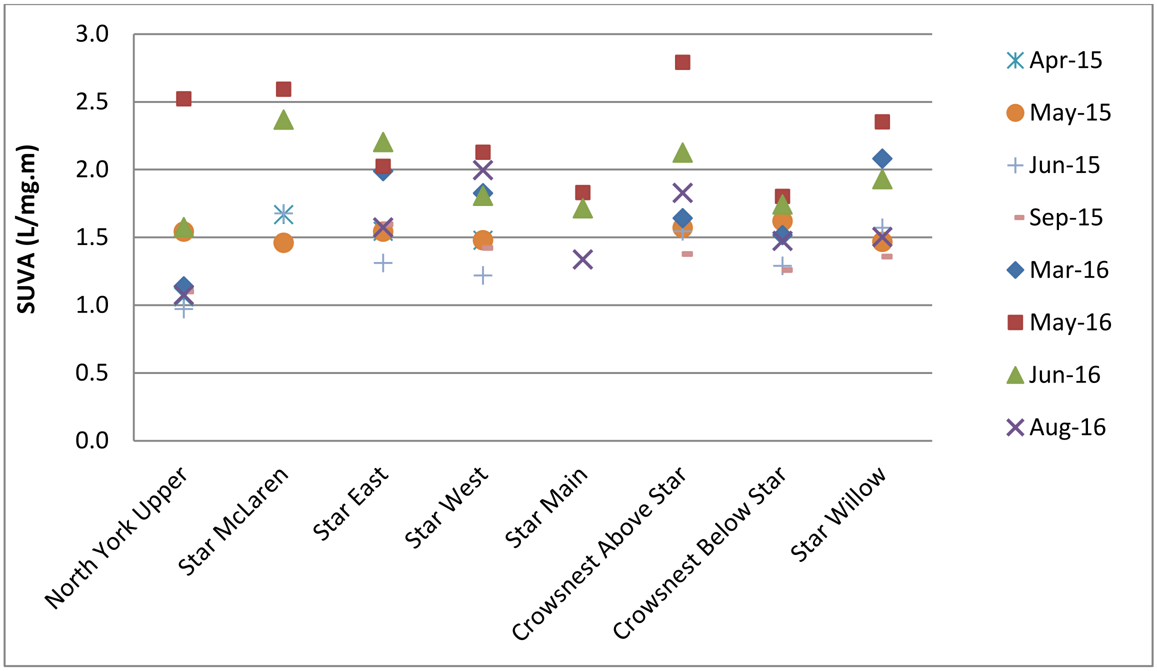
2.5
2.0
1.5
1.0
0.5
0.0
DOC (mg/L)
North York Upper
Star McLaren
Star East
Star West
Star Main
Crowsnest Above Star
Crowsnest Below Star
Star Willow
Apr-15
May-15
Jun-15
Sep-15
Mar-16
May-16
Jun-16
Aug-16

c)

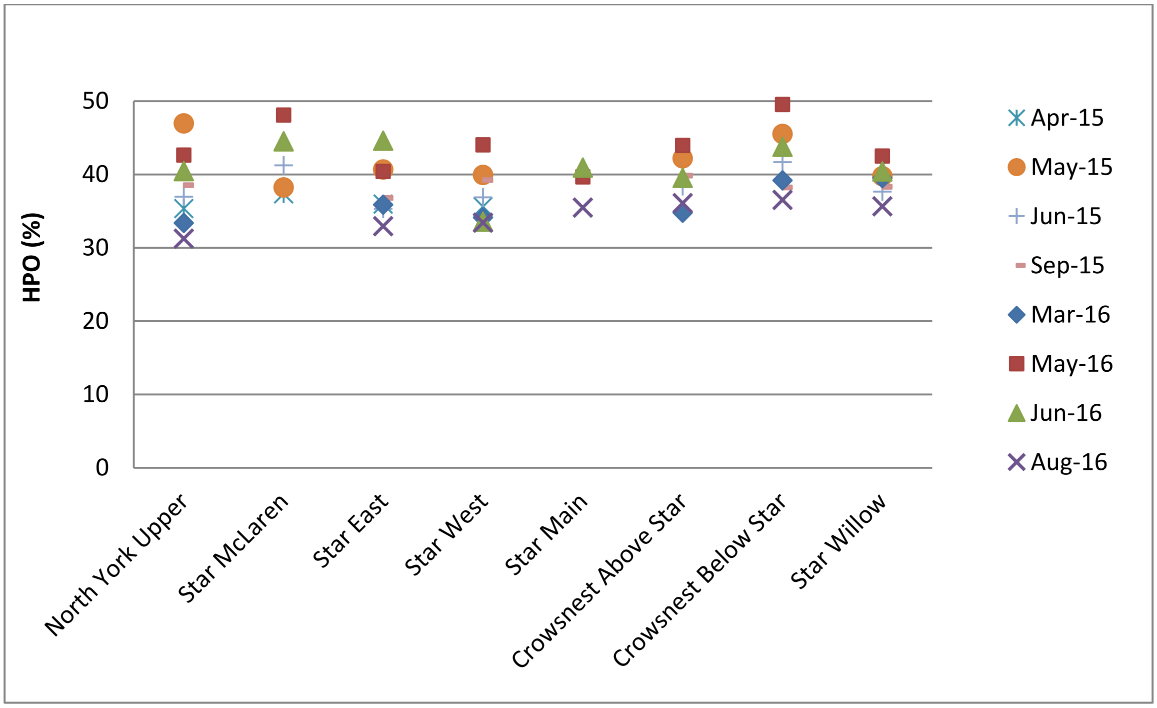


4
3
2
1
0
UV (m -1)
North York Upper
Star McLaren
Star East
Star West
Star Main
Crowsnest Above Star
Crowsnest Below Star
Star Willow
Apr-15
May-15
Jun-15
Sep-15
Mar-16
May-16
Jun-16
Aug-16

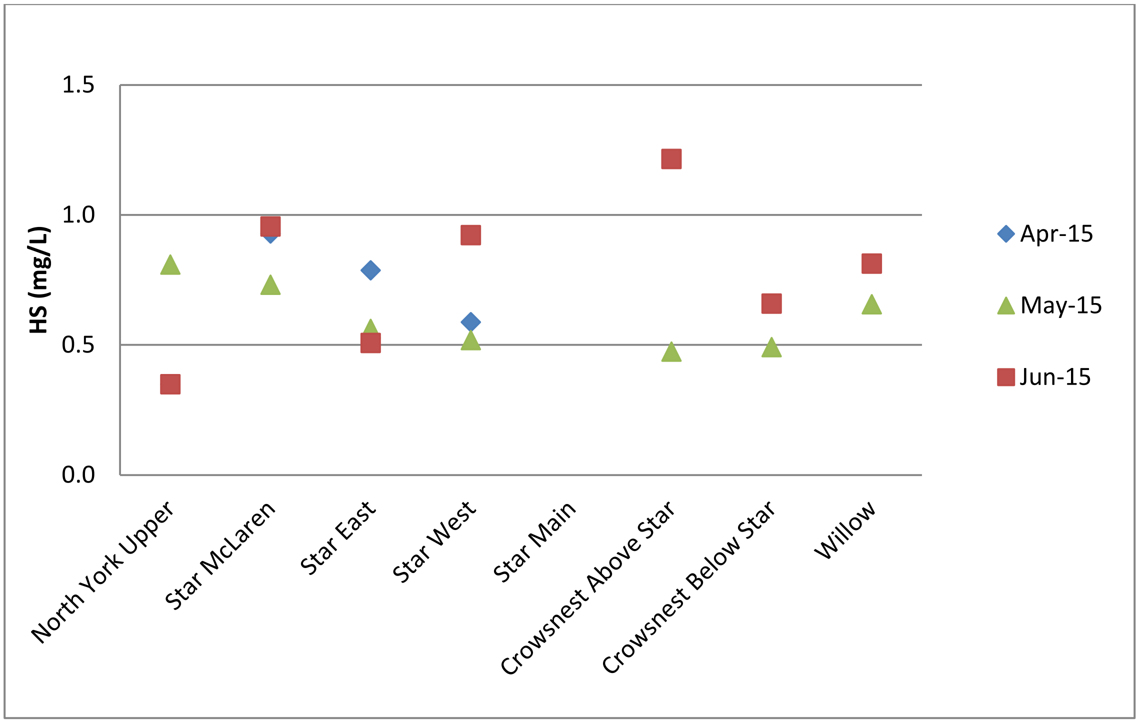
d)


SUVA (L/mg.m)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
North York Upper
Star McLaren
Star East
Star West
Star Main
Crowsnest Above Star
Crowsnest Below Star
Star Willow
Apr-15
May-15
Jun-15
Sep-15
Mar-16
May-16
Jun-16
Aug-16

e)

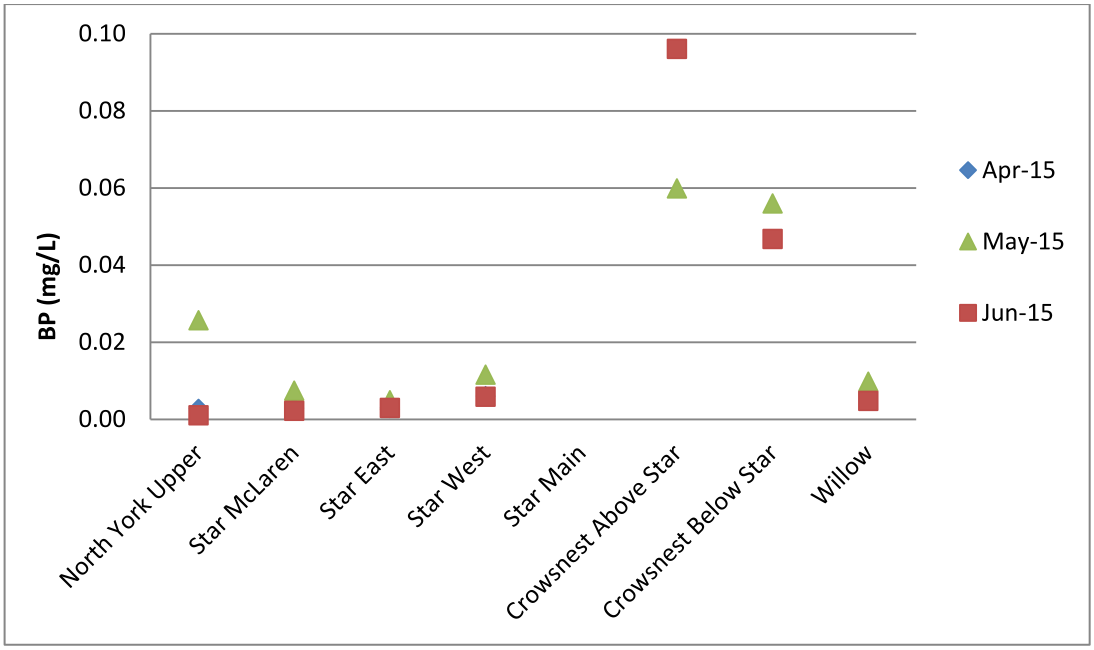

HPO (%)
50
40
30
20
10
0
North York Upper
Star McLaren
Star East
Star West
Star Main
Crowsnest Above Star
Crowsnest Below Star
Star Willow
Apr-15
May-15
Jun-15
Sep-15
Mar-16
May-16
Jun-16
Aug-16

f)



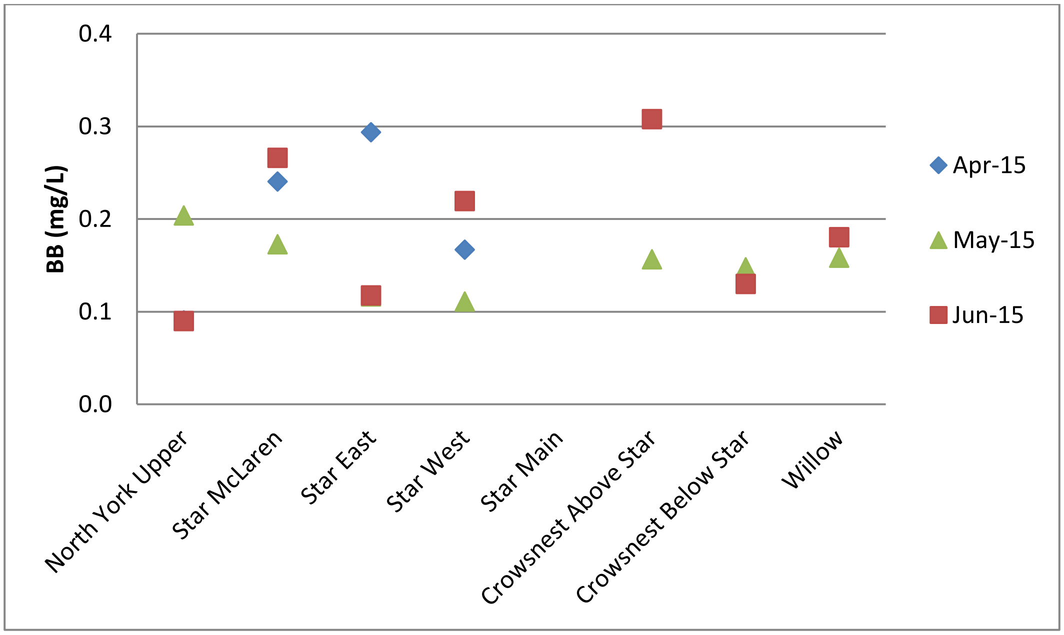
g)

Figure 6-2. NOM character described by (a) THM-FP, (b) HAA-FP, (c) DOC, (d) UV, (e) SUVA, (f) HPO, and (g) HS in streams draining reference and harvested watersheds.



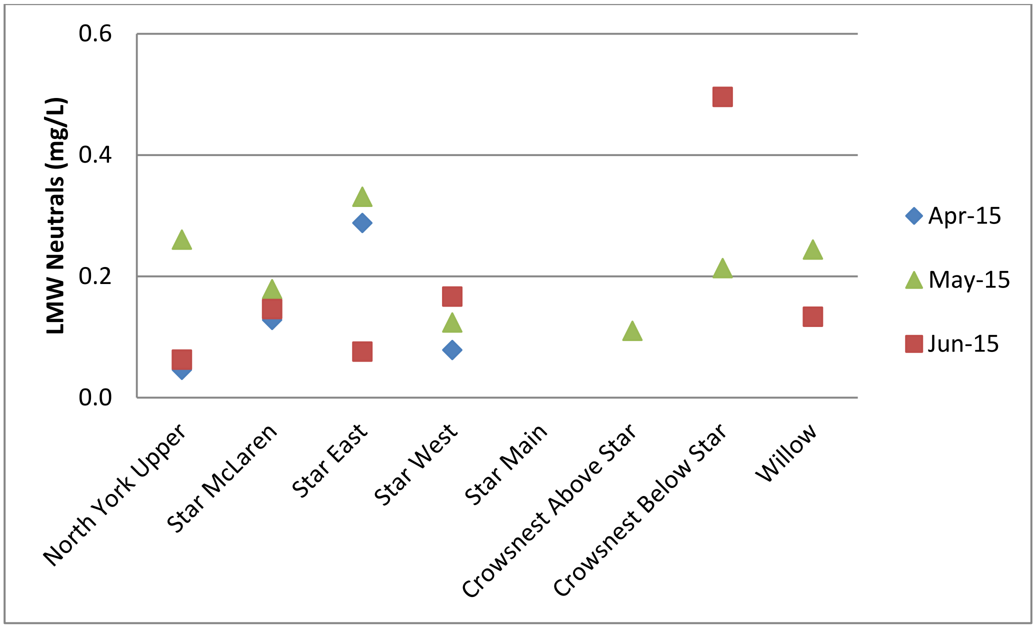
0.10
0.08
0.06
0.04
0.02
0.00
BP (mg/L)
North York Upper
Star McLaren
Star East
Star West
Star Main
Crowsnest Above Star
Crowsnest Below Star
Willow
Apr-15
May-15
Jun-15

a)



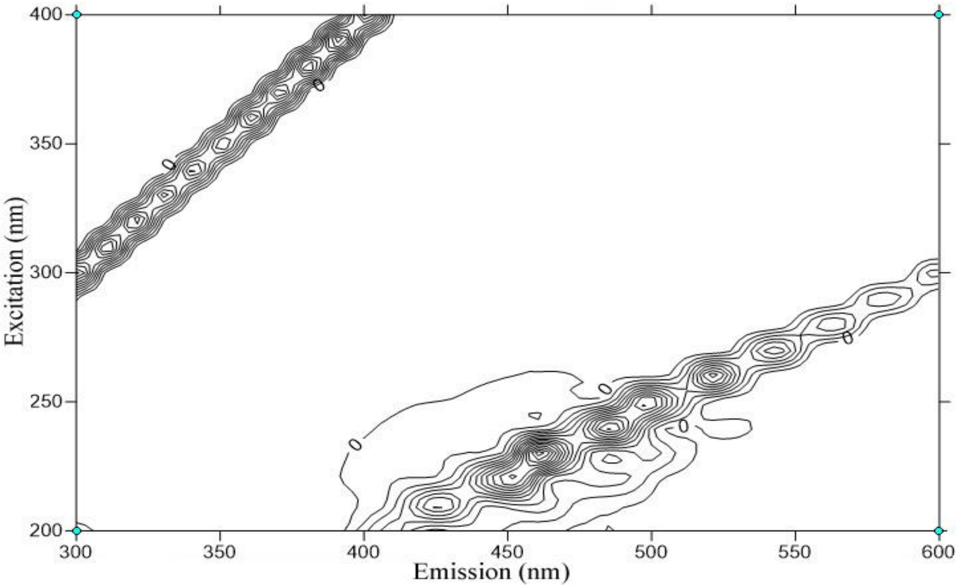
0.4
0.3
0.2
0.1
0.0
BB (mg/L)
North York Upper
Star McLaren
Star East
Star West
Star Main
Crowsnest Above Star
Crowsnest Below Star
Willow
Apr-15
May-15
Jun-15

b)

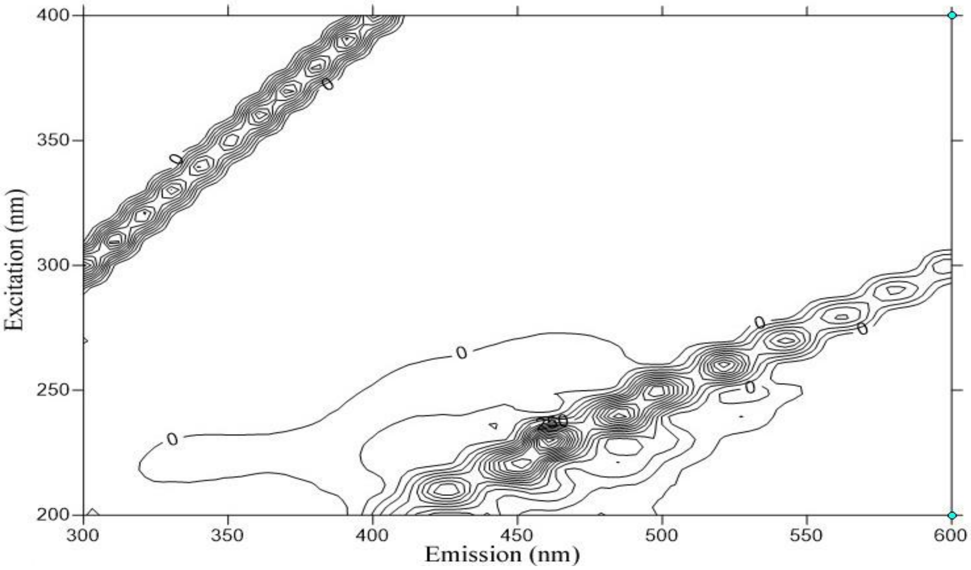


c)

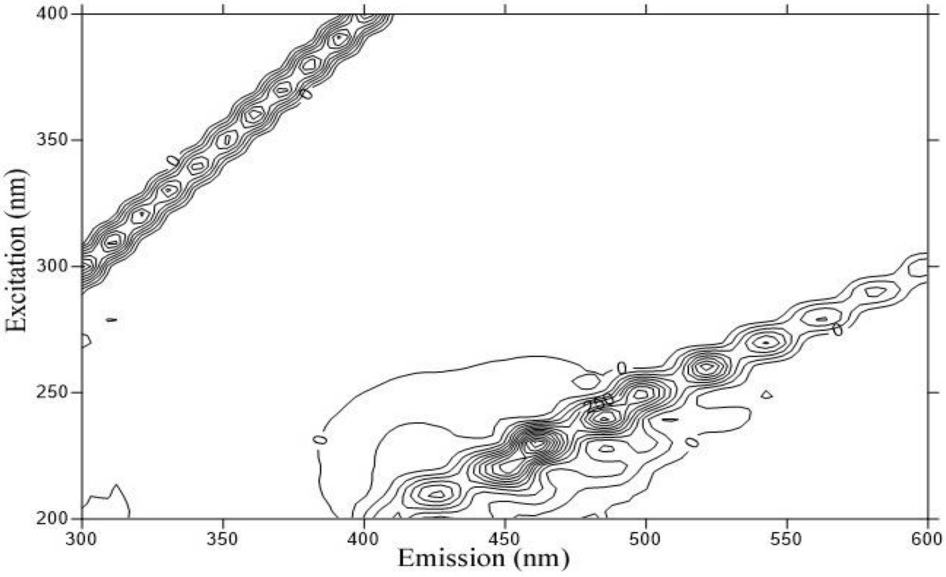
Figure 6-3. NOM character described by (a) biopolymers, (b) building blocks, and (c) LMW neutrals, fractions in streams draining unburned, burned, and post-fire salvage logged watersheds.


400
350
300
250
200
Excitation (nm)
300
350
400
450
500
550
600
Emission (nm)
0

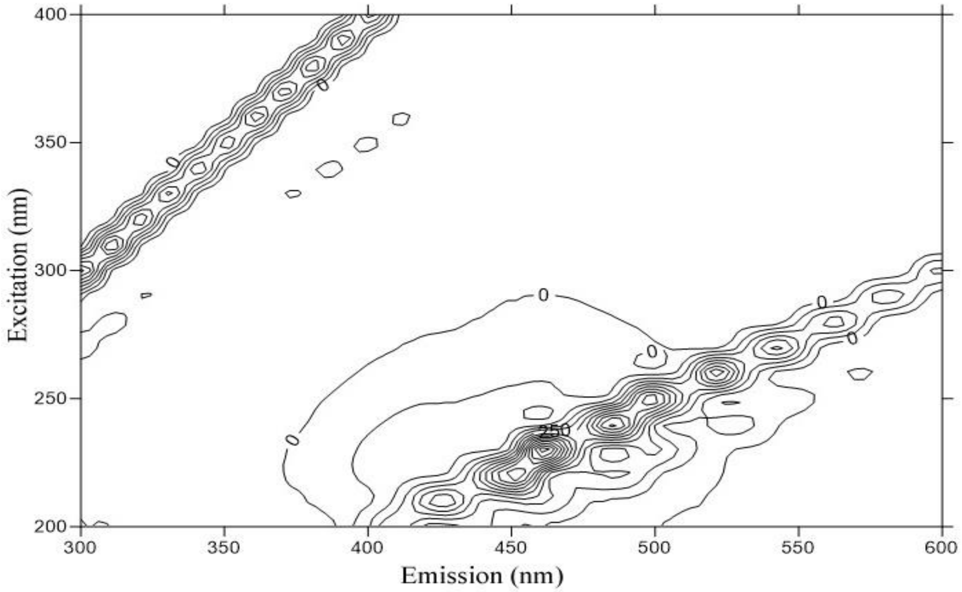
a)


400
350
300
250
200
Excitation (nm)
300
350
400
450
500
550
600
Emission (nm)
0
200

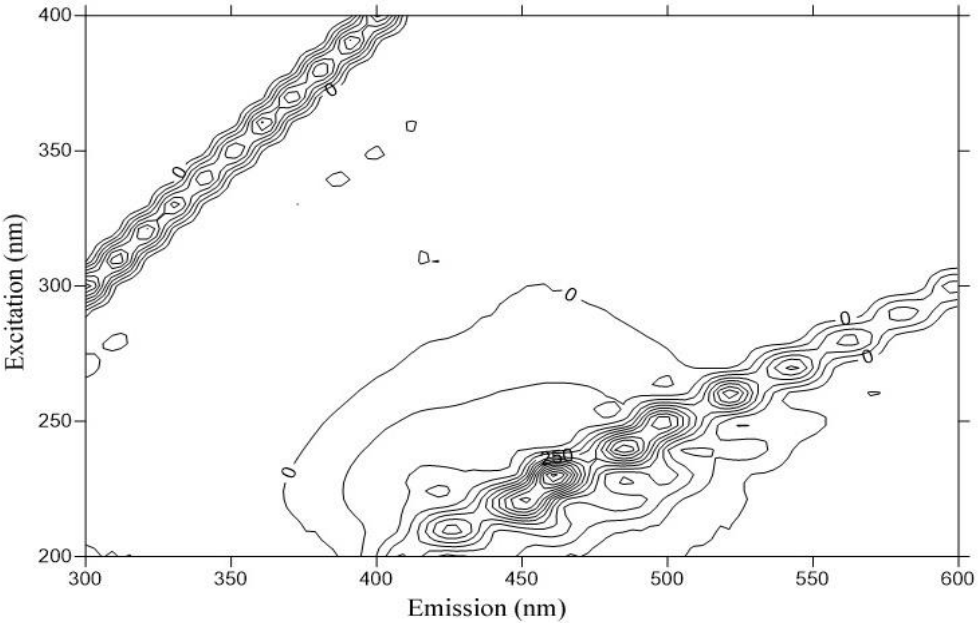
b)


400
350
300
250
200
Excitation (nm)
300
350
400
450
500
550
600
Emission (nm)
0
250

c)


400
350
300
250
200
Excitation (nm)
300
350
400
450
500
550
600
Emission (nm)
0
250

d)



e)

Figure 6-4. FEEM intensity plots for representative (a) reference, (b) partial cut, (c) strip cut, (d) clear cut, and (e) multiple cut type watersheds.

6.5 Implications for Drinking Water Treatability

Here, no impacts of forest harvesting on water quality and treatability were observed during the harvest and first post-harvest years in the eastern slopes of the Rocky Mountains in southwestern Alberta, Canada. Thus, this work suggests that forest harvesting with careful implementation of BMPs for erosion control may mitigate the potentially catastrophic impacts of wildfire on drinking water treatability without significantly compromising it. Having said that, water quality deterioration has been reported in some areas after forest harvesting—variability in impact severity has been attributed to the range of harvesting practices and management intensity, as well as hydro-climatic and geological setting. As discussed above, while previous research provides some insights, it largely reflects impacts of historic forest management practices no longer used. Current policy strategies for forest watershed management have ranged from the creation and expansion of protected areas where any type of anthropogenic disturbance including forest harvesting with the goal of mitigating potential wildfire or other disturbance risk is prohibited to integrated forest management employing BMPs to mitigate impacts on water. While forest management with BMPs may still produce some impacts to water, the degree to which effective source water protection (SWP) strategies need to employ both protective and risk mitigation strategies (i.e. avoided impacts to drinking water treatability) is unclear. Thus, the present investigation offers hope that forest management strategies that include harvesting with careful implementation of BMPs for erosion control may mitigate the potentially catastrophic impacts of wildfire and other disturbances on drinking water treatability without significantly compromising source water quality and treatability.

Chapter 7

Conclusions and Recommendations

The focus of this research was to identify, compare, and improve of strategies for characterizing challenges and threats to drinking water treatability (i.e., changes in DOC and increases in regulated DBP formation) caused by wildfire, post-fire salvage logging, and contemporary forest harvesting landscape disturbances.

The most common methods of NOM characterization and their relationship to drinking water treatability and limitations were reviewed. The efficacy of metrics of NOM character and concentration as potential proxy indicators for drinking water treatability was assessed and confirmed by comprehensive DOC characterization throughout different treatment processes at a conventional water treatment plant with aerobic biofiltration. Changes in DOC character and its relationships to regulated DBP-FPs (THM-FPs and HAA-FPs) in disturbed source water were characterized in streams draining burned, post-fire salvage logged, and harvested watersheds in the Rocky Mountains of south-western Alberta. Finally, simple strategies for enhancing prediction of THM-FP using several of the proxy indicators (particularly, of aromaticity) were investigated.

7.1 Conclusions

The following conclusions were made from the results of this research:

1) THM-and HAA-FPs as well as aromatic compounds (UV_{254}, HPO as measured by resin fractionation, and HPS as measured by LC-OCD) were efficiently removed through chemical pre-treatment (coagulation/flocculation/sedimentation). These observations highlighted that the aromatic compounds were the main reactive compounds that contributed to THM and HAA formation potentials.

2) Metrics indicative of aromatic compounds (UV_{254}) were shown to be good proxy indicators of DOC reactivity, demonstrating the best prediction of the formation of regulated carbonaceous DBPs, albeit in a site-specific manner.

3) The intensity of the fulvic and humic acid-like compounds as detected by fluorescence excitation emission matrices (FEEM) decreased following the chemical pre-treatment (coagulation, flocculation, and sedimentation) during conventional treatment. This finding, while non-quantitative, was consistent with the trends observed for other humic-descriptive metrics (UV_{254}, HPO, HS) and the formation potentials of the regulated, carbonaceous DBPs. The florescence index (FI) also demonstrated that the majority of terrestrial (aromatic) compounds were removed through chemical pretreatment.

4) Biofiltration (with GAC) demonstrated the capacity to remove aromatic compounds and regulated, carbonaceous DBP-FPs. As well, some smaller DOC fractions (low molecular weight neutrals) that are understood to contribute to microbial regrowth in the distribution systems were also removed by biofiltration.

5) THM- and HAA-FPs removal trends were generally comparable through the treatment process—this would be expected given that they share common precursors. Higher molecular weight fractions had a more substantial contribution to the formation of HAAs than THMs, however.

6) Increases in DOC concentration, aromaticity (UV_{254}) and hydrophobicity (HPO) were detected after wildfire and even more so after post-fire salvage-logging in disturbed Rocky Mountain watersheds. These findings were similar and parallel to the findings of a larger, earlier and a concurrent study conducted at the same watersheds (to which this work contributed). These observations confirmed that wildfire and salvage logging play important roles in changing the character of DOC and forming more reactive compounds that contribute to drinking water treatability threats such as the increased potential for forming DBPs.

7) The mass of humic substances (HS), biopolymers, and building blocks fractions of DOC also increased significantly in impacted streams as a result of wildfire and post-fire salvage logging, thereby suggesting that these disturbances may have significant

implications for carbonaceous DBP-FP, coagulant demand, and membrane fouling. In contrast, the mass of the low molecular weight (LMW) neutrals fraction of DOC, which contributes to microbial regrowth in the distribution system, was not significantly different in streams impacted by either wildfire or post-fire salvage logging relative to streams in reference watersheds.

8) Contemporary forest harvesting by clear-cutting with patch retention, strip-shelterwood cutting, and partial cutting with careful implementation of BMPs for erosion control did not yield any appreciable impacts on DOC concentration, aromaticity (UV_{254}) or hydrophobicity (HPO) in the harvest and first post-harvest years after harvesting in the Rocky Mountain watersheds. This suggests that forest harvesting should be further explored as a source water protection tool because it may be able to mitigate the risk of severe wildfire without having detrimental effects on drinking water treatability.

9) Wildfire and post-fire salvage logged disturbance-associated increases in DOC concentrations, aromaticity, and hydrophobicity generally correlated with increases in THM- and HAA-FPs at the watershed-scale and over multiple flow regimes in the Rocky Mountain watersheds. These results demonstrated that proxy indicators of DOC reactivity can be useful in describing threats (or lack thereof) to drinking water treatability in increasingly disturbed watersheds.

10) The intensity of the fulvic and humic acid-like compounds (as detected by FEEM) was qualitatively indicative of risks to drinking water treatability after landscape disturbance in the Rocky Mountain watersheds. In contrast, the florescence index (FI) did not meaningfully or reliably indicate impacts of wildfire-associated land disturbance on water quality and drinking water treatability—this was attributed to the lack of florescence at the associated wavelengths.

11) The aromatic metrics (UV_{254}, HPO, and HS) correlated well with each other and were good predictors of formation potential of regulated DBPs. Nonetheless, UV_{254} unequivocally offered the most precise prediction of THM-FP.

12) The prediction performance of hydrophobicity measured by resin fractionation (HPO) and the humic fraction measured by LC-OCD (HS) were noticeably enhanced when re-analyzed as mass (DOC concentration). This improvement in prediction of THM-FP, using the proxy indicators, was consistent for diverse source and treated waters and especially evident for the humic fraction obtained using LC-OCD (HS).

7.2 Recommendations

Recommendations for further investigation regarding this research are provided below.

1) Results of this study highlighted the significance of post-fire salvage logging in increasing the degree of disturbance and water treatability challenges. On the other hand, well-controlled, contemporary forest harvesting that includes extensive implementation of best management practices for erosion management and minimal density and/or duration of linear disturbances has the potential to minimize the impacts. Thus, further investigation of harvesting approaches and associated BMPs is warranted because severe land disturbance can potentially threaten source water quality and treatability, while the implementation of BMPs during forest harvesting may significantly mitigate some of the associated potential impacts.

2) Despite the annual relationships between the proxy indicators and DBP-FP by the simple regression models, these relationships are frequently spatially and temporally variable, and site specific, suggesting that other hydrological and/or biogeochemical factors (not considered herein) may have contributed to the observed differences in these relationships.

3) It is unlikely that a single, directly measured universal precursor for DBP-FP will ever be identified based on structural characteristics of NOM. As a result, data obtained from multiple NOM characterization methods must be combined and concurrently analyzed; this requires the use of appropriate multivariate analysis tools during exploratory data analysis to ensure that optimal predictive models that best extract information from available data are developed. While approaches such as principal components and parallel factor analysis have been applied to understanding FEEMs, there is a stark absence of multivariate analysis of broader NOM data. Given that several variables will likely be required to inform and develop universally predictive models for treatability metrics such as DBP-FP, the associated dispersion matrices will likely be too large to study and interpret, with too many pairwise correlations between variables that must be considered. Thus, more meaningful interpretation of the data

requires them to be reduced—thoughtful selection of the best approaches (e.g., principal components analysis, factor analysis, etc.) is required.

4) Regardless of the current absence of multivariate models for assessing the drinking water treatability implications of changes in aquatic NOM, the need to develop them is resoundingly clear. Thus, there is also a corresponding need to further develop NOM characterization/fractionation techniques and include concurrent analyses using several different characterization/fractionation methods during field investigations of NOM character and reactivity.
5) The observed lack of disturbance-associated impacts on the LMW neutrals fraction of NOM must be considered in conjunction with possible subsequent transformations of DOC that may occur during drinking water treatment, particularly if advanced oxidation processes such as ozonation are utilized in absence of biological filtration or other processes that can remove LMW neutrals, thereby reducing the potential for microbial regrowth in the distribution system.
6) Here, the work focused on comparison and improvement of strategies for characterizing changes in DOC concentration and character (proxy indicators) and formation of regulated carbonaceous DBPs formation—emerging DBPs were outside the scope of this research. Investigation of DOC characterization in identifying promising proxies for formation of emerging DBPs of health concern as well as other treatability challenges is strongly recommended.
7) The peak splitting (rather than peak separation) implicit to the commonly reported methodology of LC-OCD restricts the efficacy of this method as a suitable proxy indicator of DBP-FP. Modification of this method by increasing the elution time of the fractions and thus separating their peaks can overcome this limitations and enhance the efficiency of this method.
8) Although FEEM (especially changes in humic and fulvic acid-like substances) is qualitatively indicative of risks to drinking water treatability, research to improve reliable quantitative interpretation of FEEM is indispensable.

9) The resin fractionation method is recognized by the IHSS as a standard method. The hydrophobic fraction, as isolated by this method, was a good indicator of the formation of regulated DBPs. However, the complexity and length of this method may limit the application of it for some time-constrained studies. Modification of this method to overcome its drawbacks and development of it as a real time technique can be a significant step towards improvement of carbon characterization.

10) Data obtained from multiple NOM characterization methods must be combined and concurrently analyzed; this requires the use of appropriate multivariate analysis tools during exploratory data analysis to ensure that optimal predictive models that best extract information from available data are developed.

11) This work highlights the pressing need for 1) new knowledge regarding the <u>longer-term</u> impacts of forest harvesting on water and 2) BMP development to ensure that watershed regions critical for sustaining water supplies are optimally managed to minimize potential legacy effects of disturbance, including that by forest harvesting.

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Appendices

Appendix A - ANOVA Tables

Table A-1. ANOVA table for regression analysis of parameters reported in Table 3-2.

	ANOVA	*df*	*SS*	*MS*	*F*	*P-value*
THMFP vs HAAFP	Regression	1	224371	224371	97	1E-08
	Residual	18	41554	2309		
	Total	19	265925			
THMFP vs DOC	Regression	1	188969	188969	210	8E-17
	Residual	37	33340	901		
	Total	38	222309			
THMFP vs UV	Regression	1	196827	196827	286	5E-19
	Residual	37	25482	689		
	Total	38	222309			
THMFP vs SUVA	Regression	1	185143	185143	184	6E-16
	Residual	37	37165	1004		
	Total	38	222309			
THMFP vs HPO (%)	Regression	1	178232	178232	150	1E-14
	Residual	37	44077	1191		
	Total	38	222309			
THMFP vs HS (mg/L)	Regression	1	22	22	216	5E-17
	Residual	37	4	0.1		
	Total	38	25			
HAAFP vs DOC	Regression	1	215960	215960	78	6E-08
	Residual	18	49965	2776		
	Total	19	265925			
HAAFP vs UV	Regression	1	245300	245300	214	2E-11
	Residual	18	20625	1146		
	Total	19	265925			
HAAFP vs SUVA	Regression	1	238272	238272	155	3E-10
	Residual	18	27652	1536		
	Total	19	265925			
HAAFP vs HPO (%)	Regression	1	211464	211464	70	1E-07
	Residual	18	54461	3026		
	Total	19	265925			
HAAFP vs HS (mg/L)	Regression	1	10	10	65	2E-07
	Residual	18	3	0.2		

	ANOVA	*df*	*SS*	*MS*	*F*	*P-value*
	Total	19	13			
DOC vs UV	Regression	1	677	677	157.3	4E-15
	Residual	38	164	4		
	Total	39	841			
DOC vs SUVA	Regression	1	13	13	96.29	6E-12
	Residual	38	5	0.1		
	Total	39	18			
DOC vs HPO(%)	Regression	1	2006	2006	122	2E-13
	Residual	38	623	16		
	Total	39	2628			
DOC vs HS (mg/L)	Regression	1	21	21	160	3E-15
	Residual	38	5	0.1		
	Total	39	25			
UV vs SUVA	Regression	1	17	17	1639	7E-33
	Residual	38	0.4	0.01		
	Total	39	18			
UV vs HPO (%)	Regression	1	2237	2237	217	3E-17
	Residual	38	392	10		
	Total	39	2628			
UV vs HS (mg/L)	Regression	1	21	21	165	2E-15
	Residual	38	5	0.1		
	Total	39	25			
SUVA vs HPO (%)	Regression	1	2259	2259	232	9E-18
	Residual	38	370	10		
	Total	39	2628			
SUVA vs HS (mg/L)	Regression	1	19	19	119	3E-13
	Residual	38	6	0.2		
	Total	39	25			
HPO (%) vs HS (mg/L)	Regression	1	20	20	157	5E-15
	Residual	38	5	0.1		
	Total	39	25			

Table 0-2. ANOVA table for regression analysis of parameters reported in Table 4-1.

	ANOVA	*df*	*SS*	*MS*	*F*	*P-value*
THMFP vs DOC	Regression	1	205402	205402	57	2E-10
	Residual	63	228030	3620		
	Total	64	433432			
THMFP vs UV	Regression	1	262512	262512	97	2E-14
	Residual	63	170921	2713		
	Total	64	433432			
THMFP vs SUVA	Regression	1	183875	183875	46	4E-09
	Residual	63	249557	3961		
	Total	64	433432			
THMFP vs HPO (%)	Regression	1	174199	174199	42	1E-08
	Residual	63	259233	4115		
	Total	64	433432			
DOC vs UV	Regression	1	1278	1278	1034	9E-41
	Residual	63	78	1		
	Total	64	1356			
DOC vs SUVA	Regression	1	9	9	26	4E-06
	Residual	63	21	0.3		
	Total	64	30			
DOC vs HPO (%)	Regression	1	1855	1855	271	2E-24
	Residual	63	431	6.8		
	Total	64	2286			
UV vs SUVA	Regression	1	19	19	72	3E-12
	Residual	67	17	0.3		
	Total	68	36			
UV vs HPO (%)	Regression	1	1820	1820	246	2E-23
	Residual	63	467	7.4		
	Total	64	2286			
SUVA vs HPO (%)	Regression	1	883	883	40	3E-08
	Residual	63	1403	22.3		
	Total	64	2286			

Table 0-3. ANOVA table for regression analysis of parameters reported in Table 5-1.

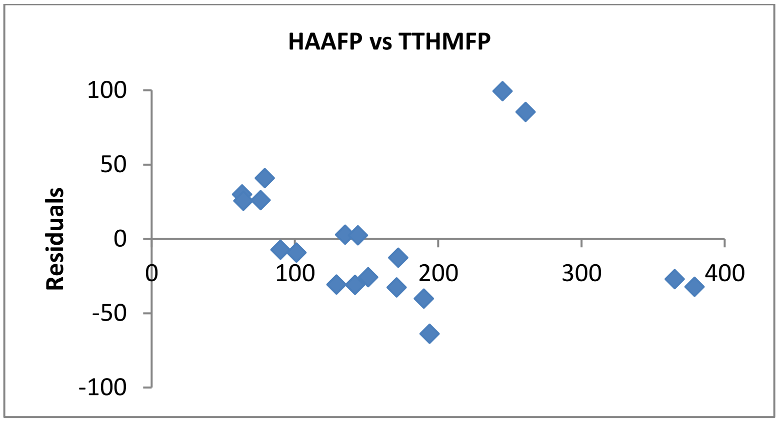
		ANOVA	*df*	*SS*	*MS*	*F*	*P-value*
Mannheim WTP	THMFP vs HPO (mg/L)	Regression	1	21	21	342	3E-20
		Residual	37	2	0		
		Total	38	24			
	THMFP vs HPO (%)	Regression	1	178232	178232	150	1E-14
		Residual	37	44077	1191		
		Total	38	222309			
	THMFP vs HS (mg/L)	Regression	1	22	22	216	5E-17
		Residual	37	4	0		
		Total	38	25			
	THMFP vs HS (%)	Regression	1	22925	22925	4	5E-02
		Residual	37	199384	5389		
		Total	38	222309			
	THMFP vs UV	Regression	1	196827	196827	286	5E-19
		Residual	37	25482	689		
		Total	38	222309			
	THMFP vs SUVA	Regression	1	185143	185143	184	6E-16
		Residual	37	37165	1004		
		Total	38	222309			
Rocky Mountain 2014	THMFP vs HPO (mg/L)	Regression	1	284874	284874	314	1E-19
		Residual	37	33525	906		
		Total	38	318399			
	THMFP vs HPO (%)	Regression	1	265089	265089	184	6E-16
		Residual	37	53310	1441		
		Total	38	318399			
	THMFP vs HS (mg/L)	Regression	1	292590	292590	902	4E-27
		Residual	36	11673	324		
		Total	37	304263			
	THMFP vs HS (%)	Regression	1	84896	84896	14	7E-04
		Residual	36	219368	6094		
		Total	37	304263			
	THMFP vs UV	Regression	1	287996	287996	350	2E-20
		Residual	37	30403	822		
		Total	38	318399			
	THMFP vs SUVA	Regression	1	125227	125227	24	2E-05
		Residual	37	193172	5221		
		Total	38	318399			

Table A-4. ANOVA table for regression analysis of parameters reported in Table 6-3.

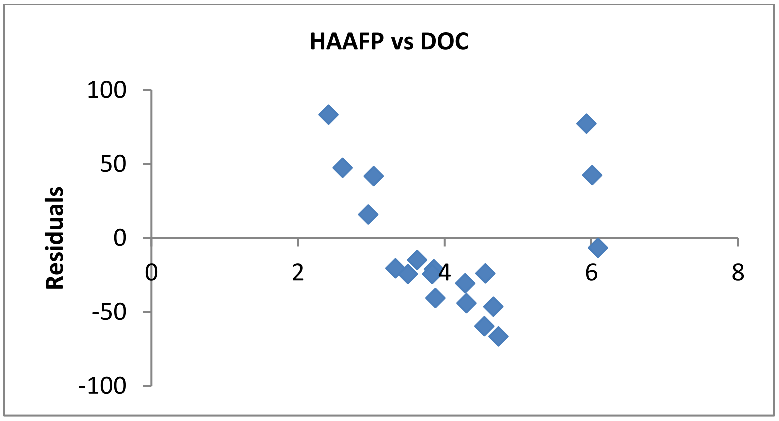
	ANOVA	*df*	*SS*	*MS*	*F*	*P-value*
HAAFP vs THMFP	Regression	1	84951	84951	289	1E-22
	Residual	51	14999	294		
	Total	52	99951			
HAAFP vs DOC	Regression	1	62218	62218	84	2E-12
	Residual	51	37733	740		
	Total	52	99951			
HAAFP vs UV	Regression	1	30931	30931	23	2E-05
	Residual	51	69020	1353		
	Total	52	99951			
HAAFP vs SUVA	Regression	1	18	18	0.01	9E-01
	Residual	51	99933	1959		
	Total	52	99951			
HAAFP vs HPO (%)	Regression	1	28115	28115	20	4E-05
	Residual	51	71836	1409		
	Total	52	99951			
HAAFP vs HPO (mg/L)	Regression	1	1	1	107	4E-14
	Residual	51	1	0.01		
	Total	52	2			
THMFP vs DOC	Regression	1	11371	11371	121	5E-15
	Residual	51	4793	94		
	Total	52	16163			
THMFP vs UV	Regression	1	8928	8928	63	2E-10
	Residual	51	7235	142		
	Total	52	16163			
THMFP vs SUVA	Regression	1	794	794	3	1E-01
	Residual	51	15369	301		
	Total	52	16163			
THMFP vs HPO (%)	Regression	1	7009	7009	39	8E-08
	Residual	51	9154	179		
	Total	52	16163			
THMFP vs HPO (mg/L)	Regression	1	12984	12984	208	1E-19
	Residual	51	3179	62		
	Total	52	16163			
Doc vs UV	Regression	1	19	19	78	8E-12
	Residual	51	13	0.25		
	Total	52	32			
DOC vs SUVA	Regression	1	0.04	0.04	0.27	6E-01
	Residual	51	8	0.16		
	Total	52	8			

	ANOVA	*df*	*SS*	*MS*	*F*	*P-value*
DOC vs HPO (%)	Regression	1	268	268	24	1E-05
	Residual	51	577	11		
	Total	52	845			
DOC vs HPO (mg/L)	Regression	1	2	2	795	9E-33
	Residual	51	0.10	0.002		
	Total	52	2			
UV vs SUVA	Regression	1	14	14	41	4E-08
	Residual	51	18	0.35		
	Total	52	32			
UV vs HPO (%)	Regression	1	17	17	60	4E-10
	Residual	51	15	0.29		
	Total	52	32			
UV vs HPO (mg/L)	Regression	1	22	22	116	9E-15
	Residual	51	10	0.19		
	Total	52	32			
SUVA vs HPO (%)	Regression	1	2	2	17	1E-04
	Residual	51	6	0.12		
	Total	52	8			
SUVA vs HPO (mg/L)	Regression	1	0.30	0.30	2	2E-01
	Residual	51	8	0.16		
	Total	52	8			

Appendix B - Residual Plots



a)



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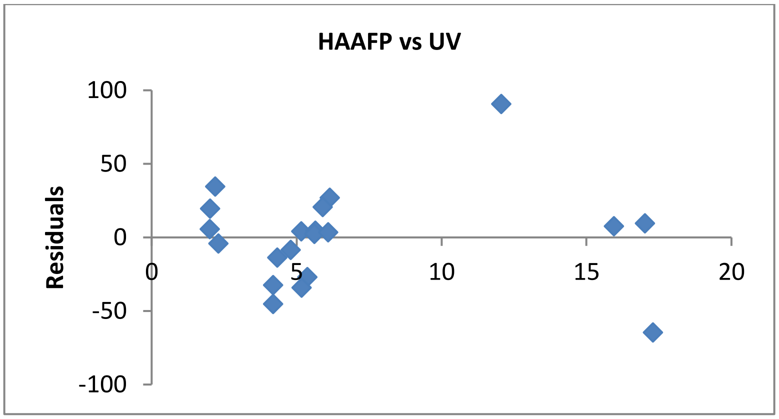
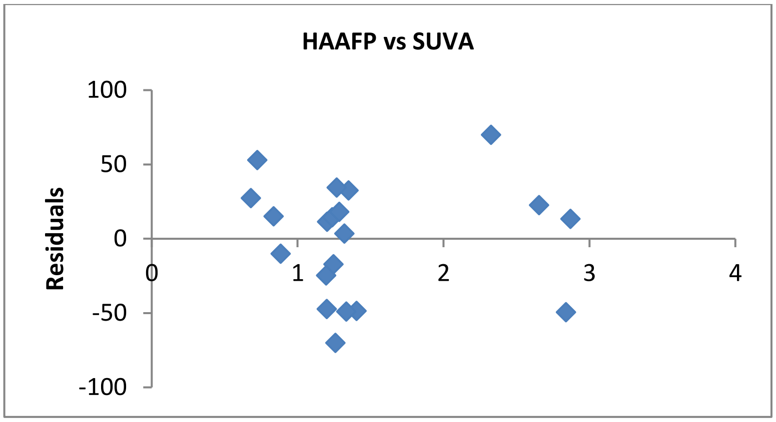
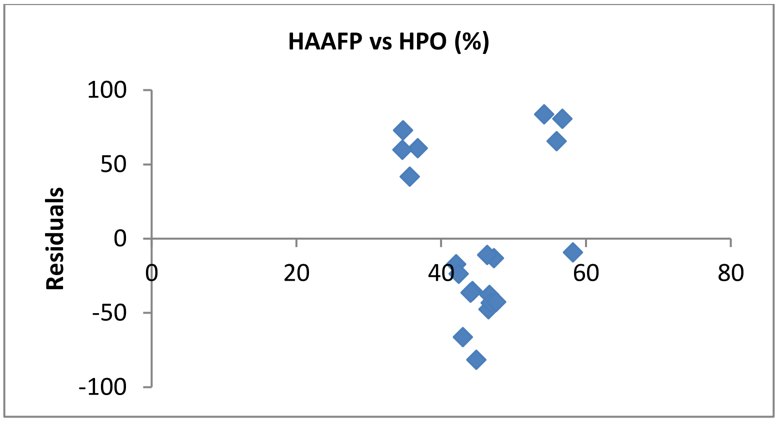


c)



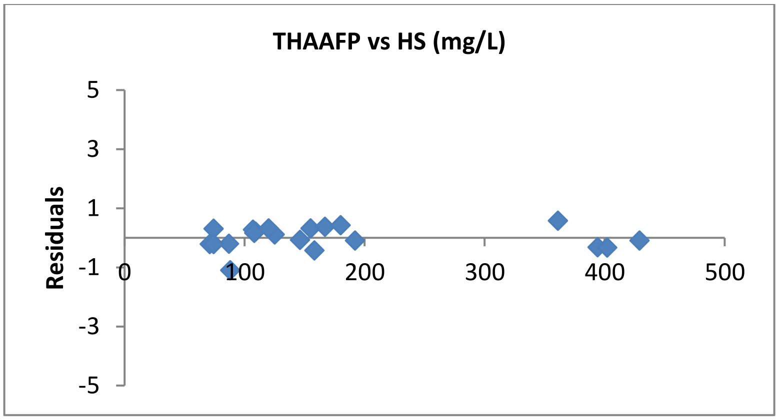
HAAFP vs SUVA
Residuals
100
50
0
-50
-100
0
1
2
3
4

d)



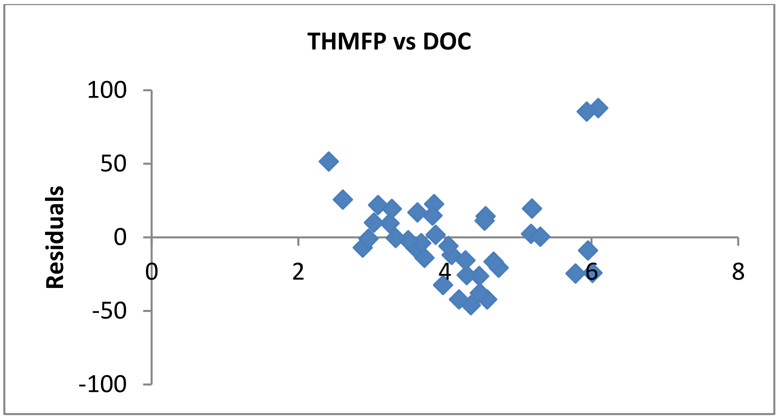
HAAFP vs HPO (%)
Residuals
100
50
0
-50
-100
0
20
40
60
80

e)

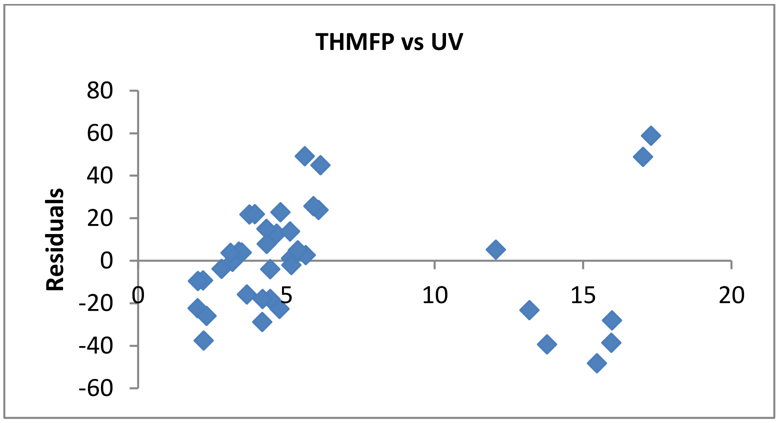


THAAFP vs HS (mg/L)
Residuals
5
3
1
-1
-3
-5
0
100
200
300
400
500

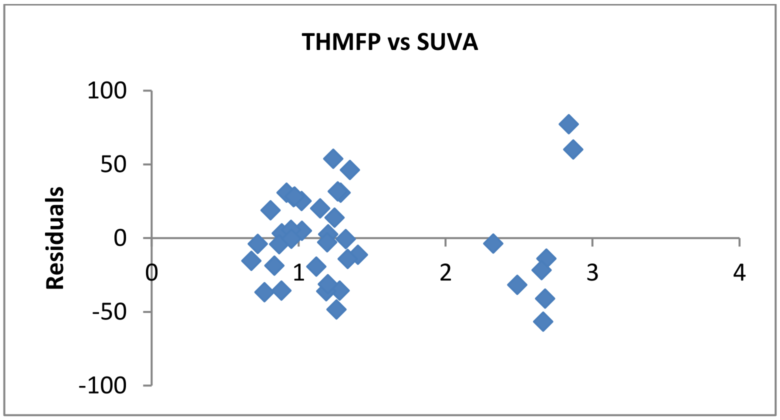
f)


THMFP vs DOC
Residuals
100
50
0
-50
-100
0
2
4
6
8

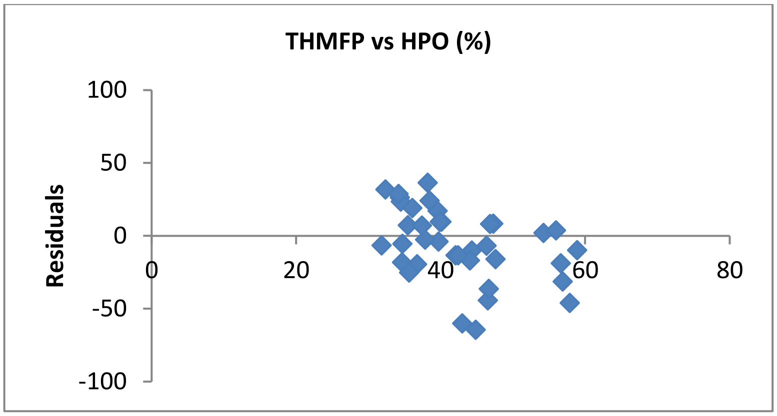
g)


THMFP vs UV
Residuals
80
60
40
20
0
-20
-40
-60
0
5
10
15
20

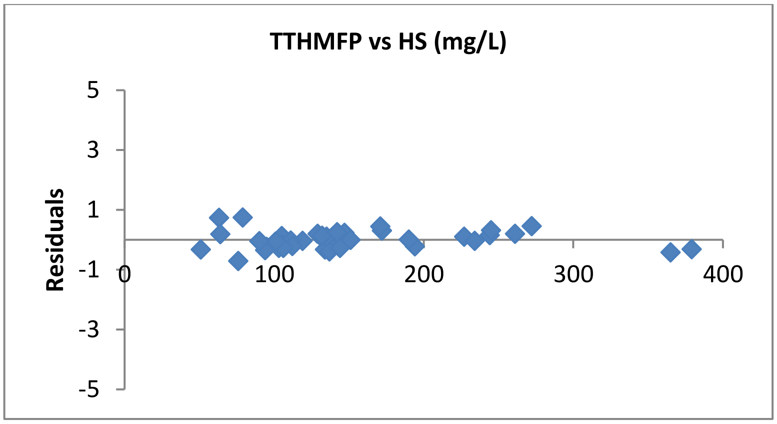
h)


THMFP vs SUVA
Residuals
100
50
0
-50
-100
0
1
2
3
4

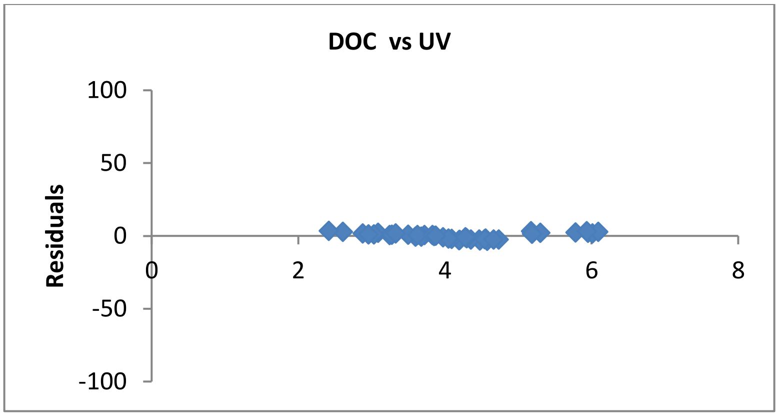
i)


THMFP vs HPO (%)
Residuals
100
50
0
-50
-100
0
20
40
60
80

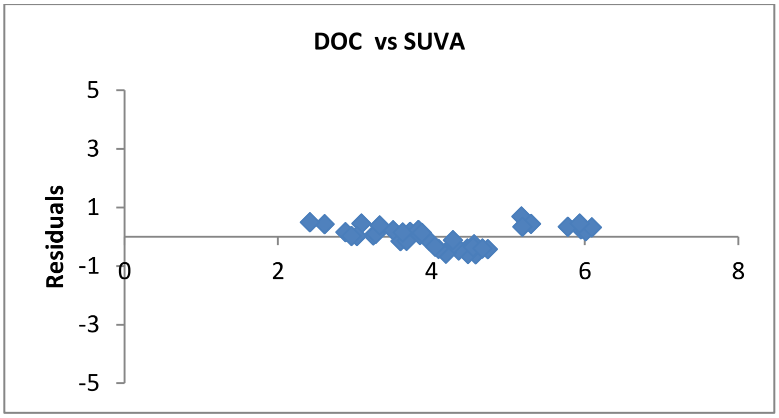
j)


TTHMFP vs HS (mg/L)
Residuals
5
3
1
-1
-3
-5
0
100
200
300
400

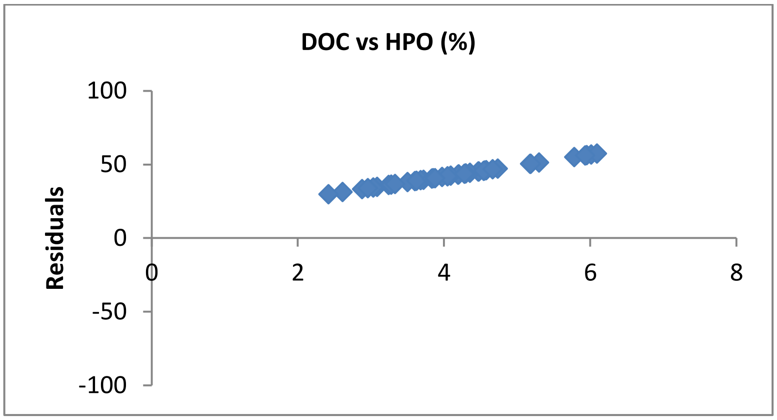
k)


DOC vs UV
Residuals
100
50
0
-50
-100
0
2
4
6
8

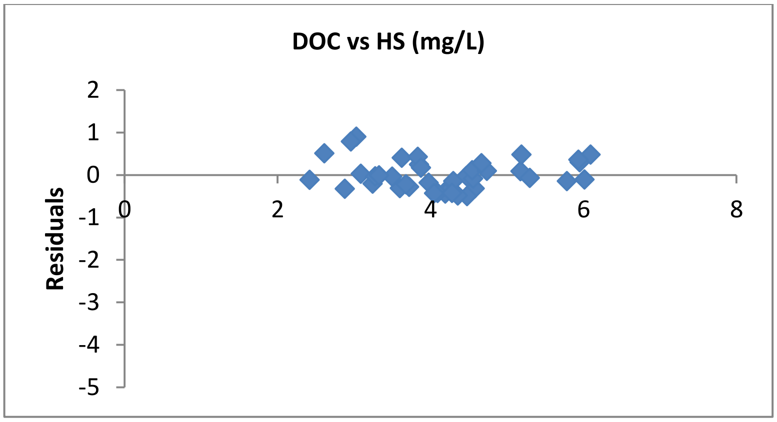
l)


DOC vs SUVA
Residuals
5
3
1
-1
-3
-5
0
2
4
6
8

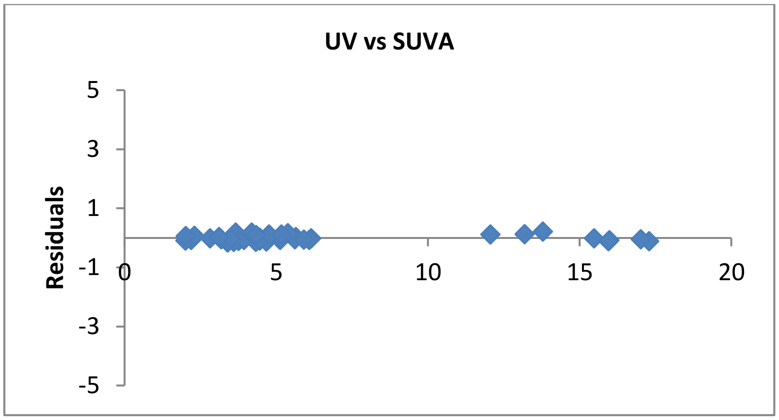
m)


DOC vs HPO (%)
Residuals
100
50
0
-50
-100
0
2
4
6
8

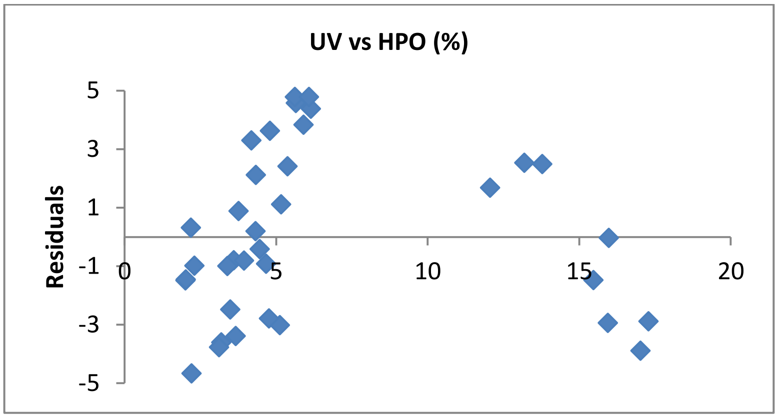
n)


DOC vs HS (mg/L)
Residuals
2
1
0
-1
-2
-3
-4
-5
0
2
4
6
8

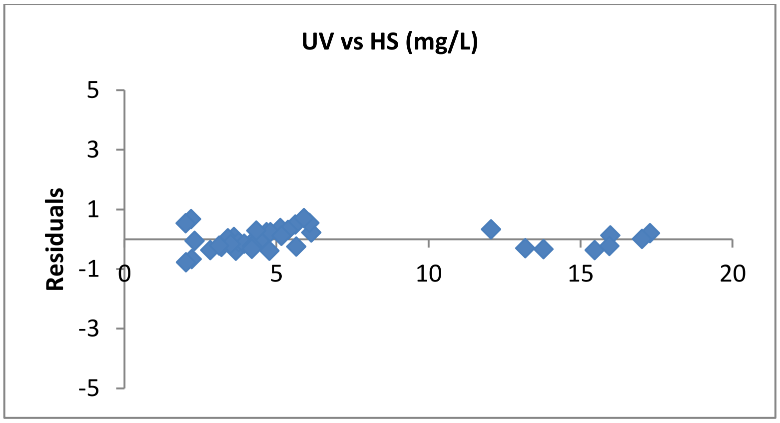
o)


UV vs SUVA
Residuals
5
3
1
-1
-3
-5
0
5
10
15
20

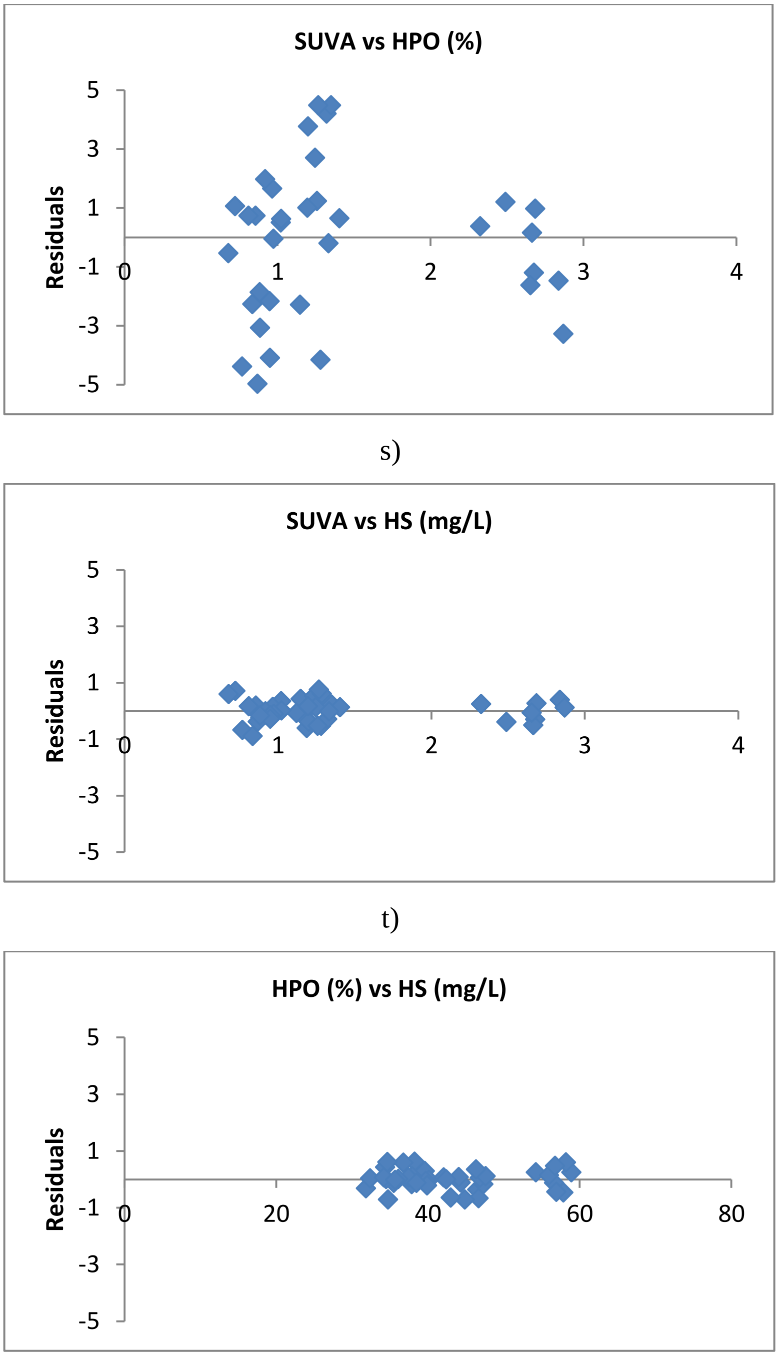
p)


UV vs HPO (%)
Residuals
5
3
1
-1
-3
-5
0
5
10
15
20

q)


UV vs HS (mg/L)
Residuals
5
3
1
-1
-3
-5
0
5
10
15
20

r)

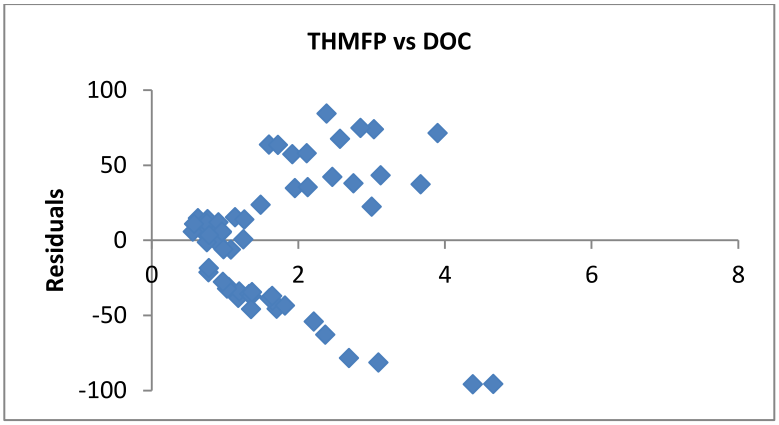


s)

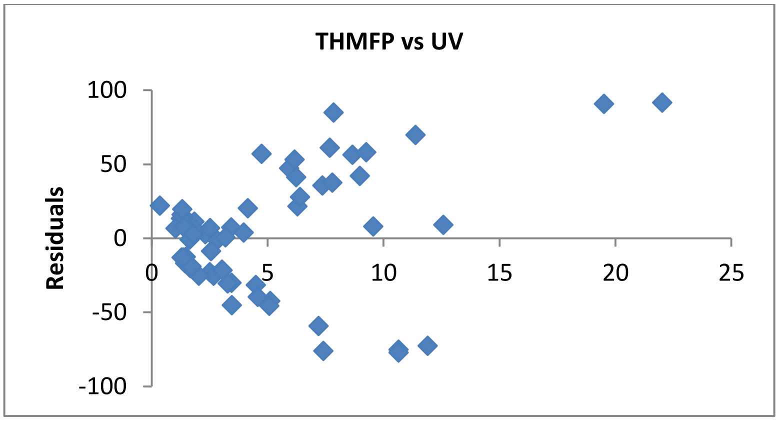
t)

u)

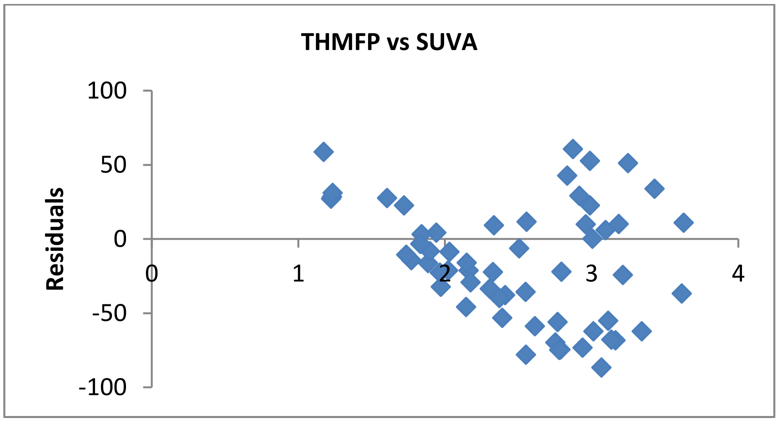
Figure B-1. Residual plots for regression analysis of Mannheim Water Treatment Plant parameters reported in Table 3-2.


THMFP vs DOC
Residuals
100
50
0
-50
-100
0
2
4
6
8

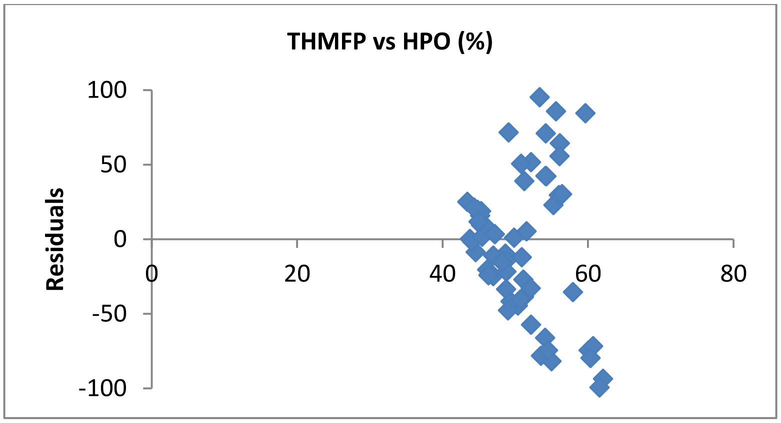
a)


THMFP vs UV
Residuals
100
50
0
-50
-100
0
5
10
15
20
25

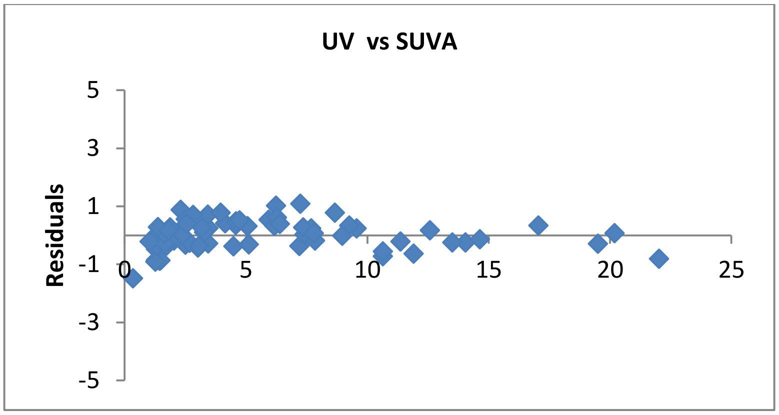
b)


THMFP vs SUVA
Residuals
100
50
0
-50
-100
0
1
2
3
4

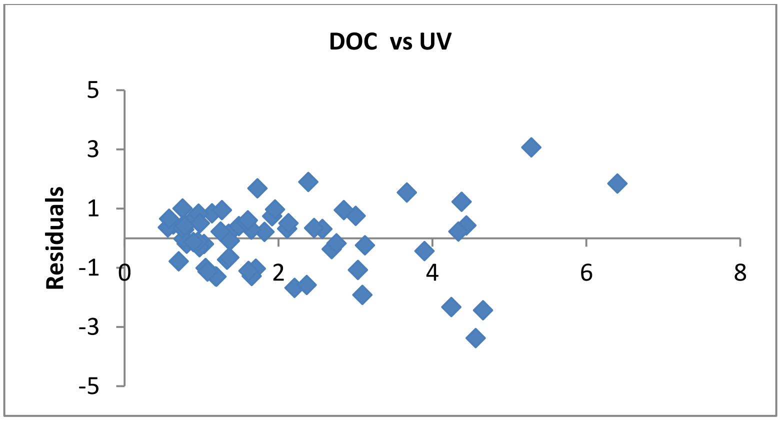
c)


THMFP vs HPO (%)
Residuals
100
50
0
-50
-100
0
20
40
60
80

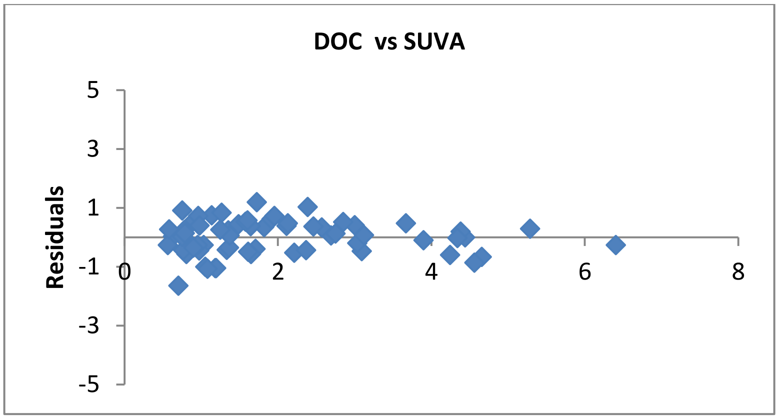
d)


UV vs SUVA
Residuals
5
3
1
-1
-3
-5
0
5
10
15
20
25

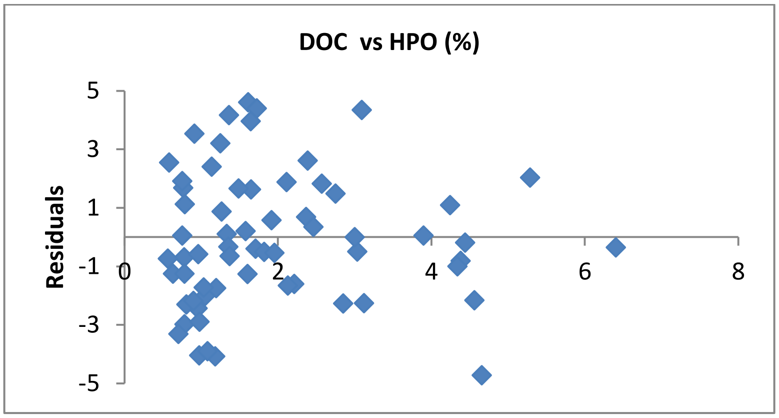
e)


DOC vs UV
Residuals
5
3
1
-1
-3
-5
0
2
4
6
8

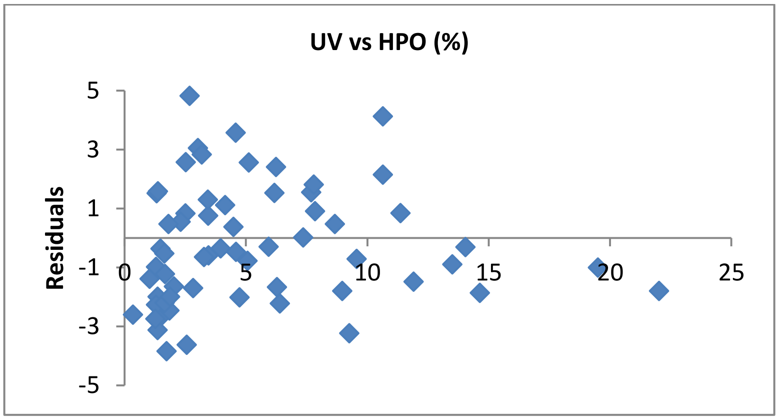
f)


DOC vs SUVA
Residuals
5
3
1
-1
-3
-5
0
2
4
6
8

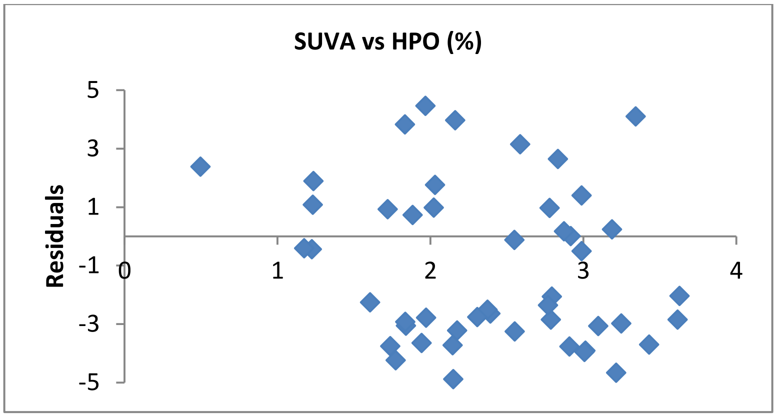
g)


DOC vs HPO (%)
Residuals
5
3
1
-1
-3
-5
0
2
4
6
8

h)

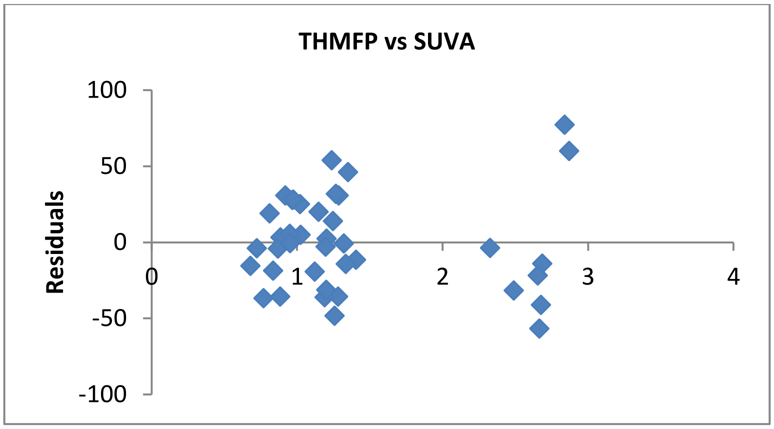

UV vs HPO (%)
Residuals
5
3
1
-1
-3
-5
0
5
10
15
20
25

i)

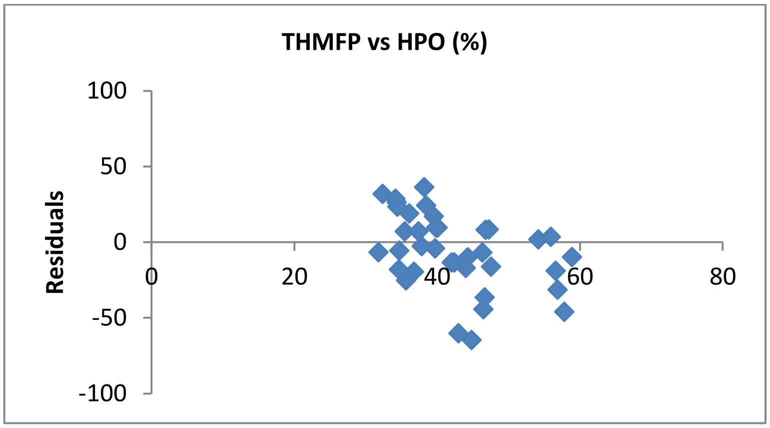


j)

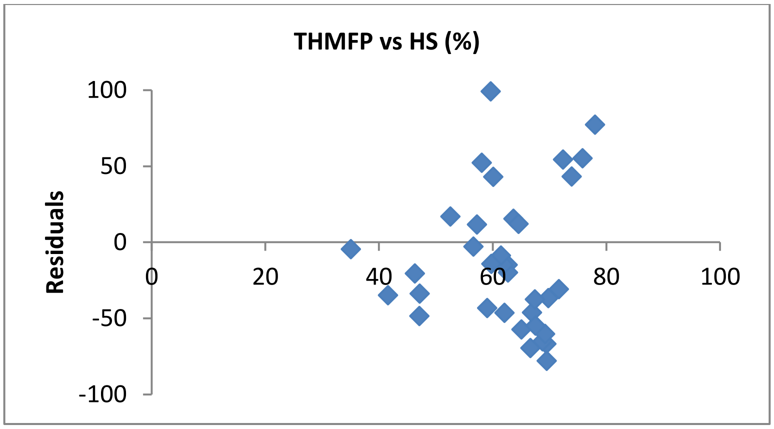
Figure B-2. Residual plots for regression analysis of Rocky Mountain (2013 and 2014) parameters after wildfire and post-fire salvage logging reported in Table 4-1.


THMFP vs SUVA
Residuals
100
50
0
-50
-100
0
1
2
3
4

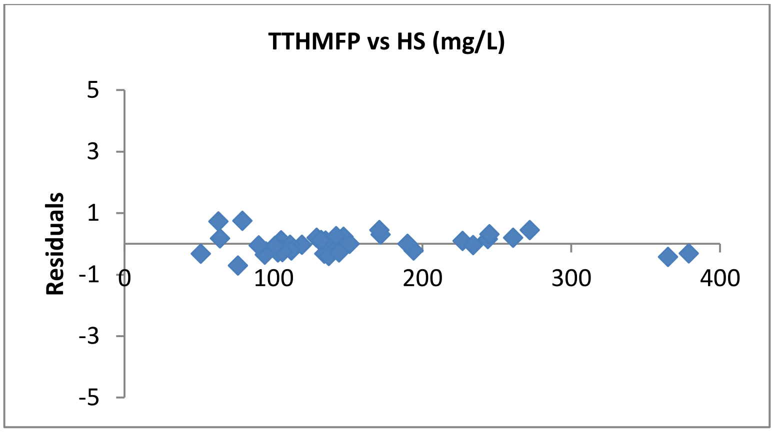
a)


THMFP vs HPO (%)
Residuals
100
50
0
-50
-100
0
20
40
60
80

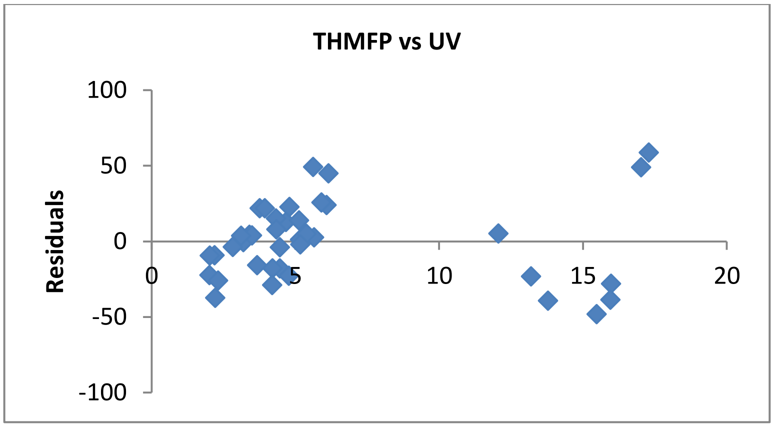
b)


THMFP vs HS (%)
Residuals
100
50
0
-50
-100
0
20
40
60
80
100

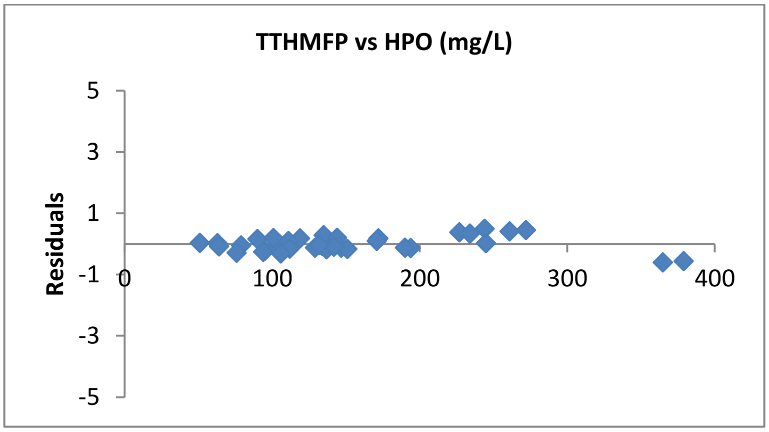
c)



d)

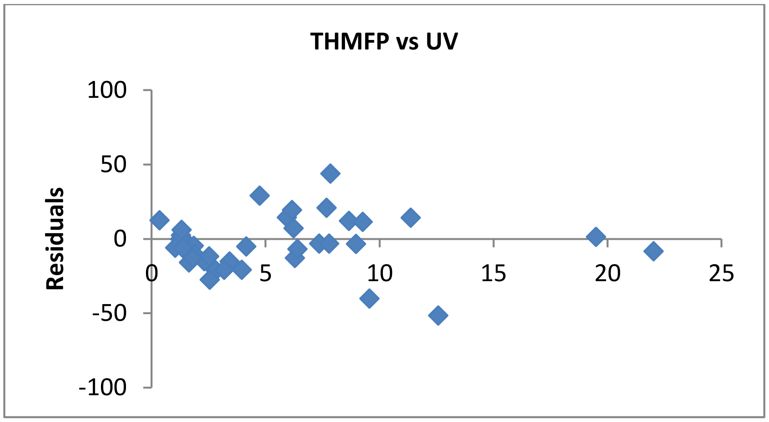


e)

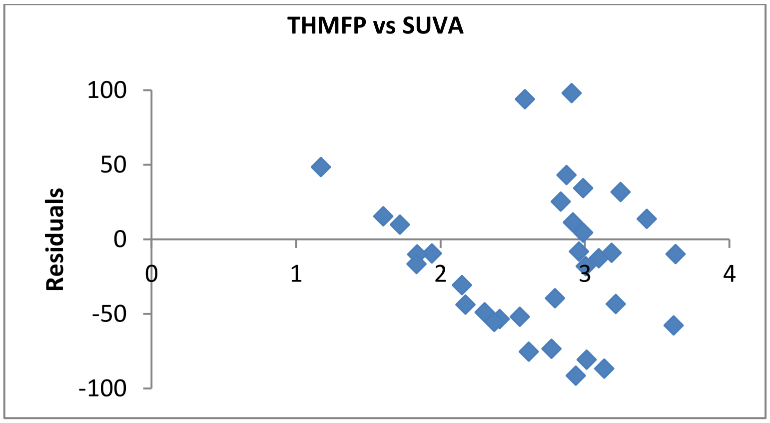


f)

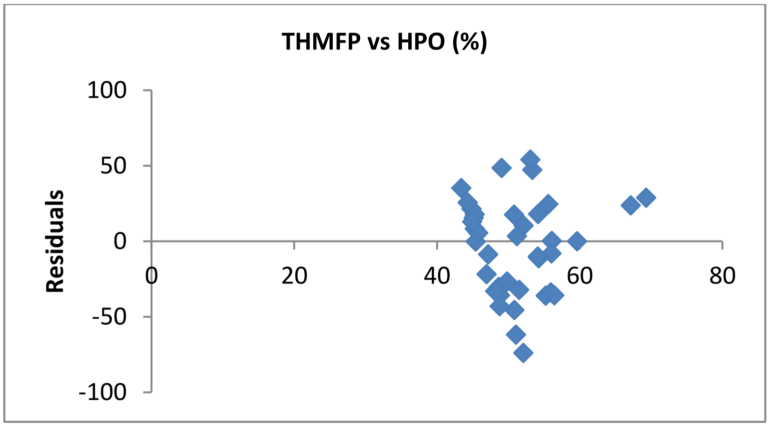
Figure B-3. Residual plots for regression analysis of Mannheim Water Treatment Plant parameters reported in Table 5-1.


THMFP vs UV
Residuals
100
50
0
-50
-100
0
5
10
15
20
25

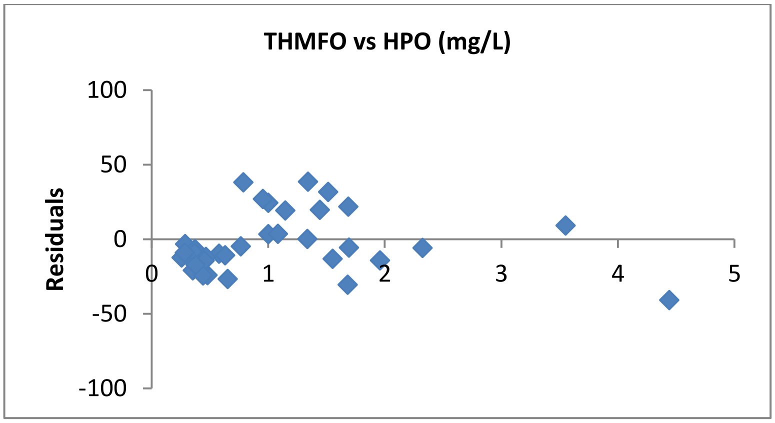
a)


THMFP vs SUVA
Residuals
100
50
0
-50
-100
0
1
2
3
4

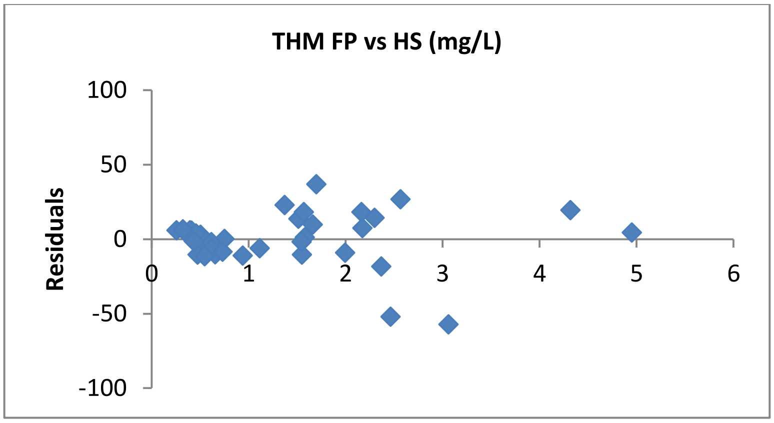
b)


THMFP vs HPO (%)
Residuals
100
50
0
-50
-100
0
20
40
60
80

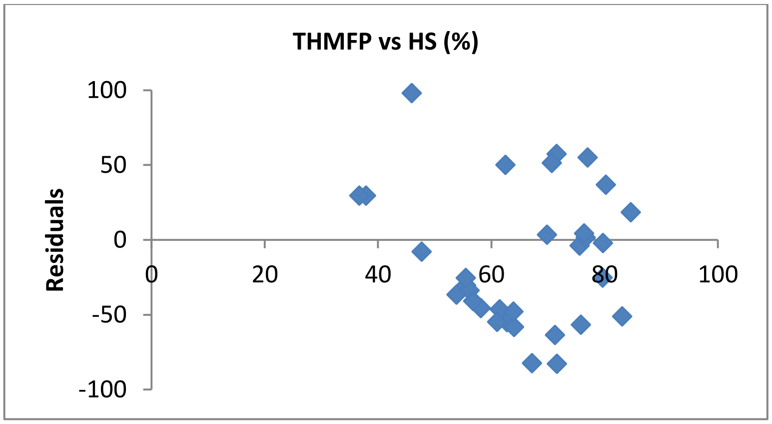
c)



d)

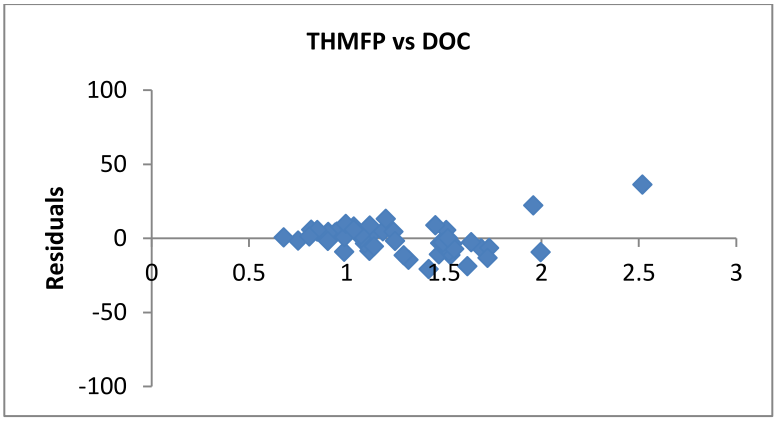


e)

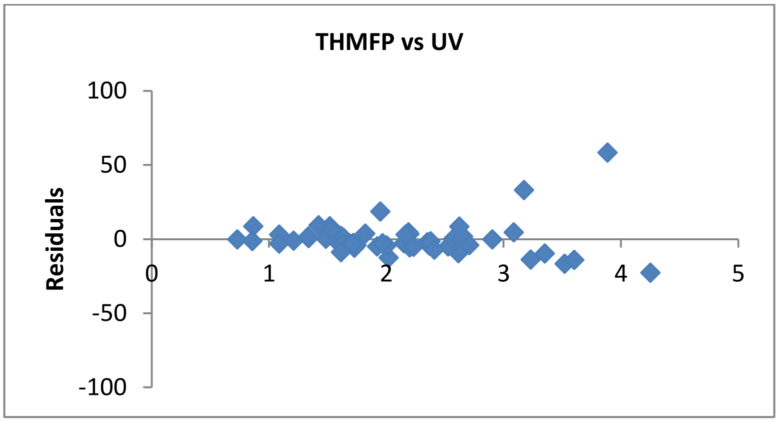


f)

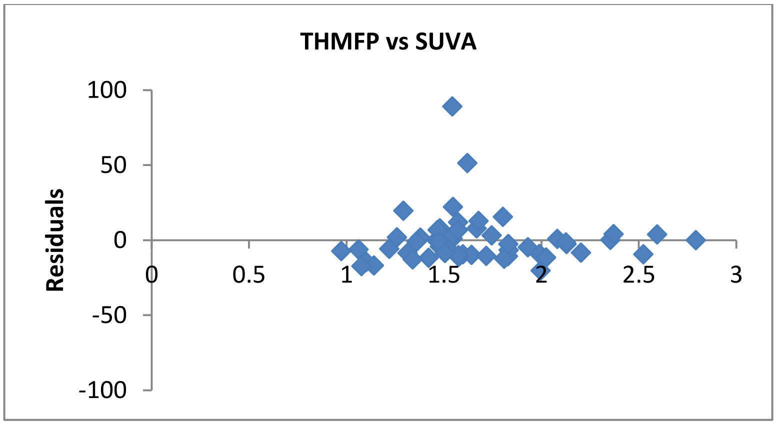
Figure B-4. Residual plots for regression analysis of Rocky Mountain (2014) parameters reported in Table 5-1.


THMFP vs DOC
Residuals
100
50
0
-50
-100
0
0.5
1
1.5
2
2.5
3

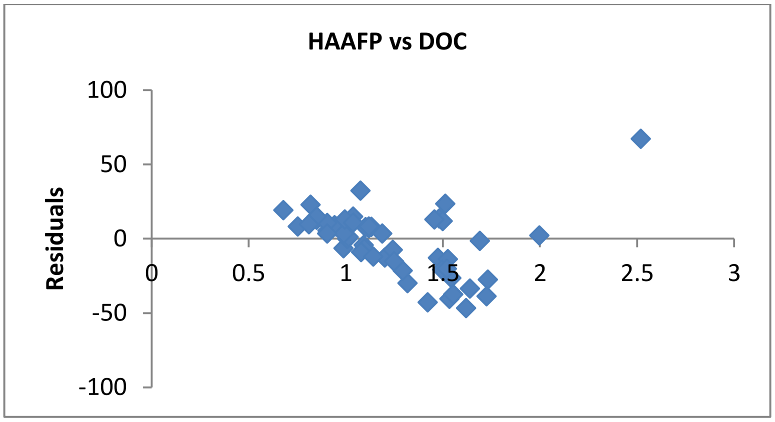
a)


THMFP vs UV
Residuals
100
50
0
-50
-100
0
1
2
3
4
5

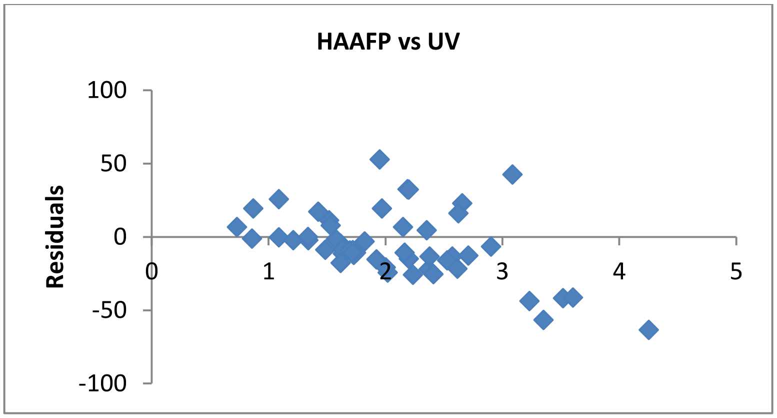
b)


THMFP vs SUVA
Residuals
100
50
0
-50
-100
0
0.5
1
1.5
2
2.5
3

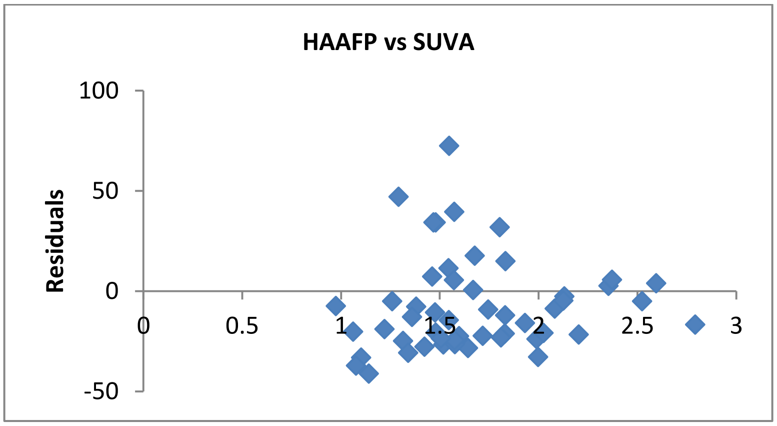
c)


HAAFP vs DOC
Residuals
100
50
0
-50
-100
0
0.5
1
1.5
2
2.5
3

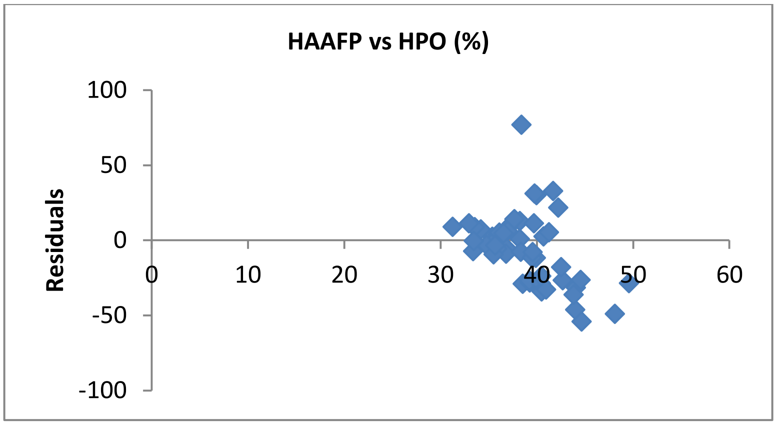
d)


HAAFP vs UV
Residuals
100
50
0
-50
-100
0
1
2
3
4
5

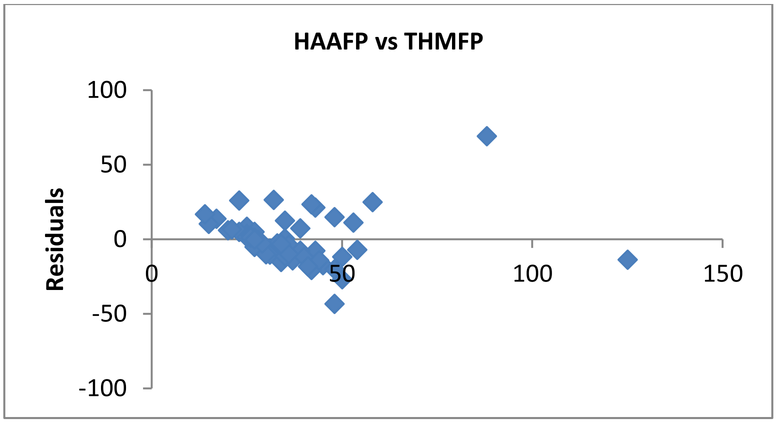
e)


HAAFP vs SUVA
Residuals
100
50
0
-50
0
0.5
1
1.5
2
2.5
3

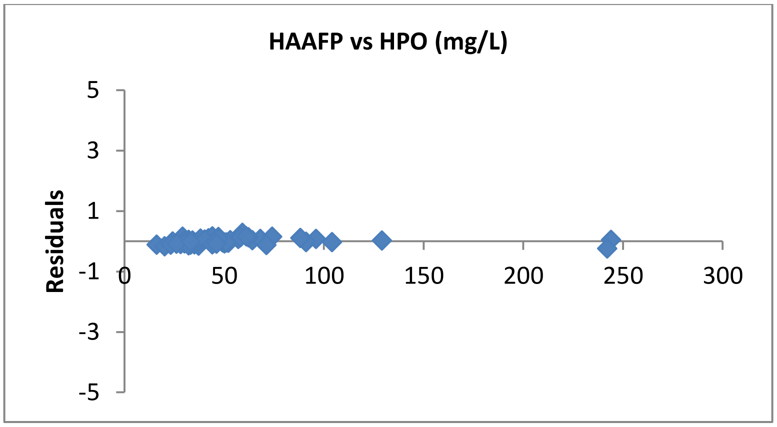
f)


HAAFP vs HPO (%)
Residuals
100
50
0
-50
-100
0
10
20
30
40
50
60

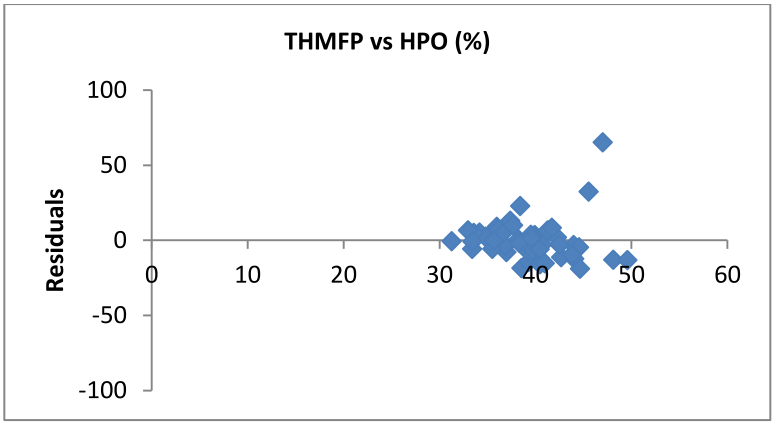
g)


HAAFP vs THMFP
Residuals
100
50
0
-50
-100
0
50
100
150

h)

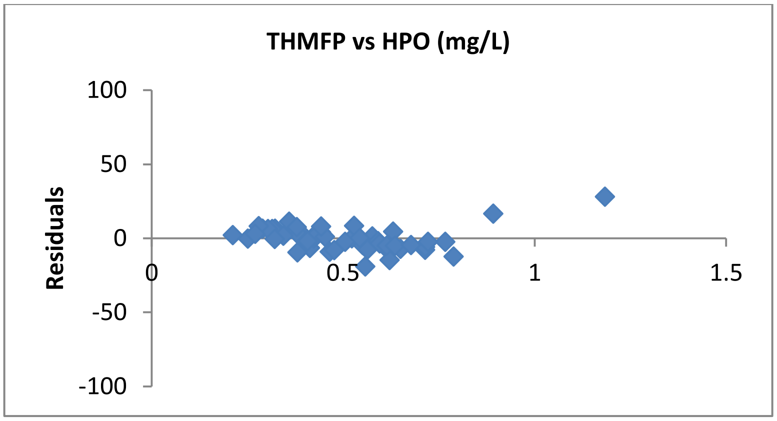

HAAFP vs HPO (mg/L)
Residuals
5
3
1
-1
-3
-5
0
50
100
150
200
250
300

i)



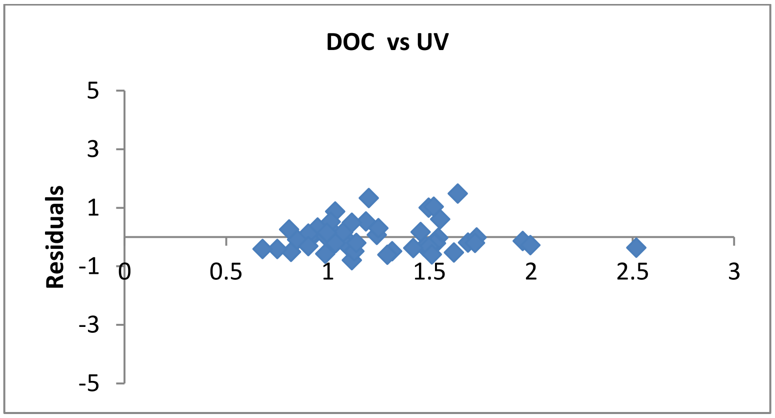
THMFP vs HPO (%)
Residuals
100
50
0
-50
-100
0
10
20
30
40
50
60

j)



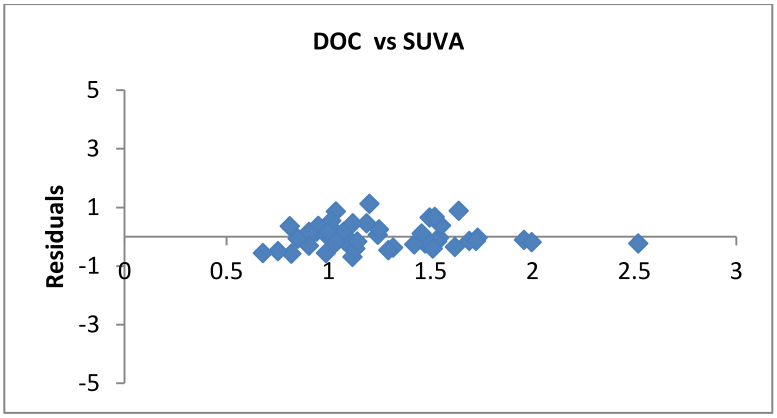
THMFP vs HPO (mg/L)
Residuals
100
50
0
-50
-100
0
0.5
1
1.5

k)

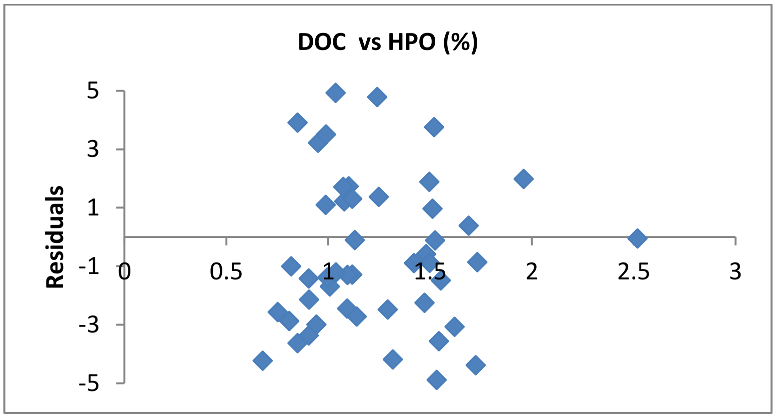


DOC vs UV
Residuals
5
3
1
-1
-3
-5
0
0.5
1
1.5
2
2.5
3

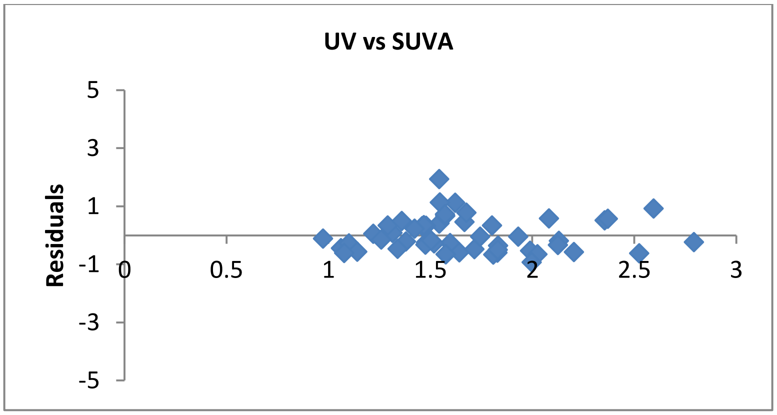
l)


DOC vs SUVA
Residuals
5
3
1
-1
-3
-5
0
0.5
1
1.5
2
2.5
3

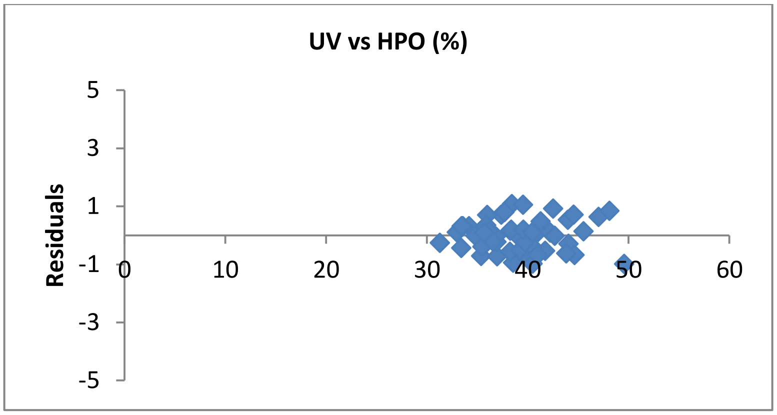
m)


DOC vs HPO (%)
Residuals
5
3
1
-1
-3
-5
0
0.5
1
1.5
2
2.5
3

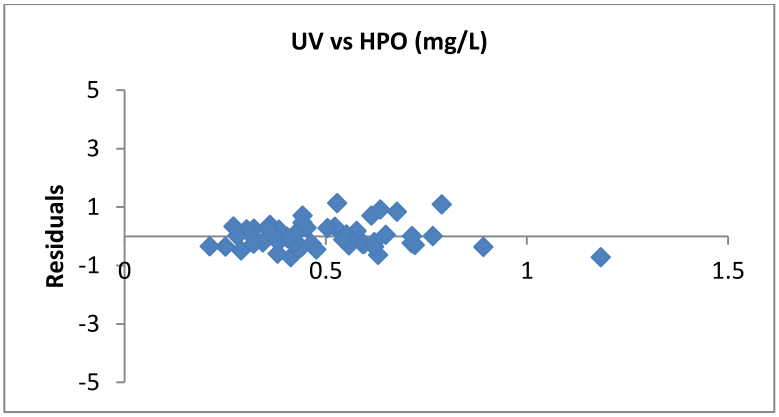
n)


UV vs SUVA
Residuals
5
3
1
-1
-3
-5
0
0.5
1
1.5
2
2.5
3

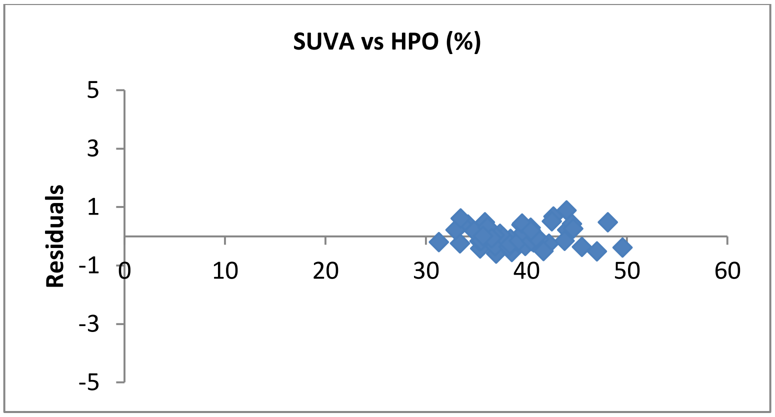
o)


UV vs HPO (%)
Residuals
5
3
1
-1
-3
-5
0
10
20
30
40
50
60

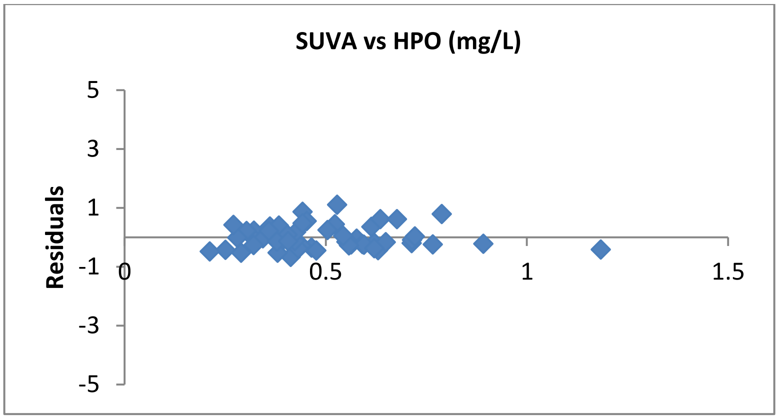
p)


UV vs HPO (mg/L)
Residuals
5
3
1
-1
-3
-5
0
0.5
1
1.5

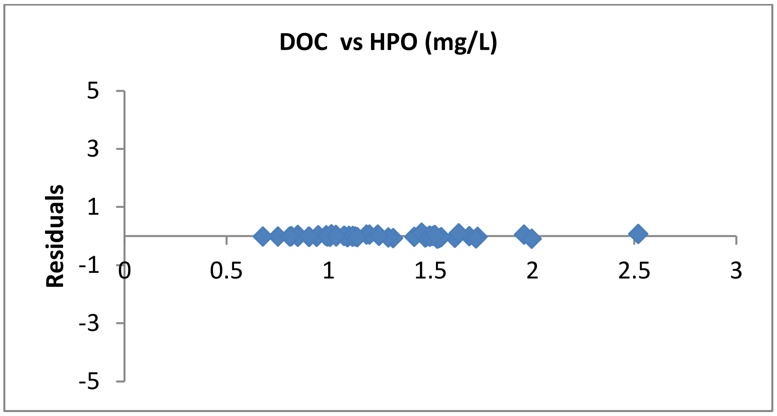
q)


SUVA vs HPO (%)
Residuals
5
3
1
-1
-3
-5
0
10
20
30
40
50
60

r)



s)



t)

Figure B-5. Residual plots for regression analysis of harvesting catchments parameters reported in Table 6-3.

Glossary

ANOVA	Analysis of Variance
AOC	Assimilable Organic Carbon
BACI	Before/After, Control/Impact
BB	Building Blocks
BCAA	Bromochloroacetic Acid
BDCM	Bromodichloromethane
BDOC	Biodegradable Organic Carbon
BMP	Best Management Practice
BOM	Biodegradable Organic Matter
BP	Biopolymers
CHA	Hydrophilic Charged Acids
DBAA	Dibromoacetic Acid
DBCM	Dibromochloromethane
DBPs	Disinfection By-products
DBP-FP	Disinfection By-product Formation Potential
DCAA	Dichloroacetic Acid
DOC	Dissolved Organic Carbon
DON	Dissolved Organic Nitrogen
ESI	Electrospray Ionization
FEEM	Fluorescence Excitation Emission Matrix
FFFF	Flow Field-Flow Fractionation
FI	Florescence Index
FTICR	Fourier Transform Ion Cyclotron Resonance
FTIR	Fourier Transform Infra-Red
GAC	Granular Activated Carbon
GPC	Gel Permeation Chromatography
HAAs	Haloacetic Acids
HAA-FP	Haloacetic Acid Formation Potential
HIX	Humification Index
HPI	Hydrophilic
HPLC	High Pressure Liquid Chromatography

HPSEC	High Performance Size Exclusion Chromatography
HPO	Hydrophobic
HS	Humic Substances
LC	Liquid Chromatography
LC-OCD	Liquid Chromatography – Organic Carbon Detector
LMW	Low Molecular Weight
MBAA	Monobromoacetic Acid
MCAA	Monochloroacetic Acid
MS	Mass Spectrometry
NDMA	N-Nitrosodimethylamine
NOM	Natural Organic Matter
NMR	Nuclear magnetic Resonance
PCA	Principal Component Analysis
PRAM	Polarity Rapid Assessment Method
Py-GC-MS	Pyrolysis-Gas Chromatography-Mass Spectrometry
RO	Reverse Osmosis
SEC	Size Exclusion Chromatography
SHA	Slightly Hydrophobic Acids
SPE	Solid Phase Extraction
SUVA	Specific Ultraviolet Absorbance
SWP	Source Water Protection
TCAA	Ttrichloroacetic Acid
THMs	Trihalomethanes
THM-FP	Trihalomethane Formation Potential
TOC	Total Organic Carbon
UF	Ultrafiltration
VHA	Very Hydrophobic Acids
WTP	Water Treatment Plant