# Wildfire Impacts on Water Quality and 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.

I understand that my thesis may be made electronically available to the public.

### ABSTRACT

Forests are critical source areas for downstream drinking water supplies in many parts of the world. However, large-scale landscape disturbance by insect infestation and wildfire—exacerbated by warming climate—can have a significant impact on downstream water quality and drinking water treatability. In 2003, the Lost Creek wildfire burned a nearly contiguous area of 20,000 ha and altered water quality in several tributaries of the Oldman River watershed in southwestern Alberta, Canada. Coagulant demand and two key water treatability proxies (turbidity and dissolved organic carbon [DOC]) were evaluated in reference (unburned), burned, and burned and salvage logged watersheds to describe the effects of these land disturbance on drinking water treatability. DOC concentration and character (hydrophobicity by resin fractionation, aromaticity by  $UV_{254}$ , and specific UV absorbance [SUVA]) were evaluated. Eight years after the disturbance, turbidities in streams draining the burned and burned and salvage logged watersheds remained elevated by factors of  $\sim$ 15 and  $\sim$ 22 on average respectively, compared to the reference watersheds. Stream DOC concentrations remained elevated by factors of ~2 and ~4 on average respectively. Stream DOC hydrophobicity respectively increased by factors of ~1.5 and ~1.4 on average and stream DOC aromaticity also increased by factors of  $\sim 1.5$  and  $\sim 1.6$  on average, as a result of these disturbances. These changes in DOC character in impacted streams suggest increased allochthonous inputs from disturbed watersheds; however, further investigation is needed to define the pathways by which these inputs would be delivered to streams, especially so long (eight years) after disturbance. Although hydrophobic and aromatic DOC is generally more amenable to removal by coagulation during drinking water treatment (relatively hydrophilic and aliphatic DOC), coagulant demand (evaluated by jar testing) significantly increased in the headwaters streams of the disturbed watersheds, thereby demonstrating potentially substantial cost implications for water treatment facilities downstream of such disturbances. Moreover, source water quality was notably more variable and changed rapidly in the streams draining disturbed watersheds; such increasingly variable and rapidly changing source water quality has the potential to challenge drinking water treatment infrastructure and operational responsiveness beyond their capacities. As a result, severe watershed disturbances such as wildfires can significantly increase the probability of service disruptions; moreover, as demonstrated herein, the effects of wildfire on water quality and drinking water treatability can be long lasting.

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## DEDICATION

To Jenna Banana,

Don't be afraid of failure don't worry about expectations.

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### **1** INTRODUCTION

#### **1.1 RESEARCH MOTIVATION**

In many parts of the world, forests are critical source areas for downstream drinking water supplies. For example, undisturbed forested regions supply high-quality potable water to more than twothirds of the population in North America (Neary, et al., 2009; Emelko, et al., 2011). Large-scale landscape disturbances by insect infestation and wildfire—exacerbated by warming climate—can have a significant impact on downstream hydrology and water quality (Bladon, et al., 2008; Silins, et al., 2009; Emelko, et al., 2011; Silins, et al., 2014). They also can have severe effects on drinking water treatability (Emelko, et al., 2011; Writer, et al., 2014; Hohner, et al., 2016). Notably, in some cases, these impacts can last for decades or longer (Emelko, et al., 2016). The severity of wildfire impacts on water quality (and thus drinking water treatability) depend on many factors such as soil type (González-Pérez, et al., 2004), vegetation type (Boerner, 1982), antecedent conditions (Richter, et al., 1982) and fuel type. Nonetheless, high quality drinking water resources originating in healthy forested regions are increasingly vulnerable to these potential catastrophic disturbances (Bladon, et al., 2014; Robinne, et al., 2016).

In 2003, the Lost Creek wildfire consumed over 20,000 ha of the Rocky Mountain headwater regions for the tributaries of the Oldman River watershed in southwestern Alberta, Canada (Bladon, et al., 2008). A long term study of water quality in wildfire impacted tributaries within this region demonstrated that key drinking water treatability indicators (turbidity and dissolved organic carbon [DOC]) were and remain increasing variable, with higher peak values, compared to streams in reference (unburned) watersheds (Silins, et al., 2009; Emelko, et al., 2011; Emelko, et al., 2016). While relatively little is known about wildfire impacts on drinking water treatability, global wildfire severity, areal extent of burn, and length of wildfire season continue to increase—it is anticipated that this will continue through the end of the century (Gillett, et al., 2004; Flannigan, et al., 2005; Westerling, et al., 2006). Thus, wildfires will pose an increasing threat to the sustainability of drinking water supply and treatment in many regions of the world (Emelko, et al., 2011; Bladon, et al., 2014; Robinne, et al., 2016). Accordingly, there is a critical need to evaluate the wildfire-associated implications of changing source water quality on drinking water treatability to enable water supply practitioners to respond and adapt to changing climate.

Dissolved organic carbon concentration and character (i.e., hydrophobicity, aromaticity) are both important indicators of drinking water treatability because they affect many processes in drinking water treatment and distribution, including chemical coagulant demand, disinfection by-product formation potential (DBP-FP), oxidant demand, and biological regrowth in the distribution system (Emelko, et al., 2011; Crittenden, et al., 2012). In recent decades, DOC concentrations in surface water supplies have been increasing worldwide (Hejzlar, et al., 2003; Monteith, et al., 2007; Erlandsson, et al., 2008). It has been demonstrated that wildfires or prescribed burning can significantly contribute to increases in aqueous DOC in high quality forested watersheds in wildfire prone areas (Carignan, et al., 2000; Minshall, et al., 2001; Allen, et al., 2003; Mast & Clow, 2008; Emelko, et al., 2011). While important post-disturbance observations suggest that wildfire can have significant implications for drinking water treatability (Emelko, et al., 2011; Writer, et al., 2014; Hohner, et al., 2016), watershed-scale investigations of wildfire impacts on drinking water treatability are rarely available. The cost and difficulty of conducting long-term evaluations that include calibrated reference watersheds and consideration of hydro-climatic variability at that scale often preclude such assessments. To enable climate change preparedness and the development of associated adaptation strategies, it is critical to invest in the long-term evaluation of wildfire impacts on water quality and drinking water treatability. In particular, an evaluation of changes in DOC concentration and character is a critical key component of any such investigation-although elevated DOC levels in impacted streams and rivers have been demonstrated after wildfire, the potential longevity of these changes in source water quality has not been reported. While a few field-scale studies have suggested that DOC aromaticity and associated DBP-FP can be elevated after wildfire (Hohner, et al., 2016), no reported investigations to date have decoupled effects of wildfire or prescribed burning from background variability at the watershed scale. Moreover, the effects of post-fire salvage logging on drinking water treatability also are unknown at present.

#### **1.2 Research objectives and scope**

The overall goal of this research was to evaluate the potential implications of wildfire and post-fire salvage logging on water quality and drinking water treatability. The specific objectives of the research were to:

1. Quantify and characterize the long-term impacts of wildfire and post-fire salvage logging on headwaters stream turbidity and DOC concentrations,

- Evaluate changes in DOC concentration for different flow regimes (bases flow, storm flow) in forested headwater regions in both undisturbed (reference) and disturbed (burned, postfire salvage logged) watersheds,
- 3. Evaluate the character (i.e., hydrophobicity, aromaticity) of DOC in forested headwater regions in both undisturbed (reference) and disturbed (burned, post-fire salvage logged) watersheds,
- 4. Evaluate the longer-term chemical dosing implications of wildfire to conventional drinking water treatment by quantifying changes in chemical coagulant demand in forested headwater regions several years after severe disturbance by wildfire and post-fire salvage logging.

#### **1.3 RESEARCH APPROACH**

In this research, the water quality impacts relevant to drinking water treatability resulting from the 2003 Lost Creek wildfire of southwestern Alberta were investigated. Turbidity and DOC data from source watersheds with varying degrees of wildfire associated land disturbance (reference [unburned], burned, and post-fire salvage logged) were evaluated during the eight years post-fire period (i.e., from 2003 to 2011). Some of the water quality impacts during these recovery years have been reported elsewhere (Bladon, et al., 2008; Silins, et al., 2014; Emelko, et al., 2011; Silins, et al., 2014; Emelko, et al., 2016), while others are reported herein. Specifically, turbidity and DOC during the eight years after wildfire. Jar tests were conducted to determine coagulant demand for turbidity and DOC and reduction. The relationships between flow regime and headwaters turbidity, DOC, and DOC hydrophobicity and aromaticity were evaluated.

#### 1.4 THESIS ORGANIZATION

Chapter 2 provides a review of disturbance (especially wildfire) impacts on water quality, with a focus on turbidity, natural organic matter (NOM), for which DOC is a key metric. NOM characterization and common water treatment methods are reviewed. Chapter 3 describes the study area, field and laboratory methods used in this investigation. Chapter 4 contains the research results and discussion. The conclusions, implications and recommendations of the study are provided in Chapter 5, which is then followed by a list of the references cited herein. Appendix A lists the

temperature and precipitation data from Environment Canada. Appendix B contains the raw data from the solid phase extraction. Appendix C provides the raw data from jar tests.

### **2 BACKGROUND AND LITERATURE REVIEW**

The effect of wildfire on water quality is well documented (Emelko, et al., 2011; Smith, et al., 2011). Wildfire negatively impacts water quality through increased aqueous nutrient (N, C, and P) (Boerner, 1982; Bladon, et al., 2008; Bladon, et al., 2014; Emelko, et al., 2011; Emelko, et al., 2016), suspended solids/turbidity (Silins, et al., 2009; Silins, et al., 2009; Emelko, et al., 2011; Murphy, et al., 2012), and metals (Silins, et al., 2009; Burton, et al., 2016) concentrations. Similarly, anthropogenic land disturbances such as prescribed burns and salvage logging also adversely affect water quality (Richter, et al., 1982; Battle & Golladay, 2003; Kreutzweiser, et al., 2008). Deteriorated water quality caused by wildfires and other land disturbances can be expected to pose challenges to drinking water treatability since turbidity and DOC that are frequently impacted by wildfire also are key drivers of water treatment infrastructure and operational needs (Emelko, et al., 2011; Crittenden, et al., 2012). However only a limited number of studies have reported on drinking water treatability implications of wildfire (Emelko, et al., 2011; Writer, et al., 2014; Hohner, et al., 2016). Notably, the longevity of wildfire and prescribed burn effects of these key aspects of water quality that inform treatability are sometime contradictory (Battle & Golladay, 2003; Evans, et al., 2017), and the longevity of these impacts neither well understood nor linked to specific physiographic settings or environmental processes.

#### 2.1 NATURAL ORGANIC MATTER

Natural organic matter broadly encompasses all carbon compounds found in soils, sediments, surface waters and groundwater that are: a) not living or b) artificially synthesized (Chen, et al., 2002). The nature of NOM ranges from simple well-known molecules (e.g. amino acids) to complex heterogeneous mixtures of compounds (Owen, et al., 1995). The majority of NOM is comprised of heterogeneous compounds known as humic substances formed from biologically mediated transformations or the decomposition of organisms and their by-products (International Humic Substances Society, 2007).

In spite of the relatively modest mass of organic matter relative to the global reservoir of carbon (2000 Gt versus 75, 000,000 Gt (Falkowski, et al., 2000)), NOM is a key component in many biogeochemical processes due to its ubiquitous, recalcitrant nature and chemical reactivity (Cole, et al., 2007). Within in an ecosystem, NOM facilitates pedogenesis (Kalbitz, et al., 2000), moderates the toxicity of organic pollutants (Hur, et al., 2006) and promotes transport of certain heavy metals in

soils (Kalbitz & Wennrich, 1998). Notably, NOM can be problematic for drinking water treatment. For example, it can alter the visual characteristics of treated water (Crittenden, et al., 2012), significantly increase chemical demand (Najm, et al., 1998), clog membrane filters (Peiris, et al., 2010), and form potentially toxic disinfection by-products (Bull, et al., 2009). The physical and chemical characteristics of NOM as well as it availability in aquatic systems, are related to environmental conditions such as geology (McKnight, et al., 1997), land use (Foley, et al., 2005), seasonal variability and hydroclimatic dynamics (O'Donnell, et al., 2010), and microbial activity (Andersen & Gjessing, 2002).

Environmental conditions and watershed processes regulate the concentration and characteristics of dissolved organic matter (DOM) (Rosario-Ortiz, et al., 2007). In forested headwater streams, allochthonous organic matter often comprises the majority of the organic matter pool and available energy in heterotrophic aquatic ecosystems (Bernhardt & Likens, 2002; Hood, et al., 2005). Discharge events such as snow melt or storms flush allochthonous organic matter from hillslopes to receiving streams, often contributing to increases in dissolved organic carbon (DOC) concentrations (Hornberger, et al., 1994; Vidon, et al., 2008). Continued flushing can deplete DOM in soils, however, and result in hysteresis of DOM with respect to discharge. (Boyer, et al., 1997; Laudon, et al., 2004). Season and antecedent precipitation/moisture conditions can affect the availability of allochthonous dissolved organic matter (Raymond & Saiers, 2010). Scott, Jones, Woof & Tipping (1998) reported changes in the seasonal character of organic matter due to microbial activity, rainfall, and soil conditions. Transport of allochthonous organic matter into streams via groundwater is further influenced by sorption reactions with mineral soils; these interactions occur over decades to thousands of years and may preferentially retain specific fractions of NOM (Gu, et al., 1994; Luthy, et al., 1997; Frank, et al., 2000; Post & Kwon, 2000). Thus, it has been hypothesized that sorption processes cause significant buffering of organic matter concentrations due to a large organic carbon pools in the soil (Michalzik, et al., 2003; Fröberg, et al., 2006). Temperature, availability of light and substrates regulate primary production of autochthonous organic matter by autotrophic organisms (Rosenfeld & Roff, 1991; Risse-Buhl, et al., 2011). Rosenfeld & Roff (1991) observed significantly higher production of DOC (by one order of magnitude) in unshaded upstream environments than forested upstream environments.

Allochthonous and autochthonous organic matter differ considerably in their characteristics. Allochthonous matter has a higher molecular weight, more aromatic content, higher C:N ratio and contains lignin as a result of its derivation from higher plants (Chin, et al., 1994; Krasner, et al., 1996; Dean & Gorham, 1998). In contrast, autochthonous organic matter is less readily mineralized and more bioavailable (Jonsson, et al., 2001; Hiriart-Baer, et al., 2008). In addition to influencing production of autochthonous organic matter, light and temperature control processes such as biological transformations and photo-degradation, which can modify the quantity and quality of both allochthonous and autochthonous stream organic matter (Meyer & O'Hop, 1983; Benner & Opsahl, 2001; Köhler, et al., 2002; Sachse, et al., 2005; Stets, et al., 2010). Stream water quality can also affect DOM concentration and characteristics. For instance, changes in pH can cause DOM to precipitate and alter DOM fluorescence (Dempsey & Ganho, 1984; Patel-Sorrentino, et al., 2002).

#### 2.1.1 Impact of land disturbance on dissolved organic matter

In North America (and many parts of the world), healthy forested watersheds are regions that produce large amounts of high quality water (Sliva & Williams, 2001; Neary, et al., 2009). Natural and anthropogenic land disturbances, including those severely exacerbated by climate change (e.g., wildfires), can dramatically alter vegetation and increase runoff rates, thereby accelerating erosion from hillslope to streams. The relative impacts on water quality are related to the type of disturbance, the geology, soil type and degree of vegetation change (Hope, et al., 1994; Carignan, et al., 2000; Smith, et al., 2011; Mikkelson, et al., 2013).

Wildfires are particularly severe watershed disturbances that threaten drinking water supplies globally (Emelko, et al., 2011; Bladon, et al., 2014; Robinne, et al., 2016). They alter watershed behaviour by affecting several key hydrological processes. In the short term (<~1 year post-fire), temporary water repellent soil layers can result from wildfire and reduce infiltration capacity, thereby increasing runoff relative to pre-burn conditions via overland flow (DeBano, 2000; Benavides-Solorio & MacDonald, 2001). Over longer periods (>1 year post-fire), wildfires can result in increased soil moisture because of reduced interception and evapotranspiration from the forest canopy. They also can heat soil to create a water repellent layer that prevents infiltration (DeBano, et al., 1998). Lower interception and infiltration rates can lead to higher surface runoff, erosion, and peak flows that wash higher loads of sediments, nutrients and pollutants into streams (Smith, et al., 2011). For example, Revchuk (2011) reported a 70% increase in the raw water DOC concentration following a wildfire in southern California. In addition, wildfires can change the composition of humic

substances and decrease their solubility (Almendros, et al., 1990) as well as their size, composition, charge and reactivity (Revchuk, 2011).

The exact changes in organic matter composition and characteristics that occur after wildfire are dependent on soil chemistry, fire severity, composition of the original organic matter (Almendros, et al., 1990; González-Pérez, et al., 2004; Knicker, 2007). Some of these complexities and interdependencies are illustrated in Figure 1.



Figure 1: Carbon cycling in soil humus during wildfire. (Source: Almendros et al, 1990)

Anthropogenic activity from logging or prescribed burning can deteriorate receiving stream and lake water quality. In a study comparing water quality of boreal lakes located in watersheds that were logged or burned by wildfire, Carignan et al., (2000) reported elevated DOC levels in lakes impacted by logging. In contrast, they found that lake DOC concentrations in burned watersheds were not significantly elevated in the first post-fire year; however, they did increase over time. While many factors (e.g., hydroclimatic variability) could have contributed to those observations, it has been

suggested that prescribed fires can result in elevated receiving stream/lake DOC concentrations at least in part because of incomplete combustion of soil organic matter (Battle & Golladay, 2003). Notably, in contrast to nutrients like nitrogen that tend to follow a better-understood recovery trajectory after disturbance as vegetation is re-established, Hope et al., (1994) observed that postdisturbance DOC concentrations were variable, depending on landscape characteristics and hydroclimatic variability. In watersheds affected by wildfires, salvage logging further devastates water quality by exposing soils and promoting erosion and runoff (Karr, et al., 2004).

#### 2.2 MEASURING NATURAL ORGANIC MATTER

Despite the prevalence of organic matter in the natural environment, efforts to accurately describe its quantity and quality in natural waters are often muddled by the multitude of measurements available to describe organic matter, while the results are often misinterpreted. Most analytical methods only measure one NOM characteristic (e.g. molecular weight, aromaticity, etc.) or one aspect of its reactivity (e.g. total organic halide formation potential, biodegradability) (Cruoé, et al., 2000; Sharp, 2002; Filella, 2009). Summarized in Table 1, aquatic DOM levels are measured and described using several different approaches that can be based on structural characterization (e.g., aromaticity [UV254 absorbance], polarity), (bio)reactivity (e.g., disinfection by-product formation potential [DBP-FP], chemical oxygen demand [COD], assimilable organic carbon [AOC], biodegradable organic carbon [BDOC]), or operational definition (e.g., DOC concentration). DOC concentration is the most common method used to represent aquatic DOM (Cruoé, et al., 2000). DOM also can be qualitatively characterized based on its composition or structure using methods such as resin fractionation, UV absorbance, fluorescence emission, HPSEC, FT-IR, <sup>13</sup>C NMR, liquid chromatography with organic carbon detection (LC-OCD), vapor pressure osmometry, flow fieldflow fractionation, low angle x-ray scattering, ultracentrifugation, elemental composition, transmission electron microscopy, and scanning electron microscopy, polar rapid assessment method (PRAM), pyrolysis gas chromatography mass spectrometry (Py-GC-MS), electron paramagnetic resonance (EPR), differential thermal analysis, modulated differential scanning calorimetry. These methods were recently reviewed by (Shams, 2018). Notably, in natural waters, DOM typically occurs at concentrations too low to be accurately measured by many of the aforementioned analytical procedures. While analytical methods with detection limits lower than 10 mg C/L (e.g. fluorescence spectroscopy) exist, other methods such as FT-IR require 10,000 mg C/L; <sup>13</sup>C NMR requires 20,000–50,000 mg C/L (Maurice, et al., 2002). Moreover, methods such as

FT-IR and elemental composition are complicated by the divergent nature of DOM, necessitating fractionation prior to analysis to minimize interfering signals. Some of the common methods used to isolate and concentrate DOM include membrane filtration, solid phase extraction, pH adjustments while other methods such as freeze concentration/freeze drying (Leenheer, 1981), solvent extraction (Thurman & Malcolm, 1981), and evaporation (Peuravuori, et al., 2005). These methods are listed in Table 1.

Table 1: Common methods used to quantify and characterize NOM

МЕТНОД	ASPECT MEASURED	References
Membrane filtration and reverse osmosis (RO)	<ul> <li>Separates particular, colloidal and dissolved organic matter</li> <li>Isolates and concentrates NOM</li> <li>Separates NOM based on molecular weight</li> </ul>	(Thurman, et al., 1982; Chowdhury, et al., 2008; Aiken, et al., 2011)
pH adjustment	Precipitates humic acid from solution	(Gaffney, et al., 1996)
DOC	<ul> <li>Quantifies amount of organic carbon</li> <li>Acts as surrogate measure for organic matter and disinfection by- product formation potential</li> </ul>	(Kaplan, 2000; Aiken, et al., 2002)
Solid phase extraction (SPE)	<ul><li>Isolate and concentrates humic substances</li><li>Separates NOM based on interactions with resin</li></ul>	(Thurman & Malcolm, 1981; Leenheer, 1981; Chen, et al., 2002; Rosario-Ortiz, et al., 2004)
High-performance size exclusion chromatography (HPSEC)	<ul> <li>Sequences NOM based on molecular weight</li> <li>Measures number average molecular weight, weight average molecular weight and molecular weight distribution</li> </ul>	(Chin, et al., 1994; Peuravuori & Pihlaja, 1997; Nissinen, et al., 2001; Allpike, et al., 2005)
DON	Quantifies amount of organic nitrogen	(Kaushal & Lewis, 2005)
Ultraviolet-visible spectrophotometry (UV- vis)	<ul> <li>Quantifies chromophores</li> <li>Quantifies relative DOM concentrations</li> <li>Detects reactive mojeties to estimate reactivity</li> </ul>	(Spencer, et al., 2007; Korshin, et al., 2009)
Fluorescence	<ul> <li>Quantifies fluorophores</li> <li>Quantifies NOM concentrations</li> <li>Detects components within NOM and other compounds</li> <li>Estimates biological activity</li> </ul>	(Ferrari, et al., 1996; Hudson, et al., 2007)
Fourier-transform infrared spectroscopy (FT-IR)	• Identifies types of bonds and compounds in bonds	(Kim & Yu, 2007)
Nuclear magnetic resonance spectroscopy (NMR)	Identifies structures and functional groups	
Liquid chromatography with organic carbon detection (LC-OCD)	Identifies hydrophobic fractions	(Baghoth, et al., 2009)
Assimilable organic carbon (AOC)	• Measures amount of biodegradable organic carbon that can be easily assimilated into biomass	(van der Kooij, et al., 1982; Huck, 1990)
Disinfection by-product formation potential (DBPFP)	• Measures treatment process efficacy in removing DBP precursors	(Hua & Reckhow, 2007)

#### 2.2.1 Membrane filtration

Membrane filtration is used in the analysis of organic matter including microfiltration, nanofiltration and RO. Microfiltration can separate organic matter into DOM and particulate organic matter (POM) by size exclusion (Vickers, et al., 1995). At the threshold pore size differentiating DOM from POM (0.22 µm or 0.45 µm) microfiltration membranes provide superior retention efficiency compared to glass fiber filters (Khan & Subramania-Pillai, 2007). The drawback of using filtration as Khan & Subramania-Pillai (2007) noted is that depending on the composition of the membrane filters used, organics contaminants may leach into the filtrate.

Nanofiltration and RO membrane filters can be used to isolate organic matter from water samples by differential solute concentration and pressure across the membrane (Crittenden, et al., 2012). Specifically, these membrane filters can be used to partition DOM by molecular weight (Kwon, et al., 2005; Chowdhury, et al., 2008). Comparisons of similar molecular weight groups of DOC between studies of different waters may be difficult to achieve as Cho et al., (2000) found the molecular weight cut-off (MWCO) for DOM was different from that specified by the manufacturer and was dependent on source water quality. The advantages of using nanofiltration or reverse osmosis membranes for DOM separation include (1) the relatively broad spectrum of DOM that they isolate (e.g., as opposed to methods like resin fractionation that largely isolate only humic substances) and (2) the lack of need for solvents that may interfere or react with the isolated DOM (Sun, et al., 1995; Ma, et al., 2001). While membrane filtration is less selective than other isolation methods, it is critical to note that pH, membrane composition, and charge interactions influence the type and amount of organic matter retained (Cho, et al., 2000). These methods also can concentrate inorganic salts on the membrane surfaces, which may interfere in analytical processes (Maurice, et al., 2002). Furthermore, the preferential removal of hydrophobic organic matter by membranes as compared to hydrophilic organic matter also can occur (Cho, et al., 1998; Lee, et al., 2002; Saravia, et al., 2006; Bond, et al., 2010). Despite these shortcomings, NF and RO are commonly used in isolating DOM.

Typically, DOC is operationally defined as the portion of total organic carbon (TOC) which passes through a 0.45 µm or 0.22 µm membrane filter. However other pore sizes have also been used (Khan & Subramania-Pillai, 2007; Filella, 2009). Furthermore, Khan & Subramania-Pillai (2007) observed that significant leaching from a number of filters could lead to inaccurate results.

DOC is measured as non-purgeable organic carbon (NPOC) by:

- 1. Removing inorganic carbon from a sample through acidification and purging.
- 2. Oxidizing the remaining carbon into CO<sub>2</sub> through combustion, chemical oxidation, UVoxidation or a combination of oxidation methods.
- Measuring the amount of CO<sub>2</sub> using a detector, such as a non-dispersive infrared (NDIR) analyzer.
- 4. Relating the amount of  $CO_2$  to a specific standard compound, typically KHP.

Although DOC can also be measured by subtraction of inorganic carbon (IC) from total carbon (TC), this method is less frequently used because IC in natural waters occurs at much higher concentrations than OC rendering imprecise results (Kaplan, 2000). Several drawbacks are associated with the NPOC method however. Acidification shifts the dominant species to carbonic acid, which volatilizes into CO<sub>2</sub> but the removal of inorganic carbon is asymptotic with a small amount of IC always remaining in solution (Sharp, 2002). Underestimation of organic carbon is possible due to inefficient oxidation methods and/or incomplete combustion of OM, which is more recalcitrant than KHP, a relatively easily oxidized compound (Aiken, et al., 2002). Furthermore, pH-dependent losses of non-volatile organic carbon can also occur due to precipitation (Kaplan, 2000).

#### 2.2.2 pH adjustment

Adjustment of sample pH is used as a preliminary step for many methods used in analysis of organic matter. These include UV-vis, DAX-8 resin fractionating, and DOC measured as non-purgeable organic carbon (NPOC). Measurement of pH is used to operationally define fractions of humic substances into humins, humic acid and fulvic acid, the portion that is insoluble, insoluble at pH <1 and soluble at all pH respectively (International Humic Substances Society, 2007). Conversely, pH may also interfere with analytic methods. Conte & Piccolo (1999) observed a drop in pH caused decreases in molecular size of humic substances measured by HPSEC; they attributed it to breakup of macromolecules into smaller molecules. Song et al., (2009) reported that small molecular sizes contributed to significantly lower retention in RO isolation. Changes in pH have also been associated with decreases in fluorescence intensity (Hudson, et al., 2007).

#### 2.2.3 Solid phase extraction

Column chromatographic SPE can isolate, concentrate and fractionate organic matter forms. SPE is favoured in NOM studies due to its specificity in concentrating organic matter without concentrating inorganic salts. Used by the United States Geological Survey and International Humic

Substances Society, non-ionic methylmethacrylate (Amberlite® XAD-8) is the most prevalently used SPE method (Ma, et al., 2001). In recent years, XAD-8 production has been replaced by a similar product called Supelite<sup>™</sup> DAX-8 (Peuravuori, et al., 2002). Isolation and fractionation of DOM using XAD-8 resin occurs by pumping an acidified sample through a column packed with XAD-8 in which hydrophobic organic solutes are adsorbed onto the resin while hydrophilic organic solutes are eluted. The following equation (1) describes the degree of hydrophobicity of the fractionated samples and its breakthrough volume:

$$V_E = V_0 (1 + k')$$
(1)

where  $V_E$  is the breakthrough volume,  $V_0$  is the void volume, and k' is the operationally defined ratio of the mass of solutes sorbed on the resin and the mass of solutes dissolved in water (Leenheer, 1981).

In natural waters, k' distribution for DOM is bimodal. Hydrophilic forms of organic matter are eluted at k' < 10 while hydrophobic forms of organic matter are retained at k' > 40 (Malcolm, 1991). In conjunction with other resins, XAD-8 is used to fractionate organic matter into a) hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral, and hydrophilic base or; b) hydrophobic, transphilic, and hydrophilic. Hydrophobic organic matter have been characterized as more aromatic, and hydrophilic organic matter contain higher nitrogenous compounds (Krasner, et al., 1996; Matilainen, et al., 2010)

Despite its popularity, fractionation of DOC with XAD-8 has many shortcomings. The method is costly and time-consuming, yields relatively low quantities of isolated organic matter when compared to other resins, and is susceptible to contamination from resin bleeding due to inadequate sample preparation (Malcolm, 1991; Ma, et al., 2001; Peuravuori, et al., 2005). Furthermore, the use of strong acids and bases in characterizing DOM is hotly debated because their use alters DOM structure (Crum, et al., 1996; Marhaba, et al., 2000). In some investigations, similar DOM reactivities were observed when DOM was characterized by UV absorbance, reconstituted from XAD-8 fractioned samples, and reconstituted from ultrafiltration, thereby suggesting that fractionation using XAD-8 did not significantly impact the chromophoric properties of the DOM (Kitis, et al., 2002)

Other methods such as the use of diethylaminoethyl cellulose (DEAE) and cross-linked polyvinylpyrrolidone (PVP) also have evolved to isolate and fractionate organic matter based on the presence of specific functional groups (Pettersson, et al., 1994; Chen, et al., 2002; Peuravuori, et al., 2002). Similarly, solid-phase extraction with multiple chromatographic columns used in parallel has also been proposed to more specifically characterize DOC character, such as in the Polarity Rapid Assessment Method (Rosario-Ortiz, et al., 2004). None of these methods has been able to further inform drinking water treatability challenges, however; thus, the continued use of XAD-8 resin fractionation has been the predominant such analysis in spite of the challenges associated with its use (Aiken, et al., 1992) even though it still lacks standardization that would enable comparisons between studies. For instance, k' values used to operationally distinguish between hydrophobic/hydrophilic organic matter and directly impact the distribution of organic matter may range from k' = 4 to k' = 100 in the literature, while many more studies do not list a k' value at all (Leenheer, 1981; Song, et al., 2009).

#### 2.2.4 High-performance size exclusion chromatography

High-performance or high-pressure size exclusion chromatography is a method used to measure the molecular weight (MW) and poly-dispersivity of DOM (Hur, et al., 2006). Organic matter is passed through a polymer-based or silica-based column (stationary phase) by an eluent (mobile phase); differential rates in the adsorption/desorption of organic matter onto the stationary phase separate the DOM and result in a chromatograph of molecular weight approximated by retention time (Nissinen, et al., 2001; Matilainen, et al., 2011). HPSEC is a popular MW measurement method that is a non-destructive, requires very little preparation, and provides values similar to those obtained from vapor pressure osmometry and field-flow fractionation (Chin, et al., 1994). The selection of calibration standards, column, and eluent is critical. For example, the popular polystyrene sulfonate (PSS) calibration standard does not accurately reflect DOM at low molecular weights (Zhou, et al., 2000)—Specht & Frimmel (2000) observed differential interactions between functional group of solutes and columns. Moreover, interpretation of chromatographs depends on detector selection in part. UV-vis detectors are commonly used, but is limited in resolving chromatographic peaks at low molecular weights (Allpike, et al., 2005; Matilainen, et al., 2011); other detectors are often used in conjunction with UV-vis including: DOC, FT-IR, etc. Currently there is no consensus on the interpretation of chromatographs based on cut-off weights, though it has been suggested that low molecular weight cut-off points can affect up to 20% of the interpreted results (Zhou, et al., 2000).

#### 2.2.5 UV-visible spectrophotometry

Aqueous NOM strongly absorbs light in the ultraviolet to visible range of wavelengths between 190 and 800 nm (Chen, et al., 2002; Spencer, et al., 2007). NOM in the visible range contributes to brownish-yellow colour in water and absorbs light restricting photosynthesis in the water column (Hudson, et al., 2007; Matilainen, et al., 2011). In the UV range, a composite of different light absorbing moieties called chromophores produce a broad and featureless absorbance spectrum that decreases monotonically with increasing wavelengths (Korshin, et al., 1997; Weishaar, et al., 2003). Many studies use UV-vis spectrophotometry to provide insight about the source, concentration, structure and reactivity of NOM by measuring the amount of light attenuated by a sample at a single wavelength or ratio of wavelengths (Kalbitz, et al., 1999; Cruoé, et al., 2000; Hur, et al., 2006). The characteristics of NOM in solution are inferred by chromophores that are primarily associated with aromatic functional groups and many other precursors or components of humic substances (particularly pedogenic humics) at wavelengths less than 400 nm (Chin, et al., 1994; Korshin, et al., 1997). DOM is frequently characterized by measuring absorbance at wavelengths between 220 - 280nm (Matilainen, et al., 2011), often with diverse interpretations of what excitation at each wavelength means. To illustrate, some of the wavelengths and interpretations used in UV-vis analysis of organic matter are summarized in table 2.

WAVELENGTH DESCRIPTION		References
Ranges		
180-210	• $\pi - \pi^*$ transition in the ethylenic band	(Her, et al., 2008)
200 - 230	Carboxylic and aromatic groups	(Korshin, et al., 2009)
>200	<ul> <li>Associated with π – π* transitions of conjugated carboxylic acids and esters</li> </ul>	(Her, et al., 2008)
250 - 295	• $\pi - \pi^*$ transition in the benzenoid band	(Her, et al., 2008)
>250	Activated aromatic groups	(Korshin, et al., 2009)
Single Wavelengths		
$\mathbf{A}_{206}$	<ul> <li>Associated with n – π* transition of non- conjugated carboxylic acids and esters</li> </ul>	(Her, et al., 2008)
$\mathbf{A}_{220}$	Associated with carboxylic and aromatic chromophores	(Korshin, et al., 2009)
$\mathbf{A}_{254}$	<ul> <li>Associated with aromatic groups with varying degrees of activation, can be correlated to concentration</li> <li>Measures DOC concentration</li> </ul>	(Mrkva, 1983; Allpike, et al., 2005; Peuravuori, et al., 2005)
A <sub>260</sub>	<ul> <li>Associated with activated benzene or polyphenols which indicate relative amount of aromatic C=C</li> </ul>	(Chen, et al., 2002)

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WAVELENGTH	DESCRIPTION	REFERENCES
$A_{340}$	• Proxy measure for DOC concentrations and to identify inner filtering effects for fluorescence methods	(Baker & Spencer, 2004)
Differential Waveleng	yths	
$\Delta A_{272}$	Correlated with TOXFP formation	(Li, et al., 1998)
Wavelength Ratios		
$A_{210}/A_{254}$	• Associated with NOM fractions and NOM source	(Her, et al., 2008)
$A_{250}/A_{365}$	• Correlated to polarity, aromaticity, humification of fulvic acids, and molecular size of aquatic humic solutes	(Edwards & Cresser, 1987; Peuravuori & Pihlaja, 1997; Li, et al., 2009)
$A_{253}/A_{203}$	• Associated with aromatic rings substituted with hydroxyl, carbonyl, ester and carboxyl groups, correlated to formation of DBPs	(Korshin, et al., 1997; Kim & Yu, 2007)
$A_{254}/A_{202}$	• Associated with activation of polyhydroxyaromatic moieties, correlated to coagulability and TOXFP and THMFP	(Korshin, et al., 2009)
$A_{254}/A_{204}$	• Associated with aromatic carbon in DOM	(Hur, et al., 2006)
A <sub>254</sub> /A <sub>400</sub>	Associated with molecular weight and composition	(Trulleyová & Rulík, 2004)
$A_{254}/A_{410}$	Associated with molecular weight	(Andersen & Gjessing, 2002)
$A_{254}/A_{436}$	• Associated with aromatic carbon from allochthonous CDOM	(Battin, 1998; Hur, et al., 2006)
$A_{280}/A_{350}$	• Estimation of electron transfer band	(Cruoé, et al., 2000; Hur, et al., 2006)
$A_{465}/A_{665}$	• Associated with degree of humification in soil sciences, differentiates fractions of NOM	(Chin, et al., 1994; Peuravuori & Pihlaja, 1997; Chen, et al., 2002)
$0.56\left(\frac{A_{254}-A_{272}}{A_{220}-A_{230}}\right)$	• Associated with aromatic content of NOM and reactivity in DBP formation	(Korshin, et al., 2009)
Normalized Wavelen	gths	
A <sub>254</sub> /DOC (SUVA <sub>254</sub> )	• Aromatic content of NOM and possible reactivity to form THMs	(Krasner, et al., 1996; Song, et al., 2009; Spencer, et al., 2010)
$A_{285}/DOC$	• Associated with benzene, carboxylic acids, and phenols in pedogenic refractory organics in unpolluted surface water	(Krasner, et al., 1996)
$\mathbf{E}_{280}$	<ul> <li>π – π* transition of various aromatic substances correlated to weight averaged molecular weight</li> </ul>	(Chin, et al., 1994; Peuravuori & Pihlaja, 1997; Maurice, et al., 2002)

While UV-vis spectrophotometry is a commonly used, economical, and rapid analytical method that requires minimal sample manipulation (Thermo-Spectronic, 2012), inorganic colloids and ions from iron, nitrates, sulfates and bromides can interfere with absorbance at wavelengths between 200 - 230 nm (Korshin, et al., 1997; Cruoé, et al., 2000; Matilainen, et al., 2011). Chin & Gschwend (1992) found similar absorbance from marine NOM and petroleum products with similar molecular

weights but different reactivity, which may limit interpretation of absorbance. UV-vis is also limited in detection of aquagenic DOMs that do not readily absorb UV (Krasner, et al., 1996).

#### 2.2.6 Fluorescence spectroscopy

Whereas UV-vis spectrophotometry measures energy absorption by chromophores, fluorescence spectroscopy measures energy emission by a group of chromophores, called fluorophores, which absorb energy and emit it back at a longer wavelength (Mopper, et al., 1996). Fluorescence can be measured by several methods, which include:

- The amount of energy emitted at a single emission wavelength due to a single excitation wavelength (Chen, 1999),
- The amount of energy emitted over a range of emission wavelengths due to a single excitation wavelength (Ferrari, et al., 1996), and
- The amount of energy emitted over a range of emission wavelengths offset by a fix wavelength from a range of excitation wavelengths (Shirshova, et al., 2009).

Fluorescence measured by the intensity of energy emitted over a range of wavelengths due to a range of excitation wavelengths is the most commonly used method today. This method produces a 3D excitation-emission matrix (EEM) that represent components of NOM, which are associated with specific fluorophores. Similar to UV-vis absorbance, there are many definitions and interpretations of the significance of the peaks. Table 3 illustrates some of the peaks identified in fluorescence EEM.

Fluorescence spectroscopy is a relatively fast and sensitive method for characterizing NOM with minimal sample preparation or manipulation (Peiris, et al., 2010). However the method is sensitive to pH, temperature, and the presence of metal ions (Hudson, et al., 2007). Additionally, due to the lack of standardization, applying machine and lab-derived correction factors for EEM can produce vastly differing results (Cory, et al., 2010; Murphy, et al., 2010).

РЕАК	FLUOROPHORE	PEAK POSITION	References
NAME		(EX/EM WAVELENGTH)	
A or A'	Humic-like	237 - 260/400 - 500	(Hudson, et al., 2007)
	Humic-like	250 - 260/380 - 480	(Parlanti, et al., 2000)
	Humic-like (UV	260/400 - 500	(Coble, 1996)
	excitation)	a ( 5 / 5 a 5	
	Humic-like	265/525	(Sierra, et al., 2005)
	Fulvıc-like	260/460	(Sierra, et al., 2005)
	Fulvic-like	320 - 350/420 - 480	(Spencer, et al., 2007)
M or B	Marine humic-like	270/450	(Peiris, et al., 2008)
	Marine humic-like	312/380 - 420	(Hudson, et al., 2007)
C or A	Humic-like (visible	300 - 370/400 - 500	(Coble, 1996)
	excitation)		
	Humic-like	320 - 350/400 - 450	(Baghoth, et al., 2009)
	Humic-like	330 - 350/420 - 480	(Parlanti, et al., 2000)
	Humic-like	360/520	(Sierra, et al., 2005)
	Fulvic-like	310/440	(Sierra, et al., 2005)
	Fulvic-like	320/415	(Peiris, et al., 2008)
	Protein-like	270 - 285/340 - 360	(Spencer, et al., 2007)
	(tryptophan)		
B or Γ	Humic-like	350 - 390/440 - 500	(Spencer, et al., 2007)
	Protein-like	225 - 237/309 - 321	(Hudson, et al., 2007)
	(tyrosine)	275/310	
	Protein-like	270 - 280/300 - 320	(Parlanti, et al., 2000)
	(tyrosine)		
	Protein-like	275/315-300	(Sierra, et al., 2005)
	Protein-like	275 - 280/310 - 320	(Baghoth, et al., 2009)
	(tyrosine)		
T or <b>D</b>	Protein-like	225 - 237/340 - 381	(Hudson, et al., 2007)
	(tryptophan)	275 - 340	
	Protein-like	270 - 280/320 - 350	(Parlanti, et al., 2000)
	(tryptophan)		
	Protein-like	275 - 280/340 - 350	(Baghoth, et al., 2009)
	(tryptophan)		,
	Protein-like	280 - 330	(Peiris, et al., 2010)
	(tryptophan)		

Table 3: Peaks in fluorescence EEM analysis of NOM

#### 2.2.7 Disinfection by-product formation potential

Disinfection by-products (DBPs) form when disinfectants oxidize organic matter. Trihalomethanes (THMs) in drinking water were originally detected in the 1970s; however, over 600 DBPs have been identified since then. Notably, DBPs that have been identified only account for approximately half of the total organic halides (TOXs) that form upon disinfection with chlorine (Richardson, 2003; Matilainen, et al., 2010). Additionally, non-halogenated DBPs also are formed during disinfection; however, most research focuses on halogenated species due to the widespread use of halogenated disinfectants, especially chlorine/hypochlorous acid (Bull, et al., 2009). The bulk of known DBPs

formed as a result of precursor reactions with chlorinated disinfectants is comprised of THMs and haloacetic acid (HAAs), which are often used as surrogate or indicators of the relative amount of DBP formation. Gas chromatographic methods are typically used to quantify the formation of halogenated DBPs once extracted from water (American Public Health Association, 2000; Hua & Reckhow, 2007).

In contrast to DBP measurement at specific treatment conditions or assessment of DBP formation that results at "uniform formation conditions" to estimate what might happen as a result of typical treatment conditions (Summers, et al., 1996), "true" DBPFP indicates the maximum concentration of DBPs that can form upon reaction of precursor material in the matrix react with disinfectant (Reckhow, et al., 1990). Specifically, DBPFP is evaluated in a manner that exposes water to excess disinfectant at optimal conditions, including controlled pH, temperature, incubation time, etc.) (Carrière, et al., 2009; Hu, et al., 2010; HACH, 2012). It is for this reason that true DBPFP is commonly used when characterizing landscape disturbance impacts on DOC character. Specifically, this approach enables identification of potential disturbance-associated impacts to drinking water treatability; more plant-specific analyses can subsequently be conducted if relevant and at conditions that are truly reflective of operations. Care should be taken to differentiate between different types of DBP evaluations so that DBPFP results are mistakenly equated with reductions in actual DBPs formed during treatment (Fabris, et al., 2008; Carrière, et al., 2009; Bond, et al., 2010). It should be highlighted that DBPs formed during treatment were up to one order of magnitude lower than DBPFPs in at least one study (Chowdhury, et al., 2008); thus, these analyses should be interpreted carefully with respect to the questions that they inform.

#### 2.3 NATURAL ORGANIC MATTER IN WATER TREATMENT

Aqueous natural organic matter is not a regulated drinking water contaminant per se; however, it is commonly recognized that it affects and frequently challenges drinking water treatment processes. Its increased presence resulted in increased coagulant demand and associated sludge production, as well as increased potential for 1) disinfection by-product formation resulting from disinfection and 2) microbial regrowth in distribution systems (Van Der Kooij, et al., 1982; Matilainen, et al., 2010). The extent of these impacts in a given system is difficult to anticipate because of the numerous, predominantly unidentified forms/fractions of aqueous NOM that exist and their various reactivities

during treatment. Some of the more typically effects of organic matter on common drinking water treatment process performance are discussed below.

#### 2.3.1 Coagulation

Coagulation in combination with flocculation and clarification (typically sedimentation) is somewhat effective at removing aqueous natural organic matter and turbidity from drinking water (Rook, et al., 1982); accordingly, it has been identified by the U.S. EPA as a best available technology for reducing NOM during treatment, especially when pH is modified to achieve "enhanced coagulation" (United States Environmental Protection Agency, 1999; AWWA, 2011). NOM is significant during "chemical pretreatment" by coagulation/flocculation/clarification because colloidal particles suspended in natural waters (especially surface waters) are negatively charged because of surface interactions with NOM (Edzwald, 1993; O'Melia, et al., 1999). Specifically, NOM adsorbs onto particle surfaces and results in repulsive forces greater than those exerted by the surfaces of the inorganic colloids alone (Edzwald, 1993; O'Melia, et al., 1999). Consequently, DOM (rather than colloid concentration or turbidity) is frequently the determinant factor in coagulant selection and dosing requirements (Crittenden, et al., 2012). One of the goals of the coagulation process is to overcome that electrostatic repulsion. Depending on the type and dose of coagulant used and the characteristics and concentration of the fine particles suspended in the water matrix, coagulation promotes flocculation by three mechanisms:

- <u>Charge neutralization</u>: At relatively low concentrations, iron and aluminum based coagulants or cationic organic polymers destabilize colloid surface charges to promote agglomeration between colloids. Destabilization occurs by adsorption of positively charged hydrolyzed metallic salts on to negatively charge surfaces decreasing the electrostatic repulsion between colloids (Dentel, 1988).
- 2. <u>Enmeshment:</u> At relatively higher coagulant concentrations, iron and aluminum based coagulants precipitate into amorphous hydroxides that enmesh and remove colloids as the precipitate settles out of the water (Duan & Gregory, 2003).
- 3. <u>Bridging:</u> Polymeric coagulants facilitate flocculation through adsorption onto different colloids along different points of the polymer (Crittenden, et al., 2012).

Coagulation processes are typically optimized for maximal turbidity removal with minimal coagulant addition; however, they can also be optimized for organic matter removal. For example, enhanced coagulation for NOM removal involves changes to pH and coagulation dose beyond those typically

required for turbidity reduction to maximize organic matter removal (Bell-Ajy, et al., 2000). The concentration and character (aromaticity, polarity, hydrophobicity, molecular weight, etc.) of organic matter also influence the efficacy of coagulation processes in removing both fine suspended particles/turbidity and associated contaminants, and NOM as well (Sharp, et al., 2006). Notably, more hydrophobic organic matter is typically associated with higher SUVA values and aromaticity. As well, higher molecular weights also are understood to control coagulant requirements and are generally more amenable to removal by coagulation (Edzwald, 1993; Owen, et al., 1995). In contrast, coagulation has limited capacity in removing hydrophilic organic matter that is relatively low molecular weight and uncharged (Volk, et al., 2000; Fearing, et al., 2004; Sharp, et al., 2006).

Sharp, et al. (2006) concluded that variations in coagulant demand were primarily due to changes in charge density of the hydrophobic fraction of organic matter. Environmental conditions strongly influence the characteristics of organic matter. Since coagulation efficiency is governed by the same solution parameters including temperature, pH, ionic strength and hardness, these common factors produce coagulant demands that are site-specific (O'Melia, et al., 1999; Crittenden, et al., 2012). Hence, while qualitative conclusions between DOM and coagulation are possible, jar testing is required to understand site-specific interactions required to optimize treatment processes.

#### 2.3.2 Granular filtration

Slow sand filtration and rapid filtration can contribute to overall treatment strategies used to remove organic matter during drinking water treatment. NOM removal by slow sand filtration processes occurs by adsorption and biodegradation. Adsorption tends to remove larger hydrophobic NOM, while filter biomass preferentially removes smaller hydrophobic NOM (Collins, et al., 1992). NOM removal by rapid filtration predominantly occurs when filters are operated in a biologically active mode—the mechanisms are the same as those that occur during slow sand filtration; however, the dynamics are not as well understood (Crittenden, et al., 2012).

#### 2.3.3 Membrane filtration and reverse osmosis

The use of membrane filtration to remove solutes, organic matter, and particulate matter during drinking water treatment is increasing globally. Mechanisms of membrane filtration for NOM removal were described in Section 2.2.1. NOM challenges membrane filtration by contributing to membrane fouling and decreased yields (Fan, et al., 2001; Jermann, et al., 2007), resulting in relatively higher operating costs, particularly for high flow rate plants (U. S. Environmental Protection

Agency, 2005). Fouling occurs when organic matter adsorbs onto membrane surfaces and increases hydraulic resistance, thereby reducing flux across membranes (Hong & Elimelech, 1997; Saravia, et al., 2006). Fouling is a function of the membrane characteristics, organic matter characteristics, and water quality (Zularisam, et al., 2006). Thus, pre-treatment processes such as coagulation or powdered activated carbon (PAC), which have the capacity to remove some aspects of NOM, also affects the degree of membrane fouling.

#### 2.3.4 Disinfection

Disinfection in drinking water treatment protects against waterborne disease and regrowth in distribution systems (AWWA, 2011). Common disinfectants include chlorine, ozonation, UV, chloramine, and chlorine dioxide. Overall, the presence of NOM in source waters decreases disinfectant efficacy, increases disinfectant demand, contributes precursor material for the formation of disinfection by-products, and promotes microbial regrowth in distribution systems (Reckhow, et al., 1990; Sadiq & Rodriguez, 2004).

Disinfection by-product formation is related to NOM characteristics, water quality parameters, pretreatment processes and disinfectants used. THMs and HAAs are surrogates for all DBPs in drinking water legislation even though these species predominantly represent DBPs formed from more aromatic organic matter (Kitis, et al., 2001). While C/F/S is one of the best available technologies to mitigate THM and HAA formation by removing hydrophobic NOM precursor material (U. S. Environmental Protection Agency, 1992), interactions between remaining organic fractions can also affect DBP formation. For example, the amount of hydrophilic organic matter also can affect the relative amount of THMs and HAAs formed (Liang & Singer, 2003), presumably due to competing oxidant demand. Similarly, in the absence of more reactive hydrophobic organic matter that competes with hydrophilic or transphilic organic matter, increased levels of halonitromethanes (HNMs)—a group of DBPs that are considered more toxic than THMs and HAAs—have been observed Hu, et al., (2010). Thus, interactions NOM, precursor materials, and DBP formation is required for improved disinfection and treatment of DBP precursor materials.

#### 2.4 **RESEARCH NEEDS**

Current source-water protection strategies focus on protecting water supplies against external inputs of contaminants and pathogens. However, both natural and anthropogenic landscape disturbances threaten many water values in many ways, including the potential for deteriorated water quality—

these challenges are further exacerbated by climate change; thus, resilient engineering is required to adapt to these water resource challenges (Parry, et al., 2007; U. S. Environmental Protection Agency, 2011). For drinking water treatment, this requires the consideration of "bigger-picture" impacts of land disturbance impacts on source water quality upstream of treatment plants and the connectivity between those changes and drinking water treatability challenges that can be anticipated in those treatment plants (Emelko, et al., 2011).

It is widely recognized that water quality and specifically different fractions and characteristics of organic matter can substantially influence the performance of a range of drinking water treatment processes. Organic matter forms that originate in watershed are related to landscape characteristics in areas upstream of the water treatment plant. However, traditional divisions between disciplines such as hydrology and water treatment research hinder the transfer of applicable knowledge between the two fields. The lack of commonality between fields is due in part to non-comparable terminology, even the threshold for "dissolved" matter is not consistent between disciplines with both 0.22 µm and 0.45 µm cut offs used respectively in the different fields (Filella, 2009).

Changes in wildfire extent and severity are amongst the earliest manifestations of climate change (Flannigan, et al., 2005); as well, severe wildfires can also substantially deteriorate water quality (Boerner, 1982; Ice, et al., 2004; Smith, et al., 2011). Given that forested headwater streams comprise more than half of the total stream length in the U.S. (Nadeau & Rains, 2007); drain up to 80% of a watershed while making up roughly 70% of the annual water volumes (Alexander, et al., 2007; MacDonald & Coe, 2007); and approximately 180 million Americans get their drinking water from forest watersheds (Stein & Butler, 2004); implications of wildfires' impact on headwater stream quality is critical to many utilities in both Canada and the U.S.

### **3** MATERIAL AND METHODS

#### 3.1 **Research methodology**

In this research, the water quality impacts relevant to drinking water treatability resulting from the 2003 Lost Creek wildfire that occurred in southwestern Alberta were investigated. Turbidity and DOC data from source watersheds with varying degrees of wildfire associated land disturbance were evaluated during an eight year post-fire period (i.e., from 2003 to 2011). Specifically, three watersheds with varying degrees of disturbance (reference [unburned], burned, and burned and salvage logged) were studied during three flow regimes (winter baseflow, spring eventflow, and summer baseflow). Stream discharge was continuously (i.e., every 10-minutes) evaluated in these watersheds and weekly samples were collected to analyze turbidity and DOC concentration. In 2011, grab samples were collected for characterization of organic matter using DOC concentration, UV<sub>254</sub>, SUVA<sub>254</sub>, and DOC hydrophobicity using resin fractionation (with DAX-8 resin after Kitis et al., (2001)).

To evaluate the implications of land disturbance by wildfire on drinking water treatability with conventional surface water treatment processes (chemical pre-treatment: coagulation, flocculation and sedimentation), jar tests were conducted to evaluate coagulant demand in waters from streams draining each of the watersheds at each of the different flow conditions. Turbidity and DOC reductions by chemical pre-treatment were determined. Quantitative and qualitative changes in DOC after treatment were determined using DOC concentration, UV<sub>254</sub>, SUVA<sub>254</sub>, and hydrophobicity assessment by DAX-8 resin fractionation. Disinfection by-product formation potential was not directly evaluated in this research but the relative disinfection by-product formation and subsequently demonstrated elsewhere (Shams, 2018).

### 3.2 STUDY SITE - OLDMAN RIVER AND LOST CREEK WILDFIRE

The Oldman River basin (Figure 2) in Southern Alberta constitutes 80% of Alberta's water demand and is thus a socio-economically significant watershed. The Oldman River has the highest precipitation and runoff ratios in Alberta and is one of the two water sources that serve the most heavily irrigated region of Canada, where approximately 90% of the total surface and groundwater are allocated to irrigation (Oldman Watershed Council, 2010). In addition, the river serves as a drinking water source for many municipalities and settlements in Southern Alberta. Originating in the eastern slopes of the Rocky Mountains, the Oldman River drains approximately 26,700 km<sup>2</sup> and is one of four rivers that discharges to the South Saskatchewan River. Water flows in the river are largely dependent on snow accumulation of in the mountainous sub-basins; discharge from the upper Oldman River and upper tributaries comprise approximately 36% of the total river flow (Oldman Watershed Council, 2010).



Figure 2: Oldman River Basin (Source: http://oldmanbasin.org/files/7613/1232/3397/Map.jpg)

In the summer of 2003, the Lost Creek wildfire—a severe, month-long, nearly contiguous crown wildfire—burned more than 21,000 ha of the headwater regions of two major tributaries of the Oldman River: the Crowsnest and Castle Rivers. The fire consumed nearly all forest cover and forest floor organic matter. The wildfire forced the evacuation of approximately 2,000 residents in the nearby communities of Hillcrest and Blairmore, while placing the community in a state of emergency for 31 days. The total cost to the province of Alberta to control the wildfire was over \$40

million (Kulig, et al., 2009). Prior to the Lost Creek fire, only 2,430 ha had previously burned in this watershed between 1961 and 2002 (Oldman Watershed Council, 2010).

#### 3.2.1 Study watersheds

The Southern Rockies Watershed Project (SRWP) was initiated to assess the impact of the Lost Creek wildfire on forest hydrology and water quality in the Oldman River basin. In the spring of 2004, several burned and unburned headwater watersheds of the Crowsnest River were instrumented with monitoring equipment to enable continuous meteorological and discharge measurements and frequent water sample collection, including event (e.g. storm) sampling. Two additional watersheds were instrumented in January 2005 to monitor the effects of post-fire salvage logging that started during the winter of 2003. Figure 3 illustrates the extent areas affected by wildfire and salvage logging and sampling locations.


Figure 3: Southern Rockies Watershed Project study watersheds in 2011 (Source: Silins et al., 2009)

In the present investigation, wildfire effects on drinking water treatability were evaluated in three watersheds: (1) an unburned reference watershed (Star), (2) a burned watershed (Drum), and (3) a burned and salvage logged watershed (Lyons East) (Silins, et al., 2009). The areal extent of disturbance in each of these watersheds is listed in Table 4.

WATERSHED	Түре	AREA (ha)	BURNED (ha)	SALVAGE LOGGED (ha)
Star	Unburned	1035	0	0
Drum	Burned	713	712	0

Table 4: Areal extent of disturbance in the study watersheds.

Lyons EastBurned & salvage logged	1309	1072	262
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Air temperature in the study area during the study period ranged from -30°C to 25°C. From 2004 to 2008, the average annual precipitation in this region was 795 mm for Drum, 852 mm for Lyons East and 1155 mm for Star; elevation and spatial differences contributed to variations in precipitation between the study sites. Snowfall in this region typically occurs between September and May, and comprises anywhere from approximately 35% to 68% of the annual precipitation. The snowmelt freshet typically starts in mid-March and lasts until early-July, with the onset occurring in approximately 3.5 weeks earlier in the disturbed watersheds relative to the reference, although this difference is somewhat confounded by the disturbed watersheds being located at lower elevations (Silins, et al., 2009). It should be noted that relatively dry conditions persisted during the study period from 2005 to 2010. Air temperature and precipitation in the study area are summarized in Figure 4.



Figure 4: Air temperature, precipitation, and snowmelt in the study area from 2004-2011. Source: (Environment Canada, 2004-2011)

No water quality or hydrological data were collected prior to the Lost Creek wildfire. To assess the effects of wildfire and salvage logging disturbances on water quality and treatability, data from reference unburned sites were compared to those from burned and salvage logged watersheds—this type of paired catchment approach is commonly utilized and described in the literature (Carignan, et al., 2000; McEachern, et al., 2000; Battle & Golladay, 2003; Silins, et al., 2009). While the watersheds used in this study differ somewhat in topography, elevation, geology, the study sites are "representative of steep, high water yielding watersheds of Cordilleran Montane region in southern Alberta" (Silins, et al., 2009). Notably, high frequency, targeted (to differentiate flow regimes) sampling of DOC and turbidity in the study watersheds for an unprecedented, extended period of time (8 years) enabled decoupling of the effects of wildfire or salvage logging from background (hydroclimatic) variability at the watershed scale; it also enabled evaluation of the impacts of flow regime on water quality and treatability.

#### 3.3 FIELD METHODS

Routine monitoring of precipitation and stream discharge began in the spring of 2004 in Star and Drum Creeks, and in early 2005 in Lyons East Creek. Continuous flow rates were determined using stage-discharge relationships and logged at 10-minute intervals. Additional instantaneous flow rates coinciding with routine water quality sampling were determined using area-velocity measurements method with velocity meters (Global FP-201 and Swoffer 2100). Collection of precipitation data began in May 2004 and occurred every 2 to 3 weeks during the summer/fall, and once every 1 to 2 months during the winter. Baseflow was determined using multi-pass separation of the hydrograph; snowmelt and stormflow were based on meteorological conditions.

Water samples were collected to evaluate a number of water quality parameters. Water temperature, pH, and turbidity were sampled continuously using water quality sondes during ice-free periods. Daily composite samples (4 sub-samples per 6 hours) were collected for turbidity. Samples for DOC/DIC analysis were collected at 10-day intervals during snowmelt, 2-week intervals during ice-free periods, and 1 to 2 month intervals during the winter, depending on accessibility. Additional samples for DOC/DIC analysis were collected whenever possible during storm events, some of those severe storm events that are relevant to the present investigation are summarized by Table 5.

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			FLOW	
	<b>PRECIPITATION*</b>		$(m^{3}/s)$	
DATE	(mm)	STAR	DRUM	LYONS EAST
Jan 19, 2005	Missing	0.48	1.10	3.00
June 2-9, 2005	1.6-40.80	0.72-1.19	0.13-0.71	0.31-1.22
June 17, 2005	16.00			
June 15, 2006	17.6	0.79	0.46	1.12
May 23-26, 2008	4.6-21.00	0.5-1.20	0.56-0.99	2.65-6.39
May 26-27, 2011	Missing	0.87	0.68	8.78

\*Precipitation at nearby Crowsnest weather station (Climate ID: 3051R4R).

Additional supplementary grab samples were collected March 22-25, 2011 during winter baseflow; May 26-27, 2011 during snowmelt/stormflow; and August 18-20, 2011 during summer baseflow conditions. It should be noted that access to remote study sites limited sampling a storm event that occurred on May 27, 2011; only Star Creek was sampled as stormflow. Drum Creek and Lyons East Creek were sampled previously on May 26, 2011 when they were at snowmelt flow conditions. Water samples collected during the snowmelt freshet were grouped and described as "eventflow" in the present investigation. Additionally, samples were not collected from Drum Creek during summer baseflow due to logistical and scheduling constraints. While a broader dataset is available, DOC concentration and character (i.e., aromaticity, hydrophobicity) were only <u>concurrently</u> analyzed by all of the methods during the spring eventflow (May 2011) and the summer baseflow (August 2011) sampling periods.

On these occasions, additional samples were collected for turbidity evaluation, and carbon analysis and characterization. These samples were collected in acid-washed triple rinsed amber coloured glass bottles, refrigerated, and shipped by air to the University of Waterloo (Waterloo, Ontario) for immediate preservation and further lab analysis. Turbidity was measured using a portable turbidity meter (VWR 66120-200) calibrated daily with 1 NTU, 10 NTU and 100 NTU standards. The pH of the grab samples was measured using a portable pH meter (Thermo Scientific Orion 290A+) calibrated with 2 point buffers at pH 7 and pH 10. DOC and related characterization analyses were conducted as described below.

In addition to the water quality analyses described above and the DOC-associated proxies for assessing drinking water treatability described below, coagulant demand was assessed. These samples required for these analyses were collected less frequently because of the water volume required and challenges associated with transporting them from remote, steep hillslopes. These samples were collected in clean 20 L plastic buckets that were triple-rinsed with stream water as per standard methods for field sampling (American Public Health Association, 2005). These samples were chilled and standard jar tests were conducted (as described below) within 48 hours of collection.

#### 3.3.1 Jar testing

Stream water coagulant demand was analyzed using standard jar tests after Arnold (2008). In brief, six 1-L beakers of untreated stream water were simultaneously dosed with a range of coagulant concentrations (list concentrations) to evaluate the optimal coagulant dose using a standard jar test apparatus (Figure 5). These tests were performed at ambient temperatures to reflect the conditions that would be expected at a water treatment plant if these waters were being treated for potable water production. Temperature and pH were monitored using a portable pH meter (as described above). Polyaluminum chloride (PACI) was chosen as a coagulant because it is widely as a coagulant in cold climates (particularly at cold water temperatures) because it can contribute to enhancing

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settling (by forming flocs that are relatively more dense than those obtained with more traditional metal salt coagulants like aluminum sulphate [alum] and FeCl<sub>3</sub>); it is also less temperature-dependent. The jars were flash-mixed with coagulant at 100 RPM for 30 seconds. Mixing was then slowed to 70 RPM for 3 minutes and followed by flocculation at 35 RPM for 10 minutes. Flocs were allowed to settle for 15 minutes.



Figure 5: Jar test apparatus

The turbidity, pH, and temperature of the supernatant were measured after sedimentation. This study focused on the turbidity reduction rather than organics reduction because that is typical practice in western Canada, and in many regions; especially those where enhanced coagulation is considered impractical because of high alkalinity. Three replicate jar tests were conducted per site, per flow condition with the exception of five jar tests that were conducted using Star Creek reference stream water during summer baseflow. The optimal coagulant doses obtained during the

three replicate jar tests were recorded and the arithmetic mean optimal coagulant dose was calculated.

Approximately 700 mL of the supernatant from the beaker with the greatest turbidity reduction from each jar test batch was decanted into acid-washed amber coloured glass bottles. The amber bottles of raw and coagulated water samples were refrigerated and couriered to the University of Waterloo for preservation and further analysis.

#### 3.4 LAB METHODS

The pH and turbidity of the samples received from the field were measured within a day of their arrival using a desktop pH meter (Orion 720A) calibrated with 3 point buffers at pH 4, pH 7 and pH 10. Turbidity was measured using a turbidimeter (HACH 2100N) calibrated with sealed turbidity standard kits (GELEX Secondary Standards).

The samples were filtered through pre-rinsed 0.45  $\mu$ m polyethersulfone membrane filters (Supor, Pall) and their absorbance at ~254 nm was measured (i.e., UV<sub>254</sub>). Specifically, absorbance was measured at 253.5 nm though a 5 cm quartz cell with a UV-visible spectrophotometer (Agilient 8453). SUVA<sub>254</sub> (with units of L/mg-C/cm) was subsequently calculated as (UV<sub>254</sub> × 100)/(DOC × 5). These filtered samples were acidified to pH 2 with concentrated HCl. They were then refrigerated in acid-rinsed 1 L amber bottles until analysis of DOC concentration and characterization by acrylic ester resin (Sigma-Aldrich Supelite<sup>TM</sup> DAX-8) fractionation. DOC was measured as non-purgeable organic carbon using TOC analyzer (Shimadzu TOC-5000A) as per Standard Method 5310 (American Public Health Association, 2005). Calibration curves were generated daily prior to analysis. Organic matter was operationally fractionated using resin, as described in the following section.

#### 3.4.1 Resin fractionation

The resin fractionation method was adapted from methods used by Song, et al., (2009). For this experiment, the column size was scaled down due to limited sample quantity as a previous investigation by Song, et al., (2009) full-scale and small-scale fractionation approaches yielded comparable results. A column coefficient (k') of 30 was selected for these analyses so that the distinction between hydrophobic and hydrophilic organic matter would fall in between the modes of the natural bimodal distribution for natural waters (Malcolm, 1991).

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Pre-cleaned DAX-8 resin was packed into a 35 mL liquid chromatography column as shown in Figure 6. The column was rinsed with Milli- $Q^{TM}$  water until no organic carbon was detected in the column effluent. Then resin was then acidified using 1.5 bed volumes of 0.1 M HCl acid; an equivalent bed volume (1.5 BV) was then subsequently discarded before the filtered and acidified sample was pumped through the column. This was done at a rate of 7.5 bed volumes per hour until the column coefficient reached k' = 30, thereby yielding the hydrophilic fraction of DOC in the sample. Next, one bed volume of 0.1 M of NaOH was pumped through the column, followed by two bed volumes of Milli- $Q^{TM}$  water, which was pumped at three bed volumes per hour to desorb the hydrophobic fraction of the sample's DOC from the DAX-8 resin. The hydrophobic eluent was immediately acidified with concentrated HCl to minimize ester hydrolysis at high pH (Malcolm, 1991).



Figure 6: Experimental set up for evaluating DOC hydrophobicity by DAX-8 resin fractionation as per (Song, et al., 2009)

The fractioned hydrophobic and hydrophilic samples were compared to the whole samples using the following equation (2):

$$Percent \ recovery = \frac{C_{SE}V_{SE} + C_D V_D}{C_{RS} V_{RS}}$$
(2)

where:  $C_{SE}$  is the DOC concentration of the collected sample effluent (Hydrophilic portion).  $V_{SE}$  is the collected sample effluent volume (Hydrophilic portion).  $C_D$  is the DOC concentration of the collected eluent containing desorbed humic substances (Hydrophobic portion).  $V_D$  is the collected eluent volume (Hydrophobic portion).  $C_{RS}$  is the DOC concentration of the raw sample.  $V_{RS}$  is the raw sample volume.  $V_{RS}=V_{SE}$ 

Samples for which the percent recovery deviated by more than 30% were excluded from the data analysis as they were deemed unreliable because they may have been contamination or impacted by resin bleeding; notably, on 33% (7 of 21 samples) were excluded from the analysis for this reason.

## **4 RESULTS AND DISCUSSION**

#### 4.1 STREAM FLOW

With the exception of June in Star Creek, baseflow conditions were similar for all three study watersheds (Figure 7). The slightly higher baseflow measured in Star Creek and Drum Creek are related to the relatively large contribution from groundwater; 68% and 75% to the annual stream flow, respectively compared to 43% in Lyons East Creek (Silins, et al., 2009). Lyons East Creek had the lowest baseflow due to its lower elevation and the lower relief of its valley.

Flow rates were typically higher in Lyons East Creek during the early months of the snowmelt freshet. These values were exceeded by higher flow rates in Star Creek over the study period (Figure 7). In disturbed watersheds, flow rates were higher than the reference stream (Star Creek) the onset and duration of snowmelt freshet was earlier (Silins, et al., 2009).



Figure 7: Median flowrate by month

The high stream flow in Star Creek during snowmelt freshet and storm events is partially related to the increased precipitation due to the rain shadow effect on the Flathead range. Rainfall interception capacity was also higher in unburned watersheds when compared to burned watersheds in the Flathead range (Silins, et al., 2009). These results are comparable to those reported by previous studies of the effects of land disturbance (i.e. wildfire, logging, beetle-infestation, etc.) on stream flow in forested watersheds (Helvey, 1980; Cheng, 1989; McIver & Starr, 2000). Table 6 summarizes the mean flow rates organized by flow regime and year for each of the watersheds studied.

			Year							
		2004	2005	2006	2007	2008	2009	2010	2011	
ωo	Star	0.213	0.212	0.132	0.163	0.078	0.073	0.113	0.151	
sefl	Drum	0.102	0.116	0.087	0.082	0.091	0.106	0.075	0.097	
Ba	Lyons East		0.121	0.071	0.070	0.093	0.073	0.071	0.046	
nelt	Star	0.159	0.438	0.238	0.558	0.379	0.332	0.344	0.548	
OWD	Drum	0.208	0.272	0.161	0.284	0.434	0.291	0.250	0.642	
Sn	Lyons East		0.602	0.439	0.656	1 <b>.2</b> 45	0.712	0.470	1.671	
low	Star	0.357	0.610	0.800	0.234	0.854	0.305	0.389	0.878	
rmf	Drum	0.288	0.394	0.464	0.090	0.781	0.189	0.529	1.643	
Sto	Lyons East		0.970	1.122	0.102	4.577	0.348	1.225	6.251	

Table 6: Mean flow rate  $(m^3/s)$ 

## 4.2 RAW WATER QUALITY

Many of the water quality parameters measured were impacted negatively by land disturbance (wildfire, post-fire salvage logging). For example, from 2004 to 2008 sediment, turbidity, phosphorus and metals were elevated Silins, et al. (2009). In the following sections, the effect of wildfire and post-fire salvage logging on turbidity, DOC and their impact on water treatability are presented and discussed in the context of the literature.

#### 4.2.1 Turbidity

Turbidity is an indicator used to gauge influent water quality in order to optimize water processes (Crittenden, et al., 2012). Higher turbidity measurements may be associated with higher pathogen concentrations and depending on the treatment technology, a threshold of 0.1 - 1 NTU is used to indicate the efficacy of treatment processes. In the present study, the observed instream turbidity was higher in incrementally more disturbed watersheds and during high flow events as shown in Table 7. However, stream turbidity in Drum Creek exceeded turbidity measured in Lyons East during some common events (i.e., during the storm event in the summer of 2007) (Figure 8).

	BASEFLOW		SNOWMELT			STORMFLOW			
	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max
STAR	0.15	0.32	1.00	0.13	1.19	19.9	0.15	2.93	33.3
DRUM	0.35	1.19	8.1	0.33	9.2	74.4	0.26	88.8	1142
LYON S EAST	0.38	2.45	9.9	0.80	24.8	135	0.22	80.5	640

Table 7: Range and average turbidity sampled by flow type and watershed



Figure 8: Precipitation and turbidity over years sampled

Turbidity is positively correlated to flowrate; an increase in turbidity were observed in response to increased flow, particularly between baseflow and event flow regimes because of more erosive forces during higher flows that suspend fines which increases turbidity (Figure 9). High flow events caused by extreme precipitation events in particular, accentuated differences in turbidity between undisturbed and disturbed watershed, varying up to a couple of order of magnitude (Table 8). During a high flow event, differences in turbidity between two sub-watersheds (Star Nix and Star Hod) are shown in Figure 10.



Figure 9: Turbidity vs flowrate of studied watersheds in under different flow regimes

Table 8: Turbidity during severe storm events

DATE	TURBIDITY (NTU)					
	STAR	DRUM	LYONS EAST			
Jan 19, 2005	1.35	40.0	90.0			
June 2-9, 2005	1.1-11.0	2.5-125.0	5.3-40.0			
June 17, 2005	5.4	37.0	63.0			
June 15, 2006	0.49	13.0	22.0			
May 23-26, 2008	0.79-5.1	7.06-19.8	69.3-640.0			
May 26-27, 2011	33.3	1142.0	625.0			



Figure 10: Comparison of colour between reference and disturbed creeks Land disturbance has an impact on turbidity and the proportion of time a given turbidity threshold is related to the level of disturbance (Emelko, et al., 2011). The incremental degradation of water quality continued to be significant four years beyond the initial disturbance event (Figure 11.) Between 2008 and 2011, turbidity was greater or equal to 1 NTU in 17% of samples measured from Star, compared to 55% and 70% for Drum and Lyons East respectively.



Figure 11: Turbidity exceedance curve

Turbidity for the 90<sup>th</sup> percentile at Star was 1.45 NTU compared to 19.2 NTU and 40.8 NTU for Drum and Lyons East, respectively. Greater range of influent turbidity requires more and costlier treatment strategies to accommodate for a wide range of turbidity levels.

### 4.2.2 DOC

In the study area, DOC concentrations were consistently elevated with increasing level of disturbance (Figure 12). A review of post-fire recovery literature (Smith, et al., 2011) indicated that there was rapid recovery of organic carbon levels post-fire. In stark contrast, this study found that relatively elevated DOC concentrations resulting from the wildfire persisted at least 7 years after the initial disturbance (Figure 12). In most observations (133 out of 153 cases), DOC concentrations in the burned watershed were nearly double (on average 1.7x higher) than the reference watershed on the same or related (e.g. following day within an event) sample dates. In nearly all cases (134 out of 137 cases), DOC concentrations in the salvage logged watershed were more than double (on average 2.4x higher) than those in the burned watershed on the same or related sample dates. ANOVA demonstrates that DOC between treatments (e.g reference, burned, salvage logged) were significantly different at baseflow: F(2,252) = 99.7, p < 0.001; snowmelt: F(2,112) = 47.7, p < 0.001; and stormflow: F(2,79) = 39.5, p < 0.001.



■ Precipitation ● Star ● Drum ● Lyons East





Figure 12: Precipitation and DOC over years sampled

As with turbidity, DOC concentration also increased with higher flowrates. Incremental increases of DOC due to land disturbance (wildfire or post-fire salvage logging) were prevalent across all flow regimes (Figure 13). During storm flows, DOC clusters for all three studied locations were more variable than baseflow. However, the organic carbon levels in Star Creek were consistently lower under all flow regimes, while Lyons East was consistently higher. Table 9 highlights some of the DOC data sampled during select severe storm events.



Figure 13: DOC vs flowrate

T 11 0 DOC		1 .		
	concentration	during	severe storm	evente
	concentration	uuinie	SUVUIC SUUTI	CVCIIIO
		()		

DATE		DOC (mg/L)	
	STAR	DRUM	LYONS EAST
Jan 19, 2005	2.73	5.64	13.68
June 2-9, 2005	1.45-4.18	2.60-8.07	6.31-9.49
June 17, 2005	5.34	5.20	8.68
June 15, 2006	1.54	4.56	7.64
May 23-26, 2008	1.70-3.30	4.60-5.3	9.1-12.3
May 26-27, 2011	3.1	4.9	8.3

Levels of DOC within the same site were similar between samples taken immediately after the disturbance events and four years post-disturbance. Exceedance curves for DOC in Lyons East were consistently above that of Drum and Star. At the 50<sup>th</sup> percentile, DOC concentrations between Star

and Drum were comparable at 1.3 mg/L and 1.9 mg/L, respectively. In contrast, Lyons East was at 4.1 mg/L. DOC levels double for each incremental disturbance to the watersheds at the 90<sup>th</sup> percentile, with 2.73 mg/L for Star, 4.51 mg/L for Drum and 8.21 mg/L for Lyons East.



Figure 14: DOC exceedance

DOC concentrations at all three sites demonstrated hysteretic behaviour on a yearly basis. DOC concentration appear to have peaked slightly after snowmelt freshet and generally coincided with stormflow events during the summer months. Subsequent high flow events in the autumn months did not typically elicit an equally high response in DOC concentration as spring/summer flow events.

One possible explanation of the high DOC spike early in the year could be caused by organic carbon buildup over the winter that gets flushed out by increased flow from snowmelt freshet or washed away by the first large storm event (Hornberger, et al., 1994). In a DOC flow pathway study, Frank, et al., (2000) observed that DOC concentrations peaked in the receding limb of the hydrograph, they attributed the delayed peak to increased DOC contributions from the topsoil. Site-specific conditions and hydrological pathways appear to dictate the peak timing and relative contribution from aquatic and terrestrial organic matter reservoirs. The resolution of the sampling makes it difficult to precisely interpret the relationship between DOC peak in relation to snowmelt discharge peak. However, the drop in hydrophobicity from spring eventflow to summer baseflow (Table 10) suggest an allochthonous input (which is typically more hydrophobic) during high flow events.



Figure 15: DOC and flowrate

The hydrophobicity of DOC in ten water samples was measured. In a few samples, particularly those with lower DOC concentrations, the amount of hydrophobic and hydrophilic fractions

recovered from the resin column exceeded 100%; this was likely due to contaminated glassware or machine error from the DOC analyzer. Two samples with greater than 130% recovery were discarded and not included in the discussion.

Although samples for all three sites were categorized as eventflow, samples for Star Creek were collected during a storm on snowmelt event that resulted in significantly elevated DOC levels. Drum and Lyons East were collected the previous day during snowmelt conditions only. The percent hydrophobic organic matter ranged from 40-70%, which is consistent with other surface water sources in North America (Malcolm, 1991; Song, et al., 2009). Despite elevated DOC concentrations in Star Creek during event flows, the hydrophobic fraction was still higher in Drum Creek. The percentage of hydrophobic material was consistently lower in Star Creek when compared to other treatments regardless of the flow conditions.

		STAR	DRUM	LYONS EAST
	n	2	1	1
M	$DOC_{Avg}$ (mg/L)	4.25	4.37	8.19
tflc	SUVA	2.281	2.404	2.788
en	(L/mg-C/cm)			
Εv	% HPO <sub>Avg</sub>	47.6%	65.5%	70.0%
	n	2	-	2
L >	$DOC_{Avg}$ (mg/L)	1.53	-	2.92
nei lov	SUVA	0.974	-	2.521
mr sef	(L/mg-C/cm)			
Su: ba:	% HPO <sub>Avg</sub>	38.9%	-	54.3%

Table 10: Percent of hydrophobic organic matter

Additionally, aromatic content in organic matter was approximated using SUVA<sub>254</sub>. The relative changes to SUVA<sub>254</sub> corroborated the changes to hydrophobicity in response to disturbances. SUVA<sub>254</sub> were highest in Lyons East irrespective of flowrate. While changes to SUVA<sub>254</sub> in samples from Star suggest allochthonous input during eventflow; persistent higher SUVA<sub>254</sub> values suggest that the organic matter pool in Lyons East was intrinsically more aromatic than Star. Given that aromatic moieties influence the rate of adsorption/desorption of organic matter in soils (McKnight, et al., 1992), the long-term effects of landscape disturbances on the characteristics of the organic matter pool in SUVA<sub>254</sub>.

Further investigations on the flow pathways and organic matter characterization are recommended to clarify the relative contributions of vegetation from overland flow and older organic matter from the fire that was retained in groundwater or sediment sources. This information is critical for developing drinking water safety plans and climate change adaptation strategies for utilities threatened or impacted by wildfire.

#### 4.3 COAGULANT DEMAND

Enhanced coagulation is widely considered as a best available technology to remove organic matter and depending on the water quality characteristics it is often triggered in raw waters with TOC concentration >2 mg/L (United States Environmental Protection Agency, 1999). Organic matter and solids generally dictate coagulant demand, and higher coagulant demand equates to higher treatment costs. The amount of coagulant required is usually estimated at bench scale using jar tests and subsequent full-scale implementation. In contrast to conventional coagulation, enhanced coagulation leverages changes to pH through increased coagulant dose and monitors TOC removal performance to optimize DBP precursor removal. Here, a traditional approach to jar tests (i.e., focused on turbidity reduction) was utilized (United States Environmental Protection Agency, 1999). Coagulant demand in this experiment is operationally defined as the minimum dose of coagulant that results in the maximum turbidity removal this is contrary to treatment plants that would aim likely aim for an operationally defined target of ~ 1 NTU. As well during winter baseflow with its low initial turbidity, a utility would likely use direct filtration rather than C/F/S to further clarify the influent. The average result of each batch of jar tests was recorded as the coagulant demand as the coagulant dosage in each batch of jar test was changed to narrow in an optimal dose.

Conditions such as temperature, water quality and flow regime all play a role in the optimal coagulant dose (Crittenden, et al., 2012); of course, available infrastructure and associated operational targets are also significant. As would be expected, coagulant demands were more pronounced in disturbed watersheds than the reference watershed (Star), especially during higher flow conditions that resulted in elevated turbidity and DOC concentrations. Table 11 summarizes the jar test results.

	Optimal coagulant dose	Темр	INITIAL TURBIDITY	Final turbidity	INITIAL pH	Final pH
Winter						
Star	25	0.22	0.07	LLD*	8.32	7.78
Drum	16.7	0.58	0.87	0.06	8.54	7.95
Lyons East	73.3	0.32	0.34	0.09	8.05	7.31
Spring						
Star	26.7	13.40	22.83	0.27	8.42	7.69
Drum	133.3	13.08	14.81	0.07	8.26	6.98
Lyons East	40	13.02	24.65	0.57	7.81	6.34
Summer						
Star	19	12.68	0.19	LLD*	8.46	7.87
Drum	-	-	-	-	-	-
Lyons East	60	13.30	0.77	0.04	6.44	6.43
*LLD = Lowe	er limit of detection	n				

Table 11: Coagulant demand and jar test result summary

Jar test results conducted on water samples collected at various flow ranges are shown in the Figures 16 - 18. Each point represents individual results from each jar test. The initial turbidity is denoted by a straight line, while the optimal dose is indicated by a large circle on the initial turbidity line.



# Winter baseflow

◆ Star ■ Drum ▲ Lyons East

Figure 16: Jar test results - winter baseflow



Figure 17: Jar test results - spring eventflow



# Summer baseflow

♦ Star ▲ Lyons East



Jar tests conducted on water samples collected from Star Creek during baseflow demonstrated that turbidity was largely unaffected by increases in coagulant dose (Figure 16). This result was expected because the low initial turbidity limited the extent of this reduction—the addition of further coagulant only added solids (Al(OH)<sub>3</sub> precipitate) to the system once the solubility product constant was exceeded. Thus, turbidity removal on a percentage basis was lowest during the winter baseflow conditions, and addition of coagulant increased turbidity at higher coagulant doses during this period. Coagulant demand during summer baseflow was similarly low (Figure 18). During eventflow, a modest increase in coagulant concentration reduced turbidity to below 1 NTU (Figure 17). Notably, treated water turbidity at any given coagulant dose was generally the lowest in samples from the reference watershed, regardless of dose (Figures 16-18).

Drum Creek had a moderately low coagulant demand during winter baseflow—it was generally consistent with that observed in Star Creek and any differences were typically below the detection limit of the instrumentation. Nonetheless, the maximum turbidity removal achieved by jar coagulation of Drum Creek water was slightly lower than for Star Creek. During spring freshest, the lowest post-coagulation turbidities were achieved for Drum Creek water, though this difference was at the limit of detection for the instrument; thus, it was neither statistically nor operationally significant. The coagulant demand of this water was significantly higher than from Star (reference); as well, the turbidity removal achieved (on a percent basis) by coagulation was lower for water from Drum. This higher coagulant demand could be attributable to higher alkalinity associated with greater groundwater inputs to Drum Creek, resulting in greater buffering relative to Lyons East Creek. Unfortunately, summer baseflow samples were not collected from Drum Creek.

Coagulant demand in Lyons East (the post-fire salvage logged watershed) was consistently higher than that for Star (the unburned reference), demand during winter and summer baseflows were both approximately three times that of Star. The jar tests performed during eventflow demonstrated that this stream was the only one that achieved a high enough suspended solids concentration to experience stoichiometric destabilization during coagulation (between 40 to 60 mg/L). Water from the other sites and at all other flow regimes were coagulated by precipitation of solid and sweep floc coagulation (Figure 17), as would be expected at such low suspended solids concentrations/turbidities.

In absolute values, organic removal was highest in disturbed watersheds than the undisturbed watershed. An increase in flow caused and increase in DOC which resulted in higher absolute value

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of DOC removal by coagulation. Conversely, coagulation showed lower efficacy in lower DOC waters within the same site when compared across flow regimes. Table 12 lists the changes in DOC from coagulation.

	n	DOC	%HPO
Spring			
Star raw	2	4.25	47.6%
Star treated	2	2.83	50.6%
Drum raw	1	4.37	65.5%
Drum treated	1	1.40	58.4%
Lyons East raw	1	8.19	70.0%
Lyons East treated	1	2.30	61.3%
Summer			
Star raw	2	1.53	39.4%
Star treated	1	1.24	41.3%
Drum raw	-	-	-
Drum treated	-	-	-
Lyons East raw	2	2.92	54.3%
Lyons East treated	1	1.14	46.6%

Table 12: Organic characteristics in raw and treated samples

The lowest absolute ( $\Delta_{spring} = 1.42 \text{ mg/L}$ ,  $\Delta_{summer} = 0.29 \text{ mg/L}$ ) and relative removal of organic matter observed during this investigation was for water from the reference watershed. Decreased coagulant efficacy coincides with the lower initial DOC concentrations within the same flow regime and lower hydrophobicity across flow regimes. This result was expected since DOC, particularly hydrophobic organic matter, is a major driver of coagulant demand (Sharp, et al., 2006). Within the same flow regime, DOC of the control after coagulation was higher than that of disturbed watersheds. Unlike other studied sites, hydrophobicity of the organic matter increased after coagulation suggesting that the hydrophobic segment is more recalcitrant towards coagulation and/or hydrophilic segment is more amenable towards coagulation. Further organic characterization is required and other coagulants or treatments may need to be explored to optimize organic removal.

Coagulation was far more effective in removing DOC in water from Drum Creek in comparison to Star. While both Drum and Star had similar initial organic carbon concentrations, 4.37 mg/L and 4.25 mg/L, respectively, the DOC concentration of Drum after coagulation was half that of Star Creek, 1.4 mg/L versus 2.83 mg/L. The observed increased removal is likely related to the higher hydrophobicity of organic matter (which is more amenable to removal by coagulation (Sharp, et al., 2006)) from Drum compared to Star.

In contrast, organic carbon removal was highest in Lyons East. Lyons East Creek is characterized by lower alkalinity due to a lower groundwater component, higher DOC with higher hydrophobicity. As stated by USEPA (1999), "TOC removal is generally more difficult in higher alkalinity waters, and source water with low TOC levels." Data from Lyons East corroborates that higher initial organic matter concentration lends to the greatest absolute ( $\Delta_{spring} = 5.89 \text{ mg/L}$ ) and percentage removal of DOC (71.9%) within the study. Hydrophobicity also appear to contribute significantly towards organic removal by coagulation. From spring freshet to summer baseflow the portion of hydrophobic organic carbon decreased from 70% to 54% while the relative DOC removal percent also decreased from 71.9% to 61.0%.

Hydrophobicity appears to play a larger role in coagulation and DOC reduction than the overall initial organic carbon concentration. Figure 19 shows the correlation between hydrophobicity increase, with increase to flow condition and disturbances with DOC removal percentage. In contrast, Figure 20 indicates that initial DOC concentration instead of hydrophobicity does not strongly predict the percent of DOC removal.

This is further evidenced by a comparison between Lyons East and Star. While initial DOC concentration for Lyons East during summer baseflow is lower than that of Star during spring event flow (2.92 mg/L versus 4.25 mg/L), both absolute and relative DOC concentration removal was higher for Lyons Creek East. Given that the jar test temperatures were similar, a higher hydrophobic content of Lyon East (54.3% versus 47.6% for Star Creek) likely contributed to a higher coagulant demand. The lower pH of Lyons East (6.44 versus 8.42) likely also contributed to the efficacy of organic carbon removal. Further carbon characterization and investigation of influence of pH and hydrophobicity on coagulation is necessary to better elucidate coagulation mechanisms relevant in these water matrices—that work was beyond the scope of this thesis.



Figure 19: Relative DOC removal based on hydrophobicity



Figure 20: Relative DOC removal based on initial DOC

Despite lower DOC reduction of the control samples, the hydrophobicity of DOC in the reference was still lowest within the same flow regime regardless of treatment with coagulation. Higher hydrophobicity has been linked to increased formation potential of regulated disinfection byproducts; this may require greater reliance on coagulation or implementation additional treatment processes to remove DOC.

		<b>OPTIMAL COAGULANT</b>	ΔDOC	% DOC REMOVAL
		DOSE		
Spring				
	Star	25.7	1.42	33.4%
	Drum	133.3	2.97	68.0%
	Lyons East	40	5.89	71.9%
Summer				
	Star	19	0.29	19.0%
	Drum	-	-	-
	Lyons East	60	1.78	61.0%

Table 13: Organic carbon removal

Although coagulation efficacy increased with incremental disturbance events, this increase was commensurate with the additional cost of increased coagulant demand. During baseflow conditions, coagulant demand in Lyons Creek East nearly tripled that of Star Creek. In comparison, coagulant demand for Star Creek remained relatively stable, even at elevated flow conditions; this consistency makes for greater predictability of the response to changes to influent water quality. A treatment facility currently operating within an undisturbed watershed may face challenges in coping with the additional chemical demands caused by an upstream disturbance. Given that the impact of forest fire and salvage logging are noticeable on organic carbon several years after the initial event; the financial legacy of the disturbance on water treatment are likely to continue to persist long after the initial devastation.

- Turbidity in streams draining burned and post-fire salvage logged watersheds was more variable, with elevated peak values, relative to reference (unburned) watersheds. Turbidities in streams draining the burned and burned and salvage logged watersheds remained elevated by factors of ~15 and ~22 on average respectively, compared to the reference watersheds. Notably, these effects were observed for at least eight years after wildfire.
- 2. Dissolved organic carbon (DOC) in streams draining post-fire salvage logged watersheds were more variable, with elevated peak values, relative to both burned and reference (unburned) watersheds. Stream DOC concentrations remained elevated by factors of ~2 and ~4 on average respectively, as a result of these disturbances. These effects also persisted for at least eight years after wildfire.
- 3. Changes in turbidity and DOC in streams draining reference, burned, and post-fire salvage logged watersheds correlated with stream discharge. Notably, for a given stream discharge, watersheds with greater levels of disturbance (i.e., wildfire and post-fire salvage logging) tended to exhibit higher turbidity and DOC levels. These relationships were consistent over eight post-fire years.
- 4. Eight years after wildfire, DOC in streams draining burned and post-fire salvage logged watersheds was more hydrophobic and more aromatic than in streams draining reference (unburned) watersheds. Stream DOC hydrophobicity respectively increased by factors of ~1.5 and ~1.4 on average and stream DOC aromaticity also increased by factors of ~1.5 and ~1.6 on average, as a result of these disturbances. The experimental design allowed for the conclusion that changes in water quality were attributable to disturbance as opposed to other factors (e.g., hydroclimatic variability, inter-watershed variability, etc.). This relatively elevated and more aromatic DOC present in streams draining the disturbed watersheds resulted in significant increases in DBP formation potential, which have been described elsewhere (Emelko, et al., 2013; Shams, et al., 2014; Emelko, et al., 2015; Shams, et al., 2015). Although it has been speculated that these changes in stream NOM may be due to either allochthonous or authochthonous sources, the origin of these post-disturbance water quality changes is not presently understood. That evaluation was beyond the scope of the present investigation.
- 5. The coagulant demand of stream water from burned and post-fire salvage logged watersheds was significantly higher (~3.2 and ~2.4 respectively) than in streams draining reference watersheds.

As would be expected, coagulation was less effective in removing the less aromatic fractions of DOC. Although an increasingly larger proportion of DOC was removed by coagulation from water supplies originating in increasingly disturbed catchments (i.e., post-fire salvage logged > burned > reference), this result suggests that conventional coagulation processes may be severely challenged post-fire by more aromatic, increasingly variable, and sometimes substantially elevated concentrations of DOC.

6. The long-term turbidity and DOC data presented herein (and elaborated upon with respect to their linkages to watershed processes elsewhere in the literature) underscore the potential for legacy effects of wildfire and post-fire salvage logging on water quality and treatability that may last for decades or longer after severe disturbance. Accordingly, it is critical that utilities whose source water originates in wildfire prone areas assess their surficial geology and the associated implications for erosion that may result in debris flows or the longer-term release of fine sediment and associated nutrients.

Further investigations are needed to elucidate organic matter source(s) and transport after wildfire and to estimate the temporal extent of wildfire impact on organic carbon recovery. This type of fundamental understanding, although likely to be regional, is critical for the development of adaptation and mitigation strategies, as well as emergency preparedness in wildfire prone regions. Disinfection by-product formation also should be investigated to determine the types and amount of organic carbon formed from undisturbed and disturbed samples to determine how best to balance regulated and emerging DBPs. Additionally, the financial impact of severe disturbances such as wildfire on water treatment and associated public health costs (including impacts of service disruptions) must be quantified to enable better-informed decisions on the impact of climate change and source water protection.

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## APPENDIX A: TEMPERATURE AND PRECIPITATION DATA FROM CROWSNEST, ALBERTA (CLIMATE ID: 3051R4R) SOURCE: ENVIRONMENT CANADA

	20	04	20	05	20	06	20	07	20	08	20	09	20	10	20	)11
Date	Temp	Prec	Temp	Prec	Temp	Prec	Temp	Prec	Temp	Prec	Temp	Prec	Temp	Prec	Temp	Prec
01/01	-11.20	0.00	-22.80	Μ	0.60	0.00	-3.60	0.00	-8.10	М	-9.90	Μ	-7.50	Μ	-13.50	Μ
01/02	-19.30	0.00	-18.20	М	-0.80	0.00	3.70	6.00	-5.20	М		М	-2.10	Μ	-10.90	М
01/03	-29.30	0.00	-17.60	М	-0.40	0.00	1.50	0.00	2.00	М		М	-3.70	Μ	-13.50	М
01/04	-28.30	0.00	-18.90	М	2.00	0.00	-4.30	0.00	2.20	М	-8.50	М	-6.80	М	-7.40	М
01/05	-26.20	0.00	-17.80	M	3.40	0.00	-9.00	0.00	0.10	M	-4 70	M	-13.90	M	-2.20	M
01/06	-17.60	0.00	-10.20	M	3.20	0.40	-2.80	0.00	-3.50	M	-0.90	M	-20.40	M	2.80	M
01/07	7.80	0.00	15.60	M	0.50	6.00	0.40	0.00	7.30	M	3.60	M	17.80	M	0.70	M
01/07	0.60	2.30	17.50	M	1.60	2.80	3 30	0.00	7.50	M	2.70	M	7.10	M	5.40	M
01/08	1.00	2.50	-17.50	M	-1.00	2.00	-5.50	0.00	-7.50	M	-2.70	M	-7.10	M	-5.40	M
01/09	1.00	0.00	-18.20	M	0.90	0.00	0.80	0.00	-5.80	111	-4.80	M	-1.80	M	-15.90	M
01/10	2.40	0.00	-11.40	M	2.20	2.40	-8.30	0.00	-2.70	M	0.50	M	2.60	M	-19.40	M
01/11	1.00	0.00	-10.00	M	1.50	3.40	-19.30	0.00	1.20	M	0.80	M	5.60	M	-20.30	M
01/12	2.40	0.00	-16.00	M	0.80	0.00	-20.30	0.00	0.10	М	-4.80	Μ	6.10	M	-9.30	M
01/13	2.20	0.00	-27.70	М	0.10	4.00	-15.60	0.00	1.00	М	2.80	М	3.50	Μ	-9.00	M
01/14	6.00	0.00	-27.30	М	0.80	2.60	-16.30	0.00	2.50	М	-0.60	М	3.20	Μ	-20.00	M
01/15	4.80	0.00	-21.70	Μ	-1.90	1.60	-10.20	0.00	-9.70	Μ	-0.70	Μ	3.70	Μ	-7.20	Μ
01/16	2.00	0.00	-11.00	Μ	-4.50	0.00	-4.80	0.00	-16.40	Μ	-0.40	Μ	-2.00	Μ	-4.10	Μ
01/17	1.70	0.00	0.20	Μ	1.00	0.00	-10.70	0.00	-7.00	Μ	-4.30	Μ	-2.10	Μ	-4.40	Μ
01/18	1.70	0.00	5.70	Μ	-1.40	0.00	-10.60	0.00	-5.80	Μ	-5.00	Μ	1.50	Μ	-10.20	Μ
01/19	-1.70	0.00	8.00	М	-3.80	0.00	-1.60	0.00	-8.00	М	-5.10	Μ	-3.10	Μ	-13.70	Μ
01/20	-4.40	0.00	6.80	М	-3.80	0.80	-3.10	0.00	-23.00	М	-6.30	М	-1.70	Μ	-10.00	М
01/21	-0.30	0.00	-0.40	М	-7.80	0.40	-8.50	0.00	-20.60	М	-1.90	М	-4.60	М	-0.30	М
01/22	1.60	0.00	2.50	М	-1.70	0.00	-0.50	0.00	-9.60	М	-8.70	M	-6.70	М	-2.10	M
01/23	-0.40	0.80	9.10	M	3.10	0.00	3.10	0.00	-10.70	M	-21.00	M	-7.10	M	-1.70	M
01/24	_9.80	3.10	6.60	M	5.10	0.00	4 50	0.00	-12.00	M	_21.00	M	-10.20	M	.3.10	M
01/24	-20.20	0.00	4.00	M	3.10	0.00	3.00	0.00	-12.00	M	-21.90	M	6.00	M	-5.10	M
01/25	26.50	5.00	4.00	M	0.70	0.00	6.40	0.00	-12.00	M	10.00	M	-0.90	M	1.40	M
01/20	-20.50	5.30	2.30	M	0.70	0.00	-0.40	0.00	-1.90	M	-18.20	M	-11.30	M	4.10	M
01/2/	-30.50	8.40	2.10	M	-0.60	0.00	-8.80	0.00	-11.60	M	-8.80	M	-8.30	M	4.90	M
01/28	-14.00	10.20	0.10	M	-0.90	0.00	-6.40	0.00	-29.60	M	-5.10	M	-5.10	M	1.10	M
01/29	-11.90	4.60	4.40	M	-0.40	0.00	-9.90	0.00	-29.90	M	-1.70	M	-1.00	M	-10.90	M
01/30	-8.10	5.90	4.20	Μ	1.40	10.00	-10.30	0.00	-15.50	М	3.80	М	-6.70	М	-24.80	М
01/31	-12.20	0.00	4.60	М	-0.10	0.00	-7.70	0.00	-7.30	М	0.30	Μ	-7.20	Μ	-21.80	М
02/01	-15.50	0.00	3.20	Μ	1.20	М	-15.30	Μ	-8.60	Μ	-4.30	Μ	-2.90	Μ	-21.00	Μ
02/02	-14.00	0.00	6.20	Μ	1.60	Μ	-11.70	Μ	-10.20	Μ	0.40	Μ	-0.10	Μ	-10.20	Μ
02/03	-10.40	0.00	8.80	Μ	-1.30	Μ	-6.90	Μ	-14.40	Μ	2.60	Μ	-2.10	Μ	-5.90	Μ
02/04	-1.90	0.00	1.90	Μ	2.00	М	0.60	Μ	-12.50	Μ	3.10	Μ	-2.10	Μ	2.90	Μ
02/05	-2.80	0.00	-9.60	Μ	1.40	М	5.50	Μ	-4.30	Μ	3.60	Μ	-4.00	Μ	-2.60	Μ
02/06	-0.90	0.00	-14.20	М	0.10	М	-3.40	М	-2.90	Μ	0.90	М	-2.60	Μ	-9.70	М
02/07	0.90	0.00	-12.30	М	1.50	М	-9.90	М	-1.70	М	-5.70	М	-5.00	М	-14.40	М
02/08	-5.00	0.00	-7.40	M	2.90	M	-12.30	M	-10.00	M	-0.70	M	-6.10	M	-14.60	M
02/09	-2.20	0.00	-4 30	M	-4.60	M	-14 60	M	-23.60	M	-1.80	M	-4.90	M	-13.90	M
02/09	-1.60	0.00	0.10	M	-8.20	M	-5.70	M	-9.00	M	-6.30	M	-2.30	M	-2.10	M
02/10	7.70	0.00	1.20	M	3.00	M	9.50	M	5.00	M	-0.50	M	-2.50	M	-2.10	M
02/11	-7.70	0.00	-1.20	M	-5.00	M	-9.50	M	-5.00	M	-7.70	M	-0.10	M	2.00	M
02/12	1.20	0.00	-1.40	M	-1.20	M	-10.00	M	2.70	M	-0.90	M	4.00	M	2.40	M
02/15	-1.30	0.00	-1.00	M	-2.30	M	-17.20	M	-5.10	M	-10.70	M	0.50	M	2.40	M
02/14	-4.80	0.00	-/.80	M	-0.10	M	-11.80	M	-7.50	M	-12.50	M	-1.80	M	4.80	M
02/15	1.50	0.00	-10.90	M	-12.20	M	1.50	M	0.80	M	-10.30	M	0.60	M	1.00	M
02/16	-1.60	0.00	-10.20	M	-19.00	M	2.90	M	-0.80	M	-6.30	M	1.00	M	-5.10	M
02/17	2.10	0.00	-6.60	M	-21.20	M	3.50	M	-7.20	Μ	-6.70	Μ	0.50	Μ	-11.70	M
02/18	2.30	1.60	-6.70	Μ	-14.20	М	2.70	Μ	-3.10	М	-0.10	Μ	-1.20	Μ	-19.00	М
02/19	2.20	0.00	-7.20	М	-11.50	М	-0.10	Μ	1.40	М	-0.20	М	-2.90	Μ	-19.50	М
02/20	-1.00	0.00	-10.20	М	-5.40	М	-1.50	Μ	-1.00	М	-3.90	Μ	-6.90	Μ	-11.60	М
02/21	-2.10	0.00	-6.40	Μ	-4.10	М	-4.60	Μ	-2.20	Μ	-0.90	М	-5.20	Μ	-3.50	M
02/22	-2.40	0.00	-4.40	Μ	-3.00	Μ	-10.80	Μ	-2.10	Μ	-0.50	Μ	-3.80	Μ	-9.80	Μ
02/23	-1.70	0.00	-2.30	Μ	-5.00	Μ	-5.70	М	-1.40	Μ	-2.40	Μ	3.20	Μ	-17.50	М
02/24	-0.80	0.00	-0.60	Μ	-10.30	Μ	-7.70	Μ	-3.60	Μ	-11.30	Μ	2.00	Μ	-27.20	Μ
02/25	1.50	0.00	0.10	Μ	-14.70	Μ	-3.80	М	-2.20	Μ	-17.80	Μ	2.60	Μ	-22.60	М
02/26	0.80	1.40	-1.20	Μ	-4.20	Μ	-6.70	Μ	-0.60	Μ	-19.90	Μ	2.60	Μ	-14.20	Μ
02/27	-0.50	0.00	0.90	Μ	2.30	Μ	-11.00	М	5.20	М	-12.00	Μ	1.50	Μ	-9.50	М
02/28	-0.70	0.00	1.30	М	-4.70	М	-10.10	М	0.70	М	-10.10	М	1.90	М	-15.30	М
02/29	-2.70	0.00							3.50	М						
03/01	-2.80	0.60	3.50	0.00	-3.30	2.40	-10.80	0.00	3.40	М	0.50	М	2.10	М	-22.70	М
03/02	-7.60	0.60	2.70	0.00	-11.00	0.00	-11.80	0.00	-1.60	M	6.60	М	2.80	М	-9.50	М
03/03	-8.40	0.00	1.60	0.00	-10.10	0.00	0.00	0.00	-0.10	М	2.80	М	5.00	M	-1.60	M
03/04	-2.40	0.00	1.80	0.20	-6.50	0.00	3 30	0.00	-4.80	M	1.20	M	3.10	M	-13.90	M
03/05	-5.30	0.00	8 30	0.00	_4.00	0.00	3.10	0.00	-5.20	M	_7.00	M	1 20	M	.0 30	M
03/05	0.80	0.00	4.20	0.00	4.20	0.60	7.30	0.00	0.20	M	15.30	M	1.10	M	18.20	M
03/00	-0.00	0.00	4.20	0.00	4.20	0.00	0.50	0.00	4.00	M	-15.50	M	1.10	M	-10.20	M
03/0/	5.10	0.00	4.00	0.00	1.30	0.20	8.50	0.00	4.00	M	-4.20	IVI M	1.60	M	-15./0	M
03/08	0.60	0.00	5.50	0.00	-1.30	0.00	5.10	1.00	1.50	M	-12.30	M	3.20	M	-9.40	M
03/09	5.60	0.60	6.50	0.00	-2.50	0.00	1.80	0.00	-0.50	M	-21.80	M		M	-1.20	M
03/10	1.20	0.00	3.50	0.00	-8.10	0.00	3.20	0.00	5.80	M	-23.80	M	-2.80	M	2.80	M
03/11	3.40	0.00	8.40	1.80	-9.40	0.00	8.30	0.40	3.70	М	-17.40	М	1.00	М	-2.50	М
03/12	4.00	2.40	-0.40	6.60	-13.50	0.00	6.20	3.20	1.00	М	-5.30	Μ	5.20	Μ	-2.40	М
03/13	1.50	0.00	-3.20	2.40	-9.00	0.00	-0.20	0.00	-2.80	М	1.30	Μ	1.20	Μ	4.20	М
03/14	1.20	0.00	-2.40	0.40	-4.20	0.00	-2.10	0.80	0.50	Μ	1.90	Μ	-0.70	Μ	4.10	М
03/15	1.20	0.00	-0.60	0.00	-2.70	0.00	-4.40	0.00	-1.60	Μ	-0.20	Μ	4.20	Μ	2.90	Μ
03/16	5.30	0.00	0.20	0.00	0.20	0.00	4.70	0.00	-0.60	Μ	-1.50	Μ	4.90	Μ	2.80	М
03/17	3.70	0.00	-5.50	0.00	-0.20	0.00	10.00	0.00	1.80	Μ	-2.00	Μ	4.20	Μ	-0.80	М
03/18	5.10	9.40	-8.90	0.00	-0.10	0.20	1.50	0.00	0.10	М	-2.90	Μ	-1.70	Μ	-1.40	М
03/19	-0.60	0.20	-13.10	0.00	-5.60	0.00	2.80	0.00	-1.50	М	1.90	М	-3.40	М	-1.80	М
03/20	-1.00	0.00	-2.90	0.00	-5.40	0.00	3.40	4.80	-1.50	М	7.30	М	2.00	М	-0.50	М
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03/22 03/23 03/24 03/25 03/26 03/27	3.90 4.20 5.10 4.70	0.00 1.80 1.20	-7.50 -8.10 -10.60	0.00	-0.90 3.80	0.00	3.80 5.80	0.00	-1.50	M M	-0.90 0.20	M M	3.60 2.20	M	0.80	M
03/23 03/24 03/25 03/26 03/27	4.20 5.10 4.70	1.80 1.20	-8.10	0.00	3.80	0.00	5.80	0.00	-1.40	M	0.20	M	2.20	M	-1.70	N4
03/24 03/25 03/26 03/27	4.70	1.20	-10.00		2 1 0	0.00	7.70	1.0	2 70	M	1.20	M	2.00	M	5.00	M
03/25 03/26 03/27	4.70	0.00	6.40	0.00	2.10	0.00	1.00	0.20	-5.70	M	1.20	M	5.90 2.40	M	-5.90	M
03/27	2.60	0.60	0.90	0.00	2.40	0.80	1.00	0.40	-4.10	M	-7.10	M	6.50	M	1.40	M
	3.90	0.00	3.70	1.40	1.60	0.00	0.10	5.20	-2.80	М	1.60	М	6.20	М	-0.20	М
03/28	3.30	0.00	2.90	1.80	0.70	0.40	1.20	0.00	-3.70	М	0.30	Μ	6.10	М	-1.60	Μ
03/29	7.90	0.00	0.50	2.60	2.10	0.00	2.40	0.00	-5.50	М	-6.80	М	3.50	М	2.10	М
03/30	7.60	0.20	0.90	0.40	3.80	0.00	5.30	0.00	-8.60	M	-7.10	M	1.20	M	5.50	M
03/31	4.90	0.00 M	-1.90	0.20	2.70	3.00	3.10	12.80	- /.50	M	2.10	M	1.30	M	6.80	M
04/01	0.80	M	4.20	2.60	3.10	0.20	-2.70	0.00	-5.10	M	-1.00	M	-0.10	M	-2.00	M
04/03	4.50	M	1.10	0.00	3.50	0.00	-11.80	0.00	2.10	M	-1.30	M	1.60	M	0.20	M
04/04	8.10	М	3.10	0.00	3.60	5.60	-3.30	0.00	3.00	М	-0.50	М	-0.20	М	2.90	М
04/05	5.90	Μ	3.40	0.00	3.30	5.60	-4.40	0.00	1.20	М	-0.10	М	-1.30	М	2.10	Μ
04/06	5.90	Μ	7.30	0.00	3.40	5.60	-3.50	0.00	1.70	М	6.90	М	1.60	М	-0.10	М
04/07	5.20	M	8.60	0.00	6.60	0.20	-1.20	0.00	1.60	M	5.60	M	4.10	M	-3.60	M
04/08	3.40	M	3.80	0.00	6.20	2.00	5.90	0.00	0.10	M	4.00	M	2.00	M	0.60	M
04/09	5 30	M	1.90	0.00	4 40	0.00	2.90	0.00	-0.50	M	5.00	M	-2.10	M	4 30	M
04/11	6.50	M	2.70	1.20	4.00	0.00	0.30	0.20	2.40	M	4.10	M	-1.60	M	3.00	M
04/12	8.40	Μ	0.60	1.60	2.90	2.80	0.70	0.00	6.00	М	5.80	М	-0.70	М	0.70	Μ
04/13	4.60	Μ	2.90	0.00	5.50	0.40	3.90	0.00	9.00	Μ	3.20	Μ	0.70	Μ	-1.50	Μ
04/14	5.50	M	3.00	3.00	6.80	0.40	8.90	0.00	9.70	M	0.30	M	5.70	M	1.70	M
04/15	3.30	M	3.60	0.00	1.70	3.80	4.00	0.00	-0.20	M	1.30	M	4.10	M	1.00	M
04/10	3.00	M	8.30 4.30	0.00	2.10	0.00	3.50	0.00	-2.30	M	2.40	M	8.80	M	-2.30	M
04/18	3.10	M	0.00	3.20	0.70	0.00	0.60	7.60	0.20	M	6.50	M	8.70	M	-7.70	M
04/19	3.70	М	2.40	0.00	4.90	0.00	2.70	1.40	-9.60	М	4.90	М	8.40	М	-6.70	М
04/20	4.20	Μ	4.60	0.00	9.50	0.00	3.20	2.60	-9.00	М	13.40	0.00	9.10	М	-2.30	Μ
04/21	4.60	Μ	6.30	0.00	7.70	0.00	3.70	0.00	-6.00	М	15.90	0.00	10.10	М	-1.00	Μ
04/22	5.70	M	8.20	0.00	3.50	0.80	6.40	0.40	0.60	M	6.00	M	8.90	M	0.40	M
04/23	/.00	M	5.70	0.00	1.30	0.00	6.90	0.00	-4.50	M	-6.90	M	6.60 5.20	M	1.60	M
04/24 04/25	5.40	M	9.90	0.00	4.00	0.20	8.30	0.00	-0.50	M	-4.80	M	4 10	M	3.40	M
04/26	9.50	M	5.50	3.80	9.60	0.00	8.10	0.00	1.80	M	0.30	M	4.30	M	3.80	M
04/27	10.30	Μ	-1.70	0.60	8.30	0.00	10.10	0.00	6.00	Μ	-1.30	Μ	3.80	Μ	4.40	Μ
04/28	2.90	Μ	-2.90	0.00	8.40	0.00	12.10	0.20	8.50	Μ	-1.10	Μ	2.50	Μ	2.10	Μ
04/29	4.40	M	-1.00	0.00	10.50	0.00	10.60	0.60	6.20	M	-0.60	M	2.90	M	1.80	M
04/30	6.20	M	1.10	0.00	4.50	19.00	7.60	0.00	4.10	M	-0.10	M	3.00	M	1.40	M
05/01	13.10	0.00	4.20	0.00	3.70	2.80	9.50	1.00	2.90	M	4.50	M	3.30	M	5.00	M
05/02	8.50	6.40	5.80	0.00	3.10	0.80	5.00	3.60	4.70	M	5.70	M	3.40	M	6.70	M
05/04	9.70	0.20	9.30	0.00	5.10	0.00	4.90	0.00	7.00	М	8.50	М	2.00	М	4.80	М
05/05	5.30	5.80	8.30	0.00	7.90	0.00	7.60	0.00	7.50	Μ	7.40	Μ	-1.90	Μ	6.50	Μ
05/06	6.00	0.00	10.30	1.60	9.80	0.00	8.00	0.00	6.60	M	6.80	M	-1.80	M	5.10	M
05/07	8.10	0.00	7.10	6.40	8.90	0.00	13.00	0.00	6.00	M	3.00	M	1.60	M	5.00	M
05/08	5.00	0.60	7.10	0.20	4.30	0.00	17.40	0.00	4.50	M	5.70	M	-1.10	M	5.00 4.20	M
05/10	4.10	2.00	5.30	2.00	4.60	0.00	9.30	0.00	2.70	M	7.10	M	2.30	M	7.10	M
05/11	0.90	3.60	6.80	0.00	7.10	0.00	8.80	0.00	4.20	М	4.40	М	3.70	М	8.20	М
05/12	1.10	1.00	8.10	0.00	9.00	0.00	10.80	0.00	4.00	Μ	5.80	Μ	6.00	Μ	7.20	Μ
05/13	2.90	2.40	10.40	0.00	5.80	0.00	7.60	19.00	4.60	М	5.40	M	7.50	M	6.10	M
05/14	6.00	0.40	9.20	1.80	9.50	0.00	7.80	0.60	10.80	0.00 M	6.40	M	9.90	M	9.80	M
05/15	6.90	4.00	12.40	2.60	15.00	0.00	11.40	0.00	12.40	M	9.70	M	9.20	M	7.40	M
05/17	7.50	1.40	10.50	7.80	15.30	0.00	12.20	0.00	13.40	M	15.00	0.00	13.50	M	4.70	M
05/18	8.40	0.20	7.90	0.00	17.30	0.00	11.30	0.00	16.50	0.00	8.20	М	14.50	М	6.40	Μ
05/19	9.40	17.80	9.10	4.40	15.70	0.00	11.40	11.60	13.60	0.00	8.60	Μ	10.80	Μ	7.30	Μ
05/20	7.80	1.80	7.30	0.00	12.30	4.20	9.10	0.00	15.30	1.60	5.00	M	6.50	M	8.90	1.20
05/21	3.90	6.60	9.30	0.00	14.00	0.00	5.20	3.60	8.40	2.20 M	5.70	M	4.00	M	0.20	M
05/22 05/23	3.60	4.00	7.10	0.00	13.90	0.00	7.40	8.60	7.50	M	9.20	M	5.40	M	10.00	M
05/24	5.70	1.00	6.10	0.40	10.30	0.60	1.70	24.80	7.70	21.00	10.90	M	4.80	M	6.10	M
05/25	7.00	0.00	8.00	0.00	10.70	0.00	7.50	0.00	9.60	0.40	9.00	Μ	6.30	Μ	6.60	Μ
05/26	12.20	0.00	9.10	0.00	7.30	20.60	8.60	0.00	7.20	4.60	9.80	Μ	5.80	Μ	5.30	Μ
05/27	9.60	0.00	10.60	0.20	6.30	1.40	10.20	1.20	7.20	1.20	14.60	0.00	3.80	M	2.90	M
05/28	10.80	0.40	9.90	0.00	7.00	8.60	8.30	20.00	11.80	M	11.50	M	4.10	M	4.00	M
05/29	8.50	2.00	8.60 9.70	0.00	9.40	2.40	11.00	0.00	11.00	M	15.50	M	1.70	M	6.30 5.20	M
05/31	9.40	0.00	10.90	0.40	10.30	0.00	12.10	0.00	11.50	M	14.90	0.00	4.30	M	7.10	M
06/01	7.90	0.00	9.60	12.40	13.80	0.00	13.40	0.00	9.50	М	8.80	0.00	8.00	М	9.30	М
06/02	9.10	0.20	9.70	13.20	14.30	0.00	15.70	0.20	11.70	0.00	8.40	М	7.80	Μ	7.40	Μ
06/03	11.90	0.00	11.10	9.60	13.40	0.00	15.30	0.00	11.40	1.20	9.20	Μ	10.50	0.20	10.20	Μ
06/04	15.80	0.00	13.00	0.20	8.40	0.80	14.80	4.80	9.80	M	11.00	M	7.20	M	10.20	M
06/05	13.70	4.00	11.00	17.00	14.20	0.00	16.20	6.80	8.30	M	8.00	M	8.80	M	11.90	M
06/06	10.50	16.40	5.90 3.40	20.80	10.50	10.60	9.20	4.60	9.40	2.20	4.00	M	9.00	0.80	9.10	15.40
06/08	8.00	0.00	8.30	3.20	12.20	10.80	13.00	0.00	8.90	M	4.60	M	9.60	M	6.60	15.60
06/09	4.50	0.20	9.40	1.60	12.30	0.00	10.60	0.20	6.50	М	3.90	М	8.60	М	10.40	Μ
06/10	10.60	0.00	9.40	0.00	9.00	2.80	13.30	0.00	5.80	М	9.10	М	8.10	М	10.40	Μ

06/11	13.10	0.00	11.60	0.00	10.80	4.60	9.40	0.00	5.20	Μ	12.30	Μ	7.40	Μ	11.40	2.20
06/12	11.60	0.00	7.80	2.80	9.50	4.80	8.40	0.00	10.00	M	11.60	М	11.00	М	11.70	М
06/13	12.50	0.00	10.20	2.00	13.00	12.40	8.10	6.40	13.50	1.60	13.00	M	12.40	M	9.40	M
06/14	7.40	2.80	8.50	1.40	14.10	4.20	8.70	9.80	9.60	M	14.90	M	12.60	0.00 M	13.40	0.00
06/15	9.00	11.00	9.20	0.20	14.20	0.20	10.80	0.20	9.40	M	15.10	0.00	7.30	18.00	8.00	1.40
06/17	8.20	1.40	11.50	16.00	11.50	0.20	7.80	1.20	11.40	M	12.00	M	6.40	26.00	10.00	0.00
06/18	6.40	0.20	10.30	0.80	10.90	0.00	10.80	0.00	10.50	M	14.20	1.20	8.00	M	10.60	0.00
06/19	8.30	0.00	12.10	0.00	10.90	2.00	12.40	0.00	9.10	M	12.10	0.20	11.20	M	13.40	0.00
06/20	7.80	6.60	13.50	0.00	10.20	0.00	13.70	0.00	12.60	Μ	14.60	0.00	11.40	М	14.40	0.40
06/21	15.50	0.20	16.10	0.00	10.80	0.00	14.80	0.00	14.70	Μ	11.80	0.80	13.60	0.20	13.50	0.00
06/22	15.30	0.80	18.80	0.00	13.10	0.00	13.80	0.00	13.60	1.20	7.10	24.20	13.30	0.00	14.00	Μ
06/23	16.20	7.20	11.40	0.40	12.80	0.00	12.40	0.00	11.80	Μ	11.40	0.00	13.40	Μ	11.30	Μ
06/24	12.80	1.80	8.20	0.20	12.90	0.00	11.10	0.00	12.30	0.00	12.90	Μ	15.60	3.20	10.70	1.00
06/25	15.90	4.60	11.10	0.80	14.80	0.00	6.80	0.20	11.30	М	14.60	1.20	13.70	1.60	9.60	М
06/26	13.40	1.40	10.90	0.20	15.60	0.00	10.30	0.00	12.40	M	12.20	0.00	13.70	M	11.30	M
06/27	14.50	0.00	11.50	28.20	18.30	0.00	12.00	0.00	11.60	M	10.60	M	15.10	0.00	11.40	M
06/28	14.70	7.20	14.00	14.00	17.70	0.00	17.00	3.60	14.80	M	13.20	M	17.30	0.00	10.70	0.00
06/29	16.50	0.00	13.90	1.20	16.30	0.00	14.00	0.00	19.30	0.00	12.70	M	12.60	0.20	12.50	2.80
07/01	10.50	M	16.30	0.00	16.50	0.00	12.30	0.00	17.60	6.40	14.50	0.00	10.00	M	12.90	0.00
07/02		M	13.10	5.40	16.80	0.00	14.60	0.00	15.70	7.00	14.90	0.00	9.60	M	14.20	0.00
07/03		М	10.90	0.20	16.70	0.00	15.20	0.00	17.80	0.00	14.40	0.00	11.00	0.00	12.70	М
07/04		Μ	12.90	0.00	17.60	3.00	17.20	0.00	17.50	3.60	16.80	0.00	10.20	0.00	12.80	Μ
07/05		Μ	15.80	0.00	20.10	0.00	19.00	0.00	17.90	0.00	17.20	0.00	9.10	М	13.60	Μ
07/06		Μ	17.90	3.20	19.50	5.40	20.60	0.00	14.30	1.00	14.80	4.80	12.20	М	15.50	Μ
07/07		Μ	14.40	0.00	16.60	0.00	15.90	0.00	13.40	М	13.60	0.80	12.90	М	16.80	М
07/08		M	13.80	0.00	18.50	0.00	16.60	0.00	13.30	M	10.40	M	15.80	M	13.80	0.60
07/09		M	13.60	0.80	18.00	0.00	13.50	0.00	16.30	0.00	11.70	2.40	16.60	M	14.20	0.00
07/10		M	12.30	0.00	15.90	3.20	14.10	0.00	14.30	9.20 M	13.00	0.00 M	17.50	4.20	12.70	M
07/11		M	15.40	0.00	14.90	0.00	18.00	0.00	11.40	M	16.80	0.00	12.70	3.00 M	16.70	19.40
07/12	14 30	0.00	16.60	0.00	16.80	0.40	19.70	0.00	14.60	M	14.00	46.00	8.20	M	16.40	13.20
07/14	17.30	4.00	13.40	4.00	19.10	0.00	21.70	0.00	16.40	0.00	12.70	6.40	14.30	0.00	14.40	0.80
07/15	18.30	0.20	15.40	0.00	20.70	0.00	20.40	0.00	17.70	М	14.80	1.40	14.40	М	12.10	0.00
07/16	20.90	0.00	14.60	21.20	15.90	0.00	19.50	0.00	14.50	0.00	16.30	0.00	16.00	0.00	13.90	Μ
07/17	18.60	0.00	15.50	2.40	16.00	0.00	18.40	0.40	13.60	М	16.50	0.00	18.10	0.00	16.20	0.00
07/18	20.10	0.00	15.30	0.00	14.60	0.00	20.40	0.80	12.90	М	17.70	0.00	14.40	2.80	19.80	0.00
07/19	20.30	0.00	15.90	0.00	15.70	0.00	19.50	2.60	13.40	Μ	18.20	0.00	13.30	1.40	18.10	1.20
07/20	14.30	0.20	19.20	0.00	17.50	0.40	18.10	0.00	14.30	M	15.60	0.00	10.90	M	13.90	0.00
07/21	13.60	0.00	14.00	0.00	17.70	0.00	18.10	0.00	16.40	M	16.50	0.00	12.50	M	12.20	0.00
07/22	15.60	0.00	16.50	0.20	20.60	0.00	19.70	0.00	16.10	0.00	17.70	5.20	16.10	M 1.40	9.60	4.80 M
07/23	16.10	0.00	11.80	0.00	19.30	2.00	19.30	0.00	15.50	0.00	18.00	2.60	15.60	1.40 M	13.80	M
07/24 07/25	10.10	M	12.40	0.00	19.40	0.40	18.30	0.20	13.50	M	17.10	11.80	17.10	0.00	14.50	M
07/26		M	12.50	0.00	18.60	0.00	18.20	0.00	16.00	0.00	18.80	6.20	17.50	0.00	14.30	0.60
07/27		М	14.90	0.00	19.40	0.00	18.60	0.00	14.70	0.00	17.30	0.00	16.30	0.00	14.90	0.00
07/28		Μ	17.10	0.00	17.20	0.00	19.40	0.00	16.40	0.00	15.10	0.00	18.30	0.00	12.60	Μ
07/29		Μ	18.00	0.00	16.00	0.00	19.30	0.00	13.60	Μ	12.20	0.20	17.40	0.00	15.50	0.00
07/30		Μ	17.10	0.00	11.40	1.00	19.80	0.00	13.30	3.40	14.50	Μ	16.80	0.00	14.60	Μ
07/31		М	17.50	0.00	12.90	0.00	15.00	0.00	12.50	М	16.20	2.20	14.10	М	16.70	0.00
08/01	13.30	0.00	17.60	0.00	11.00	0.00	18.20	0.00	14.60	2.40	18.50	7.00	15.70	0.80	16.60	0.00
08/02	16.50	6.40	13.90	0.00	12.30	0.00	12.00	0.00	10.00	15.00	15.70	15.00	12.60	1.80	14.80	M
08/03	17.10	0.40	14.00	0.00	13.30	0.00	14 70	0.00	12.10	M	12.00	8.00	11.00	M	16.40	0.00
08/05	14.90	0.00	16.00	0.00	13.10	0.00	18.00	0.00	13.20	M	12.20	4.40	13.60	M	16.20	1.00
08/06	12.90	2.20	17.10	0.00	14.50	0.00	15.00	0.00	14.80	М	15.30	0.00	16.90	2.00	16.20	0.00
08/07	13.00	11.20	14.70	0.00	16.40	0.00	14.80	0.00	19.40	0.00	12.80	0.00	14.60	Μ	17.60	0.00
08/08	11.90	0.00	15.80	2.00	18.40	0.00	14.60	0.00	18.10	0.00	13.30	Μ	14.90	0.20	16.30	0.00
08/09	14.70	0.00	14.70	0.00	19.60	0.80	11.40	0.00	18.00	3.60	15.50	1.60	13.90	Μ	15.80	2.60
08/10	12.90	0.00	12.40	14.00	18.70	1.80	12.60	0.00	14.90	0.00	15.90	0.00	13.60	5.60	14.90	М
08/11	14.60	0.00	15.10	9.80	12.70	1.80	10.40	0.00	13.50	0.00	18.60	0.40	15.60	1.40	14.80	1.40
08/12	17.10	0.00	10.00	14.20	11.20	2.00	13.70	0.00	12.80	M	14.20	5.40	13.80	5.20	15.70	0.00 M
08/15	18.50	0.00	10.90	0.00	11.10	0.00	15.00	0.00	15.00	26.40	9.50	12.20	12.20	0.20	15.50	M
08/14	18.00	0.00	15.10	0.00	15.30	0.00	14.70	0.00	16.50	20.40	9.90	12.20 M	13.20	M	10.50	M
08/16	18.90	4.80	14 60	0.00	13.10	4 20	13 50	0.00	18.90	0.00	10.50	7 40	15.60	M	9.70	M
08/17	19.80	16.40	8.70	23.60	12.30	0.00	16.10	0.00	20.30	0.00	13.40	0.00	13.30	0.20	12.30	М
08/18	17.40	0.80	10.90	0.20	13.60	0.00	14.00	0.00	21.30	0.00	15.40	0.00	19.60	0.00	12.60	0.00
08/19	16.50	1.40	10.00	0.00	14.60	0.00	12.60	0.00	17.20	0.40	14.60	0.00	16.70	0.00	11.90	М
08/20	16.70	1.80	13.60	0.00	14.80	0.00	14.60	0.00	14.00	1.00	14.80	0.00	14.00	Μ	13.20	Μ
08/21	17.60	2.00	15.50	0.00	15.80	0.00	12.40	0.00	12.80	2.20	18.00	2.00	12.50	М	14.80	Μ
08/22	13.00	21.00	14.30	0.00	15.40	0.00	11.50	0.00	11.30	M	15.30	0.00	13.60	0.40	20.20	0.00
08/23	12.30	11.20	8.80	12.00	14.70	1.60	11.10	1.80	12.70	M	12.40	M	9.30	M	18.00	0.00
08/24	13.10	0.20	8.40	6.00	12.50	0.20	11.60	0.00	14.60	M	12.30	M	12.60	M	17.80	0.00
08/25	12.60	2.00	10.90	0.00	12.30	0.00	14.20	0.00	14.20	0.00	13.00	M	14.90	M	17.50	0.20
08/27	11.00	2.40	13.90	0.20	14.90	0.00	8.00	4.80	12.10	0.00	13.00	M	13.00	10.00	16.10	0.00 M
08/27	13 70	2.20	14 70	0.00	15.60	0.00	10.30	0.00	10.10	M	14 40	M	11.00	0.00	15.70	M
08/29	14.10	0.20	12.40	0.00	15.90	0.20	13.30	0.00	18.40	0.00	14.00	M	5.60	M	16.00	M
08/30	16.40	1.00	8.70	0.00	13.00	0.00	14.00	0.00	15.70	0.00	13.50	М	9.10	М	15.80	0.00
08/31	15.00	0.20	10.40	0.00	8.20	1.80	17.20	0.00	8.10	0.40	16.40	Μ	6.80	Μ	8.00	9.00

09/01	13.70	7.60	11.20	0.00	8.90	0.00	17.70	0.80	6.70	Μ	16.40	0.00	8.10	Μ	9.80	Μ
09/02	10.20	0.20	13.50	0.00	13.30	0.00	13.50	0.00	6.70	Μ	17.40	0.20	8.00	Μ	8.20	Μ
09/03	9.00	0.00	12.10	0.00	15.50	0.00	16.30	0.00	8.70	М	16.50	0.00	11.90	М	8.20	Μ
09/04	9.70	0.00	11.70	0.00	15.20	0.00	15.60	0.00	9.70	M	13.90	0.00	13.70	M	10.70	M
09/05	11.60	0.00	9.90	0.00	16.40	0.00	13.30	0.00	8.70	M	11.50	M	5.30	M	13.20	M
09/06	8.20	0.00	8.50	0.00	15.20	2.00	(70)	0.00	8.30	M	10.80	0.20	7.10	M	14.00	M
09/07	9.70	4.00	9.30	0.00	14.20	2.00	0.70 8.10	4.00	7.50	M	10.10	0.00	5.90 8.40	N1 8 80	14.30	M
09/08	10.20	8.60	9.20	11.60	13.90	0.00	9.20	0.00	12.00	M	12.80	0.00	9.30	6.60	15.80	M
09/10	10.20	1.80	2.70	39.00	13.30	0.00	10.80	0.00	9.30	M	12.00	M	9.60	M	14.00	M
09/11	11.40	2.40	4 40	65.00	13.00	0.00	13.00	0.00	10.80	M	10.40	M	10.00	M	15.20	M
09/12	10.70	0.00	5.90	0.20	12.90	0.00	10.30	4.80	13.10	M	13.80	M	7.50	M	18.10	0.00
09/13	10.90	0.20	6.40	0.00	8.80	9.00		M	8.80	М	11.20	М	9.50	2.60	9.70	0.00
09/14	9.20	2.20	10.50	0.40	4.50	6.40		М	10.90	М	12.70	М	7.80	0.00	10.80	М
09/15	7.40	0.20	8.20	14.40	4.60	5.40		Μ	12.50	М	16.90	0.00	12.90	3.20	11.30	Μ
09/16	9.30	0.40	6.70	0.20	4.80	0.40		Μ	13.00	Μ	16.60	Μ	9.40	М	11.70	0.00
09/17	9.60	1.60	9.20	0.00	6.50	0.00		Μ	13.30	Μ	13.80	0.00	2.00	Μ	11.60	0.00
09/18	7.90	1.80	7.90	0.20	6.70	0.00		Μ	14.80	Μ	14.00	Μ	5.80	Μ	9.30	Μ
09/19	7.00	0.00	13.90	0.00	8.00	5.20		Μ	14.10	М	12.60	М	7.00	М	7.20	Μ
09/20	8.40	0.40	9.00	0.00	9.10	0.40		M	13.00	М	5.80	M	7.80	M	6.80	M
09/21	9.40	0.00	5.40	0.00	9.00	6.40		M	9.90	13.80	6.90	M	3.30	M	10.80	M
09/22	12.10	0.00	5.50	1.20	4.90	0.40		M	9.00	0.00	13.40	M	6.50	M	18.60	0.00
09/23	9.80	0.00	3.60	0.20	6.70	0.00		M	5.10	M	16.20	M	5.70	M	17.30	0.00
09/24	9.40	0.00	5.40	0.00	9.30	0.00		M	10.10	0.00	12.20	M	9.00	0.00	13.20	M
$\frac{09}{25}$	9.60	0.00	10.20	0.00	12.20	1.40		M	7.30	M	14.50	0.00	14.20	0.00	13.10	0.00
09/20	11.30	0.00	2.90	1.40	11.40	1.10		M	8.20	M	5.20	M	14.60	0.00	12.20	6.80
09/28	11.80	0.00	5.80	0.00	14.80	0.00		M	8.00	M	5.90	M	14.20	3.00	5.80	M
09/29	10.10	4.20	12.90	6.80	15.40	0.00		M	12.10	М	7.90	М	10.40	М	7.10	Μ
09/30	6.70	0.40	11.60	12.20	11.90	0.00		Μ	13.20	М	2.60	М	8.70	М	14.00	Μ
10/01	5.30	0.00	5.90	8.20	8.70	0.00		М	13.70	М	3.00	М	8.70	М	8.90	М
10/02	7.90	0.00	4.50	0.00	0.60	1.80		Μ	14.50	Μ	2.70	Μ	12.10	Μ	8.70	Μ
10/03	6.90	0.00	-0.40	3.20	4.10	2.80		М	12.40	0.20	1.70	Μ	10.90	Μ	10.80	Μ
10/04	8.50	0.20	0.40	5.60	6.70	0.00		Μ	7.10	Μ	1.50	Μ	13.80	0.20	7.70	Μ
10/05	10.90	0.00	3.30	0.00	8.70	0.00		Μ	8.40	0.00	2.40	Μ	9.90	М	3.40	Μ
10/06	12.70	1.20	7.10	0.20	7.50	0.20		М	8.00	М	5.10	М	11.20	М	3.00	М
10/07	7.60	2.40	8.10	4.20	2.10	4.60		M	8.60	5.20	-0.90	M	9.60	M	4.00	M
10/08	9.80	0.00	4.00	0.00	2.60	1.20		M	2.10	M	-1.90	M	11.10	M	6.10	M
10/09	6.90	0.00	3.30	0.20	2.90	0.00		M	-1.50	M	-9.90	M	9.70	M 0.20	6.90	M
10/10	5.80	0.00	6.40	0.00	5.00	0.00		M	-1.50	M	-11.90	M	7.80	0.20 M	7.70	M 0.60
10/11	9.50	0.00	4.40	0.00	7.20	0.00		M	0.20	M	-13.80	M	8.50	M	6.60	M
10/12	8.40	0.00	4 50	10.40	5.20	0.00		M	3.90	M	-7.20	M	8.40	M	2.40	M
10/14	9.20	19.00	5.60	0.00	6.70	0.00		M	3.10	M	-1.00	M	10.00	M	1.90	M
10/15	5.40	2.00	8.70	0.00	9.40	0.00		0.00	0.60	М	5.30	M	4.50	М	1.60	Μ
10/16	3.20	0.60	10.50	0.00	2.40	6.60	5.70	0.00	5.70	М	4.80	М	1.70	М	1.70	Μ
10/17	-4.60	0.20	12.50	8.00	2.70	0.00	6.40	0.00	9.50	0.00	12.20	6.80	1.00	М	2.00	Μ
10/18	-0.10	0.80	5.60	10.00	3.80	0.00	2.60	0.00	8.40	Μ	6.50	Μ	2.20	Μ	4.50	Μ
10/19	-2.50	0.20	4.90	0.00	7.90	0.00	4.70	3.60	0.90	Μ	2.40	Μ	6.60	Μ	6.80	Μ
10/20	1.80	1.00	4.30	5.60	4.20	5.40	1.30	0.00	3.10	М	4.10	М	7.00	М	6.60	Μ
10/21	-1.90	1.00	3.10	0.00	1.60	0.60	0.90	0.00	2.20	М	3.50	М	7.00	М	4.80	М
10/22	0.60	0.40	4.80	0.00	1.90	0.00	7.80	0.00	4.50	M	5.90	M	6.40	M	7.00	M
10/23	1.30	0.00	7.70	0.20	5.70	0.00	13.90	0.00	4.40	M	6.20	M	3.40	M	4.00	M
10/24	-0.40	0.00	9.60	0.00	2.40	0.40	2.30	2.00	2.40	M	2.20	M	4.00	M	0.10	M
$\frac{10}{25}$	-0.70	0.00	6.60	0.00	6.00	0.00	-0.70	0.00	-0.80	M	2.10	M	2.20	M	-2.10	M
10/27	0.90	0.00	2.60	0.00	9.50	0.00	1.30	0.00	7 40	M	2.70	M	0.80	M	2.00	M
10/28	3.10	0.00	1.50	0.20	9.60	0.00	10.10	0.00	7.40	M	-1.00	M	-0.40	M	1.40	M
10/29	1.30	0.00	4.10	0.00	-0.60	0.00	9.40	0.00	11.60	0.00	-3.50	М	3.70	М	4.50	М
10/30	3.10	2.80	3.00	0.00	-12.10	0.00	1.10	0.00	7.10	Μ	4.30	Μ	4.70	Μ	5.10	Μ
10/31	-2.10	0.40	3.60	1.00	-10.00	0.00	1.10	0.00	6.20	М	7.20	Μ	4.80	Μ	2.20	Μ
11/01	-5.10	0.00	2.30	3.60	-11.00	0.00	2.10	0.00	10.50	М	1.30	Μ	7.40	М	-2.10	Μ
11/02	2.60	7.40	0.50	12.60	-8.30	0.00	-0.60	0.00	8.50	М	1.40	М	6.90	М	2.80	Μ
11/03	-1.10	2.20	-1.10	0.00	4.70	0.40	6.00	0.00	1.30	М	1.00	М	3.80	М	2.10	М
11/04	0.70	0.00	0.90	0.00	8.00	0.00	3.40	3.20	-3.90	M	2.40	M	4.90	M	-6.40	M
11/05	6.60	0.00	0.20	0.20	7.80	0.80	-3.00	0.00	-0.10	M	6.50	M	8.60	M 2.00	-7.00	M
11/00	4.50	1.20	-0.50	5.20	10.20	19.20	2.90	0.00	-3.40	M	1.20	M	7.20	2.00 M	-0.50	M
11/0/	6.70	0.00	-2.50	0.00	3.40	45.00	5.40	0.00	5.90	M	1.20	M	-0.20	M	-1.20	M
11/00	3.60	0.00	1.70	0.00	-3.20	0.00	4 10	0.00	4.80	M	4 50	M	-2.40	M	0.30	M
11/10	0.00	0.00	6.90	0.00	-2.90	1.60	5.10	0.60	5.60	M	0.40	M	-3.90	M	4.70	M
,	-0.70		2 20	0.20	1 70	0.80	1.70	0.00	2.80	М	-1.70	М	-3.80	М	3.10	М
11/11	-0.70	0.00	5.50	0.20	****						5.50	1.6				
11/11 11/12	-0.70 0.30 -0.50	0.00	-1.00	0.80	-0.60	1.20	4.10	6.20	6.20	M	-5.50	M	2.40	M	-0.20	M
11/11 11/12 11/13	-0.70 0.30 -0.50 -1.00	0.00 0.00 0.00	-1.00 -0.20	0.80	-0.60 0.50	1.20 6.40	4.10 -0.40	6.20 0.00	6.20 0.10	M	-5.50	M	2.40 1.80	M M	-0.20 0.80	M
11/11 11/12 11/13 11/14	-0.70 0.30 -0.50 -1.00 0.20	0.00 0.00 0.00 0.00	-1.00 -0.20 -5.40	0.80 0.00 2.00	-0.60 0.50 -4.80	1.20 6.40 0.00	4.10 -0.40 -3.90	6.20 0.00 0.00	6.20 0.10 -4.60	M M M	-5.50 -1.70 -1.30	M M M	2.40 1.80 3.60	M M M	-0.20 0.80 -4.40	M M M
11/11 11/12 11/13 11/14 11/15	-0.70 0.30 -0.50 -1.00 0.20 7.70	0.00 0.00 0.00 0.00 0.00	-1.00 -0.20 -5.40 -6.20	0.20 0.80 0.00 2.00 0.00	-0.60 0.50 -4.80 1.10	1.20 6.40 0.00 4.00	4.10 -0.40 -3.90 3.10	6.20 0.00 0.00 0.00	6.20 0.10 -4.60 5.10	M M M M	-5.50 -1.70 -1.30 -1.80	M M M M	2.40 1.80 3.60 1.80	M M M M	-0.20 0.80 -4.40 -8.30	M M M M
11/11 11/12 11/13 11/14 11/15 11/16	-0.70 0.30 -0.50 -1.00 0.20 7.70 4.40	0.00 0.00 0.00 0.00 0.00 0.20	-1.00 -0.20 -5.40 -6.20 0.20	0.20 0.80 0.00 2.00 0.00 0.00	-0.60 0.50 -4.80 1.10 2.50	1.20 6.40 0.00 4.00 2.40	4.10 -0.40 -3.90 3.10 6.10	6.20 0.00 0.00 0.00 0.00	6.20 0.10 -4.60 5.10 2.10	M M M M M	-5.50 -1.70 -1.30 -1.80 4.20	M M M M M	2.40 1.80 3.60 1.80 -2.40	M M M M M	-0.20 0.80 -4.40 -8.30 -5.40	M M M M M
11/11 11/12 11/13 11/14 11/15 11/16 11/17	-0.70 0.30 -0.50 -1.00 0.20 7.70 4.40 1.80	0.00 0.00 0.00 0.00 0.00 0.20 0.40	-1.00 -0.20 -5.40 -6.20 0.20 -2.30	0.20 0.80 0.00 2.00 0.00 0.00 0.00	-0.60 0.50 -4.80 1.10 2.50 -0.50	1.20 6.40 0.00 4.00 2.40 0.00	4.10 -0.40 -3.90 3.10 6.10 3.00	6.20 0.00 0.00 0.00 0.00 0.00	6.20 0.10 -4.60 5.10 2.10 5.20	M M M M M M	-5.50 -1.70 -1.30 -1.80 4.20 5.20	M M M M M M	2.40 1.80 3.60 1.80 -2.40 -11.40	M M M M M M	-0.20 0.80 -4.40 -8.30 -5.40 -5.60	M M M M M
11/11 11/12 11/13 11/14 11/15 11/16 11/17 11/18	-0.70 0.30 -0.50 -1.00 0.20 7.70 4.40 1.80 3.70 4.70	0.00 0.00 0.00 0.00 0.00 0.20 0.40 0.20	-1.00 -0.20 -5.40 -6.20 0.20 -2.30 1.50	0.20 0.80 0.00 2.00 0.00 0.00 0.00 0.00 0.00 0.00	-0.60 0.50 -4.80 1.10 2.50 -0.50 -2.20	$ \begin{array}{c} 1.20 \\ 6.40 \\ 0.00 \\ 4.00 \\ 2.40 \\ 0.00 \\ 0.00 \\ 1.00 \\ \end{array} $	4.10 -0.40 -3.90 3.10 6.10 3.00 3.10	6.20 0.00 0.00 0.00 0.00 0.00 0.20	$\begin{array}{c} 6.20 \\ 0.10 \\ -4.60 \\ 5.10 \\ 2.10 \\ 5.20 \\ 6.90 \\ 1.70 \end{array}$	M M M M M M M	-5.50 -1.70 -1.30 -1.80 4.20 5.20 0.70	M M M M M M M	2.40 1.80 3.60 1.80 -2.40 -11.40 -14.90 21.40	M M M M M M M	-0.20 0.80 -4.40 -8.30 -5.40 -5.60 -14.00	M M M M M M M
11/11 11/12 11/13 11/14 11/15 11/16 11/17 11/18 11/19 11/20	-0.70 0.30 -0.50 -1.00 0.20 7.70 4.40 1.80 3.70 -4.70 6.90	0.00 0.00 0.00 0.00 0.20 0.40 0.20 0.80 2.00	-1.00 -0.20 -5.40 -6.20 0.20 -2.30 1.50 1.90	0.20 0.80 0.00 2.00 0.00 0.00 0.00 0.00 0.20 0.20	-0.60 0.50 -4.80 1.10 2.50 -0.50 -2.20 1.00 2.40	$ \begin{array}{c} 1.20 \\ 6.40 \\ 0.00 \\ 4.00 \\ 2.40 \\ 0.00 \\ 0.00 \\ 1.00 \\ 7.40 \end{array} $	4.10 -0.40 -3.90 3.10 6.10 3.00 3.10 -5.30 8.20	6.20 0.00 0.00 0.00 0.00 0.00 0.20 0.00	6.20 0.10 -4.60 5.10 2.10 5.20 6.90 -1.70	M M M M M M M M	-5.50 -1.70 -1.30 -1.80 4.20 5.20 0.70 2.10 7.20	M M M M M M M M	2.40 1.80 3.60 1.80 -2.40 -11.40 -14.90 -21.40 18.80	M M M M M M M M	-0.20 0.80 -4.40 -8.30 -5.40 -5.60 -14.00 -15.20	M M M M M M M M
11/11 11/12 11/13 11/14 11/15 11/16 11/17 11/18 11/19 11/20 11/21	-0.70 0.30 -0.50 -1.00 0.20 7.70 4.40 1.80 3.70 -4.70 -6.80 -1.20	0.00 0.00 0.00 0.00 0.20 0.40 0.20 0.80 2.00 0.00	-1.00 -0.20 -5.40 -6.20 0.20 -2.30 1.50 1.90 3.60 1.30	0.20 0.80 0.00 2.00 0.00 0.00 0.00 0.00 0.20 0.00 0.00	-0.60 0.50 -4.80 1.10 2.50 -0.50 -2.20 1.00 2.40 0.90	$ \begin{array}{c} 1.20\\ 6.40\\ 0.00\\ 4.00\\ 2.40\\ 0.00\\ 0.00\\ 1.00\\ 7.40\\ 1.60\\ \end{array} $	4.10 -0.40 -3.90 3.10 6.10 3.00 3.10 -5.30 -8.30 -9.50	$\begin{array}{c} 6.20 \\ 0.00 \\ 0.00 \\ 0.00 \\ 0.00 \\ 0.00 \\ 0.20 \\ 0.00 \\ 0.00 \\ 0.00 \\ 0.00 \end{array}$	6.20 0.10 -4.60 5.10 2.10 5.20 6.90 -1.70 -4.30 2.10	M M M M M M M M M	-5.50 -1.70 -1.30 -1.80 4.20 5.20 0.70 2.10 7.20 1.70	M M M M M M M M M M	2.40 1.80 3.60 1.80 -2.40 -11.40 -14.90 -21.40 -18.80 -22.10	M M M M M M M M M	-0.20 0.80 -4.40 -8.30 -5.40 -5.60 -14.00 -15.20 -12.90 -1.60	M M M M M M M M M M

11/22	-6.30	0.80	1.80	0.00	-1.60	0.00	-8.40	0.00	1.00	Μ	-1.40	М	-20.70	Μ	2.80	Μ
11/23	-7.00	0.00	-1.20	0.20	-4.00	3.80	-8.70	0.00	-0.90	Μ	2.50	Μ	-25.10	Μ	2.50	Μ
11/24	3.40	0.00	-1.50	0.20	-10.00	0.00	-3.60	0.00	4.00	Μ	0.70	Μ	-24.00	Μ	1.10	Μ
11/25	-0.70	0.00	1.10	0.00	-18.70	0.00	-6.60	0.00	6.30	Μ	4.60	Μ	-12.10	Μ	-4.30	Μ
11/26	-3.50	3.00	0.50	0.60	-22.00	0.00	-6.30	0.00	-1.50	Μ	7.10	Μ	-3.20	Μ	-4.40	Μ
11/27	-4.20	0.00	-3.00	4.40	-23.00	0.00	-5.30	0.00	-6.30	Μ	-0.90	Μ	-3.00	Μ	6.10	Μ
11/28	-8.20	0.00	-7.20	0.60	-22.30	0.00	-8.30	0.00	-0.10	Μ	-4.90	Μ	-10.90	Μ	2.40	Μ
11/29	-3.60	0.00	-10.50	0.00	-21.20	0.00	-14.80	0.00	2.60	Μ	2.20	Μ	-12.50	Μ	1.80	Μ
11/30	-2.20	0.00	-15.40	0.00	-8.30	0.00	-15.00	0.00	1.20	Μ	0.10	Μ	-3.90	Μ	-4.20	Μ
12/01	-2.40	0.00	-19.40	0.00	-10.40	0.00	-17.20	Μ	6.50	0.20	-10.10	Μ	0.40	Μ	-4.20	Μ
12/02	0.10	0.00	-17.10	0.00	-13.80	0.00	-10.50	Μ	-4.00	Μ	-13.40	Μ	-4.60	Μ	-5.30	Μ
12/03	2.50	0.00	-20.90	0.00	-5.50	0.00	1.40	Μ	-8.70	Μ	-15.70	Μ	-9.00	Μ	-6.50	Μ
12/04	0.50	0.00	-17.50	0.00	-1.20	0.00	5.10	Μ	-13.60	Μ	-7.50	Μ	-11.30	Μ	-8.90	Μ
12/05	-5.40	0.20	-9.90	0.00	0.50	0.20	-2.70	Μ	-1.90	Μ	-9.80	Μ	-13.30	Μ	-4.40	Μ
12/06	-12.10	0.00	-19.70	0.00	1.10	0.00	-7.50	Μ	3.90	Μ	-19.00	Μ	-9.80	Μ	-1.80	Μ
12/07	-11.80	0.00	-19.10	0.00	3.30	0.00	-14.10	Μ	1.90	Μ	-22.90	Μ	-6.50	Μ	-5.40	Μ
12/08	-4.90	1.40	-11.20	0.00	2.30	0.00	-15.00	Μ	-2.30	Μ	-24.70	Μ	3.10	Μ	-11.40	Μ
12/09	0.70	0.20	-3.90	0.00	1.20	0.00	-14.20	Μ	-6.20	Μ	-16.90	Μ	1.10	Μ	-5.40	Μ
12/10	4.50	5.20	-1.50	0.00	4.20	0.00	-10.10	Μ	3.70	Μ	-11.30	Μ	-8.40	Μ	-2.60	Μ
12/11	0.30	9.40	-1.20	0.00	4.10	0.00	-9.10	Μ	-1.00	Μ	-8.10	Μ	-8.80	Μ	-3.10	Μ
12/12	-5.50	0.00	-2.30	0.00	2.90	1.40	-3.00	Μ	-3.70	Μ	-16.40	Μ	-0.20	Μ	-9.20	Μ
12/13	-5.00	0.00	-3.30	0.60	1.70	0.80	-7.60	Μ	-17.50	Μ	-26.60	Μ	4.30	Μ	-8.60	Μ
12/14	5.50	0.00	-10.20	0.00	-0.50	0.00	-7.60	Μ	-26.20	Μ	-23.30	Μ	0.60	Μ	-4.90	Μ
12/15	4.00	0.00	-10.00	0.00	0.20	4.80	-2.70	Μ	-23.40	Μ	-9.70	Μ	-1.40	Μ	-3.70	Μ
12/16	3.30	0.00	-14.30	0.00	-10.80	0.00	-1.30	Μ	-22.10	Μ	2.10	Μ	-8.50	Μ	0.20	Μ
12/17	2.60	0.00	-18.20	0.00	-11.40	0.00	-1.50	Μ	-14.40	Μ	1.60	Μ	-13.30	Μ	4.40	Μ
12/18	3.30	0.00	-16.00	0.00	-4.60	0.00	-0.60	Μ	-19.40	Μ	1.70	Μ	-12.80	Μ	1.20	Μ
12/19	4.90	0.60	-13.00	0.00	0.50	0.00	0.30	Μ	-25.40	Μ	1.30	Μ	-14.20	Μ	-5.80	Μ
12/20	-2.00	0.00	-0.20	0.00	-0.40	0.00	-2.50	Μ	-26.90	Μ	-3.90	Μ	-11.70	Μ	0.10	М
12/21	-4.10	0.00	5.70	0.00	0.80	0.00	-12.30	Μ	-24.60	Μ	-8.30	Μ	-6.50	Μ	-4.80	М
12/22	-14.60	0.00	5.80	0.00	-2.80	0.00	-5.50	Μ	-20.50	Μ	-10.60	Μ	-8.30	Μ	-3.80	М
12/23	-13.30	0.20	5.20	0.00	-2.70	0.00	-2.00	Μ	-17.20	М	-17.60	Μ	-5.70	Μ	-1.70	М
12/24	-2.60	0.00	6.30	0.00	-7.20	0.00	-1.20	Μ	-8.80	М	-17.30	Μ	-1.20	Μ	1.60	Μ
12/25	-1.60	1.60	7.40	0.00	-4.20	3.20	-8.00	Μ	-10.40	М	-14.90	Μ	0.20	Μ	3.40	М
12/26	-11.50	2.00	3.90	0.00	-5.10	0.00	-4.60	Μ	-14.80	М	-12.80	Μ	-3.60	Μ	-0.40	Μ
12/27	-12.50	0.20	3.20	0.00	-2.90	3.20	-10.10	Μ	-3.50	М	-11.70	Μ	-1.30	Μ	0.80	М
12/28	-7.10	0.00	-0.60	0.00	-10.60	0.00	-5.80	М	-8.00	Μ	-12.80	Μ	-0.60	Μ	3.70	М
12/29	-6.30	0.00	-1.30	0.80	-11.40	0.00	-7.20	М	-11.10	Μ	-7.00	Μ	-9.60	Μ	2.20	М
12/30	-13.40	1.00	-0.50	0.00	-4.90	0.00	-4.30	М	-9.30	Μ	-14.60	Μ	-22.90	Μ	1.20	М
12/31	-20.50	0.60	0.80	0.00	-8.60	0.00	-6.40	Μ	-10.10	Μ	-18.40	Μ	-20.90	Μ	-3.80	Μ

## **APPENDIX B: RAW DATA FROM SOLID PHASE EXTRACTION**

					RAW SA	AMPLES				
Sample		Star	-1							
Date of fraction	onation	July	19, 2011							
	Concentra	ation	Volume	Mass	UV254	pН	Turbidity	Recovery	UVA	SUVA
								Ratio		
Whole	4.06		890	3.61	0.47369	8.05	31.4	1	0.094738	2.33344828
HPI	2.021		890	1.80	0.12722			0.497783251	0.025444	1.2589807
HPO	12.93		155	2.00	1.331			0.554643826	0.2662	2.05877804
DI	2.751			0.00			Total:	1.052427077		
Base	3.392			0.00						
Sample		Star	-2							
Date of fraction	onation	May	31, 2011							
	Concentra	ation	Volume	Mass	UV254	pН	Turbidity	Recovery	UVA	SUVA
								Ratio		
Whole	4.435		890	3.95	0.49416	8.06	36.9	1		0.098832
HPI	2.439		890	2.17	0.27589			0.54994363		0.055178
HPO	31.8		68	2.16	3.4832			0.547838314		0.69664
DI	1.425		925	1.32			Total:	1.097781944		
Base	6.568		33	0.22						
Sample		Lyo	ns East-1							
Date of fraction	onation	July	21, 2011 (Note	e: Sample was s	scrapped becau	ise column ran	dry)			
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	pН	Turbidity	Recovery	UVA	SUVA
								Ratio		
Whole				<del>0.00</del>	1.0457	7.2	29.4	#DIV/0!	0.20914	# <del>DIV/0!</del>
HPI				0.00				#DIV/0!	θ	#DIV/0!
HPO				0.00				#DIV/0!	θ	#DIV/0!
DI	0.577			0.00			Total:	#DIV/0!		
Base	2.046			0.00						

Sample		Lyon	ns East-2							
Date of fraction	onation	June	e 9, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	рН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	8.186		890	7.29	1.1411	7.2	28.8	1	0.22822	2.7879306
HPI	2.453		890	2.18	0.26886			0.299657953	0.053772	2.1920913
HPO	8.536		595	5.08	1.2826			0.697123343	0.25652	3.0051546
DI	1.183	)	890	1.05			Total:	0.996781296		
Base	8.987	,		0.00						
Sample		Dru	m-1						•	
Date of fraction	onation	July	22, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	рН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	4.373	1	855	3.74	0.52565	7.84	22.1	1	0.10513	2.40407043
HPI	1.51		855	1.29	0.13364			0.345300709	0.026728	1.77006623
HPO	10.34		200	2.07	0.94015			0.553101635	0.18803	1.81847195
DI	0.241			0.00			Total:	0.898402344		
Base	1.437	,		0.00						
Sample		Dru	m-2			•		•	•	
Date of fraction	onation	June	e 11, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	рН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	3.858		890	3.43	0.49144	7.8	20	1	0.098288	2.5476413
HPI	<del>1.359</del>	L	<del>890</del>	<del>1.21</del>	0.12618			0.352255054	0.025236	<del>1.8569536</del>
HPO	<del>4.962</del>	-	<del>664</del>	3.29	<del>0.50995</del>			0.959561046	0.10199	<del>2.0554212</del>
ÐI	<del>0.436</del>	,	<del>890</del>	0.39			Total:	1.311816101		
Base	<del>1.555</del>	•	<del>664</del>	1.03						

Sample		Star	-1							
Date of fraction	onation	Aug	22, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	рН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	2.025		783	1.59	0.075597	8.32	0.885	1	0.0151194	0.746637
HPI	2		<del>783</del>	<del>1.57</del>	0.055977			0.987654321	<del>0.0111954</del>	<del>0.55977</del>
HPO	<del>7.551</del>		<del>110</del>	0.83	0.31116			0.523854122	0.062232	0.8241557
DI	<del>1.141</del>			0.00			Total:	<del>1.511508443</del>		
Base	<del>2.893</del>			0.00						
Sample		Star	-2						•	
Date of fracti	onation	Aug	24, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	рН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	1.542		788	1.22	0.076229	8.09	1.01	1	0.015246	0.988703
HPI	0.9392	2	788	0.74	0.04534			0.609079118	0.009068	0.965503
HPO	7.464		80	0.60	0.42616			0.491417962	0.085232	1.141908
DI	1.045			0.00			Total:	1.10049708		
Base	2.5			0.00						
Sample		Star	-3							
Date of fraction	onation	Aug	25, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	рН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	1.526		783	1.19	0.073249	8.19	0.956	0.983345	0.01465	0.960013
HPI	0.934		783	0.73	0.04581			0.601864	0.009162	0.980942
HPO	5.408		145	0.78	0.28258			0.645348	0.056516	1.045044
DI	0.9			0.00			Total:	1.247212		
Base	1.857			0.00						

Sample		Lyo	ns East-1							
Date of fraction	onation	Sept	t 8, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	pН	Turbidity	Recovery	UVA	SUVA
						*	-	Ratio		
Whole	3.034		783	2.38	0.37413	8.26	0.602	1	0.074826	2.4662492
HPI	1.289		783	1.01	0.086533			0.424851681	0.0173065	1.342633
HPO	12.64		100	1.26	1.6658			0.53207118	0.33316	2.6357595
DI	0.4740	5		0.00			Total:	0.956922861		
Base	1.124			0.00						
Sample		Lyo	ns East-2							
Date of fraction	onation	Sept	t 8, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	pН	Turbidity	Recovery	UVA	SUVA
						Î		Ratio		
Whole	2.803		783	2.19	0.36088	8.3	0.447	1	0.072176	2.574955
HPI	1.372		783	1.07	0.100967			0.489475562	0.020193	1.471822
HPO	14.78		100	1.48	0.99404			0.673425526	0.198808	1.345115
DI	0.427	7		0.00			Total:	1.162901088		
Base	1.212			0.00						

					TREATE	O SAMPLES				
Sample		Star	-1							
Date of fracti	onation	June	e 3, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	pН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	2.889		890	2.57	0.13099	7.25	0.241	1	0.026198	0.90681897
HPI	1.566		890	1.39	0.090511			0.542056075	0.0181022	1.15595147
HPO	15.11		87	1.31	1.5883			0.511265124	0.31766	2.10231635
DI	0.718		937	0.67			Total:	1.053321199		
Base	4.38		40	0.18						
Sample		Star	-2							
Date of fracti	onation	July	27, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	pН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	2.768		855	2.37	0.10739	7.48	0.172	1	0.021478	0.7759393
HPI	1.234		855	1.06	0.065947			0.445809249	0.0131894	1.0688331
HPO	7.278		150	1.09	0.55985			0.461286888	0.11197	1.5384721
DI	0.497			0.00			Total:	0.907096136		
Base	1.478			0.00						
Sample		Lyon	ns East-1							
Date of fraction	onation	June	e 10 <b>,</b> 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	pН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	2.251		890	2.00	0.14566	6.45	0.571	1	0.029132	1.29418036
HPI	<del>1.109</del>		<del>890</del>	<del>0.99</del>	0.052225			0.492669924	0.010445	<del>0.9418395</del>
HPO	4.081		<del>590</del>	<del>2.41</del>	0.24766			1.201857851	0.049532	<del>1.21372213</del>
DI	<del>0.453</del>		<del>890</del>	0.40			Total:	<del>1.694527775</del>		
Base	<del>1.728</del>		<del>590</del>	<del>1.02</del>						
Sample		Lyon	ns East-2							
Date of fraction	onation	July	26, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	pН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	2.303		855	1.97	0.14638	6.39	0.51	1	0.029276	1.2712115
HPI	0.891		855	0.76	0.092661			0.38688667	0.0185322	2.0799327
HPO	5.218		300	1.57	0.32513			0.79499661	0.065026	1.2461863
DI	1.171			0.00			Total:	1.18188328		

Base	1.062			0.00						
Sample		Dru	m-1	•				·	•	
Date of fracti	onation	July	25, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	pН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	1.397		855	1.19	0.078703	6.59	0.288	1	0.0157406	1.12674302
HPI	0.58		855	0.50	0.072249			0.415175376	0.0144498	2.49134483
HPO	3.181		300	0.95	0.24452			0.798955155	0.048904	1.53737818
DI	0.357			0.00			Total:	1.21413053		
Base	1.814			0.00						
Sample		Dru	m-2							
Date of fracti	onation	July	24, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	рН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	1.183		855	1.01	0.073845	6.36	0.253	1	0.014769	1.2484362
HPI	<del>0.589</del>		<del>855</del>	<del>0.50</del>	<del>0.052314</del>			<del>0.497886729</del>	<del>0.0104628</del>	<del>1.7763667</del>
HPO	<del>3.151</del>		<del>300</del>	<del>0.95</del>	<del>0.1434</del>			<del>0.934584983</del>	<del>0.02868</del>	<del>0.9101872</del>
DI	<del>2.74</del>			0.00			<del>Total:</del>	<del>1.432471712</del>		
Base	<del>1.672</del>	-		0.00						
Sample		Star	-1							
Date of fracti	onation	Sept	t 6, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	pН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	0.9307	7	787	0.73	0.043191	7.57	0.818	1	0.0086382	0.9281401
HPI	0.5585	÷	787	0.44	0.025156			0.600085957	0.0050313	0.9008523
HPO	<del>3.99</del>		<del>158</del>	0.63	0.17664			0.860687581	0.035328	0.8854135
DI	0.4260	÷		0.00			Total:	1.460773538		
Base	<del>1.753</del>			0.00						
Sample		Star	-2							
Date of fracti	onation	Sept	t 7, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	pН	Turbidity	Recovery Ratio	UVA	SUVA
Whole	3.32		783	2.60	0.045083	7.73	0.845	1	0.009017	0.271584
HPI	0.7294	1	783	0.57	0.035052			0.219698795	0.00701	0.961119
HPO	11.14	,	105	1.17	0.17661			0.449960763	0.035322	0.317074
DI	0.4273	3		0.00			Total:	0.669659558		

Base	1 452			0.00						
Sample	1.432	Stor	3	0.00						
Data of fracti	onation	Star	-3							
Date of fractio	G	_ Sepi	, 2011 N. 1	2.6	1 17 7	TT		D	τττ	CLIVA
	Concentra	ation	Volume	Mass	$UV_{254}$	рн	Turbidity	Recovery	UVA	SUVA
								Ratio		
Whole	1.237		783	0.97	0.049119	7.7	0.864	1	0.009824	0.794163
HPI	0.7261	1	783	0.57	0.024564			0.586985	0.004913	0.676601
HPO	3.842		105	0.40	0.19807			0.4165	0.039614	1.031078
DI	0.4605	5		0.00			Total:	1.003485		
Base	1.249			0.00						
Samples		Lvo	ns East-1							
Date of fraction	onation	Sept	9. 2011							
	Concentra	ation	Volume	Mass	UV254	рH	Turbidity	Recovery	UVA	SUVA
	Goneentia		Volume	111435	0 1 234	P	Turbianty	Ratio	0 111	00 11
Whole	1 1/3		783	0.89	0.083050	6.97	0.712	1	0.0167918	1 4690989
LIDI	0.6101	1	703	0.87	0.065757	0.77	0.712	0.522770770	0.0107718	1.4070707
	4.721	1	/03	0.40	0.03804			0.535770779	0.011008	1.9020369
HPO	4./31		110	0.52	0.35201			0.581483828	0.070402	1.4880998
DI	0.5481	1		0.00			Total:	1.115254607		
Base	1.339			0.00						
Sample		Lyo	ns East-2							
Date of fraction	onation	Sept	: 9, 2011							
	Concentra	ation	Volume	Mass	UV <sub>254</sub>	pН	Turbidity	Recovery	UVA	SUVA
						î		Ratio		
Whole	1.287		783	1.01	0.081627	6.91	0.712	1	0.016325	1.268485
HPI	0.7213	3	<del>783</del>	0.56	0.048774			0.56045066	0.009755	<del>1.352392</del>
HPO	<del>9.329</del>		110	1.03	0.32291			1.018327493	0.064582	0.692271
DI	0.423	7		0.00			Total:	1.578778154		
Base	1.515			0.00					1	

Winter															Summer									
Site	Star							Site	Star							Site	Star							
Date	03/25/11		Collected	03/24/11	1			Date	05/28/11		Collected	05/27/11				Date	08/20/11		Collected	08/20/11				
Temp	0.4	°C						Temp	13.4							Temp	12.1							
Optimal								Optimal								Optimal								
Dose	20							Dose	20	mg/L						Dose	30	mg/L						
	Initial	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6		Initial	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6		Initial	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6	
Dose [mg]	0	10	20	30	40	50	60		0	10	20	30	40	50	60		0	10	20	30	40	50	60	
Turbidity																								
1	0.08	0.09	0.02	0.12	0.04	0.03	0.09		20.80	0.79	0.32	0.54	0.56	0.54	0.32		0.07	0.03	0.01	-0.01	-0.01	-0.01	-0.01	
Turbidity																								
2	0.06	0.11	0.03	0.14	0.01	0.05	0.11		19.40	0.81	0.29	0.51	0.63	0.56	0.38		0.09	0.01	0.02	-0.02	-0.02	-0.03	0.00	
Avg																								
Turbidity	0.07	0.10	0.03	0.13	0.03	0.04	0.10		20.10	0.80	0.31	0.53	0.60	0.55	0.35		0.08	0.02	0.02	-0.02	-0.02	-0.02	-0.01	
pH 1	8.33	8.05	7.89	7.78	7.58	7.52	7.48		8.31	8.03	7.86	7.72	7.64	7.56	7.45		8.38	8.13	7.94	7.77	7.63	7.54	7.46	
pH 2	8.30	7.98	7.92	7.79	7.64	7.54	7.50		8.33	8.10	7.90	8.81	7.68	7.56	7.44		8.40	8.10	7.91	7.80	7.68	7.54	7.47	
Avg pH	8.32	8.02	7.91	7.79	7.61	7.53	7.49		8.32	8.07	7.88	8.27	7.66	7.56	7.45		8.39	8.12	7.93	7.79	7.66	7.54	7.47	
Date	03/25/11		Collected	03/24/11				Date	05/28/11		Collected	05/27/11				Date	08/20/11		Collected	08/20/11				
Temp	0.2	°C		, ,				Temp	13.5							Temp	12.4			, ,				
Optimal		1	1	1	+	1		Optimal	1	1	1	1			1	Optimal		ł			1			
Dose	30							Dose	30	mg/L						Dose	20	mg/L						
	Initial	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6		Initial	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6		Initial	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6	
Dose [mg]	0	5	10	15	20	25	30		0	15	20	30	60	70	80		0	10	15	20	25	30	35	
Turbidity																								
1	0.06	0.02	0.05	0.06	0.14	0.00	-0.05		24.90	0.44	0.36	0.27	0.52	0.38	0.35		0.11	0.09	0.01	0.01	0.02	0.05	0.01	
Turbidity																								
2	0.05	0.01	0.07	0.07	0.13	-0.01	-0.04		25.70	0.44	0.33	0.26	0.39	0.28	0.27		0.14	0.07	0.02	0.00	0.04	0.04	0.02	
Avg																								
Turbidity	0.06	0.02	0.06	0.07	0.14	-0.01	-0.05		25.30	0.44	0.35	0.27	0.46	0.33	0.31		0.13	0.08	0.02	0.01	0.03	0.05	0.02	
pH 1	8.33	8.09	8.03	7.93	7.83	7.76	7.64		8.51	8.05	7.95	7.78	7.47	7.39	7.33		8.46	8.10	8.00	7.92	7.82	7.77	7.70	
pH 2	8.33	8.10	7.98	7.87	7.83	7.79	7.65		8.52	8.05	7.95	7.79	7.46	7.41	7.34		8.45	8.09	8.00	7.93	7.84	7.78	7.68	
Avg pH	8.33	8.10	8.01	7.90	7.83	7.78	7.65		8.52	8.05	7.95	7.79	7.47	7.40	7.34		8.46	8.10	8.00	7.93	7.83	7.78	7.69	
Date	03/25/11		Collected	03/24/11				Date	05/29/11		Collected	05/27/11				Date	08/20/11		Collected	08/20/11				
Temp	-0.1	°C						Temp	13.3							Temp	12.8							
Optimal								Optimal								Optimal								
Dose	25							Dose	30	mg/L						Dose	15	mg/L						
	Initial	Jar 1	Jar 2	Jar 3					Initial	Jar 1	Jar 2						Initial	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6	
Dose [mg]	0	20	25	30					0	30	100						0	10	15	20	25	30	35	
Turbidity																								
1	0.08	0.01	-0.03	0.03					23.40	0.25	0.32						0.20	0.02	0.00	0.01	0.00	0.01	-0.03	
Turbidity																								
2	0.09	-0.01	-0.04	0.01					22.80	0.23	0.28						0.21	0.01	-0.02	0.02	-0.02	-0.01	-0.02	
Avg																								
Turbidity	0.09	0.00	-0.04	0.02	_				23.10	0.24	0.30						0.21	0.02	-0.01	0.02	-0.01	0.00	-0.03	
pH 1	8.29	7.73	7.70	7.64					8.40	7.66	7.10						8.48	8.11	8.02	7.93	7.84	7.76	7.70	
pH 2	8.33	7.78	7.73	7.69					8.41	7.67	7.11						8.49	8.15	8.01	7.92	7.83	7.75	7.69	
Avg pH	8.31	7.76	7.72	7.67					8.41	7.67	7.11						8.49	8.13	8.02	7.93	7.84	7.76	7.70	
																Date	08/20/11		Collected	08/20/11				
																Temp	12.9							
											T					Optimal								
																Dose	15	mg/L						
																	Initial	<u>Jar 1</u>	<u>Jar 2</u>	<u>Jar 3</u>	Jar 4	<u>Jar 5</u>	<u>Jar 6</u>	
																Dose [mg]	0	10	15	20	25	30	35	
																Turbidity								
																1	0.26	0.04	0.02	-0.01	-0.05	-0.02	-0.04	
																Turbidity								
					_											2	0.22	0.08	0.01	-0.03	-0.07	-0.01	-0.01	
																Avg								
																Turbidity	0.24	0.06	0.02	-0.02	-0.06	-0.02	-0.03	

																оH 1	8 50	812	8.04	7.03	7.85	7 78	7 7 2
-			-			+	_				+			-			0.50	0.12	0.04	7.02	7.05	7.70	7.72
											-					pH Z	8.48	8.14	8.02	7.92	7.85	/.//	7.72
																Avg pH	8.49	8.13	8.03	7.93	7.85	7.78	7.72
																Date	08/20/11		Collected	08/20/11			
																Temp	13.2						
																Optimal							
																Dese	15	ma/I					
			_			-			1		-			1		Dose	15 Luitial	Ing/L	I	I 2	Len 4	I	Land
											-					D I I	Initial	Jar I	<u>Jar 2</u>	Jar 5	Jar 4	Jar 5	Jaro
-																Dose [mg]	0	10	15	20	25	30	35
																Turbidity							
																1	0.34	0.02	0.02	0.04	-0.01	0.02	0.03
																Turbidity							
																2	0.28	0.01	0.00	0.03	-0.02	0.01	-0.01
																Avg							
																Turbidity	0.31	0.02	0.01	0.04	-0.02	0.02	0.01
																pH 1	8 4 9	813	8.03	7.93	7.86	7 79	7 73
																pH 2	8.49	8.11	8.03	7.94	7.00	7.79	7.73
				+					+			+		+		Arra	0.77	0.11	0.05	7.04	7.07	7.70	7.72
		ļ				1				ļ		1				AvgpH	0.47	0.12	0.00	/.74	/.0/	1.19	1.13
Winter			-			-		Spring			-	-				Summer		-	-				
Site	Drum							Site	Drum														
Date	03/22/11		Collected	03/22/11				Date	05/27/11		Collected	05/26/11											
Temp	1.2	°C						Temp	13.1														
Optimal								Optimal															
Dose	5							Dose	100	mg/L													
	Initial	Iar 1	Iar 2	Iar 3	Jar 4	Iar 5	Iar 6		Initial	Jar 1	Iar 2	Jar 3	Iar 4	Iar 5	Iar 6								
Dose [mg]	0	5	10	15	20	25	30		0	20	40	40	40	50	100					1			
Turbidity	· ·	5	10	15	20	23	50		0	20	10	10	10	50	100								
1 arbitarty	0.59	0.04	0.03	0.02	0.21	0.04	0.19		12.10	0.52	0.18	0.15	0.18	0.45	0.08								
1 77 1 1 1	0.39	0.04	-0.03	-0.02	0.21	-0.04	0.19		12.10	0.52	0.10	0.15	0.16	0.43	0.08								
Turbidity	0.40	0.02	0.02	0.02	0.4.0	0.02	0.00		12.00	0.50	0.45	0.47	0.47	0.44	0.07								
2	0.60	0.02	-0.02	-0.03	0.18	-0.02	0.20		12.00	0.59	0.15	0.17	0.17	0.44	0.07								
Avg																							
Turbidity	0.60	0.03	-0.03	-0.03	0.20	-0.03	0.20		12.05	0.56	0.17	0.16	0.18	0.45	0.08								
pH 1	8.45	7.92	8.04	8.07	8.05	8.01	8.02		8.28	7.65	7.40	7.40	7.42	7.29	6.90								
pH 2	8.46	7.93	8.04	8.06	8.04	8.02	7.99		8.30	7.66	7.40	7.42	7.36	7.29	6.89								
Avg pH	8.46	7.93	8.04	8.07	8.05	8.02	8.01		8.29	7.66	7.40	7.41	7.39	7.29	6.90								
Date	03/23/11		Collected	03/22/11				Date	05/27/11		Collected	05/26/11											
Temp	0	°C		00/==/				Temp	13.2			,,											
Optimal	0	C						Optimal	15.2														
Dere	25							Deer	140														
Dose	23 1 1 1	T 4	1.0	1.2	T 4	1 5	I. (	Dose	140	ing/L	1.0	1.2	T 4	T	I (								
	Initial	<u>Jar I</u>	Jar 2	Jar 5	<u>Jar 4</u>	Jar 5	Jar 6		Initial	<u>Jar 1</u>	Jar 2	Jar 5	<u>Jar 4</u>	Jar 5	Jar 6		-		_				-
Dose [mg]	0	5	10	15	20	25	30		0	60	80	100	120	140	160								
Turbidity																							
1	0.72	0.23	0.27	0.19	0.20	0.11	0.09		15.28	3.13	0.73	0.22	0.22	0.13	0.22								
Turbidity									1			1											
2	0.36	0.26	0.43	0.20	0.17	0.12	0.11		7.64	31.57	40.37	50.11	60.11	70.07	80.11								
Avg																							
Turbidity	0.73	0.25	0.35	0.20	0.19	0.12	0.10		15.34	3.11	0.70	0.23	0.20	0.12	0.23								
pH 1	8.68	8.23	8.15	8.01	7.98	7.93	7.87		8.23	7.09	6.94	6.83	6.68	6.62	6.47								
pH 2	8.69	8.22	8.12	8.12	8.08	7.98	8.00	pH 2	8.22	7.11	6.94	6.81	6.70	6.61	6.48						1		
AvenH	8.69	8.23	8.14	8.07	8.03	7.96	7.94	AvgnH	8.23	7.10	6.94	6.82	6.69	6.62	6.48	1		1	1	1	-		
Data	03/22/11		Collected	03/22/11				Data	05/27/11		Collecte	05/26/11				+		+	+	+	+		
T	05/25/11	°C	Conected	03/22/11				Date	12.0		Conected	05/20/11		+							1		
1 emp	0.5	-C		ļ		-		Temp	12.8										_				
Optimal								Optimal	1														
Dose	20			ļ				Dose	160	mg/L		1						-					
	Initial	<u>Jar 1</u>	<u>Jar 2</u>	<u>Jar 3</u>					Initial	<u>Jar 1</u>	<u>Jar 2</u>	<u>Jar 3</u>											
Dose [mg]	0	20	40	60					0	120	140	160											
Turbidity												1											
1	1.26	0.02	0.13	0.72					17.26	1.16	0.11	0.01											
Turbidity			-		1					-		1			1				1				
2	1.30	0.03	0.12	0.83					16.83	1.11	0.10	0.03											
-	1.50	0.05	0.14	0.05	1	1		1	10.05		0.10	0.05	1	1	1	1	1	1	1	1	1		

٨	1	1		T	1				1	1		1	1		1			T T	-				T
Avg	1.00	0.02	0.12	0.79					17.05	1.1.4	0.11	0.02											
Turbidity	1.28	0.03	0.15	0.78					17.05	1.14	0.11	0.02											
	8.40	7.07	7.58	7.43					8.23	0./1	0.72	6.50											
Ava old	0.43 8.42	7.73	7.00	7.33	-			-	0.30	6.73	6.72	6.52											
Avg pri	0.42	/./1	7.03	7.49				<u> </u>	0.20	0.75	0.72	0.31				C							
Winter	т	1	-	1	T			Spring	T			1	1			Summer	T	1			T		
Site	Lyons							Site	Lyons							Site	Lyons						
Data	$D_{2}/25/11$		Callastad	02/24/11				Data	East $05/27/11$		Callasta d	05/26/11				Data	East = 0.0 / 1.0 / 1.1		Callasta I	00/10/11			
Tame	03/23/11	°C	Conected	03/24/11				Date	12.2		Conected	03/20/11				Tame	126		Collected	06/16/11			
Optimal	0.2	C			-			Ontimal	13.2							Ontimal	12.0						
Dose	60							Dose	40	ma/I						Dose	60	ma/I					
15030	Initial	Iar 1	Jar 2	Jar 3	Jar 4	Iar 5	Jar 6	Dose	Initial	Ing/12	Iar 2	Jar 3	Jar 4	Jar 5	Jar 6	Dose	Initial	Ing/12	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
Dose [mg]	0	10	20	30	40	<u>50</u>	<u>60</u>		0	20	40	<u>50</u>	60	80	100		0	20	30	40	50	60	70
Turbidity	0	10	20	50	10	50	00		0	20	10	50	00	00	100		0	20	50	10	50	00	10
1	0.20	0.19	0.21	0.32	0.21	0.26	0.12		25.10	0.47	0.24	0.36	1.15	4.86	26.30		0.55	0.18	0.11	0.07	0.02	0.02	0.06
Turbidity	0.20	0.07																0.00					0.00
2	0.19	0.20	0.20	0.28	0.24	0.31	0.09		24.80	0.56	0.22	0.32	1.14	4.84	26.20		0.54	0.21	0.09	0.06	0.03	0.01	0.05
Avg																							
Turbidity	0.20	0.20	0.21	0.30	0.23	0.29	0.11		24.95	0.52	0.23	0.34	1.15	4.85	26.25		0.55	0.20	0.10	0.07	0.03	0.02	0.06
pH 1	8.04	7.77	7.64	7.48	7.36	7.29	7.22		7.80	6.85	6.74	6.55	6.31	5.98	4.73		8.17	7.63	7.53	7.41	7.31	7.22	7.18
pH 2	8.04	7.75	7.55	7.43	7.33	7.26	7.23		7.83	6.85	6.75	6.66	6.37	5.95	4.74		8.18	7.65	7.54	7.42	7.31	7.22	7.20
Avg pH	8.04	7.76	7.60	7.46	7.35	7.28	7.23		7.82	6.85	6.75	6.61	6.34	5.97	4.74		8.18	7.64	7.54	7.42	7.31	7.22	7.19
Date	03/25/11		Collected	03/24/11				Date	05/27/11		Collected	05/26/11				Date	08/18/11		Collected	08/18/11			
Temp	-0.1	°C						Temp	13.1							Temp	13.2						
Optimal								Optimal								Optimal							
Dose	80							Dose	40	mg/L						Dose	60	mg/L					
	<u>Initial</u>	<u>Jar 1</u>	<u>Jar 2</u>	<u>Jar 3</u>	<u>Jar 4</u>	<u>Jar 5</u>	<u>Jar 6</u>		Initial	<u>Jar 1</u>	<u>Jar 2</u>	<u>Jar 3</u>	Jar 4	<u>Jar 5</u>	<u>Jar 6</u>		Initial	<u>Jar 1</u>	<u>Jar 2</u>	<u>Jar 3</u>	<u>Jar 4</u>	<u>Jar 5</u>	<u>Jar 6</u>
Dose [mg]	0	30	40	50	60	70	80		0	10	20	30	40	50	60		0	30	40	50	60	70	80
Turbidity																							
1	0.42	0.33	0.19	0.62	0.47	0.45	0.19		25.70	23.80	19.33	0.72	0.49	0.69	1.16		0.70	0.07	0.05	0.05	0.03	0.05	0.02
Turbidity																							
2	0.48	0.33	0.24	0.63	0.48	0.41	0.17		25.30	24.10	19.57	0.80	0.56	0.71	1.22		0.72	0.11	0.04	0.07	0.01	0.06	0.04
Avg	o. 15				0.10						10.15				4.4.9			0.00					
Turbidity	0.45	0.33	0.22	0.63	0.48	0.43	0.18	-	25.50	23.95	19.45	0.76	0.53	0.70	1.19		0./1	0.09	0.05	0.06	0.02	0.06	0.03
pH 1	8.05	7.36	7.35	7.27	/.15	7.07	7.06		/./6	7.31	7.06	6.88	6.69	6.55	6.37		8.27	7.68	7.53	7.42	7.28	/.16	7.09
pH 2	8.04	7.39	7.37	7.25	/.11	7.09	7.05		/.//	7.30	7.07	6387.00	6.70	6.51	6.3/		8.29	7.61	7.44	/.35	7.23	7.18	7.15
AvgpH	0.05	/.30	/.30	/.20	/.13	7.08	/.00	D.	1.//	/.31	/.0/	3190.94	0.70	0.55	0.3/	D	0.20	/.05	/.49	/.39	/.20	/.1/	/.12
Date	03/25/11	00	Collected	03/24/11				Date	05/2//11		Collected	05/26/11				Date	08/18/11		Collected	08/18/11			-
Temp	1.4	۳C						Temp	12.5							Temp	14.5						-
Optimal	00							Optimal	40	ma /T						Optimal	60						
Dose	00 Initial	Log 1	Log 2	Log 2				Dose	40 Traitic1	mg/L	Ior 2	Log 3				Dose	00 Initial	mg/L	Log 2	Log 2	Ior 1		
Doso [mo]	0	<u>Jai 1</u> 40	<u>jai 2</u> 60	<u>Jar 5</u> 80					0	<u>Jai 1</u> 40	<u>Jai 2</u> 100	<u>Jar 5</u> 140					0	<u>Jai 1</u> 40	<u>jai 2</u> 60	<u>jar 3</u> 80	100		
Turbidity	0	40	00	00	-				0	40	100	140					0	40	00	00	100		
1	0.37	0.05	0.01	-0.02					23 70	0.98	26.50	28.20					1 11	0.12	0.08	0.08	0.07		
Turbidity	0.57	0.05	0.01	-0.02					23.10	0.70	20.30	20.20					1.11	0.12	0.00	0.00	0.07		
2	0.40	0.06	0.03	-0.01					23.30	0.91	26.60	28.50					1.02	0.11	0.07	0.09	0.08		
Ave		0.00	0.00	0.01							20.00								0.07			1	
Turbidity	0.39	0.06	0.02	-0.02		0.09			23.50	0.95	26.55	28.35					1.07	0.12	0.08	0.09	0.08		
pH1	8.08	7.36	7.33	7.05		7.12			7.93	6.67	5.55	5.04					1.07	0.12	0.08	0.09	0.08		
pH 2	8.08	7.36	7.30	7.08	1				7.87	6.72	5.63	5.05	1			1	8.21	7.51	7.20	7.18	6.90	1	
Avg pH	8.08	7.36	7.32	7.07					7.90	6.70	5.59	5.05					4.64	3.81	3.64	3.63	3.49		1