

**The Temporal and Spatial Variability of Organic Matter
and Its Effect on Membrane Filtration**

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ABSTRACT

The Temporal and Spatial Variability of Organic Matter and Its Effect on Membrane Filtration

The overall goal of this research was to investigate spatial and temporal variations in the concentration and characteristics of organic matter (OM) in the upper Mississippi River and the effects of these variations on the treatability of the water, specifically membrane filtration. OM is ubiquitous in surface waters as a result of natural and anthropogenic inputs. Although not directly harmful to human health or water quality, OM challenges drinking water utilities by increasing chemical consumption, serving as a precursor for disinfection byproducts, and fouling filtration membranes as seen through permeability or transmembrane pressure-normalized flux decline. It is therefore critical to understand how the concentration and composition of OM changes spatially and temporally in a watershed. Temporal OM variability in the upper Mississippi River was assessed by near-real time monitoring of dissolved organic carbon (DOC) concentration and ultraviolet absorbance at 254 and 280 nm for approximately one year. Spatial OM variability was assessed by collecting water samples along a 648-mile stretch of the upper Mississippi River from its headwaters at Lake Itasca to La Crescent, Minnesota and analyzing the samples for OM concentration and composition. In addition, monthly sampling of eight upper Mississippi River tributaries with varying dominant watershed land uses was performed for nine months to simultaneously assess both spatial and temporal OM variability. The water samples from these campaigns were filtered through four different ultrafiltration membranes to assess how the various combinations of membrane characteristics, such as hydrophobicity and pore size, and OM characteristics would affect membrane fouling.

Near real-time monitoring of the Mississippi River, the water source for the 70 MGD Columbia Heights Membrane Filtration Plant (Columbia Heights, Minnesota), over an 11-month

period showed that the permeability of hydrophilic ultrafiltration membranes with a pore size of 0.02 μm was negatively correlated with river flow ($p < 0.01$) and raw water specific ultraviolet absorbance (SUVA) ($p < 0.01$), but not raw water dissolved organic carbon (DOC) concentration ($p = 0.865$).

From a spatial aspect, the concentration (as measured by TOC and DOC) and character (as observed through SUVA and fluorescence spectroscopy) of OM were relatively constant along the length of the upper Mississippi River during a late summer to early fall sampling period despite inputs from tributaries rich in organic matter and wastewater effluent. The estimated DOC export from the upper Mississippi River was 0.0088 kg/d. Overlaying sampling points on a digital elevation model and land use map showed that concentrations of TOC and DOC were negatively correlated with the percent of agricultural land and positively correlated with percent shrubland area.

Stirred cell membrane trials on seasonal waters collected from the upper Mississippi River before and after lime softening showed that pretreatment significantly reduces membrane fouling (12.0 - 47.5%) by preferentially removing larger hydrophobic OM. Although performance varied, the most hydrophilic membrane tested (contact angle 22.6°) exhibited the lowest permeability decline of all of the membranes for all water samples before and after fouling. When compared to organic matter standards from International Humic Substances Society, the natural, unfractionated waters fouled the membranes more, possibly as a result of increased interactions between the hydrophobic and hydrophilic fractions. Additional stirred cell membrane trials on seasonal waters collected from tributaries of the upper Mississippi River with varying land uses indicated that both membrane hydrophobicity and seasonal factors such as snow melt and storm events and land use were important in determining overall membrane performance.

The results of this research encourage extensive near real-time monitoring and membrane pilot studies as well as pretreatment and large-scale watershed assessments for utilities considering

membrane filtration systems for surface water treatment. In addition, this work could aid in the formulation of policies and regulations governing land use, land development, stormwater management, and wastewater discharges.

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Chapter 1

Introduction

1.1 Background

1.1.1 Overview

Natural organic matter (NOM) is a mixture of complex compounds ubiquitous in natural waters and is derived from two natural sources: production by aquatic organisms and leaching of decaying vegetation from terrestrial sources (Thurman, 1985). NOM also comes from anthropogenic sources such as wastewater, urban stormwater, and runoff from agricultural activities. The export of NOM from water bodies will vary based on the land type, retention time, climate, vegetation, and water flow paths (Table 1-1).

Table 1-1. Average natural organic matter export (as dissolved organic carbon) in world biomes (Alvarez-Cobelas, 2012)

Biome	Average Export (kg C / ha / yr)
Arctic/Subarctic	10.43
Cold temperate	40.57
Warm temperate/Arid	7.74
Tropical/Subtropical	81.27
Agricultural	10.84
Desert	6.20
Mountain	57.38
Savanna	224.13
Taiga	45.63
Temperate forest	28.31
Temperate shrubland	56.56
Tropical forest	72.84

Observed as the yellow or brown coloration of water, the molecular weight of NOM is between 200 - 20,000 Daltons with 10 - 35% aromaticity (Thurman, 1985). Almost all (> 90%) NOM contains carboxyl functional groups. At pHs typical of surface waters, these functional

groups are deprotonated and NOM thus typically has a negative charge. The complexity of NOM means that compositional classification of NOM is difficult and categories are thus operationally or arbitrarily defined; however, there are ways of exploring the general characteristics of a mixed sample.

Humic substances are widely defined as all generic, unidentifiable, complex organic compounds within a water sample and can comprise up to 80% of what is termed organic matter (Thurman, 1985) (Figure 1-1). Humic substances include hydrophobic, hydrophilic, and transphilic acids, bases, and neutrals as compared to more readily identifiable compounds and functional groups such as carbohydrates, carboxylic acids, amino acids, and hydrocarbons. Hydrophobic NOM can further be differentiated between humic acids (soluble below pH 2), fulvic acids (soluble at any pH), and humins (insoluble at any pH). Part of the complexity of organic substances can be attributed to the tendency of smaller molecules to act as building blocks and formation, non-polar, or hydrogen bonds with each other, creating more complex macromolecules (Leenheer et al., 2001). As the exact composition of humic substances is not known, they can instead be described operationally. Extraction of specific fractions is performed by initially filtering the water through a 0.45 μm filter then using hydrochloric acid to drop the pH to 2. Hydrophobic NOM (e.g. humic and fulvic acids) is adsorbed onto XAD-8 resins made of acrylic ester. When eluted with sodium hydroxide, hydrophobic acids and bases are flushed from the resin while hydrophobic neutral fraction remains adsorbed. From the XAD-8 effluent, transphilic NOM is adsorbed on XAD-4 resins made of styrene divinylbenzene. When eluted with sodium hydroxide, the transphilic acid fraction is flushed from the resin while the transphilic neutral fraction remains adsorbed. Hydrophilic NOM does not adsorb to either resin (Figure 1-2). Fulvic acids tend to remain in solution and in general, have a lower molecular weight and a higher aromaticity (Thurman, 1985).

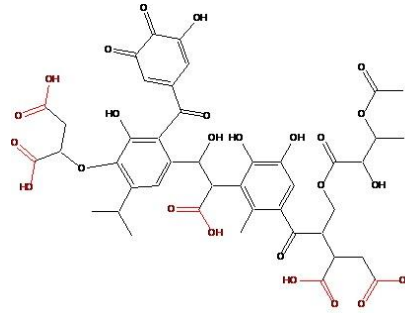


Figure 1-1. Hypothetical fulvic acid structure (Leenheer et al., 1998)

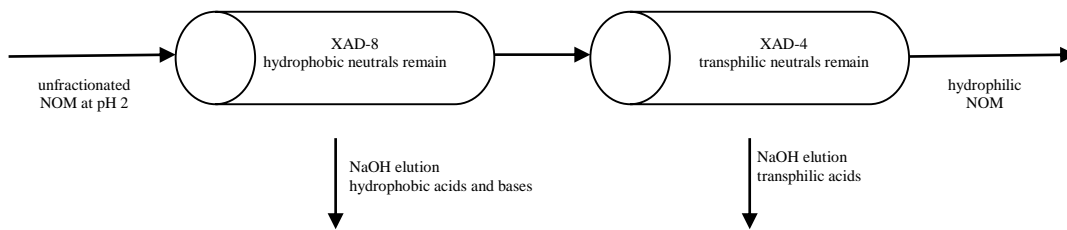


Figure 1-2. NOM separation procedure using XAD resins

Allochthonous organic matter originates external to the water body, typically in the decomposition of soils or leaf litter on land. It may include particulate matter in the form of whole branches or leaves. This terrestrial based NOM has a molecular weight greater than 1 kDa and numerous aromatic rings, making it more hydrophobic. In contrast, autochthonous organic matter derives from sources internal to the water body, typically bacterial exudates or decomposition byproducts. With a molecular weight less than 500 Da, autochthonous NOM is nitrogen rich due to the presence of peptides and more hydrophilic due to the presence of carboxylic acid functional groups (Leenheer, 1994). Point sources, such as wastewater treatment plant outflows may also contribute autochthonous NOM to a water body.

1.1.2 *NOM characterization methods*

The study of NOM behavior as a function of its component species focuses on the importance of each broad compound type within the NOM moiety; however, this approach is hampered by the fact that the compounds within in the NOM interact with each other to form more complex interactions and influence overall behavior. Separating the NOM into their component parts may result in data, but it is unknown how well that data represents the original, whole NOM (Abbt-Braun et al., 2004). Individual compounds, such as oxalate and glyoxal, or elements can be also quantified. Non-destructive methods of evaluating NOM concentration and composition are therefore important tools in the characterization of NOM.

1.1.2.1 NOM concentration

The complexity and lack of specific compounds within NOM means that a surrogate measurement, such as organic carbon, must be used to measure concentration. Organic carbon is often used as a surrogate for NOM because it is the primary element in organic matter and primary reactant for degradation or transformation reactions. Additional quantitative analysis of organic matter can be performed by elemental analysis (e.g. specific to nitrogen, carbon, etc.) or pyrolysis in conjunction with mass spectrometry (Abbt-Braun and Frimmel, 2002; Schulten et al., 2002). To measure organic carbon, samples are typically collected in 40 mL vials that have been washed in 3 M nitric acid and baked at 550°C for six hours with caps that have been soaked in 10% sodium persulfate to remove trace amounts of organic matter. The water sample is initially acidified below pH 2 to convert inorganic carbon compounds to carbon dioxide. A portion of the acidified water sample is then exposed to a chemical oxidant and ultraviolet light to convert the organic carbon present to carbon dioxide. The concentration of carbon dioxide can be measured through direct conductometric detection, membrane conductometric detection, and non-dispersive infrared detection. Organic carbon is determined as the difference between the total carbon (from acidification and

oxidation) and inorganic carbon (from acidification). New organic carbon analyzers may be self-standardizing, reducing the need for repetitive standards runs.

Dissolved organic carbon (DOC) refers to compounds that can pass through a 0.45 μm pore size or GF/F glass-microfiber filter (Kaplan, 1994). The remaining fraction, particulate organic carbon (POC), comprises only about 10% of the total organic carbon (TOC) in surface waters (Thurman, 1985). POC can be further divided into fine and coarse classes with a 0.25 inch distinction. Additional subgroups of organic carbon, such as biodegradable dissolved organic carbon and assimilable organic carbon, can be categorized according to biological factors, such as culture growth and oxygen consumption.

1.1.2.2 NOM composition

Spectroscopy is the study of how matter interacts with various types of radiation. In general, spectroscopic methods provide quantitative and/or qualitative information about a molecule's functional groups, size, and structure. Bonds, electrons, and nuclei will absorb radiation at various wavelengths of the electromagnetic spectrum. The absorption of radiation can then be measured. Because NOM is a complex mixture of organic compounds, spectroscopy is useful to track the occurrence of common functional groups such as aromatic rings, phenols, and carboxylates. For NOM, the phenolic and carboxylate functional groups are the most studied because of their reactivity and tendency to form intra- and inter-molecular bonds. Spectroscopy can also be used to identify specific compounds or classes within fractionated NOM samples.

Nuclear magnetic resonance (NMR) spectroscopy measures the energy absorbed when spinning nuclei change quantum states within an applied magnetic field. All nuclei with an odd number of neutrons spin, generating a magnetic dipole and observable angular momentum. The quantum states of some atoms, such as ^1H and ^{13}C , are relatively easy to observe because they have only two discrete spin states (spin number equal to one half). While ^1H NMR is commonly used

for chemical analyses, ^{13}C NMR is the most applicable for studying NOM because it provides information about the carbon structure of the complex molecules. ^{13}C NMR can even be used to track the relative abundance of functional groups over time. McKnight et al. (1988) observed a decrease in t-methyl esters associated with phenolic functional groups in the fulvic acids of Spirit Lake in the three years following the eruption of Mt. St. Helens. A study of NOM from the Ribou River in France demonstrated significant differences in composition between isolated fractions. Peaks corresponding to aliphatic (0-60 ppm), aromatic (110-160 ppm), and ketone (190-220 ppm) bonded carbons were more prominent in the hydrophobic fractions. In contrast, peaks representing aliphatic ethers and carboxylic acids were more common in the hydrophilic fractions (Croué, 2004).

Chemical bonds can absorb infrared radiation when a molecule is experiencing a change in dipole. As a result of the absorption, the rotational, vibrational, stretching, and bending properties of the bonds change. The degree of absorption corresponds to the change in the bond's dipole moment (Skoog et al., 2007) and the transmitted infrared radiation is then directed to a detector where it is Fourier transformed into a frequency representation. Fourier transform infrared (FTIR) spectroscopy is preferred over dispersive spectrophotometers with a monochromator because of its speed, reliability, and lack of environmental interferences. FTIR provides a rapid means of determining the functional groups within a molecule and (depending on how the base wavenumbers shift) their proximity to each other. The complexity of NOM means that FTIR spectra for natural waters can be extremely indistinct. However, the prevalence of specific functional groups can be qualitatively determined. FTIR spectra on NOM fractionated water from the Neversink Reservoir in upstate New York showed distinct differences between fractions separated by reverse osmosis and resins. For this water, hydrophobic NOM had more aliphatic hydrocarbon bonds (3400-2900 $1/\text{cm}$) and basic NOM had a peak at 591 $1/\text{cm}$, possibly indicative of organic salts (Wershaw et al., 2005).

Attenuated total reflection Fourier transform spectroscopy (ATR-FTIR) is especially useful for examining membranes that have been fouled with NOM. An internal reflection crystal is positioned within the infrared beam to direct infrared radiation onto a solid surface. The radiation slightly penetrates the surface and reflects back to the detector. The reflected radiation is still infrared, but the intensity is altered by the absorption of energy by chemical bonds within the solid. Howe et al., (2002) evaluated the effect of pH on Beaver Lake water fouling a polypropylene membrane. The ATR/FTIR showed little change over a range of pHs suggesting that the foulant had an insignificant number of carboxylate functional groups that could be protonated. Rabiller-Baudry et al. (2002) observed shielding of the membrane's functional groups and additional amide (1500 – 1600 1/cm) and lactose bands (1064 1/cm) after filtering skimmed milk through a membrane. Other researchers have demonstrated through ATR-FTIR that phenolic and carboxylate functional groups can interact and increase the binding strength of a NOM surrogate to a metal hydroxide (Guan et al., 2004).

Ultraviolet/visible (UV/Vis) spectroscopy measures the absorbance of radiation between the wavelengths of 10 – 780 nm. Unlike other forms of spectroscopy, it does not provide a detailed structural analysis, but it can indicate the relative presence of specific atomic configurations known as chromophores. Chromophores are groups of atoms within a molecule that have unsaturated bonds and valence electrons that can be easily excited out of their ground state. When a molecule is exposed to UV/Vis radiation, valence electrons (usually in the nonbonding ρ or bonding π orbitals) will absorb the light and become excited. The excited electrons move to next higher energy orbital (antibonding π^* or σ^*). Either the loss of light (absorbance) or fraction of light not lost (transmittance) through the sample is measured and plotted as a function of wavelength. UV/Vis spectra are continuous rather than banded because the amount of energy absorbed by a molecule is not discrete, but affected by rotational and vibrational energy (Skoog et al., 2007). For specific organic and inorganic compounds, UV/Vis spectroscopy is a useful method of detection

because of its consistent accuracy and selectivity, but more generally, it can be used for identifying ring structures within a water sample. Ring structures react with disinfectants such as chlorine during water treatment to form disinfection by-products (Reckhow et al., 1990). Water sources and isolated NOM fractions are often evaluated for their disinfection by-product formation potential because the concentrations of trihalomethanes and some haloacetic acids in finished drinking water are regulated by the EPA (Kitis et al., 2001). Absorbance at 254 nm is most commonly measured and can be combined with DOC to measure specific ultraviolet absorbance (SUVA). The absorbance at 254 gives a general indication of the concentration of NOM and, when combined with the dissolved organic carbon concentration, its source (Leenheer and Croué, 2003). SUVA values greater than 4 indicate a terrestrial while SUVA values less than 2 indicate an aquatic source of the NOM. Absorbance at 285 nm has also been used to determine the source of refractory organic matter through changing phenolic concentrations in the upper Rhone River (Rostan and Cellot, 1995).

Although a wavelength of 254 nm is commonly provides information about the source of NOM in natural waters, other wavelengths are used as well. Chin et al. (1994) formed empirical links between molar absorptivity at 280 nm and the molecular weight and percent aromaticity of NOM. Aromatic rings will absorb at 184, 204, and 256 nm while phenolic compounds will absorb at 210.5 and 270 nm. Carboxylic functional groups will also absorb at 184 and 204 nm. pH adjustment will protonate or deprotonate many functional groups and thus change the absorbed wavelength and molar absorptivity (Bloom and Leenheer, 1989).

When excited electrons return to their ground state, they often fluoresce or emit radiation. The emitted wavelength is equal to the energy difference between the ground and excited states. However, the emitted wavelength is usually longer than the original radiation because some of the electron's energy has been lost of vibrational and rotational movement. These emissions can also be measured and combined with the original absorbance (excitation) spectra to create three-

dimensional excitation-emission matrices (EEMs). Peaks within a matrix indicate which general classes of compounds are present and are especially useful for determining the constituents of complex mixtures such as NOM (Figure 1-3). Her et al. (2003) differentiated source waters by applying fluorescence spectroscopy after size exclusion spectroscopy. Humic acid-like NOM was prevalent in groundwater and surface water samples (Region V of Figure 1-3) while wastewater effluent samples had both protein-like and humic acid-like characteristics (Regions IV and V of Figure 1-3, respectively). Protein-like NOM produced in the water column was found concentrated in the deep dead zone of a dam, isolated there because of the configuration of the outflow structure (Region IV of Figure 1-3) (Hur et al., 2007). The presence of protein-like soluble microbial byproducts in wastewater effluent was also observed in EEMs developed by Chen et al. (2003) with humic and fulvic contributions dependent on the characteristics of the source water. Fluorescence is highly sensitive, but of limited applicability since fewer species fluoresce than absorb light. The most intense fluorescence occurs in fused ring structures or aromatic groups with low energy $\pi-\pi^*$ bonds (Skoog et al., 2007). Fluorescence will decrease when the excited electron is in a bond close to a halogen. Fluorescence can also be quenched by calcium and manganese ions.

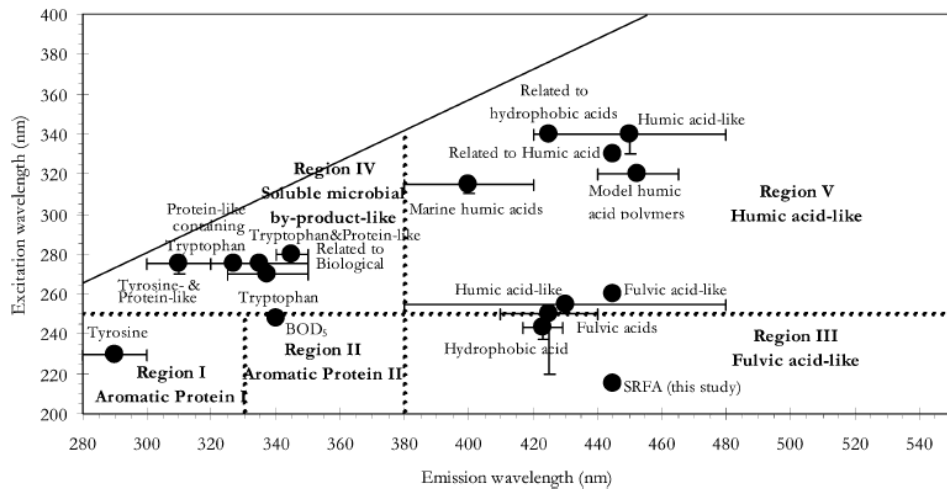


Figure 1-3. EEM peaks from selected compound classes (Chen et al., 2003)

Absorbance ratios can also be used to estimate the molecular weight and character of NOM since functional groups may not produce distinct peaks in the spectrum. Bloom and Leenheer (1989) note that the ratio of absorbances at 465 and 665 nm can indicate whether the NOM is humic ($E_{465}/E_{665} < 5$) or fulvic ($E_{465}/E_{665} > 5$). The applicability of this ratio is limited due to the difficulty in obtaining reproducible absorbance readings at 665 nm (Chin et al., 1994). Other ratios such as E_{250}/E_{365} and E_{300}/E_{400} have also been used to operationally define humic substances (Uyguner and Bekbolet, 2005). Hernes et al. (2008) used the exponentially fitted slopes of absorbance spectra from 290 – 350 nm to estimate molecular weights and aromaticities of seasonal water samples from an agricultural watershed. A steeper slope indicated low molecular weight and aromaticity.

Mass spectroscopy provides information about the structure and molecular mass of a ionized compound by fragmenting it and observing the masses of the resulting pieces. Molecules fragment in certain patterns based on their structure. For example, the mass spectrum of an alkane would be expected to show a peak corresponding to the molecular ion as well as fragment peaks in intervals of 17 (the mass of $-\text{CH}_2-$) as the ions created by splitting the carbon backbone are observed. In studying NOM, high resolution mass spectroscopy is used to elucidate the structure of the complex molecules and identify prevalent functional groups; however, mass spectroscopy is not relevant for unfractionated or unpurified environmental samples as there are too many closely grouped peaks to infer information about any specific fragment (Leenheer and Croué, 2003). Multiple mass spectroscopy runs, chromatographic methods, pyrolysis, electrospray ionization, or membrane filtration can be employed to reduce the complexity of samples containing NOM or any complex mixture of compounds. The identification of molecular formulas for specific humic and fulvic acids in environmental samples has been achieved using a combination of electrospray ionization mass spectroscopy, quadrupole time-of-flight mass spectroscopy, and Fourier transform

ion cyclotron resonance mass spectroscopy and can be used as a foundation for studying more complex compounds (Kujawinski et al., 2002).

Some spectroscopic methods are more applicable to identifying elements and specific compounds rather than characterizing properties of NOM. However, they have possible applications for future spectroscopic investigations of NOM. When radiation is scattered at the same wavelength as the incident radiation, it is termed elastic or Rayleigh scattering. Elastic scattering is used for particle counters and turbidimeters. Inelastic scattering occurs when the scattered wavelength is different from the incident wavelength due to electron shifts to virtual vibrational states and temporary polarization. The scattered radiation may be longer (Stokes) or shorter (anti-Stokes) than the incident radiation. Raman spectroscopy quantifies Stokes and is useful for examining bonds between like atoms (Bloom and Leenheer, 1989). Raman spectroscopy is not typically used to characterize NOM, but scattering must be compensated for when developing EEMs.

Energy dispersion of X-ray spectroscopy (in which inner shell electrons are forced away from the atom) can be paired with microscopy to identify the character of foulants on a membrane surface by quantifying elemental ratios (Rabiller-Baudry et al., 2002). Mössbauer spectroscopy utilizes gamma rays to study the metal ion binding sites and specific metal compounds on solid samples. Iron, with cobalt-57 as a gamma source, is the most common metal studied by Mossbauer spectroscopy (Bloom and Leenheer, 1989). Although this requires the isolation and desiccation of NOM, this technique is used to study NOM-metal complexes and metal binding properties of soils.

1.1.3 NOM standards

As part of its purpose to promote research of humic and fulvic acids, the International Humic Substances Society (IHSS) collects, processes, and sells standardized samples of organic matter, isolated from both soils and natural waters, to researchers. Samples are first acidified to

pH 2, then concentrated using reverse osmosis, fractionated with an XAD-8 resin, saturated with hydrogen ions to remove salt cations, and finally freeze-dried for long-term storage (IHSS, 2007; Sun et al., 1995; Thurman and Malcolm, 1981). One limitation of this procedure is that it only gathers the hydrophobic humic and fulvic acids and does not represent the complete spectrum of organic matter in the original water sample

Two commonly used organic matter samples are from the Suwannee River, a black river in Georgia, USA with high DOC (up to 75 mg/L), and Pony Lake, a saline Antarctic lake dominated by autochthonous production. The elemental, functional group, and spectrographic compositions of humic acids, fulvic acids, and unfractionated NOM from these standards have been well documented. For example, aquatic fulvic acids have more carboxyl functional groups than aquatic humic acids while humic acids have more carbon in aromatic rings, but both have similar amounts of phenolic subgroups (Richie and Perdue, 2003; Thorn et al., 1989). Modern spectrographic analysis through EEMs showed that humic acids fluoresce at longer excitation and emission wavelengths, but fulvic acids have higher maxima and more distinct peaks (Mobed et al., 1996; McKnight et al., 2001). Although natural waters are a mix of humic and fulvic acids, as well as many other components, these characterizations of standard organic matters allow for the classification of unique samples as 'humic-like' or 'fulvic-like' and may predict their behavior in natural or man-made systems.

1.1.4 Impacts of NOM

Although typically not directly harmful to human health or water quality, NOM can have a variety of negative effects on the production of safe drinking water. For example, NOM can increase the consumption of water treatment chemicals (Sharp et al., 2006), react with chlorine to form potentially harmful disinfection by-products (Hui, 2004; Carlson, 2002; Galapate et al., 1999; Reckhow et al., 1990), stimulate bacterial growth (Wetzel et al., 1995), and foul filtration

membranes (Kaplan, 1994; Li and Chen, 2004). In particular, NOM in wastewater treatment plant effluent (EfOM) is dominated by humic substances and hydrophilic acids of low molecular weight (Imai et al., 2002). Broader concerns with NOM in surface waters include the mobilization of metals (McKnight and Bencala, 1990), acting as a carbon source for bacterial growth (Moran and Zepp, 1997), and shading other compounds and aquatic organisms from light penetration through the water column (Schindler and Curtis, 1997).

1.1.5 Sources, transformations, and variability of NOM

A major complication in dealing with NOM fouling is that NOM concentration and composition is a moving target, exhibiting significant spatial and temporal variability. The concentration and composition of NOM in a water body at a given location and time results from a complex series of processes including inputs from the land surface of allochthonous NOM, production of autochthonous NOM within the water body, transport processes, and transformation and loss processes (Thurman, 1985; Hope et al., 1994). NOM concentration and composition varies spatially due to differences in climate, topography, land use, precipitation, and other factors (Correll et al., 2001; Thomas et al., 2004; Pinney et al., 2000).

In temperate climates such as Minnesota, the concentration and composition of NOM in surface waters varies throughout the year, especially in response to seasonal changes in precipitation, sunlight, and temperature (Hope et al., 1994; Mulholland, 1997). For example in the Rhode River watershed in Maryland, total organic carbon (TOC) concentrations varied from a low of 5.11 mg/L in the winter to a high of 12.80 mg/L in the summer (Correll et al., 2001). Flood events appear to be particularly important as these events lead to leaching of dissolved organic carbon (DOC) from upper soil horizons (Mulholland, 1997) and high fluxes of particulate organic carbon (POC) (Veyssy et al., 1999). Rainfall was positively correlated with TOC during a long term study of eight watersheds in the Maryland coastal plain (Correll et al., 2000). While flood

events may be more likely to initiate the movement of POC into a water source, DOC concentrations are often independent of discharge (Grubaugh and Anderson, 1989). In particular, rainfall after an extended dry or snow-covered period will flush organic matter from the upper layers of the soil into the receiving water. This 'first flush' effect will result in increasing NOM concentration concurrent with the rising limb of hydrograph followed by a rapid decrease prior to the descending limb of the hydrograph. The path of the flood waters (overland, shallow subsurface, deep subsurface) will dictate which the source of the flushed NOM as well as its molecular weight and degradability (Dalzell et al., 2005; Findlay et al., 2001). Hornberger and colleagues (1994) were able to model the first flush of a non-conservative DOC pool for the Snake River in Colorado, establishing a relationship between upland soil characteristics and resulting downstream DOC concentrations, but did not see any correlation between DOC and flow due to flushing.

Changes in DOC inputs are frequently linked to non-precipitation driven events such as leaf fall and primary productivity (Hope et al., 1994; Meyer et al., 1998). Autochthonous NOM production and thus DOC concentration can change significantly over the course of a day (Kaplan and Bott, 1982) and seasonally due to changes in temperature and sunlight. Watershed factors such as the presence of lakes and reservoirs (Kendall et al., 2001) and minimal canopy cover (Kaplan and Bott, 1982) also contribute to increased production of autochthonous NOM in rivers. In some cases, increases in autochthonous production during warm summer months can be offset by increases in the rates of degradative processes such as photolysis, hydrolysis, and biodegradation (Neff and Asner, 2001; Moran and Zepp, 1997). Further transformations can occur when streams and rivers meet the ocean. The mid-salinity portion of an estuary is characterized by high biological activity resulting in rapid turnover of NOM. Lignins specifically can be lost at low salinity due to flocculation or 'salting out' (Benner and Opsahl, 2001).

Forests contribute DOC to surface waters mainly through leaf litter (Meyer and Tate, 1983) with DOC leached from leaf litter contributing about 30% of the DOC generated in a small forested

stream (Meyer et al., 1998). A comparison of a forest and a moorland watershed in Scotland determined that the forested catchment had twice the DOC in receiving streams as the moorland due to higher accumulation of detritus (Grieve et al., 1990). Meyer and Tate (1983) observed lower carbon exports from a forested watershed two years after clear cutting when compared to a non-cleared control forested watershed. Agricultural land uses, including pasture, concentrated animal feeding operations, orchards, and row crops, have varying fluxes of organic matter from animal or vegetal waste (Chomycia, et al., 2008), erosion (Correll et al., 2001), and irrigation (Hernes et al., 2008). A comparison of intensively grazed pasture and pine forest in New Zealand showed that the runoff from the pasture had less than half the DOC concentration of the runoff from the planted pine forest plot (Findlay et al., 2001). Streams in the Amazon basin, however, had higher DOC following pastures than following forests (Thomas et al., 2004). Urbanization may reduce NOM variability due to impoundments, channelization, and wastewater flows (Westerhoff and Anning, 2000), but increase the trihalomethane formation potential of the water (Galapate et al., 1997).

Wetlands, due to their long hydraulic residence time, anaerobic conditions, organic soils, and high amount of primary productivity, can be a source of or sink for NOM (Mulholland and Kuenzler, 1979; Dalva and Moore, 1991; Kaplan et al., 2006). Pinney and coworkers (2000) observed a decrease in DOC concentrations, ranging from 9% in June to 47% in February, through a constructed wetland receiving treated wastewater effluent from an aerated lagoon system. SUVA increased along the wetland, especially in the summer, as the labile compounds with low SUVA values in the wastewater were biodegraded and NOM with high SUVA values was leached from plant materials within the wetland.

Another source of NOM in natural waters is wastewater treatment plant effluent. In addition to the NOM present in the initial source water, wastewater will contain chlorinated organic compounds formed during disinfection, synthetic organic matter from human or animal chemical consumption and industrial processes, soluble microbial byproducts from the treatment process,

and non-OM constituents that degrade water quality or effect NOM behavior and decomposition (Shon et al., 2006). The concentration and character of wastewater effluent organic matter (EfOM) is thus highly diverse and demonstrates the same range of compositional variation as NOM. Fractionation of EfOM from seven wastewater treatment plants in Japan found hydrophilic acids comprised 32 - 74% and hydrophobic acids comprised 3 - 28% of the organic matter (Imai et al., 2002), but Singapore effluent had 39.4-52.7% hydrophilic acids and 47.3 - 60.6% hydrophobic acids (Hu et al., 2003), while two wastewater treatment plants in France had 24 - 27% colloids, 25-30% hydrophobic acids, 18 - 19% transphilic acids, and 28 - 29% hydrophilic acids (Jarusutthirak et al., 2002). A high percentage of smaller, more hydrophilic NOM may cause additional trihalomethane formation in downstream water treatment facilities (Shon et al., 2006).

1.1.6 Membrane water treatment

Membranes are a selective, size-based barrier for removing compounds or particles from a liquid or gaseous medium and are widely used to separate or purify compounds in public works, food, industrial, and chemical systems. They are classified based on their hydrophobicity, material, thickness, pore tortuosity, surface roughness, zeta potential (e.g. the electrical potential between the edge of the membranes electrostatic double layer and the bulk fluid), and molecular weight cutoff or pore size (Table 1-2). Membranes are created by randomly or deliberately assembling polymers in a liquid solution then performing phase inversion to form a solid sheet while controlling the porosity. Solvent etching or controlled precipitation may also be used to form the membrane. The polymer concentration, temperature, evaporation time, and solvent solutions must be highly controlled (Mulder, 1996).

Table 1-2. Characteristics of membranes used in water treatment (Shon et al., 2006; Mulder, 1996)

Membrane	Reverse Osmosis	Nanofiltration	Ultrafiltration	Microfiltration
Molecular Weight Cutoff (kDa)	< 0.15	0.15 - 1	1 - 100	100 to 0.01 μm
Thickness (μm)	top layer: 1 support: 150	top layer: 1 support: 150	150	10 - 150
Pressure (bar)	10 - 100	5 - 20	1 - 5	0.1 - 2
Flux ($\text{L}/\text{m}^2\text{-hr-bar}$)	0.05 - 1.4	1.4 - 12	10 - 50	> 50
Mechanism	diffusion	diffusion	sieving	sieving

Membrane filtration is a relatively new water treatment technology that is increasingly being used as a replacement for sand filtration because it provides consistent and effective pathogen removal. In membrane filtration, the water is forced through synthetic polymer membrane material in a flat sheet or hollow fiber configuration under pressure or vacuum to produce a clean permeate water. Looser (micro- or ultrafiltration) membranes function as a sieve leaving particles, bacteria, and viruses behind on the retentate side of the membrane while tighter (nanofiltration or reverse osmosis) membranes only allow the diffusion of the solvent. Membranes are susceptible to fouling, or a decrease in water production, as they are exposed to small particles and foulants present in the water. With regular maintenance and cleaning, water treatment membranes can be expected to last five to seven years before they become irreversibly fouled and can no longer produce sufficient permeate at the plant's operating pressure. Membranes provide an additional pathogen removal method for wastewater treatment plant effluent, especially if the effluent is intended for water reuse, aquifer recharge, or agricultural use. Pretreatment of this water source is critical, with flocculation followed by absorption removing up to 90% of the colloidal and hydrophilic EfOM, which are more likely to clog pores and lead to steep permeability declines (Shon et al., 2004; Jarusutthirak et al., 2002)

1.1.7 Membrane fouling by NOM

The fouling of membranes by NOM is dependent on the membrane surface characteristics as well as the NOM composition and concentration (Fan et al., 2001). Foulants such as NOM may slow the passage of the water through the membrane by sorbing to the membrane surface, pore entrances, or within the pores as well as inducing electrostatic or steric exclusion (Mulder, 1996). NOM can deposit on the surface of the membrane and clog the pores and can be very difficult to remove by physical or chemical means (Kaiya et al., 1996; Cherkasov et al., 1995). During filtration, the solute becomes concentrated near the membrane surface (concentration polarization) as a result of the separation process and solvent flux. Eventually, some of the solute will diffuse back into the bulk solution. Additionally, foulants can form a high concentration gel or cake layer on the membrane surface. These processes reduce the overall flux of the permeate (Blatt et al., 1970). Integral forces influencing the behavior of foulants include inertial, drag, lift, electrostatic, vander Waals, and hydrophobic attractive forces (Mulder, 1996). With many water utilities switching to membrane filtration to ensure pathogen removal, the urgency of understanding and mitigating the impacts of NOM on membrane fouling has increased; however, descriptions of membrane-foulant interactions are often hard to compare and conflicting because of the range of membranes, NOM, and research goals.

In general, waters with higher concentrations of NOM (Braghetta et al., 1998; Her et al., 2004; Amy and Cho, 1999) and lower pH with increasing electrostatic interactions (Braghetta et al., 1998, Teixeira and Rosa, 2006; Hong and Elimelech, 1997; Kabsch-Korbutowicz et al., 1999) will foul membranes faster. Both hydrophobic (Hong and Elimelech, 1997; Violleau et al., 1998) and hydrophilic (Lee et al., 2004; Fan et al., 2001; Gray et al., 2007; Park et al., 2006; Makdissy et al., 2004) NOM fractions have been found to be the primary membrane foulant. Hydrophobic NOM - hydrophobic membrane and hydrophilic NOM - hydrophilic membrane pairings are

particularly susceptible to fouling because membrane surface groups are neutralized rapidly (Cho et al., 1998; Lee et al., 2006). The wide variety in results has been attributed to the membrane's method of exclusion and operating flux. At low fluxes, the decline in permeate production may be due to size exclusion and electrostatic repulsion while at higher fluxes it may be due to membrane hydrophobicity inducing the formation of a gel layer and pore blockage by ions and larger, aromatic NOM (Cho et al., 1999; Schäfer et al., 2000).

1.2 Objectives and Approach

1.2.1 Objectives

Although not directly harmful to human health or water quality, NOM challenges drinking water utilities by increasing chemical consumption, serving as a precursor for disinfection byproducts, and fouling filtration membranes. It is therefore critical to understand how the concentration and composition of NOM changes spatially and temporally in a watershed. The overall goal of this research is to investigate spatial and temporal variations in the concentration and characteristics of NOM in the upper Mississippi River and the effects of these variations on treatability, specifically membrane filtration. The results of this research will be useful for improving the design and operation of membrane filtration systems for surface water treatment by informing membrane selection and plant operation. In addition, this work could aid in the formulation of policies and regulations governing land use, land development, stormwater management, and wastewater discharges.

1.2.2 Research approach

The research performed in this dissertation was mainly experimental and field-based. Continuous monitoring of dissolved organic carbon and ultraviolet light absorption followed by data filtering and analysis were performed to track the temporal variability of NOM in the

Mississippi River. This was combined with membrane filtration plant performance data provided by the Minneapolis Water Works and river flow data from the United States Geological Survey to statistically analyze how NOM effects water treatment.

Field work required the sometimes dangerous collection of water samples from the Minneapolis Water Works, Mississippi River, and Mississippi River tributaries for snapshot and long term monitoring.

Experimental analyses, including measurement of total organic carbon, absorbance, and fluorescence, were performed on all water samples. Membrane filtration experiments were performed to record the rate of permeate production was recorded for each water and sampling time. The decrease in permeate production was an indication of the degree of fouling from the interaction of the membrane and the water sample.

Statistical analyses were performed to link temporal NOM characteristics with membrane plant performance, land use with NOM characteristics, land use with membrane filtration performance, and land use over time with membrane filtration.

1.3 Dissertation Outline

The research chapters of this dissertation are composed in research paper format, compiled where appropriate from published or submitted papers. Chapter 2 describes the results of a year-long monitoring of NOM and membrane performance at the Minneapolis Water Works Columbia Heights Membrane Filtration Plant. Chapter 3 presents the effects of land use in the upper Mississippi River basin on NOM character and concentration. Chapter 4 explains the link between NOM, pretreatment, and membrane fouling in a series of batch filtration experiments. Chapter 5 illustrates a large-scale relationship between land use, season, and membrane fouling in additional batch filtration experiments. Chapter 6 provides the concluding remarks and ideas for future research in this area.

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Chapter 2

Temporal Variation of NOM and Effects on Membrane Treatment

2.1 Executive Summary

Near real-time monitoring of natural organic matter (NOM) concentration and composition in the upper Mississippi River was performed for eleven months. Distinct seasonal trends in dissolved organic carbon (DOC) concentration and ultraviolet light absorbance at 254 nm were observed as well as short-term (i.e. hours to days) increases that correlated with increases in river discharge during storm and snowmelt events. The permeability (i.e. transmembrane pressure-normalized flux) of hydrophilic ultrafiltration membranes was negatively correlated with river flow ($p < 0.01$) and raw water specific ultraviolet absorbance (SUVA) ($p < 0.01$) but not raw water DOC concentration ($p = 0.865$). Overall, the potential benefits derived from the increased data provided by an on-line monitoring system should outweigh the maintenance requirements for such instrumentation. Such data potentially could be used for real-time control of chemical dosing rates as well as membrane backwash and cleaning schedules.

2.2 Introduction

Natural organic matter (NOM) is ubiquitous in natural waters and is primarily derived from two sources: production by aquatic organisms (i.e. autochthonous NOM) and leaching of decaying vegetation from terrestrial sources (i.e. allochthonous NOM) (Thurman, 1985). Although typically not directly harmful to human health or the environment, NOM can have a variety of negative effects on the production of safe drinking water. For example, NOM can increase the consumption of water treatment chemicals, react with chlorine to form potentially harmful disinfection

byproducts, stimulate bacterial growth in water distribution systems, and foul filtration membranes (Li and Chen, 2004; Kaplan, 1994). With many water utilities switching to membrane filtration to ensure pathogen removal and meet new treatment standards, the urgency of understanding and mitigating the impacts of NOM on membrane fouling has increased.

NOM can foul membranes by adsorbing to the membrane surface and plugging pores as well as forming organic-cation complexes that lead to cake formation on the membrane surface (Goosen et al, 2004). Membrane-foulant interactions are influenced by the properties of the membrane, NOM concentration, hydrophobicity, and molecular weight as well as general water quality parameters, such as pH, temperature, ionic strength, and turbidity (Fan et al, 2001). Often, the surface characteristics of the membrane, including charge and dominant functional groups, are altered by the foulant (Violleau et al, 2005; Cho et al, 1998). Some studies have implicated hydrophobic NOM as the main contributor to membrane fouling (Violleau et al, 2005; Tu et al, 2001; Braghetta et al, 1998). The hydrophobic fraction is typically comprised of molecules with high molecular weight and high aromaticity and is thus associated with allochthonous sources (Pontie et al, 2007; Fan et al, 2001). Other studies have suggested that the hydrophilic fraction, which is often associated with autochthonous sources, is responsible for membrane fouling (Park et al, 2006; Lee et al, 2004). In general, hydrophobic membranes in contact with hydrophobic NOM are more likely to experience rapid and irreversible flux declines due to the formation of low permeability gel layers on the membrane surface or NOM sorption within the membrane pore structure (Pontie et al, 2007). Thus, hydrophilic membranes have been recommended for treating waters with high concentrations of hydrophobic NOM (Schäfer et al, 2000; Kabsch-Korbutowicz et al, 1999). Interactions between the hydrophobic and hydrophilic NOM fractions may further complicate the fouling process (Braghetta et al, 1998). Overall, the main concern is that NOM adsorbed onto membranes can be very difficult to remove by physical or chemical cleaning (Cherkasov et al, 1995).

A major complication in addressing membrane fouling is that NOM concentration and composition exhibit significant temporal variability. The concentration and composition of NOM in a water body at a given location and time results from a complex series of processes including inputs from the land surface of allochthonous NOM, production of autochthonous NOM within the water body, transport processes (e.g., flow, mixing, diffusion, sedimentation, resuspension), and transformation and loss processes (e.g., sorption, precipitation, photolysis, hydrolysis, biodegradation) (Hope et al, 1994; Thurman, 1985). NOM concentration and composition varies spatially due to differences in climate, topography, land use, and precipitation. Temporal variations in NOM concentration and composition have been linked to storm events and daily cycles in the short term (hours) and seasonal weather changes at intermediate time scales (weeks to months). Changes in land use and climate are the likely drivers at longer time scales (years to decades).

In temperate climates, the concentration and composition of NOM in surface waters varies throughout the year, especially in response to seasonal changes in precipitation, sunlight, and temperature (Mulholland, 1997; Hope et al, 1994). In the Rhode River watershed in Maryland, total organic carbon (TOC) concentrations varied from a low of 5.11 mg/L in the winter to a high of 12.80 mg/L in the summer (Correll et al, 2001). Surface runoff is a significant contributor to variations in NOM concentration and composition as runoff transports allochthonous NOM into surface waters (Hope et al, 1994). Flood events appear to be particularly important because such events cause leaching of dissolved organic carbon (DOC) from upper soil horizons (Mulholland, 1997) and high fluxes of particulate organic carbon (Veyssy et al, 1999). Rainfall was positively correlated with TOC during a long-term study of eight watersheds in the Maryland coastal plain and the importance of spring floods was noted (Correll et al, 2001). While flood events may be more likely to initiate the movement of particulate organic carbon into a water source, DOC concentrations do not always correlate with discharge (Meyer et al, 1998; Hope et al, 1994; Grubaugh and Anderson, 1989). For example, in large rivers such as the Mississippi, processes

such as internal production, dilution, and transformation may dictate NOM concentration and character (Duan, 2007). Autochthonous NOM production and DOC concentration can change significantly over the course of a day (Kaplan and Bott, 1982) and seasonally due to changes in temperature and sunlight. Watershed factors such as the presence of lakes and reservoirs (Kendall et al, 2001) and low canopy cover (Kaplan and Bott, 1982) also contribute to increased production of autochthonous NOM in rivers. In some cases, increases in autochthonous production during warm summer months can be offset by increases in the rates of degradative processes such as photolysis and biodegradation (Neff and Asner, 2001).

The Mississippi River watershed upstream of Minneapolis, Minnesota, USA is comprised of a mix of land uses including forests, wetlands, agriculture, and urban centers. The NOM contributions of different land uses in the watershed and the effects of these inputs on membrane fouling are poorly understood. Although there is some understanding of seasonal changes in NOM concentration and composition in the Mississippi River near Minneapolis from weekly grab samples analyzed by local water utilities, the short-term variability has not been investigated. In this part of the Mississippi River, it is unknown how rapidly NOM can change, whether those changes are significant from a treatment perspective, and what factors drive NOM change. The overall goal of this research was to investigate temporal variations (both short-term and seasonal) in the concentration and characteristics of NOM in the upper Mississippi River and the effects of these variations on treatability, specifically on membrane filtration. Herein, we demonstrate with near-real time monitoring that significant seasonal and short-term (i.e. hours to days) changes in NOM concentration and composition occur and that these short-term changes can be linked to storm and snow melt events. In addition, these changes in NOM composition can be linked to the fouling of ultrafiltration membranes used for water treatment.

2.3 Materials and Methods

2.3.1 Sampling site

Near real-time monitoring of the Mississippi River was done at the Minneapolis Water Works (MWW) treatment facility located in Fridley, Minnesota, USA. At that location, the river has an average daily flow of approximately 178,000 L/s and ranges from 40,000 to 682,000 L/s. MWW supplies water to over 100,000 service connections in Minneapolis and several neighboring cities. MWW treats water from the Mississippi River by lime softening followed by coagulation/flocculation/sedimentation before directing it to one of two filtration plants with a combined capacity of 180 million gallons per day (MGD). At the time of this study, one of those filtration plants (capacity of 70 MGD) employed Norit X-Flow hydrophilic, hollow-fiber, ultrafiltration membranes made of a polyethersulfone/polyvinylpyrrolidone blend with a nominal pore size of 0.02 μm . The 36 membrane skids (a skid consists of 112 modules with 35 m^2 of filtration area per module) are operated in inside-out, dead-end mode at a design flux of 97 $\text{L}/\text{m}^2\text{h}$ at 20°C. The membranes are cleaned by two-minute backwashes every 25 minutes, daily chemical washes (which could include sodium hypochlorite, sodium bisulfate, and/or hydrochloric acid), and extended chemical soaks as necessary. Membrane permeability (i.e. water flux through the membrane normalized by the applied pressure) is monitored continuously for each of the membrane skids and the values are averaged to obtain a permeability for the entire filtration plant. Permeability is a useful indicator of membrane fouling because permeability decreases with increased fouling. For the purposes of this study, the average daily plant permeability was used as the indicator of fouling rate to avoid the temporal variability associated with periodic cleaning of single skids.

2.3.2 *Near-real time water quality monitoring*

On-line water quality monitoring instrumentation was installed at the MWW treatment facility to provide near-real time data on NOM concentration (as DOC) and composition (as specific ultraviolet light absorbance or SUVA) in the upper Mississippi River. The on-line instrumentation was installed on February 5, 2007 and was operated for eleven months until December 24, 2007. The organic carbon concentration was measured every four minutes using a Sievers 900 Portable TOC Analyzer (GE Analytical Instruments, Boulder, Colorado, USA). The accuracy of the TOC analyzer was typically evaluated weekly in off-line or “batch” mode by analyzing blanks and 5, 10, or 20 mg as C/L TOC standard solutions prepared by diluting a purchased 1,000 mg/L standard solution (Sigma Aldrich, St. Louis, Missouri, USA). Ultraviolet absorbance at wavelengths from 178 to 891 nm was measured every four minutes using a USB4000 spectrometer and 1 cm path length Z flow cell (Ocean Optics, Dunedin, Florida, USA). The raw water was passed through a 3 µm Peplyn Plus Demicap polypropylene cartridge filter (Domnick Hunter, Charlotte, North Carolina, USA) to remove particles and reduce the possibility of instrument clogging before entering the spectrometer and TOC analyzer (Figure 2-1). Although this is a departure from the recommended use of ~0.7 µm pore size glass microfiber filters⁵ (Kaplan, 1994), there was no significant difference ($p < 0.03$, $n = 3$) between organic carbon measurements on surface water samples prepared by filtering through the glass microfiber filters or the 3 µm cartridge filter. Hence, the near-real time organic carbon results are termed DOC results.

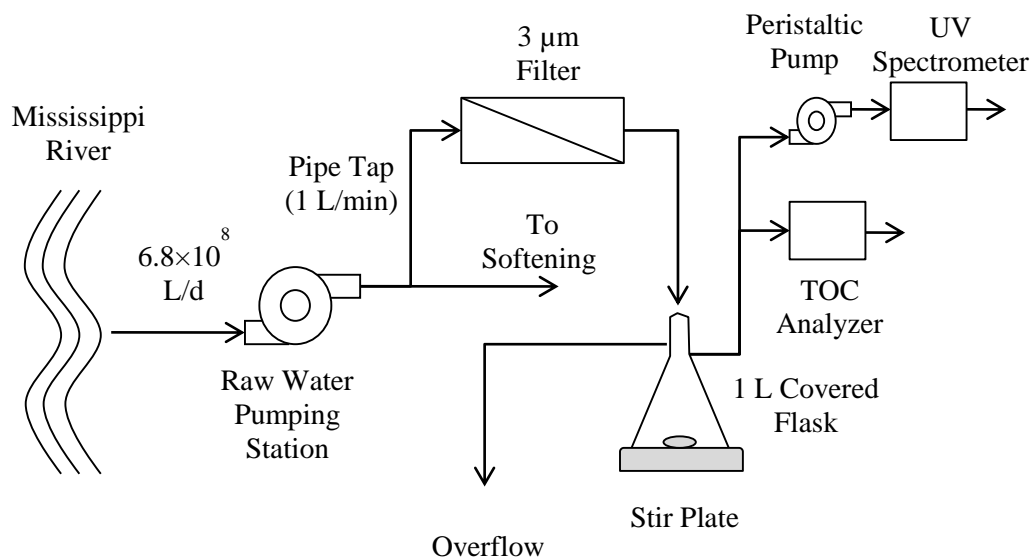


Figure 2-1. Schematic diagram of the near-real time water quality monitoring system installed at the Minneapolis Water Works.

2.3.3 Grab sampling

To compare with the results from the near-real time TOC analyzer, biweekly grab samples were collected directly from the pipe tap (i.e., upstream of the cartridge filter). Samples were collected in glassware that had been rendered organic carbon free by soaking overnight in 3 M nitric acid, rinsing with distilled water, and then baking for six hours at 550°C. Caps were soaked for one hour in a 0.63 M solution of reagent grade sodium persulfate and then rinsed with distilled water. Grab samples were typically filtered (Whatman Model 1825-047(GF/F), Florham Park, New Jersey, USA) within a few hours of collection and stored at 4°C for a maximum of one month before being analyzed on a Phoenix 8000 TOC Analyzer (Teledyne Tekmar Instruments, Mason, Ohio, USA) calibrated with dilutions of a purchased TOC standard solution (Sigma Aldrich, St. Louis, Missouri, USA) and a UV-1601PC UV/Vis Spectrophotometer (Shimadzu Scientific Instruments Incorporated, Columbia, Maryland, USA).

2.3.4 Data analysis

Daily averages of DOC, SUVA, Mississippi River flow, and treatment plant permeability were computed and then analyzed using the Kendall tau rank correlation test (Wessa, 2008). This method of analysis compares how two sets of time-dependent data vary with respect to each other. Each set of data is ordered from small to large and then each value within that set is assigned a rank from 1 to N. The assigned ranks of all paired values are then compared by the Kendall correlation coefficient (Equation 1). The Kendall correlation coefficient ranges from -1 (i.e. perfect negative correlation) to 1 (i.e. perfect positive correlation) with zero indicating no correlation (Abdi, 2007).

$$\tau = 1 - [2(\Delta P_1 P_2)/N(N-1)] \quad (1)$$

where: N = number of pairs

$\Delta P_1 P_2$ = number of times that rankings differ between paired data sets

Mississippi River flow data were obtained from the United States Geological Survey (USGS) National Water Information System: Web Interface for Station No. 05288500 (USGS, 2008). To examine seasonal changes in water quality, the seasons were defined as follows: Winter (January 1st – February 28th, December 1st – 31st), Spring (March 1st – May 31st), Summer (June 1st – August 31st), Autumn (September 1st – November 30th).

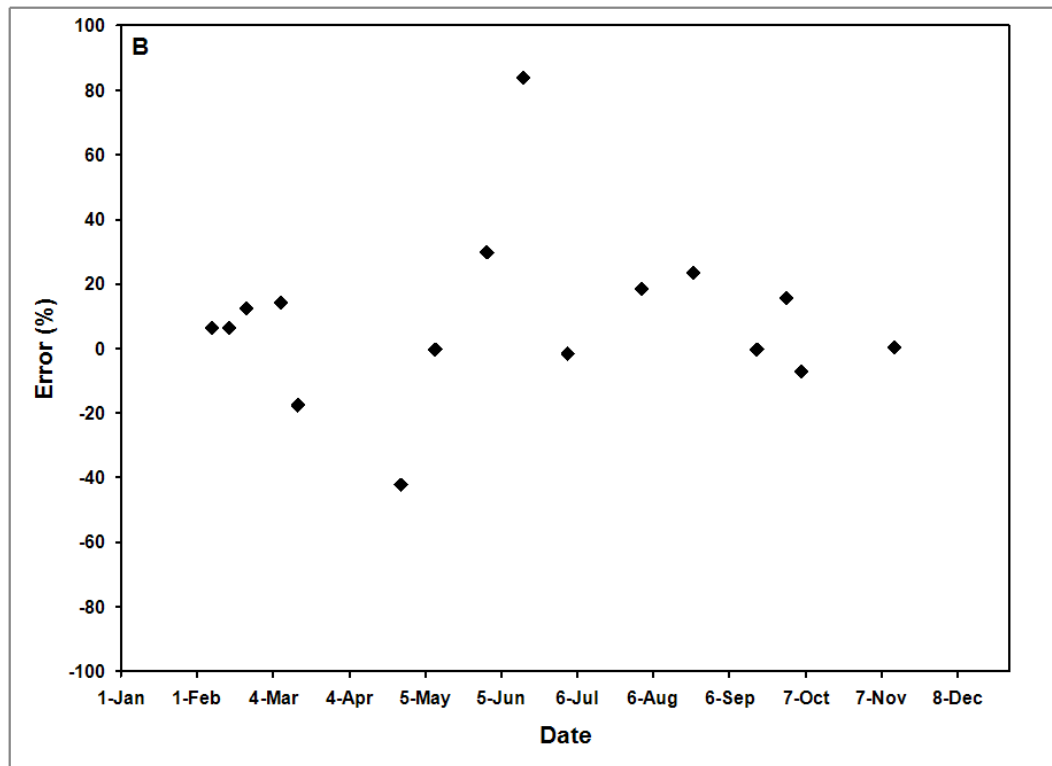
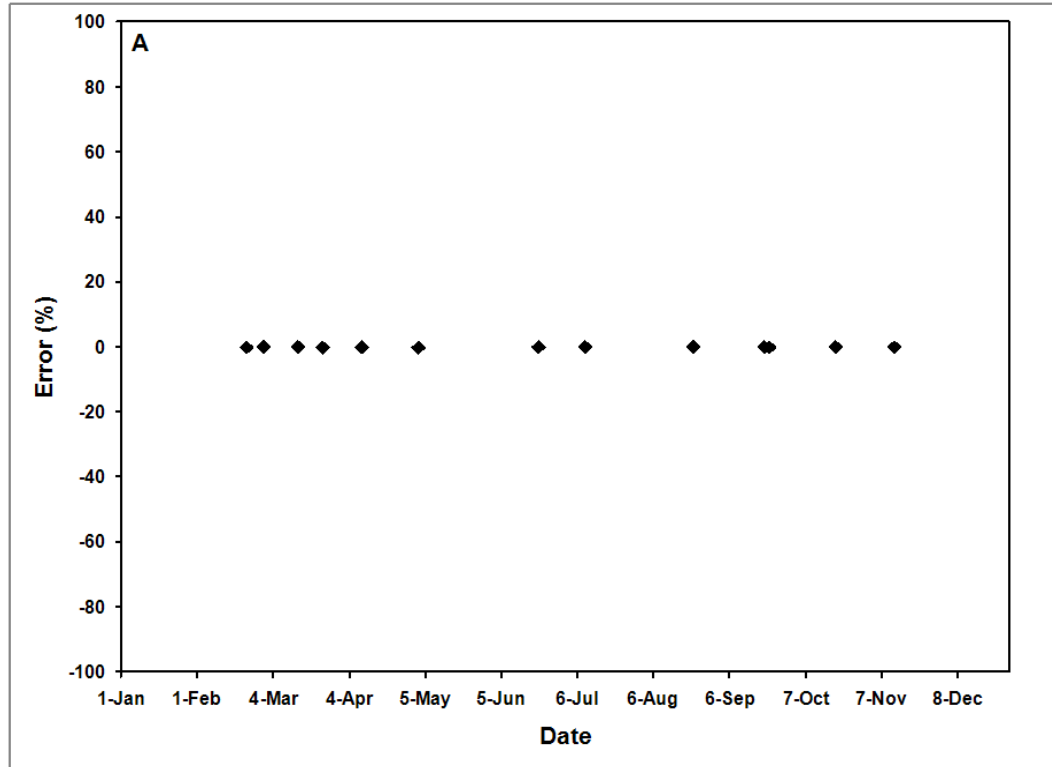
2.4 Results and Discussion

2.4.1 Near-real time water quality monitoring

During the eleven-month testing period, the organic carbon analyzer was operational 70% of the time and the UV-Vis spectrophotometer was operational 60% of the time. The calculation of percent on-line time does not include two weeks in April 2007 during which the instrumentation was taken off-line for class demonstrations. Maintenance of the instruments consisted mainly of scheduled replacements of consumable items (i.e. reagents, filters) and periodic checks of instrument calibration. Off-line time was attributed to clogged sample lines and periodic power

interruptions at the water treatment plant. Because the equipment was checked approximately weekly, a short-term power outage or other problem could result in up to a week of downtime.

The accuracy of the on-line organic carbon analyzer, as indicated by the small error values for the analyses of TOC standard solutions ([online-known]/known), was consistently good over the duration of the testing (Figure 2-2A). The DOC and ultraviolet absorbance at 254 nm (UV_{254}) results from weekly grab samples were compared with the corresponding data from the on-line monitoring systems. Results from grab samples collected when sampling lines were clogged or noticeably fouled with biological growth ($n=5$) were removed from the regressions. The error of the DOC results ([online-grab]/grab) ranged from -42 to 84% (Figure 2-2B). A regression of the on-line versus grab sample DOC data also indicates some deviation between the two sets of data ($\text{On-line} = 0.70(\text{Grab}) + 2.76$, $r^2 = 0.47$, $n = 16$). The on-line spectrophotometer tended to underestimate the UV_{254} , especially when the values were relatively high during spring snow melt. The error of the UV_{254} results ranged from -18 to 59% (Figure 2-2C). Again, a regression of the on-line versus grab sample UV_{254} data also indicates some deviation between the two sets of data ($\text{On-line} = 1.24(\text{Grab}) - 0.04$, $r^2 = 0.46$, $n = 11$). The accurate results from the analysis of standard solutions in batch mode coupled with the significant errors observed in the comparisons with the grab sample results suggest that there were issues with the maintenance of the cartridge filter and the sample tubing. Discrepancies between the on-line and grab samples were attributed to biofouling of the sampling lines and clogging or breakthrough of the 3 μm filter. The cartridge filter was replaced on April 2, May 29, June 20, August 15, and October 10, 2007 and it appears that the largest errors in on-line DOC and UV_{254} occurred just prior to filter replacements.



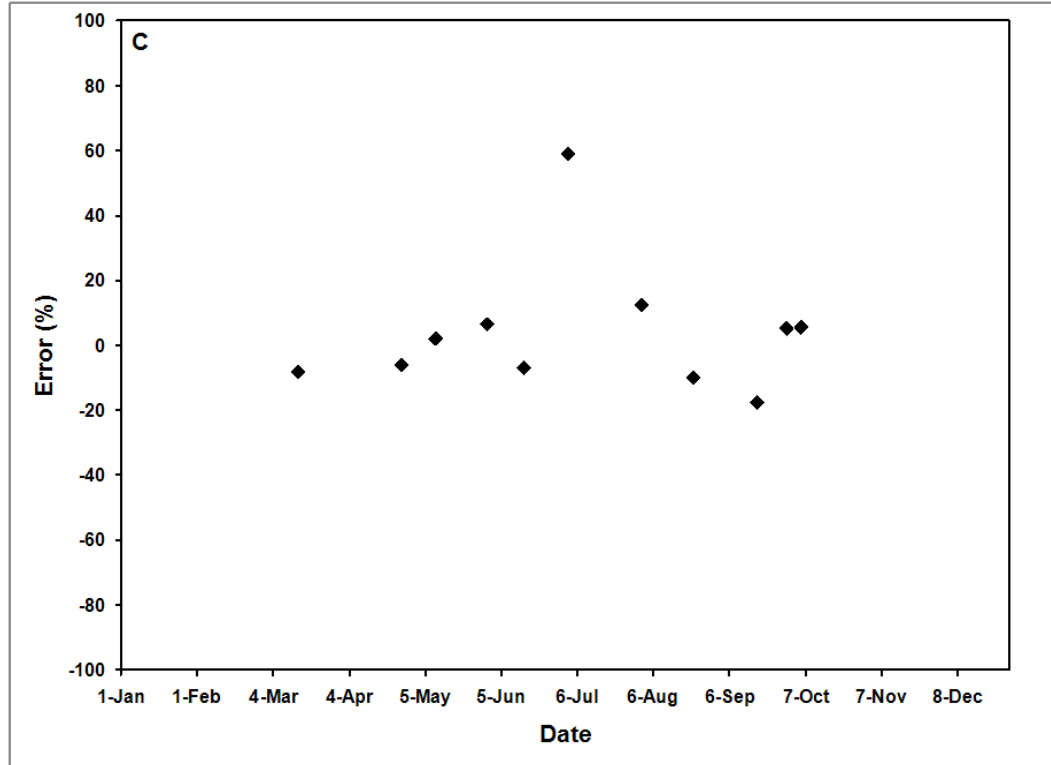


Figure 2-2. Error from the analysis of DOC standard solutions (A) and from comparison of grab and on-line DOC (B) and UV₂₅₄ (C) analyses of Mississippi River water during 2007.

2.4.2 Seasonal trends in water quality parameters

Seasonal trends in DOC, UV₂₅₄, and SUVA are shown in Figure 2-3 by plotting the average daily values of each parameter. DOC concentrations were the highest in the summer months (June – August) and lowest during the winter months (December – February) when the river had relatively low flows and was covered by ice. Similar seasonal trends were observed for the White River in Indiana (Volk et al, 2004). UV₂₅₄ was relatively stable throughout the winter and summer months, but increased during spring snow melt and autumn storms. SUVA values were greatest in the winter and decreased in the summer suggesting an increase in the fraction of autochthonous NOM in the summer months (Table 2-1). The highest variability, as indicated by relative standard deviation, occurred in the spring and autumn for all measured parameters.

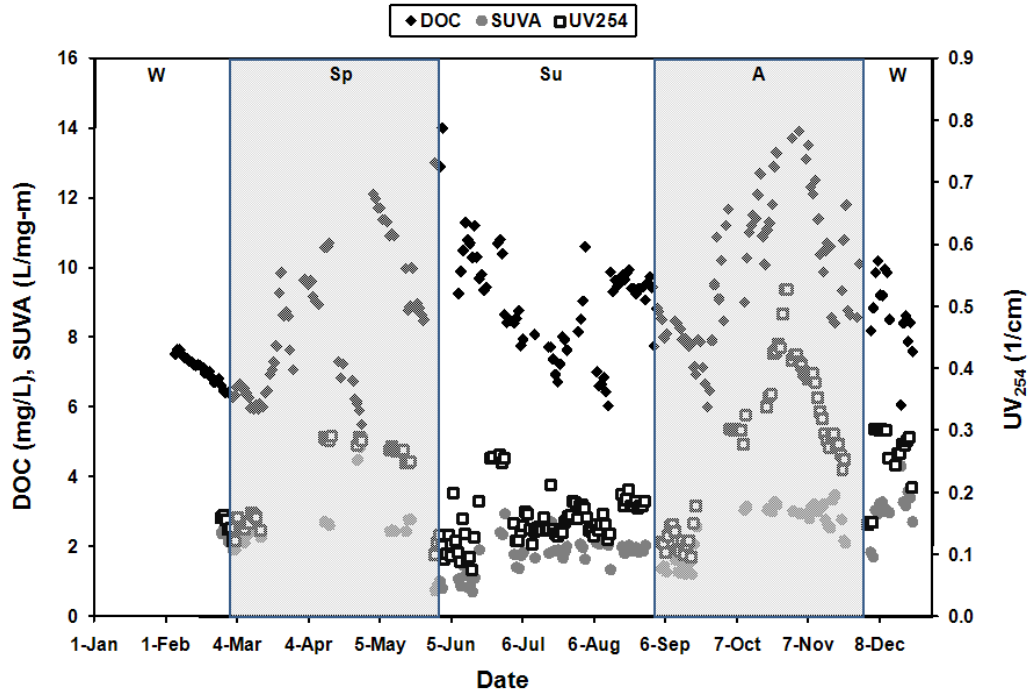


Figure 2-3. Daily average DOC concentration, UV_{254} , and SUVA for the upper Mississippi River from February 5, 2007 to December 24, 2007.

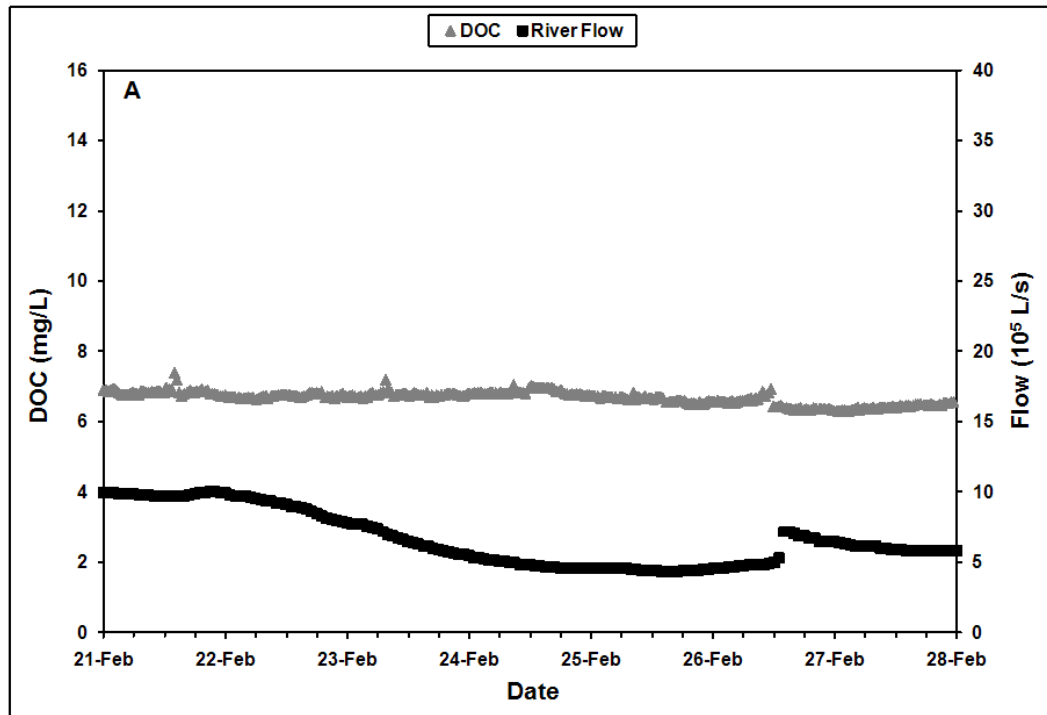
Table 2-1. Mean (\pm standard deviation) DOC concentration, UV_{254} , and SUVA as a function of season for the upper Mississippi River

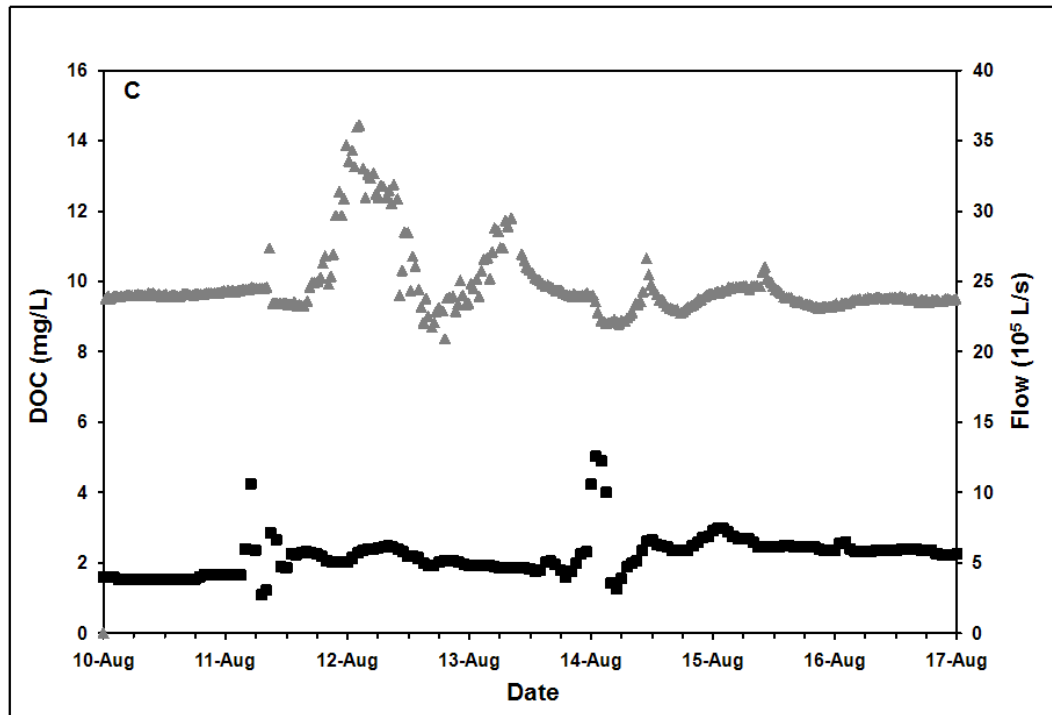
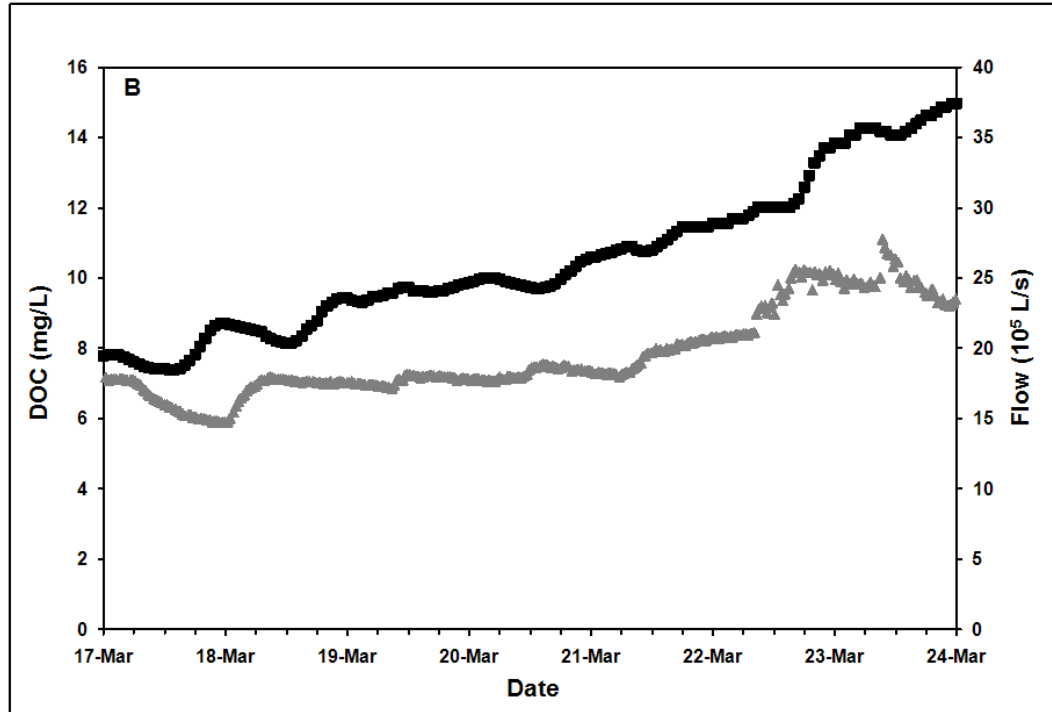
Season	DOC (mg/L)	UV_{254} (1/cm)	SUVA (L/mg-m)
Winter	7.08 ± 0.38 (n = 7,870) ¹	0.153 ± 0.011 (n = 2,029)	2.18 ± 0.16 (n = 1,826)
Spring	8.31 ± 2.24 (n = 16,488)	0.161 ± 0.054 (n = 5,063)	1.92 ± 0.55 (n = 4,050)
Summer	9.52 ± 0.81 (n = 7,099)	0.138 ± 0.071 (n = 13,263)	1.45 ± 0.42 (n = 4,969)
Autumn	8.31 ± 1.48 (n = 9,336)	0.123 ± 0.046 (n = 5,297)	1.48 ± 0.72 (n = 3,111)

1. n is the number of data points

Near real-time DOC data from a few selected weeks of the eleven-month monitoring campaign are shown in Figure 2-4. The surface of the Mississippi River was frozen for most of February 2007 and the water quality was relatively stable (Figure 2-4A). In contrast, the water quality of the Mississippi River historically changes rapidly during snow melt in March, April, and May (Brinkman and Bankston, 2007). In 2007, the DOC concentration increased concurrently with

discharge starting in mid-March. Over the course of a week, both discharge and DOC increased by approximately 50% (Figure 2-4B). The increase in DOC is attributed to snow melt water carrying allochthonous NOM into the river via overland flow or percolation through the riverbanks. During the summer months, increases in discharge due to storm events resulted in a corresponding increase in DOC (Figure 2-4C). This is consistent with other studies of rivers and streams in the temperate United States (McDowell and Likens, 1988; Meyer and Tate, 1983). In this study, two days of heavy rains on August 11th and 13th (4.4 mm and 5.2 mm, respectively) resulted in an increase of up to 50% in DOC concentration and 140% in flow. Two distinct DOC peaks occurred for each rainfall, possibly representing delayed storm flows from drainage ponds or upstream tributaries. The impact of rainfall on DOC concentration is dissipated by the volume of flow in the Mississippi River and its 19,100 square mile watershed north of Minneapolis.





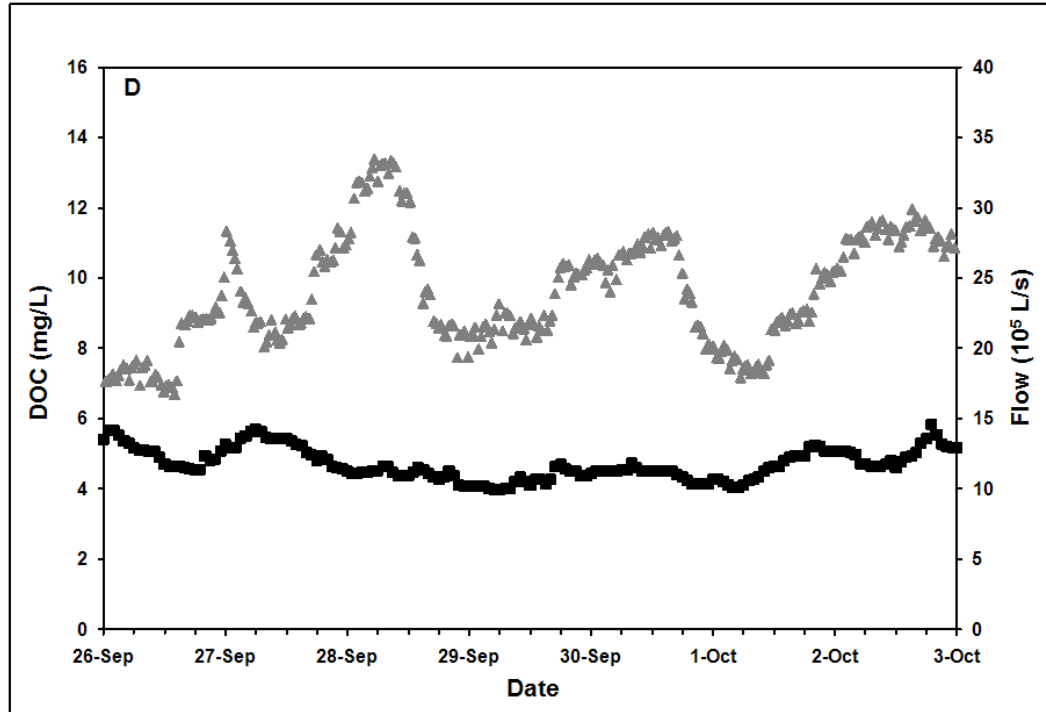


Figure 2-4. Four-minute DOC concentrations and one-hour upper Mississippi River flows (USGS Station No. 5288500, Anoka, Minnesota, USA) for selected weeks during the winter (A), spring (B), summer (C), and autumn (D) of 2007

Periodic fluctuations in the DOC concentration were observed in late September and early October (Figure 2-4D) when flow in the river was at a minimum (~57,000 L/s). SUVA values for this time period were consistent and typically below 2 L/mg-m, suggesting that the NOM is predominantly from autochthonous sources (Karanfil et al., 2002; Thurman, 1985). A lack of canopy cover over the upper Mississippi River, which is up to 650 feet wide in places, and the presence of upstream reservoirs permit internal production of NOM. The times between peaks in DOC concentration were between 29 to 43 hours and did not correspond to typical diel variations in DOC concentrations resulting from primary productivity (Kaplan and Bott, 1982).

2.4.3 River flow and water quality

DOC concentration positively correlated with river flow in the winter, spring, and autumn seasons (Table 2-2). The increase in DOC concentration during the autumn is likely due to mobilization of carbon from upper soil layers during storm events and leaf fall. For the upper Mississippi River, Grubaugh and Anderson (1989) observed similar correlations between peak flow and high TOC values at a location approximately 450 miles downstream from the sampling site in the current study. SUVA positively correlated with river flow during the spring and autumn, but not in the winter and summer. As SUVA indicates the aromaticity of NOM, it is expected that SUVA would increase as spring snow melt and autumn storms mobilize allochthonous NOM from the upper soil layers (Dalzell et al, 2005; McDowell and Likens, 1988).

Table 2-2. Kendall tau rank correlation coefficients (τ) and probability values (p) for comparisons of daily mean DOC concentration and river flow and SUVA and river flow

Season	DOC and River Flow	SUVA and River Flow
Year	$\tau = 0.179$ $p < 0.01$ $n = 155$	$\tau = 0.362$ $p < 0.01$ $n = 71$
Winter	$\tau = 0.393$ $p < 0.01$ $n = 28$	$\tau = 0.255$ $p = 0.454$ $n = 8$
Spring	$\tau = 0.294$ $p < 0.01$ $n = 57$	$\tau = 0.463$ $p < 0.01$ $n = 24$
Summer	$\tau = 0.215$ $p = 0.083$ $n = 33$	$\tau = -0.103$ $p = 0.592$ $n = 17$
Autumn	$\tau = 0.324$ $p < 0.01$ $n = 37$	$\tau = 0.523$ $p < 0.01$ $n = 22$

Note: Significant p values (< 0.05) are in bold

2.4.4 Membrane fouling and water quality

Permeability for the Columbia Heights Membrane Filtration Plant was highly variable in the late spring and mid-autumn due to runoff from storm events, but more stable during the summer

due to low flow conditions and early winter due to ice cover (Figure 2-5). Permeability and raw water SUVA were negatively correlated in the autumn and summer months (Table 2-3), indicating that a decrease in permeability occurred as SUVA increased (i.e. as NOM aromaticity increased). For water utilities concerned with maintaining high permeability and membrane integrity, NOM associated with runoff may be of more concern than NOM associated with primary production. In general, NOM with higher SUVA is more hydrophobic and can cause more fouling on hydrophobic membranes than hydrophilic NOM because of hydrophobic-hydrophobic interactions (Lee et al, 2006; Fan et al, 2002). Other researchers have suggested, however, that hydrophilic NOM and its associated colloids are primary foulants of membranes treating surface waters (Park et al, 2006; Lee et al, 2004).

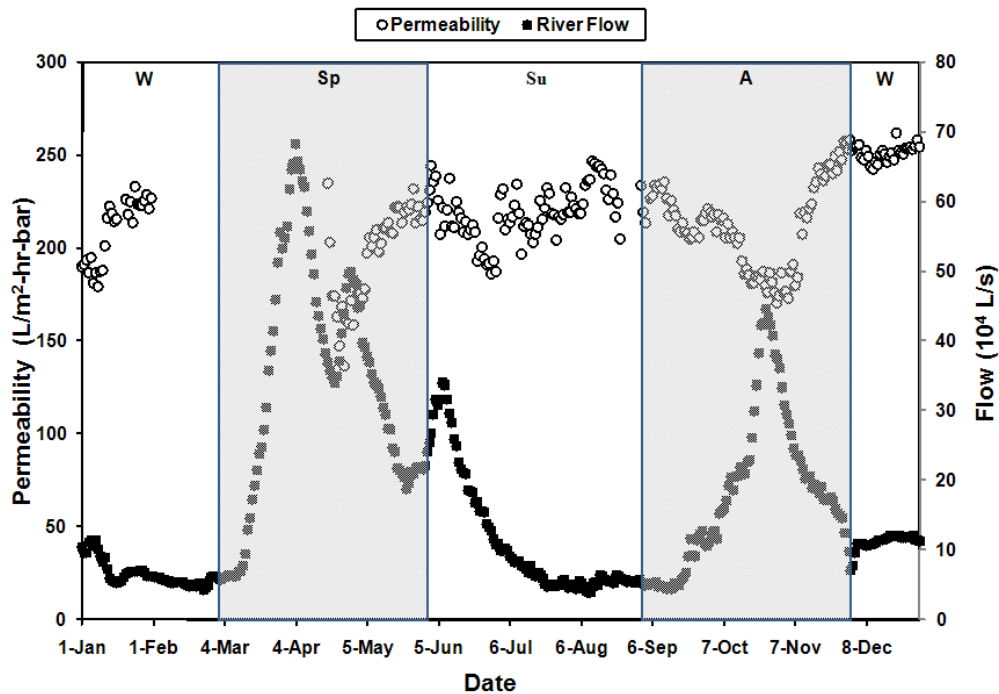


Figure 2-5. Average 2007 daily membrane permeability for the Minneapolis Water Works Columbia Heights Membrane Filtration Plant

Table 2-3. Kendall tau rank correlation coefficients (τ) and probability values (p) for comparisons of daily mean DOC concentrations, SUVA values, Mississippi River flow, and membrane plant permeability

Season	Permeability and DOC	Permeability and SUVA	Permeability and River Flow
Year	$\tau = -0.129$ $p = 0.865$ $n = 84$	$\tau = -0.294$ $p < 0.01$ $n = 50$	$\tau = -0.313$ $p < 0.01$ $n = 276$
Winter	$\tau = 0$ $p = 1$ $n = 4$	$\tau = -1$ $p = 0.089$ $n = 4$	$\tau = 0.341$ $p < 0.01$ $n = 59$
Spring	$\tau = 0.228$ $p = 0.172$ $n = 20$	$\tau = -0.278$ $p = 0.348$ $n = 9$	$\tau = -0.650$ $p < 0.01$ $n = 44$
Summer	$\tau = 0.110$ $p = 0.455$ $n = 25$	$\tau = -0.433$ $p = 0.022$ $n = 16$	$\tau = -0.226$ $p < 0.01$ $n = 84$
Autumn	$\tau = 0.0152$ $p = 0.910$ $n = 35$	$\tau = -0.423$ $p < 0.01$ $n = 21$	$\tau = -0.466$ $p < 0.01$ $n = 89$

Note: Significant p values (< 0.05) are in bold

Permeability and Mississippi River flow were negatively correlated in the spring, summer, and autumn (Table 2-3). Surface runoff from snow melt or storm events and high river flows typically result in increases in NOM loading and suspended solids (i.e. turbidity), both of which can contribute to membrane fouling. Surprisingly, permeability did not correlate with DOC concentration even though DOC concentration was positively correlated with Mississippi River flow and Mississippi River flow was negatively correlated with membrane permeability. The membrane plant was not in service from February 1 to April 17, 2007. The lack of correlation between permeability and DOC concentration was attributed to the lack of membrane permeability data during this time of elevated DOC.

In this analysis, the composition and concentration of the raw water NOM were compared with membrane permeability although the water undergoes several treatment steps in between. Water treatment processes such as softening can change the composition and concentration of

NOM by selectively removing NOM based on its hydrophobicity and/or size (Chen et al, 2007). For example, lime softening at MWW removed $54 \pm 10\%$ of the raw water TOC and reduced the UV_{254} by $36 \pm 8\%$ during 2007. Earlier research on Mississippi River water showed a 33% removal of raw water TOC and 52% reduction in UV_{254} via lime softening (Semmens and Staples, 1986). Ideally, two on-line setups would have been employed to measure DOC concentration and composition in the raw water and just prior to the membranes. Nevertheless, the raw water characteristics still provided some useful information on membrane fouling potential as the results of grab samples indicate that the raw water NOM characteristics significantly correlate with the NOM characteristics of the membrane feed water (TOC: $\tau = 0.767$, $p < 0.01$, $n = 28$; DOC: $\tau = 0.672$, $p < 0.01$, $n = 28$; and UV_{254} : $\tau = 0.721$, $p < 0.01$, $n = 30$).

2.5 Conclusions and Recommendations

On-line analyzers were used to monitor NOM concentration (as DOC) and composition (as SUVA) in the upper Mississippi River near Minneapolis, Minnesota, USA over the course of 11 months in near-real time. Analysis of NOM at high temporal resolution yielded information on significant short-term variations that are missed by a typical weekly grab sampling routine. For example, significant increases in DOC resulted from spring snowmelt and from large storm events. Also, during a period of low flow in August, short-term variations were observed that were likely due to variation in production of autochthonous NOM. Seasonal patterns were also observed. DOC concentrations increased during the spring months concurrently with snow melt and remained high throughout the summer rainy season. These major short-term and seasonal changes in NOM concentration and composition can have significant impacts on water treatment, including chemical dosage requirements and membrane fouling. Membrane permeability, which is an indicator of fouling, was negatively correlated with river flow and raw water SUVA. Surprisingly, permeability did not correlate with raw water DOC, but this may have been due to a lack of membrane

permeability data during a period of relatively high and variable DOC concentration and severe fouling. It is suggested that water utilities, especially those with highly variable water sources, consider on-line instrumentation for monitoring of NOM to ensure a consistent high quality finished water and to protect valuable water treatment infrastructure such as membranes.

Near real-time monitoring of raw water quality parameters such as DOC and SUVA using on-line instrumentation can be used to improve plant performance and to safeguard the operational integrity of membrane filters. The on-line instrumentation must be properly maintained, however, to ensure that it is operational and that the data are accurate and consistent with grab sample results. Operation of the monitoring instruments should be verified daily and restarted in the event of shutdown due to power outages and tubing or connection failures. In addition, cleaning and/or replacement of fouled sample lines and pre-filters should be performed on an as needed basis (~weekly for our site). Visual assessment of the lines and filters can be used to estimate required cleaning or replacement intervals. Use of grab sampling (at least for the first few months) and routine analysis of standards also can be used to diagnose problems and determine maintenance schedules. Although not employed in this study or evaluated in the field, installation of pre-filters in series (e.g., a 3 μm filter followed by a 0.45 μm filter) may aid in protecting the on-line instruments and tubing from particles and clogging due to bacterial growth. Other routine maintenance of the on-line TOC instrumentation includes replacing reagents, filters, and the UV lamp, with an expected time commitment of approximately two hours every three months. Overall, the potential benefits derived from the increased amount of data should outweigh the maintenance requirements for such on-line instrumentation.

2.6 Acknowledgements

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Chapter 3

Spatial Variations in Organic Carbon Concentration and Composition in the Upper Mississippi River and Tributaries

3.1 Executive Summary

Variation in the concentration and composition of natural organic matter (NOM) as a function of land use was studied along the length of the upper Mississippi River in Minnesota and at selected tributaries. Total (TOC) and dissolved organic carbon (DOC) concentrations were relatively constant at 7 – 9 mg/L along the length of the river despite inputs from tributaries with much higher concentrations (> 12 mg/L). The character of NOM, as observed through specific ultraviolet absorbance and fluorescence spectroscopy, did not change significantly; however, chlorinated wastewater effluent, which can contribute almost 4% of river flow, had significantly higher occurrences of oxidized quinones and the highest fluorescent intensity. For this late summer - early autumn time period, estimated DOC export from the upper Mississippi River was 0.0088 kg C/ha/day. Overlaying sampling points on a digital elevation model and land use map showed that concentrations of TOC and DOC were negatively correlated with the percent of agricultural land and positively correlated with percent shrubland area. This survey of the upper Mississippi River and its tributaries could help inform policy and engineering decisions regarding watershed and surface water quality management and treatment plant design by showing how land use influences NOM in both small-scale tributaries and large-scale river systems.

3.2 Introduction

Natural organic matter (NOM) is ubiquitous in surface waters and is derived from two sources: production by aquatic organisms (i.e. autochthonous) and leaching of decaying vegetation from terrestrial sources (i.e. allochthonous) (Thurman, 1985). Aquatic organic matter (OM) also

comes from anthropogenic sources such as wastewater, urban stormwater runoff, and agricultural runoff. Both natural and anthropogenic sources are believed to be important in our study site, the upper Mississippi River basin. OM can differ in chemical characteristics dependent on where it originates (Pinney et al., 2000; Correll et al., 2001; Thomas et al., 2004). Unfortunately, the relationship between source (i.e. land use) and the concentration and composition of OM supplied to surface water is poorly understood. Although most OM is not directly harmful to human health or aquatic biota, OM challenges drinking water utilities by increasing chemical consumption, serving as a precursor for disinfection byproducts, and fouling filtration membranes (Li and Chen, 2004; Kaplan, 1994). OM plays many roles in surface waters, including facilitating the mobilization of metals (McKnight and Bencala, 1990), acting as a carbon source for bacterial growth (Moran and Zepp, 1997), and protecting aquatic organisms from exposure to UV irradiation (Schindler and Curtis, 1997). It is therefore critical for water utilities and watershed managers to understand how the concentration and composition of OM may be affected by changes in upstream land uses.

Predominant land uses in the Mississippi River watershed in Minnesota include row crop agriculture, forests, wetlands, and urban areas. Agricultural land uses include pasture, concentrated animal feeding operations, orchards, and row crops, but each of these may have varying fluxes of organic matter from animal or vegetal waste (Chomycia, et al., 2008), erosion (Correll et al., 2001), and irrigation (Hernes et al., 2008). Large-scale agricultural impacts on organic matter are therefore difficult to quantify and are often conflicting. A comparison of intensively grazed pasture and pine forest in New Zealand showed that the runoff from the pasture had less than half the DOC concentration of the runoff from the planted pine forest plot (Findlay et al., 2001). Streams in the Amazon basin, however, had higher DOC following pastures than following forests (Thomas et al., 2004). Forests contribute DOC to surface waters mainly through leaf litter (Meyer and Tate, 1983) with DOC leached from leaf litter contributing about 30% of the DOC generated in a small forested stream (Meyer et al., 1998). A comparison of a forest and a moorland watershed in Scotland

determined that the forested catchment had twice the DOC in receiving streams as the moorland due to higher accumulation of detritus (Grieve et al., 1990). Meyer and Tate (1983) observed lower carbon exports from a forested watershed two years after clear cutting when compared to a non-cleared control forested watershed.

Wetlands, due to their long hydraulic residence time, anaerobic conditions, organic soils, and high amount of primary productivity, can be a source of NOM (Mulholland and Kuenzler, 1979; Dalva and Moore, 1991; Kaplan et al., 2006). Wetlands may also serve as sinks of organic matter. For example, Pinney et al. (2000) observed a decrease in dissolved organic carbon (DOC) concentrations, ranging from 9% in June to 47% in February, through a constructed wetland receiving treated wastewater effluent from an aerated lagoon system. Specific ultraviolet light absorbance (SUVA) at 254 nm increased along the wetland, especially in the summer, as the labile compounds with low SUVA values in the wastewater were biodegraded and OM with high SUVA values was leached from plant materials within the wetland. Studies of shrubland influences on OM have mainly been limited to Scottish peatlands. In an analysis of DOC in the Glen Dye catchment, waters from three peat-dominated subwatersheds had the highest DOC concentrations, up to an average of 18.3 mg/L, compared to those with humic podzols (Dawson et al., 2004). A seasonal survey of 56 Scottish watersheds found that upland peat/shrub land use was only positively correlated to DOC export during the autumn and winter when overland and subsurface flows were not common (Aitkenhead-Peterson, 2007). Urbanization may reduce NOM variability due to impoundments, channelization, and wastewater flows, but not necessarily affect concentration and composition (Westerhoff and Anning, 2000).

The relative contribution of upland sources and internal production to OM in surface waters is not well understood and depends on a number of factors including stream characteristics (i.e. discharge, channel dimensions, shading), local land use, time of year, and precipitation. The OM in headwaters tends to be dominated by allochthonous OM rather than autochthonous OM (Meyer

et al., 1998). Inputs of allochthonous OM, however, are highly dependent on storm events. During baseflow conditions, allochthonous OM mobilized from deeper mineral soils is transported to surface waters via groundwater (Vidon et al., 2008). Such organic matter is primarily in the dissolved form. During storm events, stormwater infiltration and rising water tables together with overland flow can result in increased mobilization of the relatively young soil OM that is at or near the ground surface as both DOC and particulate organic carbon (POC) (Dalzell et al., 2005; Vidon et al., 2008). Storm events resulted in increases in DOC loadings in small streams (Dalzell et al., 2005; Vidon et al., 2008) and the Mississippi River (Brinkman and Hozalski, 2011) compared to base flow because of increases in both flow and concentration. The opposite effect has been reported for some large rivers (Benedetti et al., 2003; Bianchi et al., 1997; and Moreira-Turcq et al., 2003), however, which may be due to dilution of autochthonous NOM (Dalzell et al., 2005). Furthermore, there is evidence that the NOM composition changes during storm events, with increases in SUVA (Vidon et al., 2008) and in DOC that is 'less degraded' or more labile (Dalzell et al., 2005; Buffam et al., 2001) in comparison to baseflow conditions. In addition, increased solar irradiation and warmer temperatures in the summer months lead to increased production of autochthonous NOM (Duan et al., 2007). Thus, a significant amount of work has been done to investigate NOM dynamics in streams and rivers and an important conclusion is that the timing of a sampling campaign must be considered when interpreting OM data. Unfortunately, we are unaware of any studies that tracked spatial NOM variability over a large scale for a major river and its tributaries.

Thus, the purpose of this research was to evaluate the spatial variability of NOM and effects of land use on NOM concentration and composition by sampling along a 650-mile reach of the upper Mississippi River along with selected tributaries. Through this trip down the Mississippi River in Minnesota, we will demonstrate that during the late summer - early fall there is little variability in NOM concentration and composition along the river despite significant variation in

these parameters in the tributaries. Furthermore, we will show that certain land uses, particularly agriculture and shrubland, have a significant influence on NOM concentration and composition in this part of the river.

3.3 Materials and Methods

3.3.1 Study site

The Mississippi River begins at Lake Itasca in northern Minnesota and flows nearly 640 miles through the state, draining approximately 65% of Minnesota's land area. The entire Mississippi River watershed covers approximately 41% of the land area in the continental United States. Land use in the Mississippi watershed in Minnesota is dominated by agriculture in the southern two-thirds of the state, while forests and wetlands are predominant in the northern third. Urban/suburban land uses and their associated stormwater and wastewater inputs become more important in the southern part of the watershed. For example, during the time of our sampling, approximately 3.9% of the river flow immediately downstream of the Twin Cities metropolitan area (144,000 L/s at the Lilydale gauging station) was comprised of treated wastewater from the Metropolitan (5,300 L/s) and St. Cloud (400 L/s) wastewater treatment plants. Major soil classifications for Mississippi River watershed in Minnesota are Udalts, Psamments, and Udepts with subsurface geology dominated by glacial till and outwash (University of Minnesota Extension, 2013). Water samples from the Mississippi River (23 locations) and selected tributaries (30 locations) in Minnesota were collected during ten trips from August 18 through October 17, 2008 and analyzed for organic carbon concentration and OM composition. A travel time of 47 days from Lake Itasca to the confluence of the Mississippi and Minnesota Rivers was estimated based on the watershed area and average discharge (Søballe and Kimmel, 1987) and sampling trips were timed to approximately follow a parcel of water as it flowed down the Mississippi River. Sampling sites

were selected from descriptions in the Minnesota Department of Natural Resources' Canoeist's Guide to the Mississippi (MNDNR, 2005-2008) and include major tributaries as well as small streams (Figure 3-1). In this manuscript, location on the river (in river miles) refers to the distance upstream from the confluence of the Mississippi and Ohio Rivers as established by the U.S. Army Corps of Engineers. River or stream discharges for locations with gauging stations monitored by the United States Geological Survey (23% of sampling locations) were obtained from the National Water Information website (USGS, 2008) for the date and time the water sample was collected. For sampling locations without gauging stations, the discharge was estimated when the water depth was sufficiently shallow to cross the channel safely on foot (i.e. maximum depth <1 m, 62% of sampling locations) as no boat was available for the sampling campaign. At these shallow locations, depth and width were determined using a tape measure. Then, surface velocity was estimated by timing floating debris over a predetermined distance. For 75% of the sampling locations, the river or tributary width was too wide to measure with a tape measure, so web-based Google Earth (Google, Inc., Mountain View, California, USA) was used to determine the river width. Finally, discharge was computed by multiplying the surface velocity by the channel cross-sectional area.

3.3.2 *Analytical methods*

At each site, water grab samples were collected in two 40 mL screw top glass bottles by submerging the bottle 6 inches below the water surface and opening the cap. The bottles had been rendered organic carbon free by soaking overnight in 3M nitric acid, rinsing with distilled water, and then baking for six hours at 550°C and the caps had been cleaned by soaking for one hour in a 10% solution of reagent grade sodium persulfate

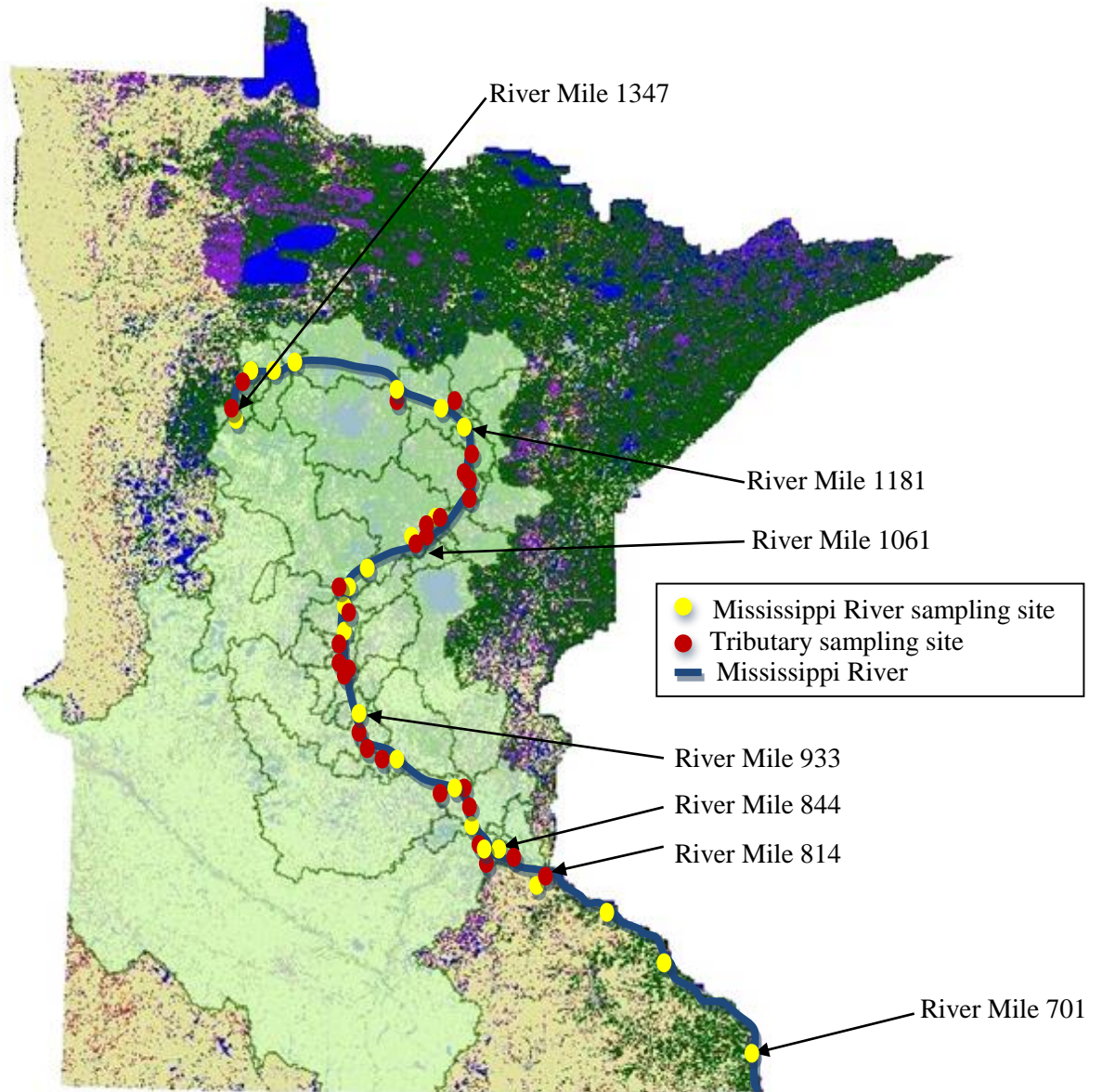


Figure 3-1. Land use by color (grey = urban, light sage = agriculture, maroon = grassland, green = forest, blue = water, purple = wetland, orange = shrubland) and location of sampling sites (August 18 – October 17, 2008) along the upper Mississippi River and tributary watersheds shaded in transparent light green.

(Sigma Aldrich, St. Louis, Missouri, USA). The water samples were filtered through baked glass microfiber filters (Whatman GF/F, Piscataway, New Jersey, USA) within 24 hours of return to the laboratory. The filtered water samples were stored at 4°C for a maximum

of one month before being analyzed for organic carbon using a Sievers 900 Portable TOC Analyzer (GE Analytical Instruments, Boulder, Colorado, USA) that was calibrated with dilutions of a TOC standard solution (Sigma Aldrich, St. Louis, Missouri, USA). UV/Vis light absorbance scans from 200 – 600 nm were obtained for filtered samples using a UV-1601PC UV-Visible spectrometer (Shimadzu Scientific Instruments, Inc., Columbia, Maryland, USA).

Fluorescent spectroscopy was performed on selected samples: the Mississippi River at Itasca, Prairie River, Minnesota River, Metropolitan Wastewater Treatment Plant effluent, Mississippi River at Hastings, St. Croix River, and Mississippi River at La Crescent. Water samples were filtered through 0.2 µm nitrocellulose membrane filters (Millipore Corporation, Billerica, Massachusetts, USA) and stored in organic carbon-free glassware prepared as described above. Excitation-emission matrices (EEMs) were generated on a Fluoromax-3 fluorometer (Horiba Instruments, Irvine, California, USA). The excitation range was 200 – 400 nm with an interval of 5 nm while the emission range was 290 – 550 nm with an interval of 2 nm. The raw scans were adjusted according to baseline scans to account for Raman scattering, variations in lamp intensity, and cuvette imperfections. Contour plots representing the resulting matrix were created using a MatLAB (The Mathworks, Inc., Natick, Massachusetts, USA) script. Parallel factor analysis was also performed in MatLAB using the thirteen reference components identified by Cory and McKnight (2005).

3.3.3 Watershed delineation and land use correlation

A digital elevation model (DEM) for the State of Minnesota was created from state topographic maps (MNDNR, 1999-2008) in ArcView 9.0 (ESRI, Redlands, California, USA). Watershed terrain models, based on the Universal Transverse Mercator (Section 15) coordinates of

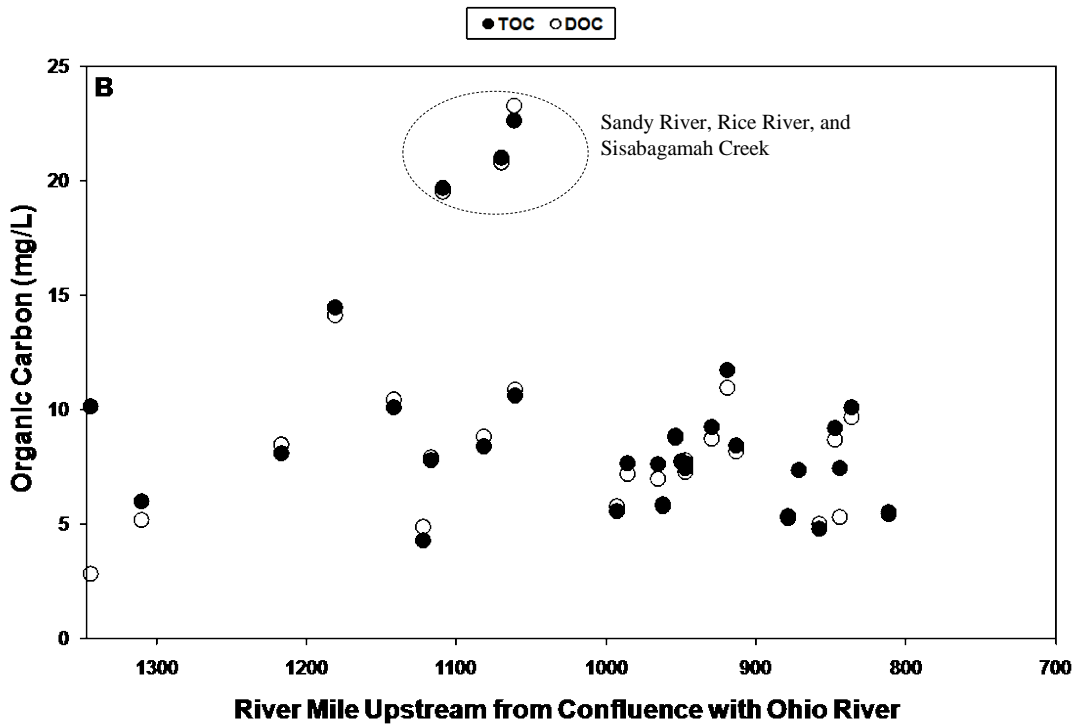
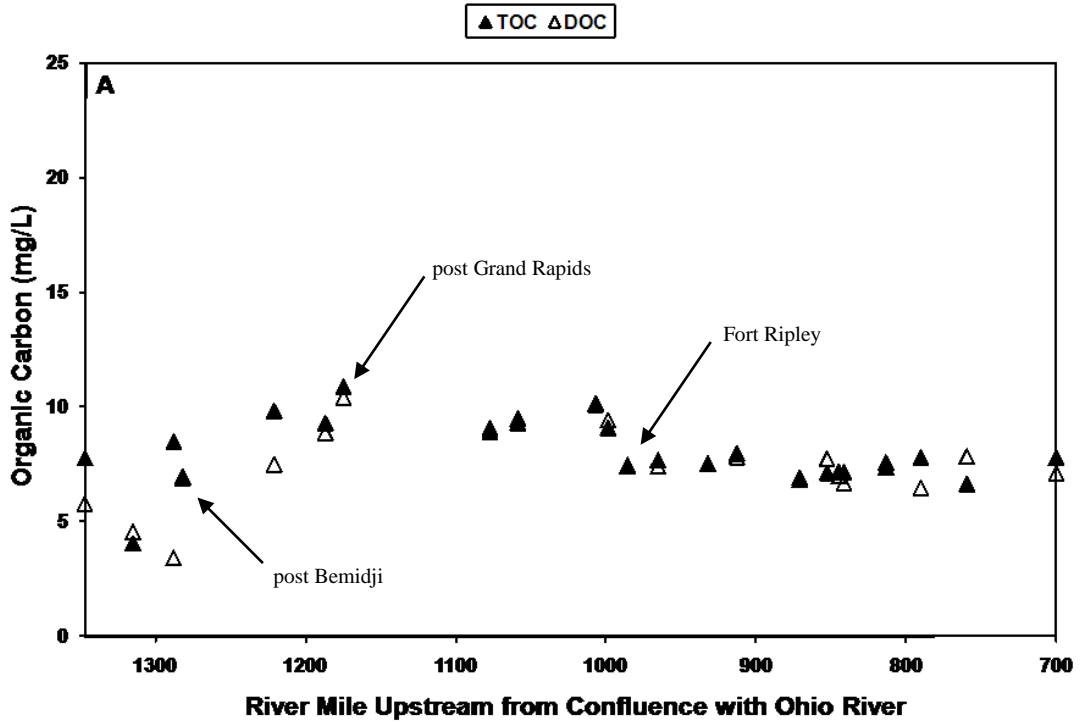
the sampling points were then developed. Major watershed boundaries were confirmed with the boundaries developed by the Minnesota Department of Natural Resources (MNDNR, 1999). The watersheds were then overlaid with Minnesota 2000 Level 1 Landsat Landcover Classification data (University of Minnesota Remote Sensing and Geospatial Lab, 2006) to estimate the contributing area of each land use within each watershed.

Stepwise regression analysis was performed using a MatLAB script to determine correlations between land uses and the measured or computed NOM descriptors. Relationships were deemed significant if the p-value was less than 0.10. This analysis was performed for all Mississippi River subwatersheds, all tributary watersheds, and all watersheds combined.

3.4 Results and Discussion

3.4.1 Spatial variability in OM concentration

TOC and DOC concentrations along the length of the Mississippi River remained relatively constant (Table 1, Figure 3-2A), despite high TOC concentrations (> 20 mg/L) in several tributaries from river mile 1109 to 1061 (Figure 3-2B). Although TOC and DOC concentrations in the Mississippi River declined initially downstream of the headwaters, they increased prior to Bemidji (river mile 1288), the first small city downstream, and peaked with a concentration of 10.9 mg/L at river mile 1175, downstream of Grand Rapids, Minnesota. Contributing sources of organic matter in this portion of the river included autochthonous production in several lakes with surface areas greater than 4 km² and treated wastewater effluent from papermills. Organic carbon concentrations decrease after the confluence with the Crow Wing River, which drains a predominantly forested watershed (49%), at river mile 993. TOC and DOC concentrations for the tributaries of the Mississippi River had a larger range and were more variable (Table 3-1) than those in the main river.



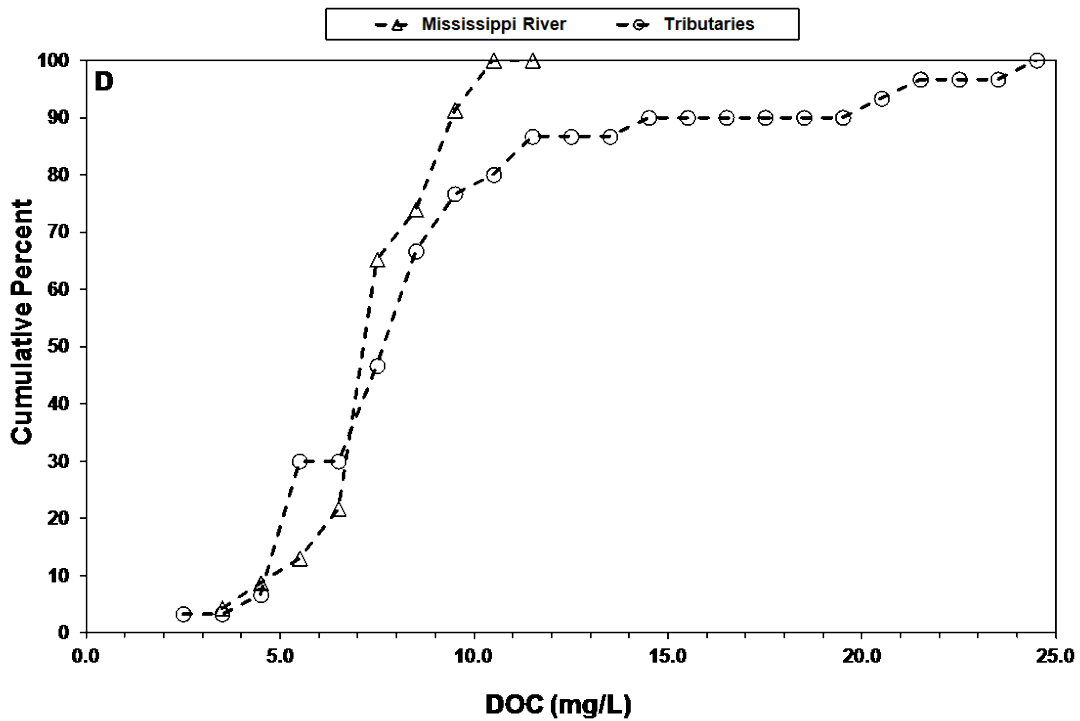
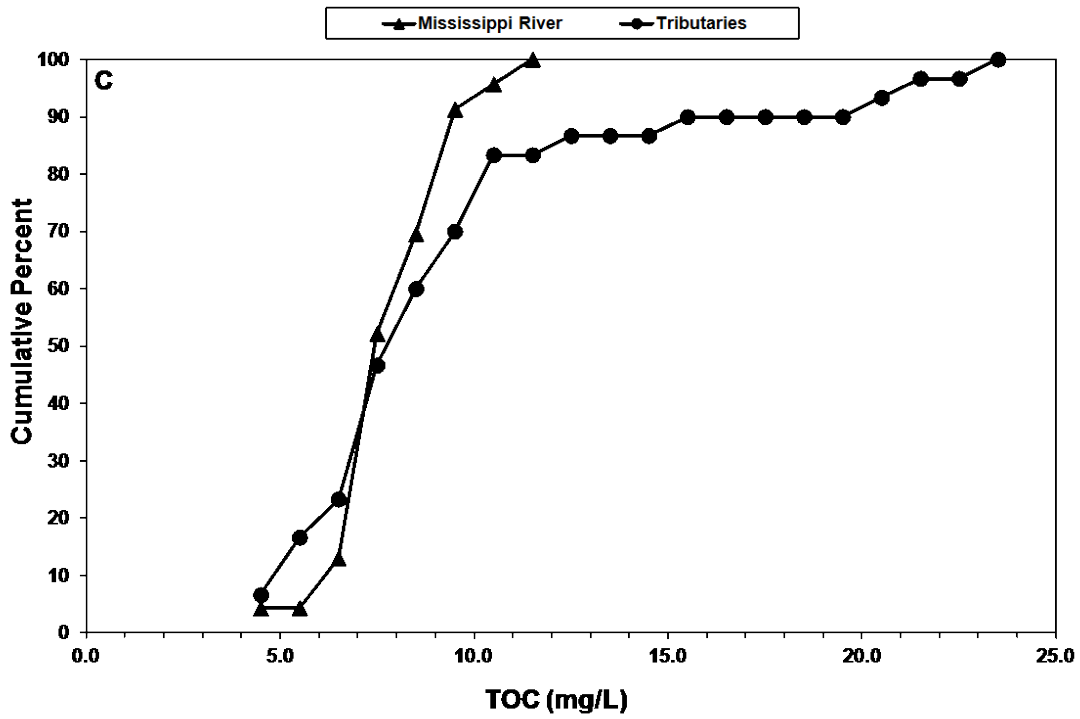


Figure 3-2. Total and dissolved organic carbon concentrations of the upper Mississippi River (A) and tributaries (B). Cumulative distribution of total (C) and dissolved (D) organic carbon concentrations of the upper Mississippi River and tributaries.

Table 3-1. Summary of water quality parameters for the Mississippi River and tributaries.

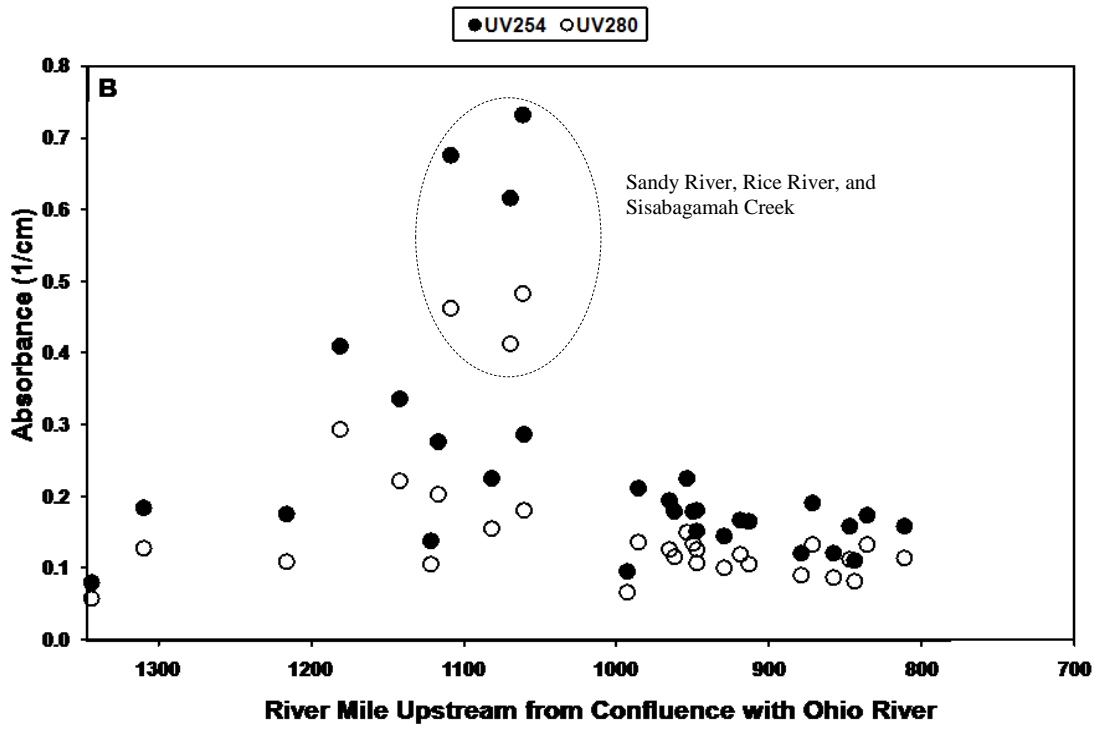
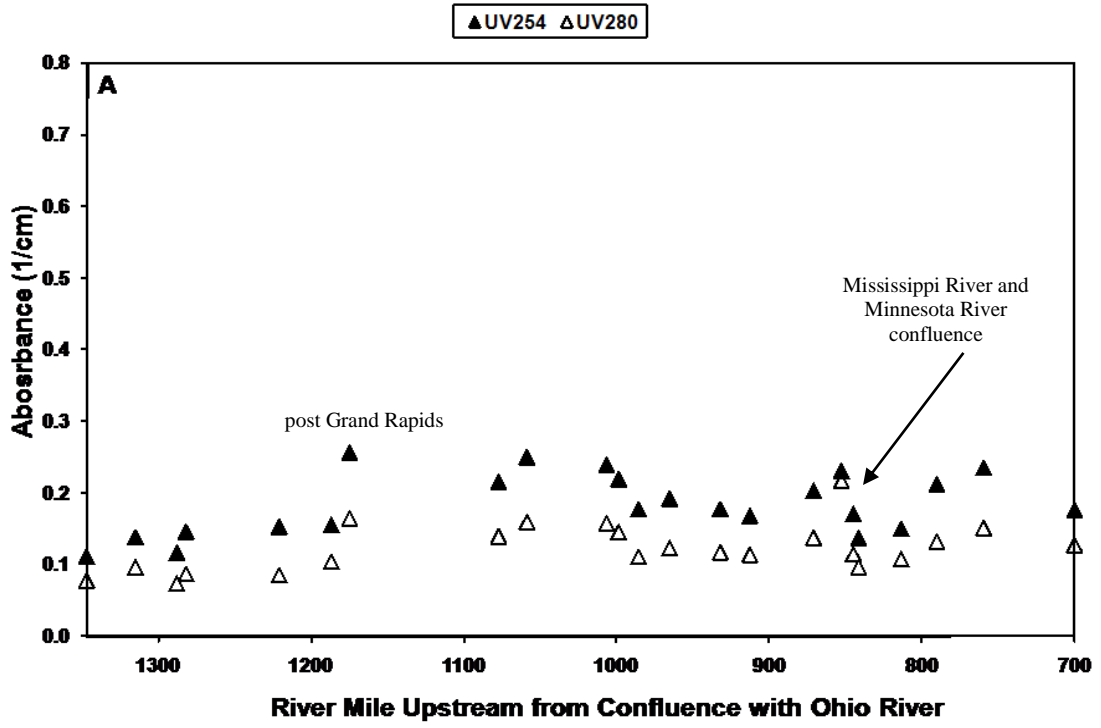
Parameter	Mississippi River (n=23)					Tributaries (n=30)				
	TOC (mg/L)	DOC (mg/L)	UV ₂₅₄ (1/cm)	UV ₂₈₀ (1/cm)	SUVA (L/mg-m)	TOC (mg/L)	DOC (mg/L)	UV ₂₅₄ (1/cm)	UV ₂₈₀ (1/cm)	SUVA (L/mg-m)
Mean	7.99	7.53	0.185	0.124	2.49	9.37	8.97	0.237	0.163	2.57
Minimum	4.07	3.46	0.112	0.073	1.76	4.31	2.84	0.081	0.059	1.53
Maximum	10.9	10.4	0.257	0.218	3.39	22.63	23.29	0.733	0.484	3.57
Standard Deviation	1.43	1.63	0.043	0.034	0.44	4.54	4.75	0.165	0.110	0.57
Coefficient of Variation, %	18	22	23	27	18	48	53	70	67	22

The mean (\pm standard deviation) ratio of DOC to TOC was $96\% \pm 15\%$, indicating that there was minimal contribution from or variation in POC. Because sampling was conducted at end of the summer during a time of low flow for the Mississippi River (46 - 132 m³/s average flow at Anoka, Minnesota) and many of its tributaries, low POC concentrations were expected. High fluxes of POC would be expected during periods of high flow initiated by storm events or snowmelt (Grubaugh and Anderson, 1989).

DOC concentrations in the Mississippi River obtained in this investigation were within the range of concentrations reported for other large rivers of the world (5 - 60 mg/L) and were at the upper range of DOC concentrations (2 - 8 mg/L) reported for rivers in temperate climates (Thurman, 1985, Schmidlin and Baur, 2007). For example, the White River in Indiana with yearly average flow of 5,600 L/s had a mean DOC of 4.00 mg/L (Volk et al., 2002). The results were also in agreement with previous studies of the Mississippi River, which reported DOC concentrations of 5.87 ± 1.96 mg/L south of New Orleans, Louisiana (Bianchi et al., 2004), 12.5 mg/L at river mile 400 near Burlington Island, Iowa (Grubaugh and Anderson, 1989) and 6.27 mg/L in Fridley, Minnesota (Semmens and Staples, 1986).

3.4.2 *Spatial variability in OM composition*

Similar to the trends observed for the TOC and DOC concentrations, UV absorbance values at both 254 nm (UV₂₅₄) and 280 nm (UV₂₈₀) for the upper Mississippi River were relatively constant (Table 3-1, Figure 3-3A). Absorbance values peaked at river mile 1175 in Grand Rapids, but a rapid decrease in absorbance values from river miles 853 to 842 occurred due to the confluence of the Mississippi and Minnesota Rivers (Mississippi River: DOC = 7.76 mg/L, flow = 114.2 m³/s; Minnesota River: DOC = 5.30 mg/L, flow = 29.8 m³/s).



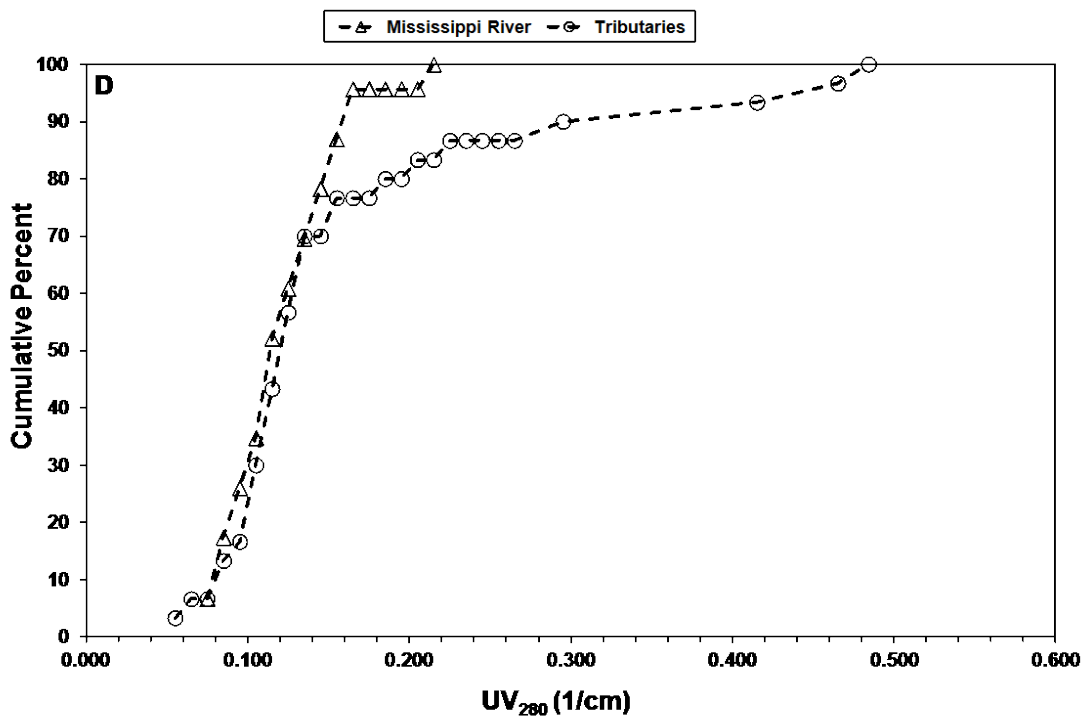
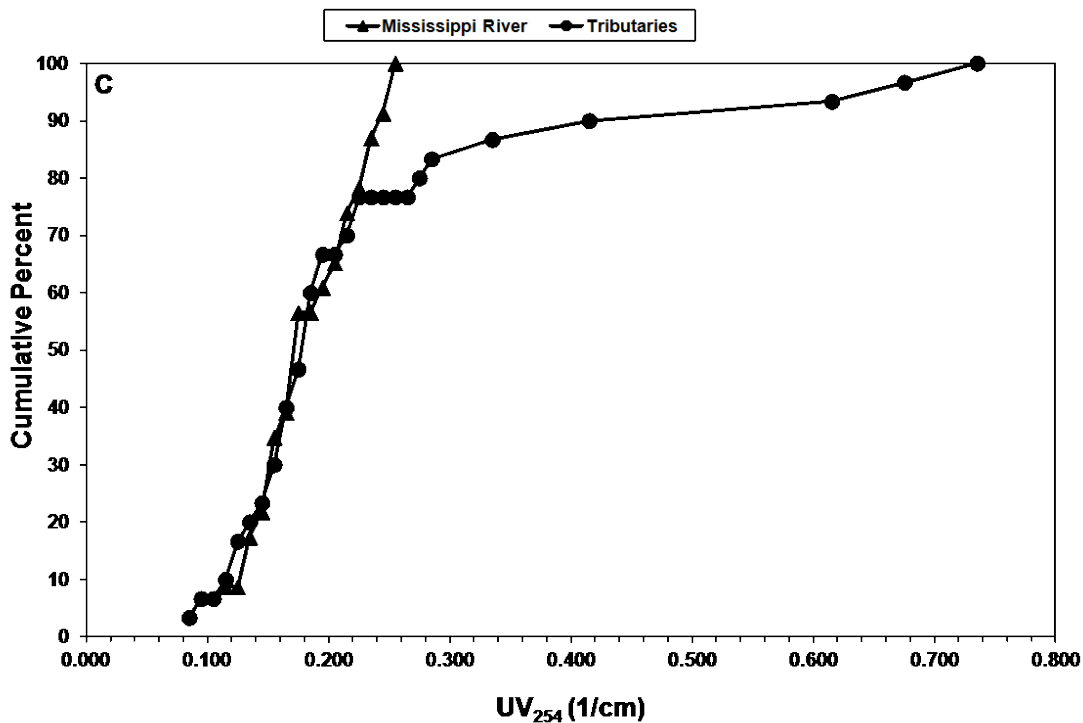


Figure 3-3. Ultraviolet absorbance at 254 and 280 nm of the upper Mississippi River (A) and tributaries (B). Cumulative distribution of ultraviolet absorbance at 254 nm (C) and 280 nm (D) of the upper Mississippi River and tributaries.

Similar to TOC and DOC, UV absorbance values at both 254 and 280 nm in the tributaries were more variable than those in the river (Table 3-1, Figure 3-3B). High UV_{254} values (> 0.6 1/cm) in several tributaries near Aitkin, Minnesota did not alter the overall absorbance of the Mississippi River because of the tributaries' relatively low flows (0.4 - 1.1 m³/s).

SUVA values for the upper Mississippi were generally between 2 and 4 L/mg-m (Figure 3-4), indicating that the NOM was of both terrestrial and aquatic origin (Karanfil et al., 2002). SUVA values in the tributaries decline going downstream from a high of 3.57 L/mg-m at Hennepin Creek (River Mile 1310). Two of the lowest SUVA values occurred at the outfalls of the St. Cloud (1.53 L/mg-m) and Twin Cities Metropolitan (1.82 L/mg-m) wastewater treatment plants. These SUVA values for wastewater effluent are in agreement with other reported values ranging from 0.99 - 1.78 L/mg-m (Shon et al., 2004; Hu et al., 2003; Her et al., 2003).

Excitation-emission matrices (EEMs) from the Mississippi River and several tributaries were generated to further analyze the composition of dissolved organic matter (DOM) and how it changed based on land use. EEMs can often be used to distinguish between water sources based on the location and magnitude (intensity) of the resulting Raman peaks in the three-dimensional graphs (Her et al., 2003). For example, groundwaters tend to have higher concentrations of aliphatic compounds compared to the more protein-like character of wastewater effluent samples (Chen et al., 2003). EEMs were performed on three Mississippi River samples from Itasca, Hastings, and La Crescent (Figure 3-5). EEMs were also performed on water samples from several tributaries, including the Prairie and St. Croix Rivers, which drain predominantly forested land areas, the Minnesota River (river mile 842), whose watershed is dominated by agricultural land uses, and the Metropolitan Wastewater Treatment Plant effluent (Figure 3-6). Peak intensity increased with distance downstream in the Mississippi River (Table 3-2). Two distinct peaks were visible in the samples. The broadest, at an excitation of 250 nm and emission of 400 – 450 nm,

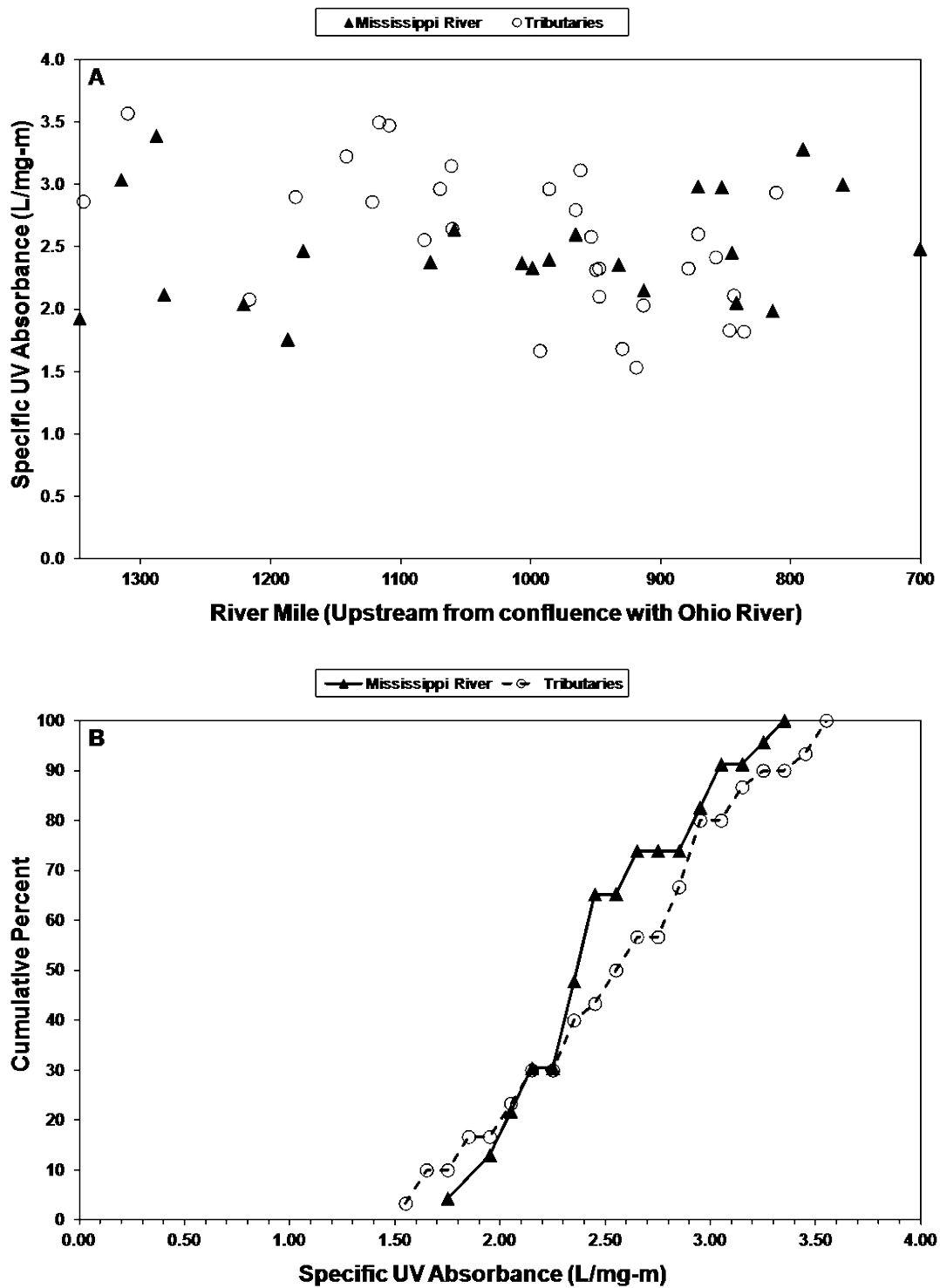


Figure 3-4. Specific ultraviolet absorbance (A) and cumulative distribution of specific ultraviolet absorbance (B) of the upper Mississippi River and tributaries

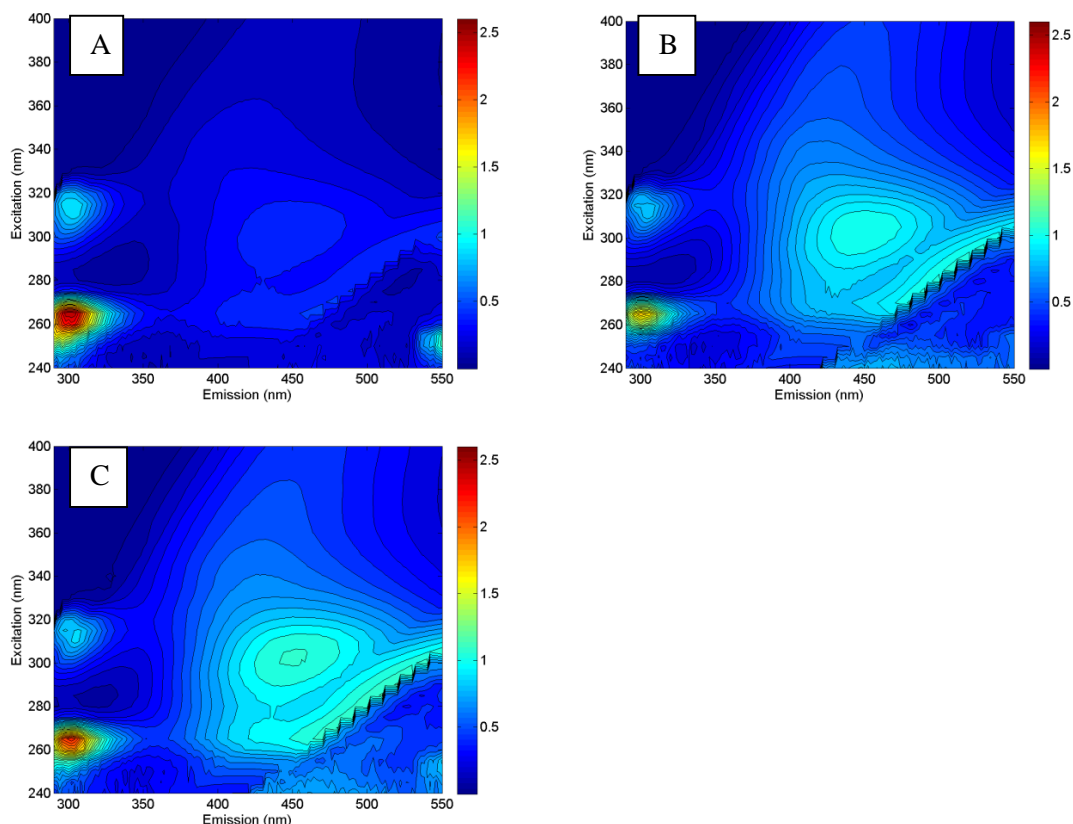


Figure 3-5. Excitation-emission matrices of the upper Mississippi River at Itasca headwaters (river mile 1347, FI = 1.49) (A), Hastings (river mile 814, FI = 1.48) (b), and La Crescent (river mile 701, FI = 1.40) (C)

indicated DOM that could be characterized as humic and fulvic acid-like while a smaller, but more intense peak at an excitation of 265 nm and emission of 294 - 310 nm indicated DOM of aquatic origin (Chen et al., 2003; McKnight et al., 2001). The peaks of the Prairie River and Metropolitan Wastewater Treatment Plant effluent EEMs representing humic and fulvic acid-like NOM are broader, representing a wider range of DOM within those waters. The fluorescence index (FI), the ratio of emission intensities at 450 and 500 nm at an excitation at 370 nm, can also be used as an indicator of the source of NOM (McKnight et al., 2001). FIs for the samples ranged from 1.32 for the Prairie River to 1.61 for the Metropolitan Wastewater Treatment Plant, indicating that the organic matter was derived from a mixture of terrestrial (~1.4) and microbial (~1.9) sources (McKnight et al., 2001).

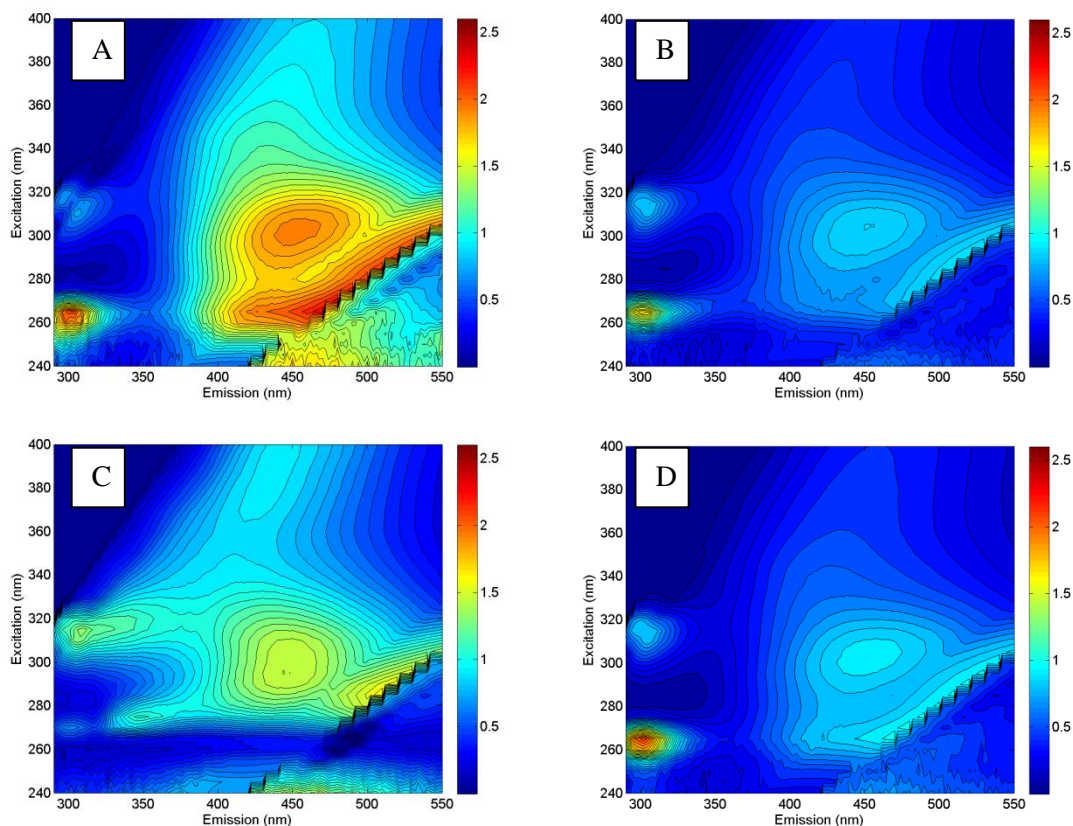


Figure 3-6. Excitation-emission matrices from selected tributaries of the upper Mississippi River: Prairie River (river mile 1181, FI = 1.32) (A), Minnesota River (river mile 844, FI = 1.45) (B), Metropolitan Wastewater Treatment Plant (river mile 836, FI = 1.61) (C), and St. Croix River (river mile 812, FI = 1.39) (D)

The EEMs of the DOM samples were modeled using parallel factor analysis (PARAFAC) to determine the approximate composition of the DOM in the water samples (Stedmon and Bro, 2008; Cory and McKnight, 2005; Stedmon et al., 2003; Mobed et al., 1998). For this analysis, thirteen reference components were used including three oxidized quinones, three reduced quinones, one hydroquinone, two amino acids, and four unknown components as identified in a model developed by Cory and McKnight (2005). Using a two-sided Student's t-test at a confidence level of $\alpha = 0.01$, the distribution of the reference components for each sampling site were compared. Most notably, the Metropolitan Wastewater Treatment Plant effluent had significantly less reduced quinone-like components and significantly more tryptophan-like,

Table 3-2. Fluorescent intensity and peak data from excitation-emission matrices for the upper Mississippi River and selected tributaries.

	River Mile	DOC (mg/L)	SUVA (L/mg-cm)	Fluorescent Intensity	Maximum Intensity (Raman)	Peak Location¹ (nm)
Mississippi River						
Itasca	1347	5.81	1.93	1.49	2.52	(302, 265)
Hastings	814.2	7.59	1.99	1.48	1.78	(300, 265)
La Crescent	700.8	7.12	2.84	1.40	2.26	(302, 265)
Tributaries						
Prairie River	1181	14.14	2.90	1.32	2.31	(470, 265)
Minnesota River	844	5.30	2.11	1.45	1.73	(302, 265)
Metropolitan WWTP	836.2	9.66	1.82	1.61	1.68	(520, 290)
St. Croix River	811.5	5.45	2.94	1.39	2.18	(302, 265)

1. Peak location is given in EEM coordinates: (emission, excitation)

tyrosine-like, and two of the three oxidized quinone components than the other samples. The higher occurrence of oxidized components is likely due to the use of chlorination for wastewater disinfection that occurs during the summer. The unique characteristics of wastewater effluent were also noted for two samples of Arizona wastewater, which contained more protein-like components, indicating soluble microbial products, than comparable surface waters (Chen et al., 2003). The EEM analysis confirms the SUVA results showing that the wastewater effluent had a substantially different OM composition than the Mississippi River or its tributaries.

3.4.3 *OM export*

Where flow could be obtained or estimated, export coefficients for TOC and DOC from the Mississippi and its tributaries were computed. At the time of sampling, DOC export was 8.8 g C/ha/day from the upper Mississippi River at Lilydale in the Twin Cities metropolitan area (Figure 3-7). Extrapolation of this value results in an estimated yearly DOC export from the upper Mississippi River basin of 3.2 kg C/ha/yr which significantly underestimates the actual annual export of the basin owing to the timing of sample collection (i.e., dry period). Using mean daily DOC and river flow data collected in 2007 by Brinkman and Hozalski (2011), the computed export of DOC from the watershed was much greater (10.1 kg C/ha/yr). This highlights the generally well known danger of extrapolating single time point values for such a dynamic system as a river in a temperate climate. The value; however, compares reasonably well with other reported export values for rivers in temperate climates of 15 kg C/ha/yr (Meybeck, 1993) and agricultural biomes of 10.84 kg C/ha/yr (Alvarez-Cobelas et al., 2012). Leenheer (1982) estimated a DOC export specifically from the Mississippi River of 11.18 kg C/ha/yr. The upper Mississippi River DOC export, however, is much lower than the average DOC export from cold conifer and deciduous forests of 38.4 kg C/ha/yr (Aitkenhead and McDowell, 2000). The latter result is not surprising given the complex mix of land uses including the predominance of agricultural and urban land uses in the southern part

of the watershed. Several tributaries in the northern part of the watershed with predominantly forested land use, including the Ripple River (66.1 g C/ha/day), exhibited much greater DOC export than those in urban (e.g., Shingle Creek at 12.7 g C/ha/day) and agricultural (e.g., Platte River (47.0 g C/ha/day) areas. This difference would likely be magnified during periods of high precipitation. Certainly, the transport of organic matter is not only a function of land used but also can be correlated with other factors such as annual precipitation, channel slope, channel width, and streambed area (Mulholland, 1997).

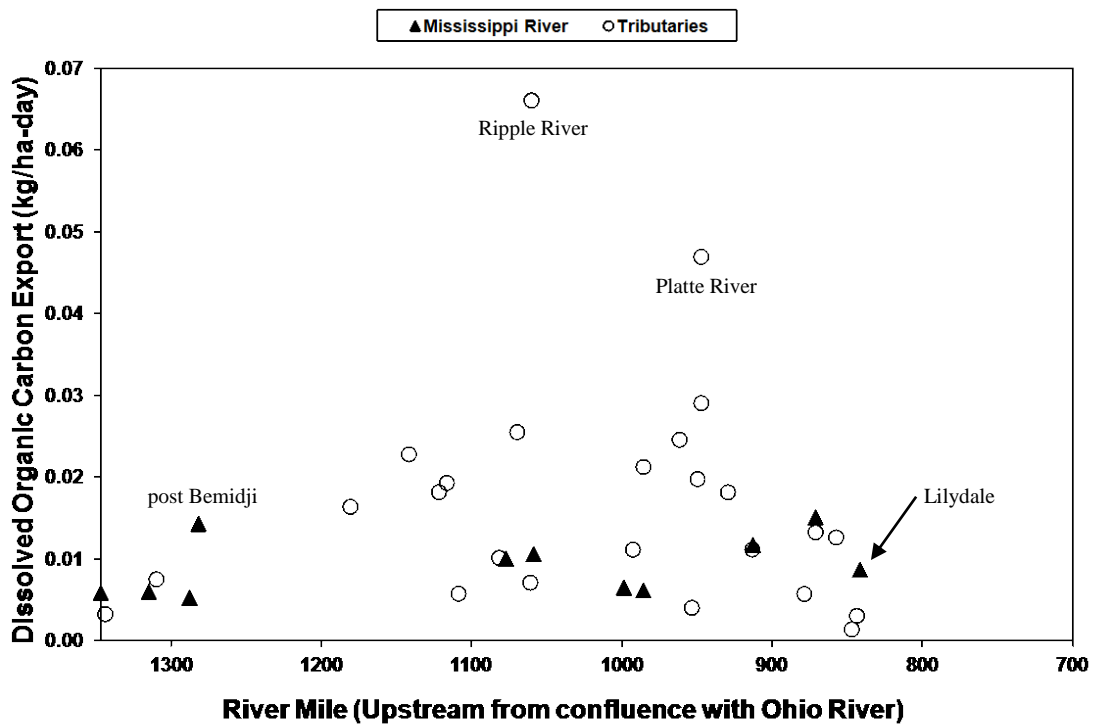


Figure 3-7. Dissolved organic carbon export from the upper Mississippi River and tributaries

3.4.4 Effect of land use on OM concentration and composition

Forest is the dominant land use in the upper Mississippi River watershed until it approaches Little Falls, Minnesota at river mile 986. At this location, row crop agriculture begins to dominate the local watersheds although the dominant land use for the combined upper Mississippi River

remains forest. Wetlands also comprise up to 27% of land use in the northern portions of the watershed. Following the confluence with the Minnesota River, which has a watershed area of 44,000 km² that is comprised of 65% agricultural lands, the dominant land use of the Mississippi River becomes agriculture. Although urban land uses dominate some of the sub-watersheds in the southern part of the state, urban land uses comprise less than 8% of the total watershed of the Mississippi River in Minnesota.

For all of the studied watersheds, TOC, DOC, UV₂₅₄, and UV₂₈₀ were negatively correlated with the percent of agricultural land (Table 3-3). SUVA was negatively correlated with the percents of grassland and water areas. TOC, DOC, UV₂₅₄, UV₂₈₀, and organic carbon export were positively correlated with the percent of shrubland area. Regression equations were generated from the stepwise analysis of the data as shown below. The resulting equations explain 15 – 37% of the variation in the specified water quality parameters:

$$\text{TOC (mg/L)} = 8.25 - 0.0600*(\% \text{ agricultural area}) + 1.5787*(\% \text{ shrubland area}) \quad (1)$$

$$\text{DOC (mg/L)} = 6.12 - 0.0550*(\% \text{ agricultural area}) + 1.8514*(\% \text{ shrubland area}) \quad (2)$$

$$\text{UV}_{254} \text{ (1/cm)} = 0.18 - 0.0023*(\% \text{ agricultural area}) + 0.0732*(\% \text{ shrubland area}) \quad (3)$$

$$\text{UV}_{280} \text{ (1/cm)} = 0.12 - 0.0015*(\% \text{ agricultural area}) + 0.0482*(\% \text{ shrubland area}) \quad (4)$$

$$\text{SUVA (L/mg-m)} = 3.09 - 0.1568*(\% \text{ grassland area}) - 0.0474*(\% \text{ water area}) \quad (5)$$

$$\text{TOC Export (kg C/ha/yr)} = -13.38 + 19.5853*(\% \text{ shrubland area}) \quad (6)$$

$$\text{DOC Export (kg C/ha/yr)} = -12.45 + 18.3221*(\% \text{ shrubland area}) \quad (7)$$

Forest, urban, and wetland land uses had no significant influence on the concentration and composition of OM. A similar study of the New York City drinking water supply watersheds found positive correlations between DOC and wastewater discharge, wetland area, grassland area, and orchard area and a negative correlation between forest area and DOC (Kaplan et al., 2006). Forest lands typically export relatively high OM loads (Aitkenhead and McDowell, 2000; Cronan et al., 1999) and OM with higher aromaticity (e.g., lignin-like) in comparison to

Table 3-3. Stepwise regression coefficients, p-values, constant, and r-squared values relating percent land use and total (TOC) and dissolved organic carbon (DOC), ultraviolet absorbance at 254, specific ultraviolet absorbance (SUVA), and yearly TOC and DOC export for the upper Mississippi River and selected tributaries. Significant coefficients and p-values are in bold.

	Urban	Agriculture	Grass	Forest	Water	Wetland	Shrub	Constant (r ²)
TOC	-0.0286 p = 0.565	-0.600 p = 0.037	0.383 p = 0.463	.00254 p = 0.956	0.0646 p = 0.611	0.0253 p = 0.798	1.58 p = 0.015	8.24 (0.193)
DOC	-0.0175 p = 0.743	-0.0550 p = 0.066	-0.332 p = 0.336	0.0313 p = 0.189	0.166 p = 0.175	0.0539 p = 0.606	1.851 p = 0.008	6.12 (0.150)
UV₂₅₄	-4.78*10 ⁻⁴ p = 0.782	-0.00229 p = 0.023	7.84*10 ⁻⁴ p = 0.966	5.06*10 ⁻⁵ p = 0.975	-0.00264 p = 0.549	0.00282 p = 0.411	0.0732 p = 0.002	0.180 (0.269)
UV₂₈₀	-2.12*10 ⁻⁴ p = 0.858	-0.00145 p = 0.035	0.00248 p = 0.843	2.61*10 ⁻⁵ p = 0.981	-0.00243 p = 0.422	0.00182 p = 0.438	0.0481 p = 0.002	0.122 (0.248)
SUVA	-0.00469 p = 0.415	-0.00928 p = 0.124	-0.157 p < 0.001	0.00486 p = 0.253	-0.0474 p = 0.001	0.0120 p = 0.224	0.121 p = 0.105	3.09 (0.374)
TOC Export	0.187 p = 0.616	0.103 p = 0.632	-1.13 p = 0.643	-0.101 p = 0.549	-1.13 p = 0.190	0.872 p = 0.232	19.6 p < 0.001	-13.4 (0.285)
DOC Export	0.176 p = 0.613	0.0887 p = 0.658	-1.11 p = 0.627	-0.0908 p = 0.565	-1.08 p = 0.177	0.847 p = 0.213	18.3 p < 0.001	-12.4 (0.286)

other land uses (Grieve et al., 1990). Despite increasing urbanization proceeding downstream, urban land uses did not appear to exert a major influence on OM concentration and composition in the upper Mississippi River. Hatt et al. (2004), however, observed a strong positive correlation between DOC concentration and percent impervious surface for small streams near Melbourne, Australia. The rationale is that impervious surfaces together with urban drainage systems, which are typically designed to collect and rapidly transport stormwater runoff to local surface waters, facilitate rapid movement of NOM with little opportunity for adsorption or transformation as might occur in the soil matrix of a non-impacted watershed (Hatt et al., 2004). The lack of a significant effect of urban land use is partly due to the rather small fraction of urban land in this large watershed (< 8%). Furthermore, the lack of correlation between some land uses, such as forest and urban, and OM concentration and composition may be a result of the time of sampling. Samples were taken over a period of two months in late summer - early fall when there was little rainfall in the watershed and the streams and rivers had low discharges. As a result, OM contributions were mainly from base flow, autochthonous production, or a combination of the two.

3.5 Implications

The established correlations between land use and OM parameters allow us to predict how downstream processes may be affected by upstream conditions. Chin et al. (1994) formed empirical links between molar absorptivity at 280 nm and the molecular weight and percent aromaticity of NOM. These correlations suggest that as molar absorptivity at 280 nm decreases with increasing percents of agriculture land use or decreasing amounts of shrubland, OM molecular weight and aromaticity will decrease, resulting in OM that is more hydrophilic, degradable, and bioavailable. Some studies have found smaller, more hydrophilic molecules to be the primary

cause of water treatment membrane fouling (Lee et al., 2004; Park et al., 2006). In particular, hydrophilic NOM - hydrophilic membrane and hydrophobic NOM - hydrophobic membrane pairings are susceptible to fouling because the charge of membrane surface groups are neutralized rapidly with more aliphatic NOM (Cho et al., 1998). Land use and its effects on OM composition must therefore be a factor when considering downstream water treatment options.

One limitation of this study was that it was performed during a single late summer - early fall time period. More research is needed to observe if the correlations between agricultural and shrubland land uses and OM concentration and composition holds for wetter and more variable water flow conditions in the complex upper Mississippi River system. In addition, differentiation between row crops, hay pasture, and animal grazing may more accurately define the influence of agricultural land use on water NOM.

3.6 Conclusion

The Mississippi River and selected tributaries in Minnesota were sampled over two months in late summer to determine the spatial variation of NOM concentration and composition. Although the Mississippi River flows for 640 miles and the predominant land use in the watershed changes from forest to agriculture as it passes through the state of Minnesota, TOC and DOC concentrations and NOM composition, as determined by SUVA and fluorescence spectroscopy, were relatively stable. Much more variability in NOM concentration and composition was observed in the tributary samples. NOM concentration and SUVA were negatively correlated with percent of agricultural land use in the watershed, most likely due to increased autochthonous production of more labile NOM compounds stimulated by nutrient inputs. NOM concentration and export were positively correlated with the percent of shrubland area in the watershed. These correlations suggest that upstream land use and resulting NOM characteristics and composition must be considered when planning engineering or water management projects downstream.

3.7 Acknowledgements

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Chapter 4

Temporal Variations in Organic Carbon Concentration and Composition in the Upper Mississippi River and Effects on Membrane Filtration

4.1 Executive Summary

Seasonal water samples from the upper Mississippi River at Fridley, Minnesota were collected before and after pretreatment at the Minneapolis Water Works. Batch filtration experiments were performed using a stirred-cell device to determine the impact of pretreatment and seasonal water quality changes on membrane fouling. Four ultrafiltration membranes were selected representing a range of different materials, molecular weight cutoffs, and hydrophobicities. Lime softening followed by coagulation, flocculation, and sedimentation reduced the average fouling of the membranes, as measured by permeability decline, for the spring, summer, and autumn by 35.0, 47.5, and 12.0%, respectively. The most hydrophilic membrane experienced the least decline in permeability (3.1%) across all seasons compared to the more hydrophobic membranes (4.0 - 14.8%). Furthermore, the unfractionated raw and settled waters fouled the membranes more than International Humic Substances Society standards prepared in carbonate buffer due to increased interactions between hydrophobic and hydrophilic compounds. Excitation-emission matrices for the seasonal waters indicated that humic and fulvic-acid like natural organic matter (NOM) was predominant, but hydrophilic, soluble microbial byproduct-type NOM increased during the coagulation process due to oxidation. The results suggest that lime softening followed by filtration using hydrophilic membranes may be best processes for treating upper Mississippi River water.

4.2 Introduction

Natural organic matter (NOM) in surface waters presents a challenge to water utilities, especially those employing membranes for filtration, as it can foul membranes by absorbing to the membrane surface and plugging pores as well as forming organic-cation complexes that lead to cake formation on the membrane surface (Goosen et al., 2004). Membrane-foulant interactions are influenced by the properties of the membrane (e.g., surface roughness, contact angle, zeta potential, molecular weight cutoff or MWCO), NOM concentration and composition (e.g., hydrophobicity, molecular weight), and general water quality parameters (i.e., pH, temperature, ionic strength, and turbidity) (Fan et al., 2001). The forces controlling these interactions between membranes and foulants include permeation drag, van der Waals, acid-base attractive, electrostatic forces, hydrogen bonding, and hydrophobic interactions (Lee et al., 2006). As water utilities install membranes to meet drinking water quality regulations, the role of membrane and NOM hydrophobicity in relation to the character and degree of NOM fouling has significant implications. Both hydrophobic (Violleau et al., 2005) and hydrophilic (Lee et al., 2004; Park et al., 2006) molecules have been suggested as the primary cause of fouling and both can alter the hydrophobicity, surface functional groups, and isoelectric point of a membrane (Cho et al., 1998; Violleau et al., 2005). The hydrophobic fraction of NOM is typically comprised of molecules with larger molecular weights and greater aromaticities than the hydrophilic fraction (Fan et al., 2001; Pontie et al., 2007). As a result, hydrophobic membranes fouled with hydrophobic NOM are more likely to experience rapid and permanent flux declines as the hydrophobic interactions create low permeability gel layers on the membrane surface or adsorb strongly within the membrane pore structure (Pontie et al., 2007). Thus, hydrophilic membranes have been recommended for treating waters with high concentrations of hydrophobic NOM (Kabsch-Korbutowicz et al, 1999; Schäfer et al., 2000).

A major complication in dealing with NOM fouling is that NOM concentration and composition is a moving target, exhibiting significant spatial and temporal variability. The

concentration and composition of NOM in a water body at a given location and time results from a complex series of processes including inputs from the land surface of allochthonous NOM, production of autochthonous NOM within the water body, transport processes, and transformation and loss processes (Thurman, 1985; Hope et al., 1994). NOM concentration and composition varies spatially due to differences in climate, topography, land use, precipitation, and soil type. Temporal variations in NOM concentration and composition have been linked to precipitation events and daily cycles in the short term (hours), seasonal weather changes at intermediate time scales (weeks to months), with changes in land use and climate the likely drivers at longer time scales (years to decades).

In temperate climates, the concentration and composition of NOM in surface waters varies throughout the year, especially in response to seasonal changes in precipitation, sunlight, and temperature (Hope et al., 1994; Mulholland, 1997). For example, total organic carbon (TOC) concentrations in the Rhode River watershed in Maryland varied from a low of 5.11 mg/L in the winter to a high of 12.80 mg/L in the summer (Correll et al., 2001). Surface runoff is a significant contributor to variations in NOM concentration and composition as runoff transports allochthonous NOM into surface waters (Hope et al., 1994). Changes in DOC inputs are frequently linked to non-precipitation driven events such as leaves dropping in the autumn and primary production (Hope et al., 1994; Meyer et al., 1998). In some cases, increases in autochthonous production during warm summer months can be offset by increases in the rates of biodegradation or photolysis (Neff and Asner, 2001).

This seasonal variation of NOM in a surface water can present some issues for membrane pretreatment processes in water treatment plants. Semmens and Staples (1986) studied the effects of various pretreatment strategies on organic removal from Mississippi River water. They and others found that alum and lime dosing resulted in the preferential removal of hydrophobic, high molecular weight NOM (Chen et al., 2007); however, control of the

coagulation/flocculation/sedimentation process (i.e. pH, dosage, and settling time) is critical to ensure large floc formation and removal (Choksuchart et al., 2006; Randtke, 1988). Pretreatment processes are often optimized to reduce the formation of disinfection by-products following chlorination, but may not remove all of the fractions responsible for membrane fouling (Chen et al., 2007; Howe and Clark, 2006).

Although seasonal changes in NOM concentration and composition in the Mississippi River near Minneapolis can be tracked from utility weekly grab samples, experimental knowledge on how the NOM is altered through the treatment process and whether those changes are significant from a treatment perspective is required. The overall goal of this research was thus to investigate seasonal variations in the concentration and characteristics of NOM in the upper Mississippi River through grab samples and the effects of these variations on treatability, specifically softening and membrane filtration.

4.3 Materials and Methods

4.3.1 Sampling site

Sampling of the Mississippi River was done at the Minneapolis Water Works (MWW) treatment facility located in Fridley, Minnesota, USA. At that location, the river has an average daily flow of approximately 178,000 L/s and ranges from 40,000 to 682,000 L/s. The MWW supplies water to over 100,000 service connections in Minneapolis and several neighboring cities. The MWW treats water from the Mississippi River by lime softening followed by coagulation/flocculation/sedimentation before directing it to one of two filtration plants with a combined capacity of 180 million gallons per day (MGD).

4.3.2 Analytical methods

At four times during the year, raw water samples were collected from the MWW intake and at three times during the year, settled water samples were collected from the effluent of the sedimentation basins at the MWW. At each sampling time, water samples were collected in two five-gallon polyethylene containers, which had been cleaned by soaking for one hour in a 10% solution of reagent grade sodium persulfate (Sigma Aldrich, St. Louis, Missouri, USA).

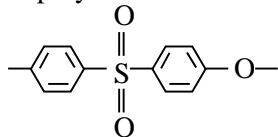
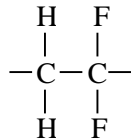
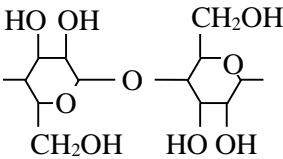
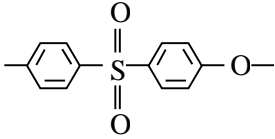
Upon return to the laboratory, the water samples were immediately analyzed for total organic carbon then filtered through baked glass microfiber filters with an average pore size of 0.7 μm (Whatman, Psicataway, New Jersey, USA) to remove particulates. The filtered water samples were stored at 4°C for a maximum of one week before being analyzed for dissolved organic carbon. Organic carbon measurements were made using a Sievers 900 Portable TOC Analyzer (GE Analytical Instruments, Boulder, Colorado, USA) that was calibrated with dilutions of a standard potassium hydrogen phthalate solution (Sigma Aldrich, St. Louis, Missouri, USA). UV/Vis light absorbance scans from 200 – 600 nm were obtained for filtered samples using a UV-1601PC UV-Visible spectrometer (Shimadzu Scientific Instruments, Inc., Columbia, Maryland, USA).

Fluorescent spectroscopy was performed on all water samples. Water samples were filtered through 0.2 μm nitrocellulose membrane filters (Millipore Corporation, Billerica, Massachusetts, USA) and stored in organic carbon-free glassware prepared as described above. Excitation-emission matrices (EEMs) were generated on a Fluoromax-3 fluorometer (Horiba Instruments, Irvine, California, USA). The excitation range was 240 – 400 nm with an interval of 5 nm while the emission range was 290 – 550 nm with an interval of 2 nm. The raw scans were adjusted according to baseline scan accounting for Raman scattering, variations in lamp intensity, and for cuvette imperfections. Contour plots representing the resulting matrix were created using a MatLAB (The Mathworks, Inc., Natick, Massachusetts, USA) script.

4.3.3 Membrane filtration

Filtered water samples were stored at 4°C until fouling experiments could be performed. Four flat-sheet ultrafiltration membranes of various materials and properties (Table 4-1) were soaked overnight in ultrapure water from a Milli-Q Q-Gard 2 System (Millipore Corporation, Billerica, Massachusetts, USA) then placed in an Amicon 8200 stirred cell with a bottom surface area of 28.7 cm² (Millipore Corporation, Billerica, Massachusetts, USA). The membranes were then flushed with additional ultrapure water. To establish an initial clean water flux for the new membrane, 75 mL of ultrapure water was filtered through the membrane. The test water (200

Table 4-1. Properties of membranes tested in fouling experiments

Membrane	Material	MWCO (kDa)	Contact Angle (°)	Source
K-131	polyether sulfone 	30	50.9	Koch Membrane Systems
M-100	polyvinylidene fluoride 	75	68.8	Koch Membrane Systems
YM30	regenerated cellulose 	30	22.6	Millipore
PM30	polyether sulfone 	30	47.9	Millipore

mL) was then placed in the stirred cell and approximately 150 mL was filtered through the membrane. Then, 75 mL of ultrapure water was filtered through the membrane to determine the final clean water flux for the fouled membrane. A constant stirring speed of approximately 120 rpm was maintained during all filtration runs. Flux was determined by measuring the mass of permeate over time using a Mettler Toledo PG-S Balance with integrated BalanceLink software (Mettler Toledo Incorporated, Worthington, Ohio, USA). Constant pressure in the stirred cell (0.5 to 3.8 bar, depending on the membrane, for a flux of approximately 0.03 L/m²-s) was maintained during the filtration experiments with a nitrogen cylinder and regulator. The permeability was calculated by dividing the flux by the applied pressure and the initial and final clean water permeabilities were compared to determine the percent permeability decline for each fouling experiment. At the end of the test water run, the retentate and permeate were analyzed for organic carbon concentration and light absorbance using the instrumentation described previously. Two or three trials were performed with each membrane and each water.

Filtration experiments were also performed with Suwannee River whole NOM (SRNOM, Catalog No. 2R101N), Suwannee River humic acid (SRHA, Catalog No. 2S101H), Suwannee River fulvic acid (SRFA, Catalog No. 1S101F), and Pony Lake fulvic acid (PLFA, Catalog No. 1R109F) standards purchased as dried powders from the International Humic Substances Society (IHSS, St. Paul, Minnesota). The Suwannee River is a black river in Georgia while Pony Lake is an Antarctic Lake containing only autochthonous NOM. For these experiments, the NOM standards were dissolved to a concentration of 10 mg/L of carbon in a carbonate buffer solution that mimics a natural water with 0.5 mM CaCl₂, 1 mM NaHCO₃, and 20 mM NaCl (Schäfer et al., 2001). The filtration procedure described above was modified slightly to prevent NOM desorption during the fouling experiment by adding a filtration run of 150 mL with the carbonate buffer between the initial clean water flux and test water run and again between the test water run and final clean water flux to minimize membrane-buffer chemical interactions.

The hydrophobicities of the membranes were determined by the sessile drop method on an Automatic Microscopic Contact Angle, Model MCA-3 (Kyowa Interface Science Company, Ltd., Tokyo, Japan). Images were captured every 67 milliseconds for 2 seconds and the contact angle was calculated using the ‘tangent’ method by placing three data points on each side of the droplet on the first image after settlement and measuring the angle formed with the membrane surface.

4.4 Results and Discussion

4.4.1 Water quality parameters of IHSS standards

The four IHSS standards prepared in carbonate buffer exhibited a range of characteristics typical of Pony Lake and the Suwannee River (Table 4-2). Measured DOC and UV₂₈₀ values were used to estimate the molecular weight and aromaticity of the NOM from the correlations developed by Chin and co-workers (1994) with the SRHA having the highest calculated molecular weight and aromaticity as expected (Sensei, 1993). Values for molecular weight are comparable to those determined through high-pressure size exclusion chromatography (SRHA: 3305 - 3409 Daltons, SRFA: 2310 Daltons, SRNOM: 2190 – 2310 Daltons, PLFA: 1260 – 1470 Daltons) (Chin et al., 1994; Her et al., 2002; Brown et al., 2004) while values for aromaticity are equivalent to those determined through ¹³C-NMR (SRHA: 31%, SRFA: 24%, SRNOM: 23%, PLFA: 12%) (Thorn et al., 1989). As expected, the SRFA absorbance spectrum lacked a shoulder at 280 nm, which is characteristic of OM derived from more mineral soils (Baes and Bloom, 1990). The SRNOM and SRFA have similar characteristics because whole NOM in most surface waters is comprised of approximately 80 - 90% fulvic acid (Thurman, 1985). The specific UV absorbance (SUVA), aromaticity, molecular weight were lowest for the PLFA sample as its NOM is primarily derived from autochthonous production and thus has less aromatic carbon and more aliphatic carbon.

Table 4-2. Water quality parameters for IHSS NOM standards in carbonate buffer

Sample	UV₂₅₄ (1/cm)	UV₂₈₀ (1/cm)	DOC (mg/L)	SUVA (L/mg-m)	Molecular Weight¹ (g/mol)	Aromaticity¹ (%)	Conductivity (uS)	pH	Fluorescent Index	Relative Intensity	Peak Location² (nm)	C/N Ratio³
Suwannee River Humic Acid	0.591	0.483	10.7	5.54	2657	34	17.61	7.23	1.05	1.49	(540, 300)	45
Suwannee River Fulvic Acid	0.401	0.303	10.3	3.89	1896	24	19.02	7.26	1.27	1.99	(530, 295)	73
Suwannee River Whole NOM	0.355	0.278	9.55	3.72	1884	24	15.57	7.40	1.24	1.44	(530, 295)	40
Pony Lake Fulvic Acid	0.249	0.191	9.51	2.62	1452	19	16.27	7.60	1.61	1.63	(530, 295)	8

1. Per relationships developed by Chin et al., 2004
2. Peak location is given in EEM coordinates: (emission, excitation)
3. Huffman Laboratory data published by the IHSS

Excitation-emission matrices (EEMs) of the IHSS standards in carbonate buffer were generated to further analyze the composition of the organic matter (Figure 4-1). For all of the samples, broad peaks at (450 - 500, 300), (450 - 500, 240), and (540, 295) indicated that the majority of the NOM could be characterized as humic and fulvic acid-like. Previous studies of humic standards have consistently found these fluorophores in aquatic NOM samples (Patel-Sorrentino et al., 2002; McKnight et al., 2001; Coble, 1996) and more specifically in IHSS standard and reference humic substances (Takacs and Alberts, 2013; Cory et al., 2010; Chen et al., 2003; McKnight et al., 2001; Mobed et al., 1996). A secondary peak at approximately (300, 265) showed the presence of microbial byproducts (Chen et al., 2003). The fluorescence index (FI), the ratio of emission intensities at 450 and 500 nm at an excitation at 370 nm can also be used as an indicator of terrestrial (~1.4) or microbial (~1.9) NOM sources (McKnight et al., 2001). FIs for the IHSS samples ranged from 1.05 (SRHA) to 1.61 (PLFA), indicating that the organic matter was derived from primarily terrestrial sources with microbial sources more important in the PLFA sample. Aquatically derived fulvic acids typically have peaks at lower emissions than terrestrially derived fulvic acids and previous studies have reported a range of FI values (1.46 - 1.7) for PLFA and (Cory et al., 2010; McKnight et al., 1994).

4.4.2 Water quality parameters of seasonal waters

NOM in the Mississippi River grab samples collected for the membrane filtration experiments displayed distinct seasonal trends (Table 4-3). TOC concentrations in the raw water samples were lowest in the winter (6.33 mg/L) and higher during the spring, summer, and autumn (12.4, 11.2, and 12.7 mg/L, respectively). Lime softening and pretreatment reduced TOC

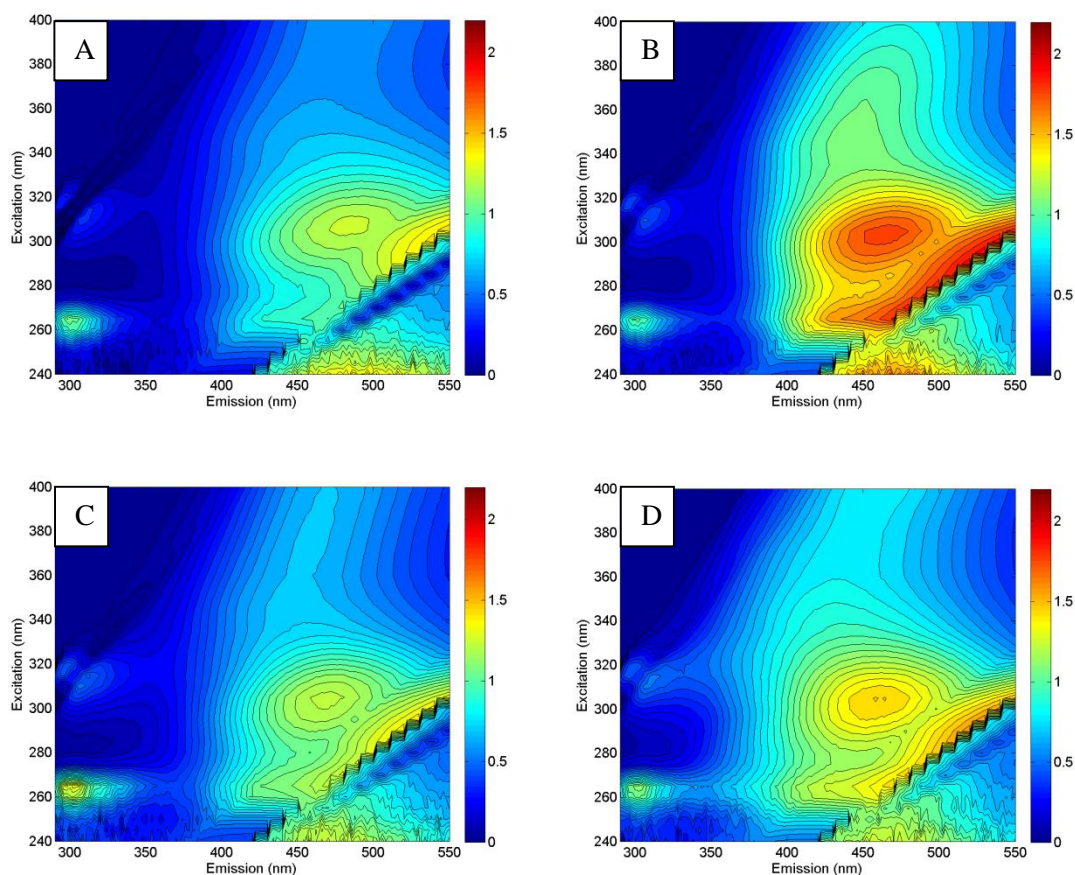


Figure 4-1. Excitation-Emission Matrices in units of relative intensity of IHSS Standards NOM Samples (10 mg C/L) in Carbonate Buffer from Suwannee River Humic Acid, FI = 1.05 (A), Suwannee River Fulvic Acid, FI = 1.27 (B), Suwannee River Whole NOM, FI = 1.24 (C), and Pony Lake Fulvic Acid, FI = 1.61 (D)

concentrations by 20 – 34% and DOC concentrations by 6 – 49%. Aromatic NOM was preferentially removed during pretreatment, with a 93 – 99% decrease in UV₂₅₄ absorbance observed. For a northern England water treatment plant, when the fulvic acid portion of the DOC increased from 36 to 61%, the coagulant demand increased due to the high charge density of the fulvic acid fraction and pretreatment preferentially removed the hydrophobic fraction of NOM (Sharp et al., 2006; Randtke, 1988). Semmens and Staples (1986) performed lime softening and

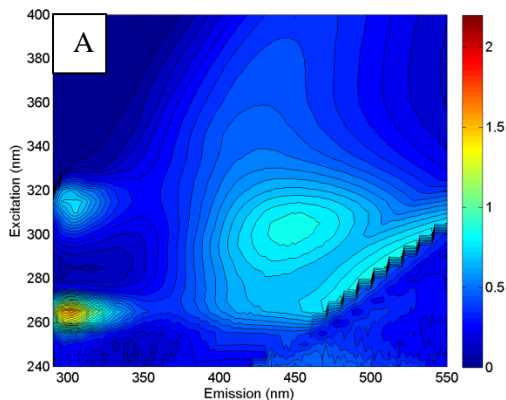
Table 4-3. Water quality parameters for seasonal water samples from the upper Mississippi River

Sample	Date	UV₂₅₄ (1/cm)	UV₂₈₀ (1/cm)	TOC (mg/L)	DOC (mg/L)	SUVA (L/mg-m)	Molecular Weight (g/mol)	Aromaticity (%)	Conductivity (uS)	pH	Fluorescent Index	Maximum Intensity (Raman)	Peak Location¹ (nm)
Winter Raw	2/7/07	0.118	0.083	6.33	5.39	2.19	1227	16	8190	8.19	1.52	1.63	(302, 265)
Spring Raw	4/30/07	0.325	0.239	12.4	11.6	2.80	1475	19	7960	7.96	1.35	2.19	(520, 290)
Spring Settled	4/30/07	0.096	0.061	8.24	7.67	1.25	871	12	7580	7.58	1.77	1.84	(302, 265)
Summer Raw	8/17/07	0.143	0.102	11.2	8.80	1.63	1045	14	7640	7.64	1.50	1.70	(302, 265)
Summer Settled	8/17/07	0.060	0.036	8.14	4.51	1.33	872	12	7460	7.46	1.88	1.71	(304, 265)
Autumn Raw	10/15/07	0.203	0.146	12.7	8.32	2.44	1330	17	8110	8.11	1.42	1.35	(450, 305)
Autumn Settled	10/15/07	0.075	0.047	10.1	7.82	0.96	778	10	7820	7.82	1.81	1.97	(302, 265)

1. Peak location is given in EEM coordinates: (emission, excitation)

recarbonation on a 200 L sample of Mississippi River water withdrawn at the same location as this study and reported TOC removal of 4.21% and UV_{254} removal of 52% during pretreatment for initial values of 4.21 mg/L and 0.406 1/cm, respectively. Conductivity decreased after treatment and was the lowest in the summer sample. pH was controlled by the Minneapolis Water Works for optimal treatment of the raw water.

Excitation-emission matrices (EEMs) were created for these seasonal Mississippi River samples to further analyze the composition of dissolved organic matter (DOM) and how it changed over time and from pretreatment (Figure 4-2). For all of the samples, broad peaks at (450 - 500, 300), (450 - 500, 240), and (540, 295) indicated that the NOM could be characterized as humic and fulvic acid-like without much influence from microbial byproducts (Chen et al., 2003). Relative intensity decreased after treatment as total DOM was removed, but the FI increased by an average of 28%, indicating a relative increase in microbially derived NOM. Seasonal trends were not as pronounced, but FI peaked for the raw water samples in the winter and summer.



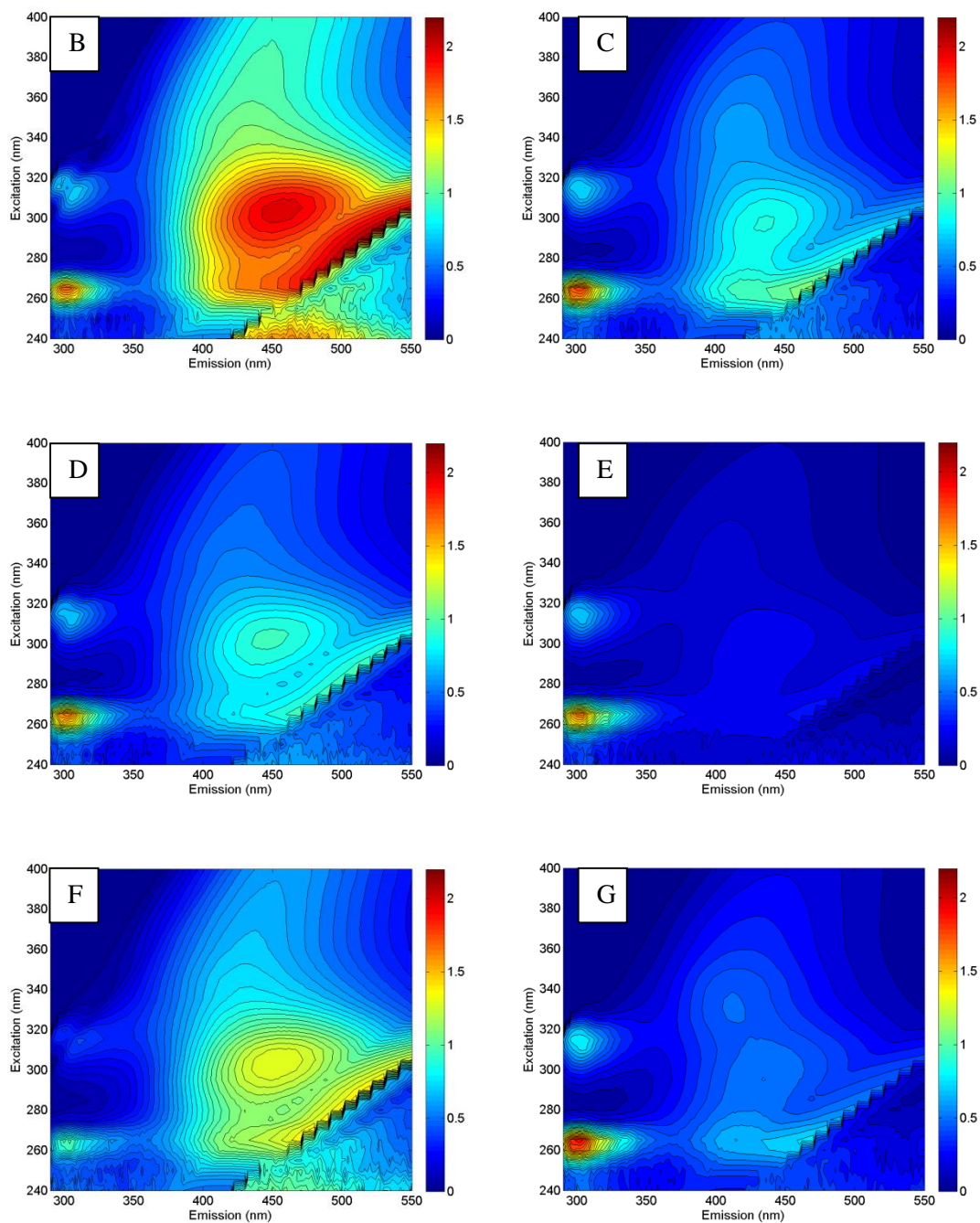


Figure 4-2. Excitation-Emission Matrices in units of relative intensity of Raw and Pretreated Water Samples from Mississippi River at Anoka of Winter Raw, FI = 1.52 (A), Spring Raw, FI = 1.35 (B), Spring Settled, FI = 1.77 (C), Summer Raw, FI = 1.50 (D), Summer Settled, FI = 1.88 (E), Autumn Raw, FI = 1.42 (F), and Autumn Settled, FI = 1.81 (G).

In all seasons, the raw Mississippi River water had higher relative intensities than the settled water, supporting the TOC/DOC measurements and UV scans which indicated a loss of organic matter through the softening process. With respect to seasonal differences, the spring raw sample had the highest FI, in agreement with the DOC measurements. Coagulation, flocculation, and sedimentation removed the humic acid-like NOM associated with a broad EEM peak at approximately (450, 300) in the spring, summer, and autumn by 55.7, 72.3, and 57.9%, respectively because pretreatment preferentially removes the larger molecular weight NOM (Chen et al., 2007). Concurrently, the peak associated with soluble microbial by-products (SMPs) at approximately (302, 265) increased in intensity by 4.5, 0.6, and 95.0% per respective season. This increase in SMP-type NOM is possibly due to the oxidation during preliminary chlorination prior to coagulation (Wenk et al., 2013). FIs for the samples ranged from 1.33 (Spring Raw) to 1.84 (Summer Settled), indicating that the organic matter was derived from both terrestrial (~1.4) and microbial (~1.9) sources (McKnight et al., 2001), again emphasizing the SMP characteristics of the settled waters. When compared to the EEMs of the IHSS standards, the Mississippi River samples had more varied peak locations and intensities with a well-defined SMP presence.

4.4.3 Membrane performance with IHSS standards

All tested membranes experienced fouling by the IHSS NOM standards in carbonate buffer (Figure 4-3). As measured by permeability decline, the hydrophilic YM30 membrane in general fouled less (3.5 – 8.6%) than the hydrophobic membranes. Average membrane permeability across the IHSS standards ranged from 13.5% (SRFA and SRNOM) to 16.5% (PLFA) and 17.5% (SRHA). Other studies have observed the most fouling from SRHA due to NOM absorption within the pores (Jones and O'Melia, 1999). The permeability declines were likely enhanced by the carbonate buffer matrix used to mimic natural waters. The presence of divalent cations, such as calcium, increases the rate of fouling as the cations act as intermolecular bridges, allowing the

formation of more dense fouling layers and preventing back diffusion (Li and Elimelech, 2004; Li and Elimelech, 2006; Hong and Elimelech, 1997; Hartman and Williams, 2002).

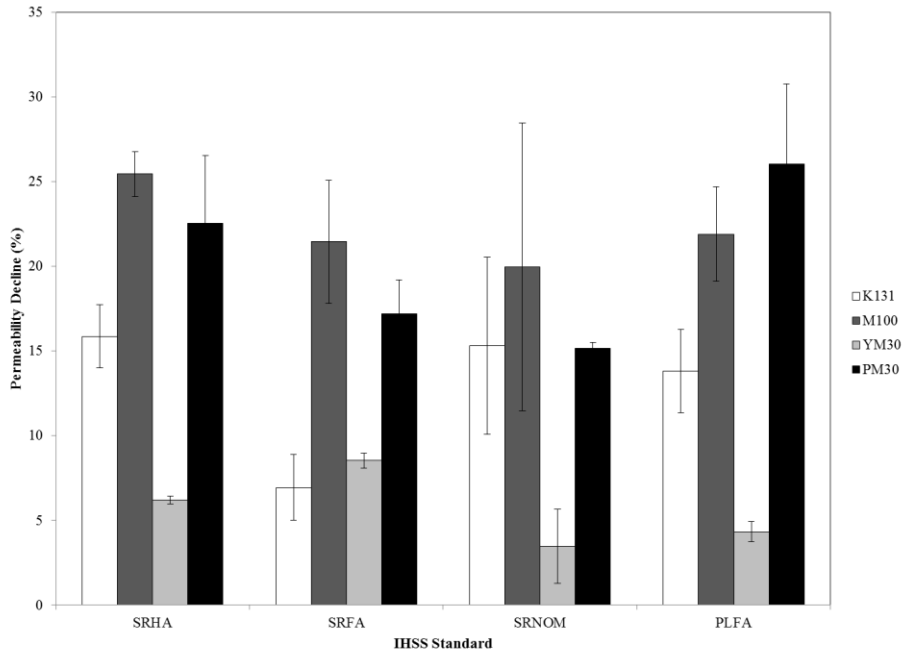


Figure 4-3. Percent permeability decline (\pm standard deviation) for four membranes filtering IHSS NOM standards (10 mg C/L) in carbonate buffer

Trends for DOC and UV_{254} removal from the IHSS standard samples were similar. SRHA was preferentially removed by all membranes (DOC: 21.0 - 54.1%, UV_{254} : 15.1 - 61.6%) in most contrast to SRFA (DOC: 0.3 - 24.3%, UV_{254} : 1.3 - 33.4%) (Figures 4-4 and 4-5). In general, the M100 membrane removed the most NOM (DOC: 9.5 - 54.1%, UV_{254} : 29.9 - 61.6%) across all IHSS standards with the YM30 membrane removing the least NOM (DOC: 5.0 - 21.0%, UV_{254} : 1.3 - 15.1%). At the end of filtration, the majority of the NOM was still present in the filtrate, although it must be kept in mind that the volume of the filtrate is approximately three times that of the retentate (Figure 4-6). The M100 membrane consistently showed the most retention of NOM mass on the membrane itself (16.2 - 36.0%). As a 'loose' ultrafiltration membrane, it may have

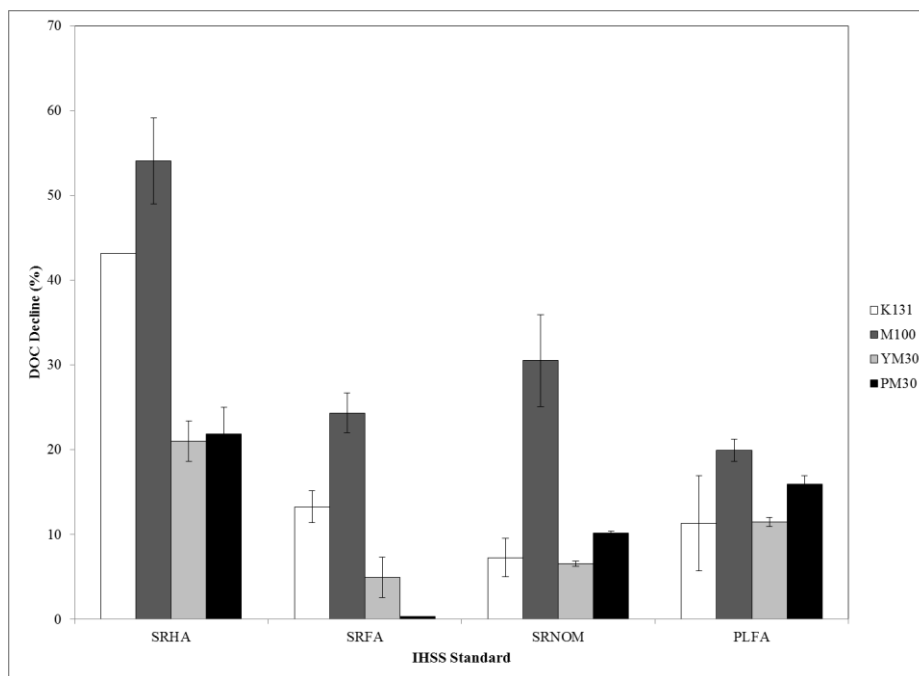


Figure 4-4. Percent DOC decline (\pm standard deviation) for four membranes filtering IHSS NOM standards (10 mg C/L) in carbonate buffer

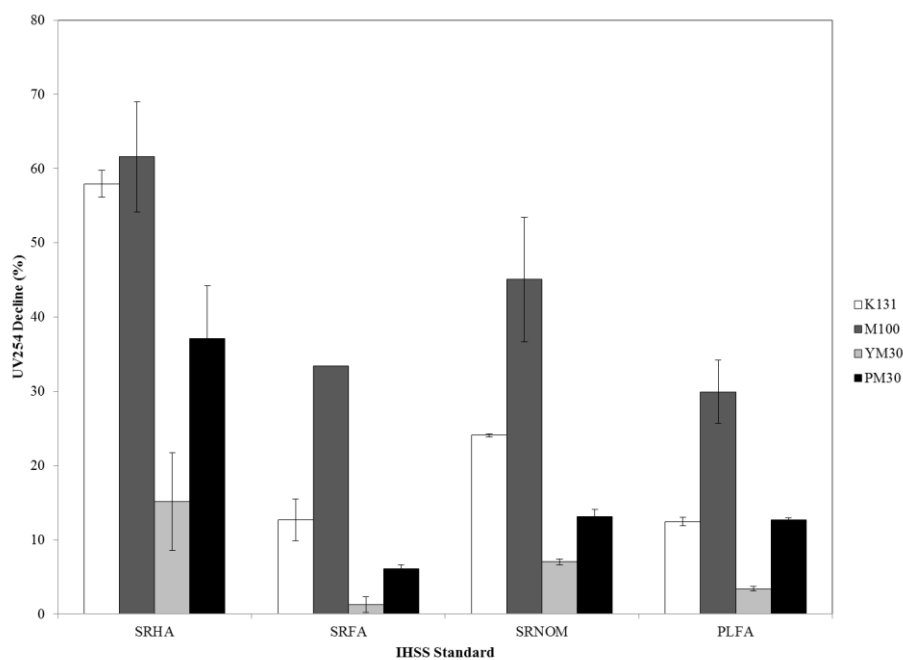


Figure 4-5. Percent UV₂₅₄ decline (\pm standard deviation) for four membranes filtering IHSS NOM standards (10 mg C/L) in carbonate buffer

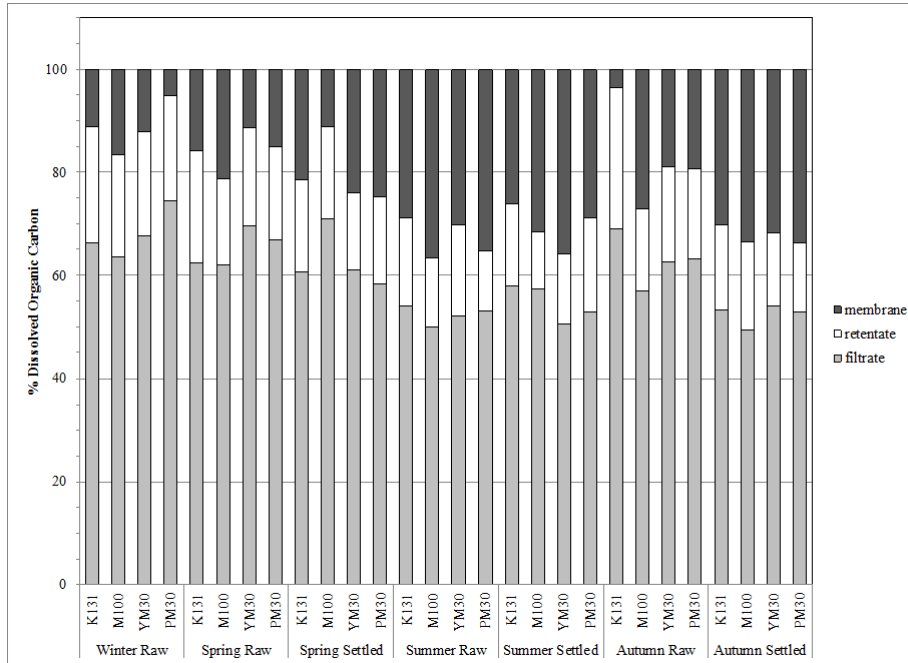


Figure 4-6. Fate of DOC following filtration for four membranes filtering IHSS NOM standards (10 mg C/L) in carbonate buffer

experienced more pore surface plugging and cake formation rather than internal pore absorption (Schäfer et al., 2000).

4.4.4 Membrane performance with seasonal waters

All tested membranes experienced fouling from the Mississippi River samples (Figure 4-7). The M100 membrane, which has the highest hydrophobicity, typically had the highest declines in permeability, followed by PM30. Fouling of the hydrophilic YM30 membrane was typically less than that of the comparable hydrophobic membranes. The gel polarization layer typically forms more slowly on hydrophilic membranes due to weaker interactions between functional groups in the NOM and those on the membrane surface (Cherkasov et al., 1995). Hydrophilic membranes have therefore been suggested as a means of treating waters with high concentrations

of hydrophobic NOM (Kabsch-Korbutowicz et al, 1999; Schäfer et al., 2000). Nevertheless, high hardness concentrations and alkaline pH present in many surface waters, including the Mississippi River, may reduce the effectiveness of hydrophilic membranes and cause serious fouling. When normalized for carbon loading on the surface, the average relative rate of fouling of the membranes across all seasons did not change (PM30 > M100 > K131 > YM30) (Table 4-4). Carbon normalized seasonal fouling of membranes averaged across all membranes indicated that the spring raw water still fouled the most and winter raw still fouled the least; however a more pronounced differentiation between permeability declines resulting autumn/winter and spring/summer waters became evident, emphasizing that autochthonous production and NOM of lower molecular weight may play an important role in membrane fouling.

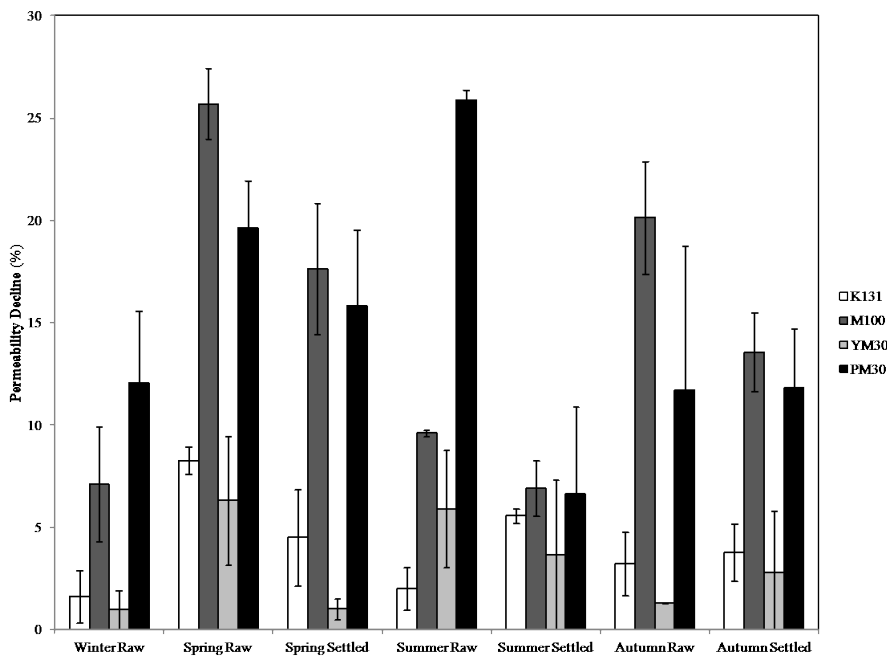


Figure 4-7. Percent permeability decline (\pm standard deviation) for four membranes filtering seasonal raw and settled waters from the Mississippi River

Table 4-4. Average percent permeability decline normalized per mg/L carbon load for four membranes filtering seasonal raw and settled waters from the Mississippi River

Membrane	Winter Raw	Spring Raw	Spring Settled	Summer Raw	Summer Settled	Autumn Raw	Autumn Settled	Avg
K-131	0.30	0.71	0.59	0.23	1.23	0.39	0.48	0.56
M-100	1.32	2.22	2.30	1.09	1.53	2.42	1.73	1.80
YM30	0.18	0.54	0.13	0.67	0.81	0.16	0.36	0.41
PM30	2.24	1.69	2.06	2.94	1.47	1.41	1.51	1.90
Average	1.01	1.29	1.27	1.23	1.26	1.09	1.02	

In general, settled waters fouled the membranes less than their comparable raw waters, indicating that the decrease in overall DOC and more specifically, humic and fulvic acids as seen in the EEMs, improved membrane longevity (Lee et al., 2005). Permeability declines between raw and settled waters were on average 35.0, 47.5, and 12.0% less in the spring, summer, and autumn, respectively. Coagulation prior to membrane filtration increases floc size, preventing pore blockage and particle deposition on the membrane surface while preferentially removing high molecular weight, high charge density and the hydrophobic humic and fulvic acids; however, coagulation does not typically remove low molecular weight neutral and hydrophilic compounds (Sharp et al., 2006; Choksuchart et al., 2002). In this study, the relative concentration of more hydrophilic, SMP-type NOM increased during the coagulation process, possibly due to oxidation during chlorination prior to coagulation. When compared to the IHSS standards, the Mississippi River seasonal waters consistently caused greater permeability declines in the four tested membranes despite lower DOC concentrations in all samples except the Spring Raw water. Unfractionated NOM has been found to foul membranes more readily than individual fractions because of increased interactions between hydrophobic and hydrophilic components (Braghetta et al., 1998).

DOC and UV₂₅₄ removals were consistent across membrane type, season, and pretreatment, falling within the wide range of removal efficiencies (10 - 95%) reported by Schäfer et al. (2000) for ultrafiltration membranes (Figure 4-8). The highest DOC removals for all membranes were

seen for the Summer Raw, Summer Settled, and Autumn Settled waters (34.2, 32.8, and 34.4%, respectively). The M100 membrane reduced UV_{254} absorbance the most (26.0 - 48.3%) across seasons and pretreatments (Figure 4-9). The interactions between the hydrophobic (68.8°) M100 membrane and the NOM likely neutralized membrane surface groups to induce the formation of a thick fouling layer (Cho et al., 1998), resulting in internal pore blockage and a decrease in permeability (Pontie et al., 2007). The Autumn Settled water saw the most UV_{254} removal by all membranes (22.8 - 48.33%), possibly due to the water's low SUVA value, indicating NOM of lower molecular weight and aromaticity compared to the other waters. Low SUVA molecules are typically small, neutral, and aliphatic and have been implicated in irreversible membrane fouling due to their tendency to absorb within the pores (Kimura et al., 2004; Fan et al., 2001; Cho et al., 2000). At the end of filtration, mass fractionation of the NOM indicated that the majority of the NOM was still present in the filtrate although an average of 22.9% of the DOC was retained on or within the membranes (Figure 4-10). The M100 membrane once again showed the most retention of NOM mass on the membrane itself (11.2 - 36.7%).

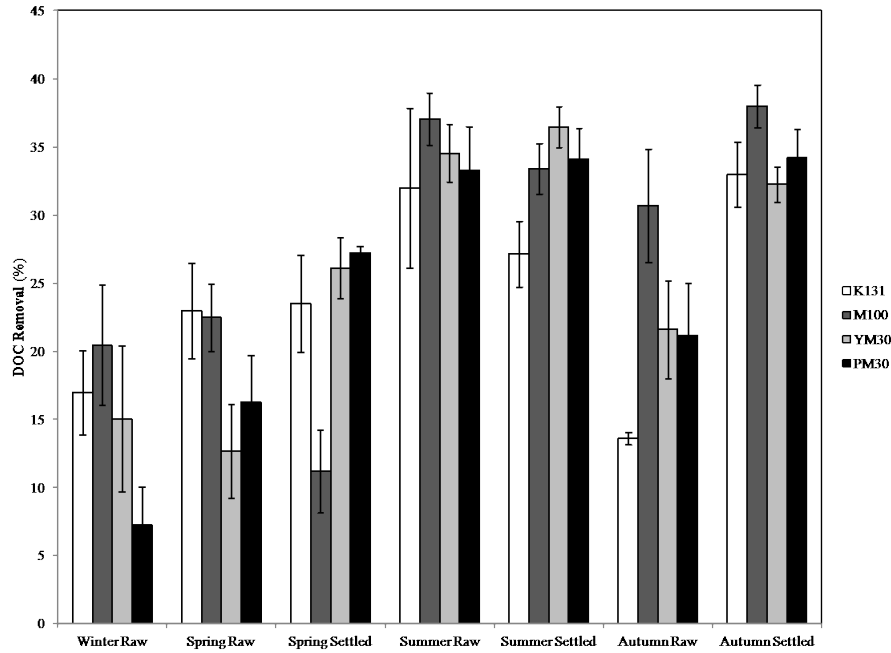


Figure 4-8. Percent DOC Removal (\pm standard deviation) for four membranes filtering seasonal raw and settled waters from the Mississippi River

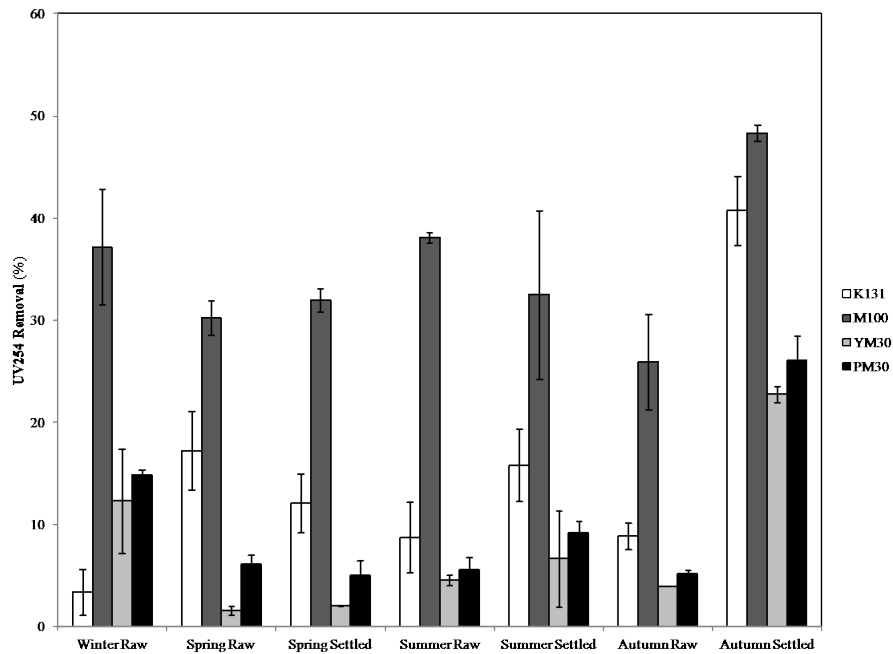


Figure 4-9. Percent UV₂₅₄ removal (\pm standard deviation) for four membranes filtering seasonal raw and settled waters from the Mississippi River

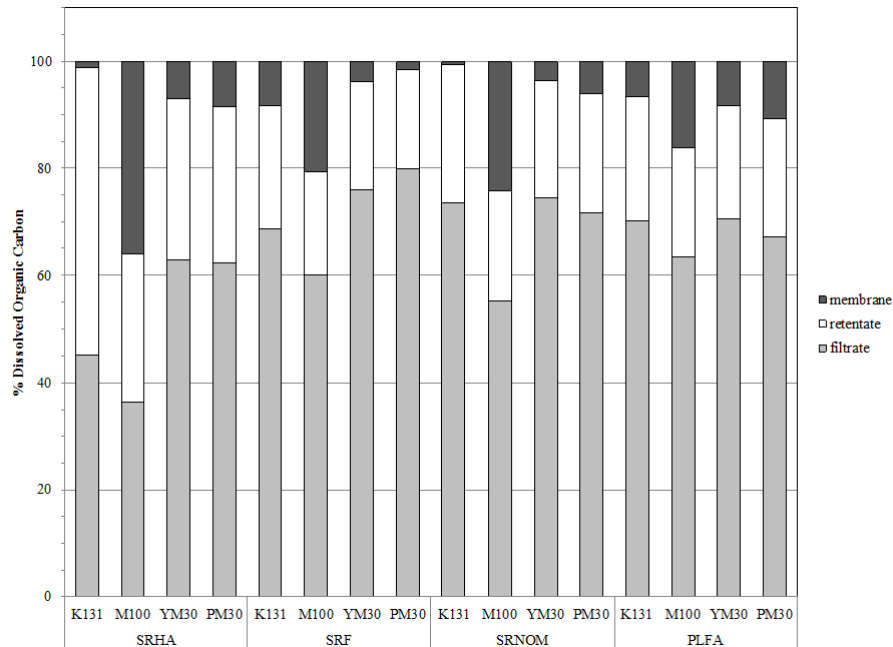


Figure 4-10. Fate of DOC following filtration for four membranes filtering seasonal raw and settled waters from the Mississippi River

4.5 Conclusion

Raw and lime-softened Mississippi River water and IHSS organic matter dissolved in carbonate buffer were filtered through four membranes in a stirred cell system. The softening/coagulation process decreased membrane fouling by preferentially binding high molecular weight, hydrophobic humic- and fulvic-like NOM to flocs for removal during settling. Fouling, however, still occurred from smaller, hydrophilic and neutral molecules that formed from the oxidation of NOM during preliminary chlorination. Across all membranes, the Spring Raw sample caused a greater permeability decline than the other waters. Traditionally, spring snow melt has been the most challenging time for the full-scale Columbia Heights Membrane Filtration Plant because of the Mississippi River's low alkalinity and high DOC concentration (Brinkman and Bankston, 2007). This grab sample was thus indicative of the membranes' seasonal performance.

The most hydrophilic membrane had the least permeability decline from the natural waters and IHSS standards. Spring and summer waters caused greater permeability declines on a carbon loading basis compared to the winter and autumn waters; however the test membranes were loaded at 0.52 g C/m² with no water or air or chemical cleaning processes, which would be implemented in a full-scale water treatment plant. Future studies may also want to perform EEMs on filtrate and retentate samples to see which specific NOM fractions are retained on or passed through the membrane. Removal of DOC and UV₂₅₄ in the seasonal waters was not consistent by degree of treatment, season, or membrane. These factors suggest that the complexity of NOM in the Mississippi River precludes studying individual components of NOM, such as humic or fulvic acids.

4.6 Acknowledgements

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Chapter 5

Spatial and Temporal Variations in Organic Carbon Concentration and Composition in Tributaries of the Upper Mississippi River and Effects on Membrane Filtration

5.1 Executive Summary

Monthly sampling of eight selected tributaries to the upper Mississippi River was performed to evaluate temporal changes in the concentration and character of natural organic matter (NOM) with respect to land use in the tributaries' watersheds. Batch filtration experiments were also performed using a stirred-cell device to determine the impact of seasonal water quality changes on membrane fouling with two ultrafiltration membranes of differing hydrophobicity. Dissolved organic carbon (DOC) concentrations were variable between the tributaries (5.0 - 35.1 mg/L), with obvious temporal variations due to spring snow melt and storm events. Excitation-emission matrices determined that relative amounts of low molecular weight NOM consisting of soluble microbial byproducts increased in the summer. The hydrophilic membrane experienced less fouling, as measured by decline in permeability, than the hydrophobic membrane (1.73 - 9.8% vs. 25.1 - 33.0%). DOC and UV₂₅₄ removal were more consistent across land uses, but varied temporally. These results suggest that membrane hydrophobicity, temporal water quality, and land use influence membrane fouling by NOM and NOM rejection.

5.2 Introduction

Organic matter (OM) in surface waters is derived from aquatic organisms, decomposing terrestrial vegetation, and anthropogenic sources (Thurman, 1985). The concentration and composition of OM in a water body can vary based on where it originates (Thomas et al., 2004; Correll et al., 2001), the path it takes to the receiving water (Dalzell et al., 2007), and transformations within the water body (Pinney et al., 2000). This complex series of processes means that the resulting aquatic OM is highly variable both spatially and temporally, especially in

response to land use and seasonal changes (Hope et al., 1994; Mulholland, 1997). Within a water body, OM can mobilize metals (McKnight and Bencala, 1990), increase bacterial growth (Moran and Zepp, 1997), and shield aquatic organisms from ultraviolet irradiation (Schindler and Curtis, 1997). From an engineering standpoint, OM can challenge drinking water utilities by increasing chemical consumption, serving as a precursor for disinfection byproducts, and fouling filtration membranes (Li and Chen, 2004; Kaplan, 1994). An understanding of the variable and complex factors affecting OM concentration and composition is thus crucial for watershed managers and water utilities.

Past studies of natural organic matter (NOM) in surface waters have shown that NOM concentration and composition varies throughout the year in temperate climates. For example, Correll and colleagues (2001) demonstrated that total organic carbon (TOC) concentrations in the Rhode River watershed in Maryland varied from 5.11 mg/L in the winter to 12.80 mg/L in the summer. NOM concentration and composition change as runoff transports particulate and terrestrially derived (allochthonous) OM into surface waters from upper soil horizons (Veysy et al. 1999; Hope et al., 1994; Mulholland, 1997). A long term study of eight watersheds in the Maryland coastal plain positively correlated rainfall with TOC (Correll et al., 2001). Dissolved organic carbon (DOC) concentrations are often independent of discharge (Mattsson et al., 2005; Grubaugh and Anderson, 1989). In these cases, DOC concentrations are instead linked to events such as leaves dropping in the fall and primary productivity (Hope et al., 1994; Meyer et al., 1998). Temperature and sunlight changes seasonally and throughout the course of a day (Kaplan and Bott, 1982), significantly altering in-stream (autochthonous) NOM production. Production of autochthonous NOM in rivers also increases with the presence of lakes and reservoirs (Kendall et al., 2001) and low canopy cover (Kaplan and Bott, 1982), but increases in autochthonous production during warm summer months can be offset by degradative processes such as photolysis and biodegradation (Neff and Asner, 2001).

Row crop agriculture, forests, wetlands, and urban areas comprise the predominant land uses in the upper Mississippi River watershed in Minnesota. Organic matter fluxes in agricultural areas can be caused by animal and vegetal waste (Chomycia, et al., 2008), erosion (Correll et al., 2001), and irrigation (Hernes et al., 2008). For example, one study in New Zealand showed that the runoff from the pasture had less than half the DOC concentration of the runoff from a planted pine forest plot (Findlay et al., 2001) while a study in the Amazon basin showed higher DOC following pastures than following forests (Thomas et al., 2004). In forested area, DOC leached from leaf litter contributes about 30% of the generated DOC in the streams (Meyer and Tate, 1983; Meyer et al., 1998). Comparing forest and a moorland watershed in Scotland, Grieve and colleagues (1990) determined that the forested catchment had twice the DOC in receiving streams as the moorland due to higher accumulation of detritus while Meyer and Tate (1983) observed lower carbon exports from a forested watershed two years after clear cutting when compared to a non-cleared control forested watershed.

Wetlands can also be a source of NOM due to their long hydraulic residence time, anaerobic conditions, organic soils, and high amount of primary productivity (Mulholland and Kuenzler, 1979; Dalva and Moore, 1991; Kaplan et al., 2006). Wetlands may also serve as sinks of organic matter. For example, Pinney et al. (2000) studied a constructed wetland receiving treated wastewater effluent from an aerated lagoon system and observed that in June DOC concentrations decreased 9%, while in February DOC concentrations fell 47%. They attributed this difference to the concurrent summer biodegradation of labile OM and leaching of more recalcitrant OM from plant materials. Several studies of Scottish peatlands have examined shrubland influences on OM. In the Glen Dye catchment, waters from three peat-dominated subwatersheds had the highest DOC concentrations, up to an average of 18.3 mg/L, compared to those with humic podzols (Dawson et al., 2004). A seasonal survey of 56 Scottish watersheds found that upland peat/shrub land use was only positively correlated to DOC export during the autumn and winter when overland and subsurface flows were not common (Aitkenhead-Peterson, 2007). While urbanization does not

necessarily affect concentration and composition of NOM, urban impoundments, channelization, and wastewater flows do impact the variability of NOM (Westerhoff and Anning, 2000).

The purpose of this research was to evaluate the spatial and temporal variation of organic carbon concentration and composition in eight tributaries of the upper Mississippi River in Minnesota. Previous research had indicated the importance of shrubland and agricultural land uses in determining the variance of OM concentration and composition in a late summer through early fall sampling period, but the specific effects of land use on water treatment, specifically membrane filtration, was of interest.

5.3 Materials and Methods

5.3.1 Sampling sites

Eight tributaries of the Mississippi River in Minnesota were selected for monthly sampling during the ice-free portion of 2009 (March - November). Tributaries were selected to represent a range of dominant land uses (Figure 5-1, Table 5-1). A digital elevation model (DEM) for the State of Minnesota was created from state topographic maps (MNDNR, 1999-2008) in ArcView 9.0 (ESRI, Redlands, California, USA). Watershed terrain models, based on the Universal Transverse Mercator (Section 15) coordinates of the sampling points were then developed. Major watershed boundaries were confirmed with the boundaries developed by the Minnesota Department of Natural Resources (MNDNR, 1999). The watersheds were then overlaid with Minnesota 2000 Level 1 Landsat Landcover Classification data (University of Minnesota Remote Sensing and Geospatial Lab, 2006) to estimate the contributing area of each land use within each watershed. The eight selected tributaries of the Mississippi River were grouped into three land use categories: forest/wetland (Leech Lake, Sandy, and Rice Rivers), agriculture/forest/wetland (Nokasippi, Swan and Clearwater Rivers), and urban (Shingle and Minnehaha Creeks). Major soil classifications for Mississippi River watershed in Minnesota are Udalts, Psamments, and Udepts with subsurface geology dominated by glacial till and outwash (University of Minnesota Extension, 2013). Rainfall

data from the St. Cloud Airport and Minneapolis St. Paul International Climatological Data Sites was also evaluated for the sampling period (Figures 5-2 and 5-3) (National Weather Service, 2010). When available, discharges for the Shingle and Minnehaha Creek locations as monitored by the United States Geological Survey were obtained for the dates and times of sampling (USGS, 2009). The other six sampling locations did not have a safe means of measuring flow and/or were not monitored by the USGS. As a result, correlations between rainfall, flow, and water quality parameters could not be obtained.

Table 5-1. Percent land use per Minnesota 2000 Level 1 Landsat Landcover Classification data within selected Mississippi River tributaries

Tributary	River Mile ¹	Land Use Percent						
		Urban	Agriculture	Grassland	Forest	Water	Wetland	Shrubland
Leech Lake River	1216.5	2.3	5.8	0.1	58.5	18.9	14.1	0.2
Sandy River	1109	4.2	6.8	0.2	61.0	6.2	19.6	2.0
Rice River	1070	2.9	7.6	0.5	65.2	3.9	18.1	1.6
Nokasippi River	986	4.2	25.7	0.3	41.6	4.2	22.7	1.4
Swan River	962	5.7	35.7	1.2	24.6	3.0	27.7	2.2
Clearwater River	913.6	9.3	45.3	5.9	11.7	7.1	19.4	1.4
Shingle Creek	857.8	71.5	14.5	0.0	9.4	4.5	0.0	0.0
Minnehaha Creek	847.4	32.4	9.4	3.2	21.2	18.3	15.0	0.6

1. River mile refers to the distance upstream from the confluence of the Mississippi and Ohio Rivers as established by the U.S. Army Corps of Engineers

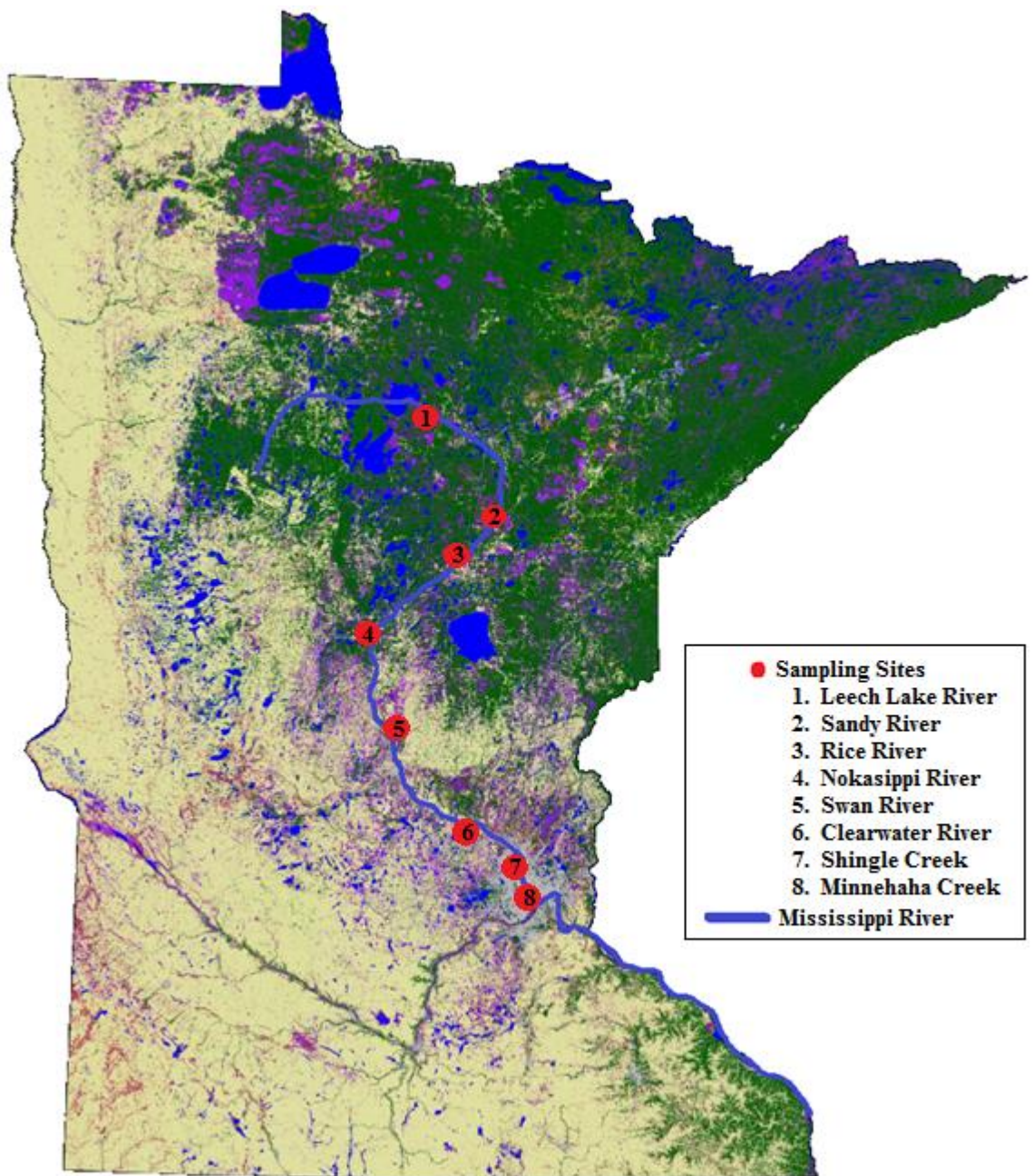


Figure 5-1. Land use by color (grey = urban, light sage = agriculture, maroon = grassland, green = forest, blue = water, purple = wetland, orange = shrubland) and location of sampling sites along tributaries of the upper Mississippi River in Minnesota

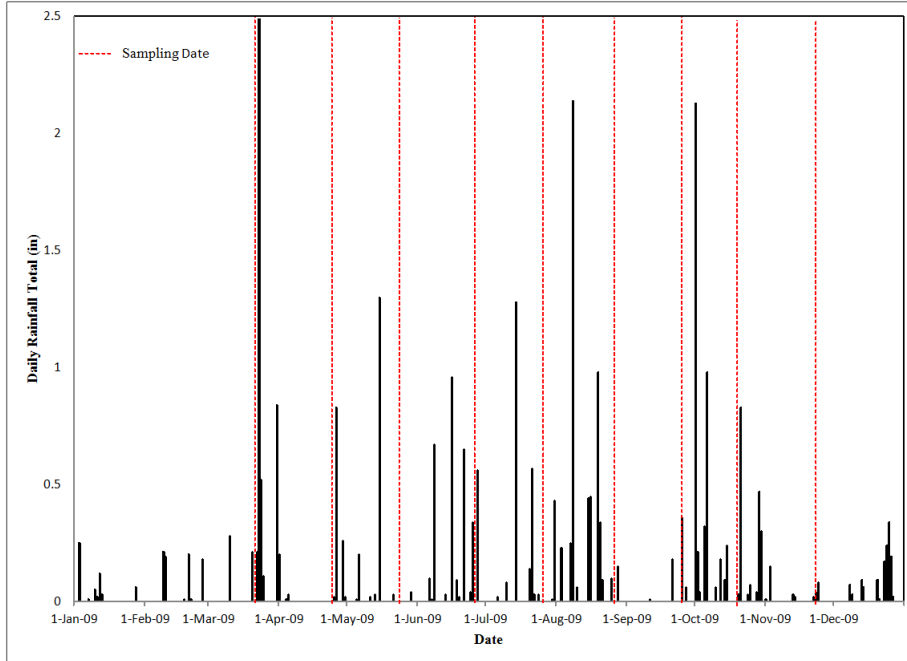


Figure 5-2. 2009 rainfall data for the National Weather Service Primary Local Climatological Data Site at the St. Cloud Airport and tributary sampling dates (dotted vertical lines)

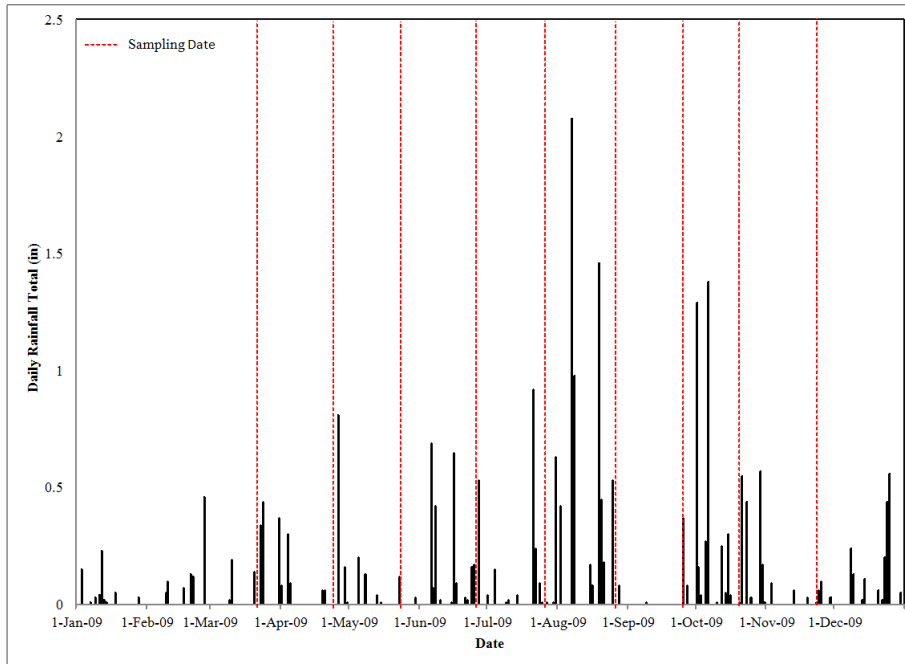


Figure 5-3. 2009 rainfall data for the National Weather Service Primary Local Climatological Data Site at the Minneapolis St. Paul International Airport and tributary sampling dates (dotted vertical lines)

5.3.2 Analytical methods

At each site, a grab sample of water was collected in a 1 L screw top glass bottle by submerging the bottle 6 inches below the water surface and opening the cap. The bottles had been rendered organic carbon free by soaking overnight in 3M nitric acid, rinsing with distilled water, and then baking for six hours at 550°C and the caps had been cleaned by soaking for one hour in a 10% solution of reagent grade sodium persulfate (Sigma Aldrich, St. Louis, Missouri, USA). Upon return to the laboratory, the water samples were immediately analyzed for total organic carbon then filtered through baked glass microfiber filters with an average pore size of 0.7 µm (Whatman GF/F, Piscataway, New Jersey, USA) within 48 hours. The filtered water samples were stored at 4°C for a maximum of one week before being analyzed for dissolved organic carbon. Organic carbon measurements were made using a Sievers 900 Portable TOC Analyzer (GE Analytical Instruments, Boulder, Colorado, USA) that was calibrated with dilutions of a standard potassium hydrogen phthalate solution (Sigma Aldrich, St. Louis, Missouri, USA). UV/Vis light absorbance scans from 200 – 600 nm were obtained for filtered samples using a UV-1601PC UV-Visible spectrometer (Shimadzu Scientific Instruments, Inc., Columbia, Maryland, USA).

Fluorescent spectroscopy was performed on all water samples. Water samples were filtered through 0.2 µm nitrocellulose membrane filters (Millipore Corporation, Billerica, Massachusetts, USA) and stored in organic carbon-free glassware prepared as described above. Excitation-emission matrices (EEMs) were generated on a Fluoromax-3 fluorometer (Horiba Instruments, Irvine, California, USA). The excitation range was 240 – 400 nm with an interval of 5 nm while the emission range was 290 – 550 nm with an interval of 2 nm. The raw scans were adjusted according to baseline scan accounting for Raman scattering, variations in lamp intensity, and for cuvette imperfections. Contour plots representing the resulting matrix were created using a MatLAB (The Mathworks, Inc., Natick, Massachusetts, USA) script.

5.3.3 *Membrane filtration*

Two flat-sheet membranes of differing materials and properties (Table 5-2) were soaked overnight in ultrapure water from a Milli-Q Q-Gard 2 System (Millipore Corporation, Billerica, Massachusetts, USA) then placed in an Amicon 8200 stirred cell with a bottom surface area of 28.7 cm² (Millipore Corporation, Billerica, Massachusetts, USA). The membranes were then flushed with additional ultrapure water. To establish an initial clean water flux for the new membrane, 75 mL of ultrapure water was filtered through the membrane. A test water (200 mL) was then placed in the stirred cell and approximately 150 mL was filtered through the membrane. Sample waters from April, July, and September from the Leech Lake, Rice, and Clearwater Rivers and Shingle Creek were chosen for filtration experiments to represent seasonal variations in the tributaries. At the end of the test water run, the retentate and permeate were analyzed for organic carbon and UV absorbance at 254 nm (UV₂₅₄) using a Sievers 900 Portable TOC Analyzer (GE Analytical Instruments, Boulder, Colorado, USA) and a UV-1601PC UV/Vis Spectrophotometer (Shimadzu Scientific Instruments Incorporated, Columbia, Maryland, USA), respectively. Then, 75 mL of ultrapure water was filtered through the membrane to determine the final clean water flux for the fouled membrane. A constant stirring speed of approximately 120 rpm was maintained during all filtration runs. Flux was determined by measuring the mass of permeate over time using a Mettler Toledo PG-S Balance with integrated BalanceLink software (Mettler Toledo Incorporated, Worthington, Ohio, USA). Constant pressure in the stirred cell (0.5 to 3.8 bar, depending on the membrane) was maintained during the filtration experiments with a nitrogen cylinder and regulator. The permeability was calculated by dividing the flux by the applied pressure. Finally, the initial and final clean water permeabilities were compared to determine the percent permeability decline for each fouling experiment. Two trials were performed with each membrane and each water.

Table 5-2. Properties of membranes tested in fouling experiments

Membrane	Material	MWCO (kDa)	Contact Angle (°)	Source
YM30	regenerated cellulose	30	22.6	Millipore
PM30	polyether sulfone	30	47.9	Millipore

The hydrophobicities of the membranes were determined by the sessile drop method on an Automatic Microscopic Contact Angle, Model MCA-3 (Kyowa Interface Science Company, Ltd., Tokyo, Japan). Images were captured every 67 milliseconds for 2 seconds and the contact angle was calculated using the ‘tangent’ method by placing three data points on each side of the droplet on the first image after settlement and measuring the angle formed with the membrane surface.

5.4 Results and Discussion

5.4.1 Water quality parameters

DOC concentrations in the tributaries ranged from 5.1 mg/L for Shingle Creek in April to 35.1 for Rice River in July (Figure 5-4). The Rice and Sandy Rivers were visibly colored by tannins and humic substances and consistently had the highest DOC concentrations and UV₂₅₄ absorbances (Figure 5-5). Six of the tributaries saw a drop in DOC concentrations in April. The tributaries were bank full at this sampling time, suggesting that flooding at the end of spring snow melt had flushed and diluted allochthonous OM from the top layers of soil (Grubaugh and Anderson, 1989). Minnehaha Creek had an elevated DOC concentration and UV₂₅₄ absorbance in September as sampling was done on a day with 9.4 mm of rainfall; however the NOM parameters of Shingle Creek, 10 miles upstream, did not reflect this increase. SUVA values for the tributaries were generally between 2 and 4 L/mg-m (Figure 5-6), indicating that the NOM was of both terrestrial and aquatic origin (Karanfil et al., 2002). SUVA values ranged from 0.66 for Shingle Creek in July as small molecular weight NOM from primary production dominated NOM to 5.41 L/mg-m for Minnehaha Creek in April from the spring melt flush of allochthonous NOM (Hope, 1994; Kaplan

and Bott, 1982). No land use trends were apparent for the concentration or composition of NOM in the tributaries.

Conductivity was most variable in the urban systems of Shingle and Minnehaha Creek (Figure 5-6). April conductivities in these waters dropped by over 30% from the March values. A study of urban drainage systems in Melbourne, Australia found that conductivity was positively correlated with imperviousness and connectivity (Hatt et al., 2004), resulting in storm water releases that are 'flashy' and may be high in particulate NOM/ pH followed a trend similar to conductivity, but land use differences were not pronounced (Figure 5-7). Waters increased in acidity during the spring snow melt, but generally remained between 7 and 8 pH units.

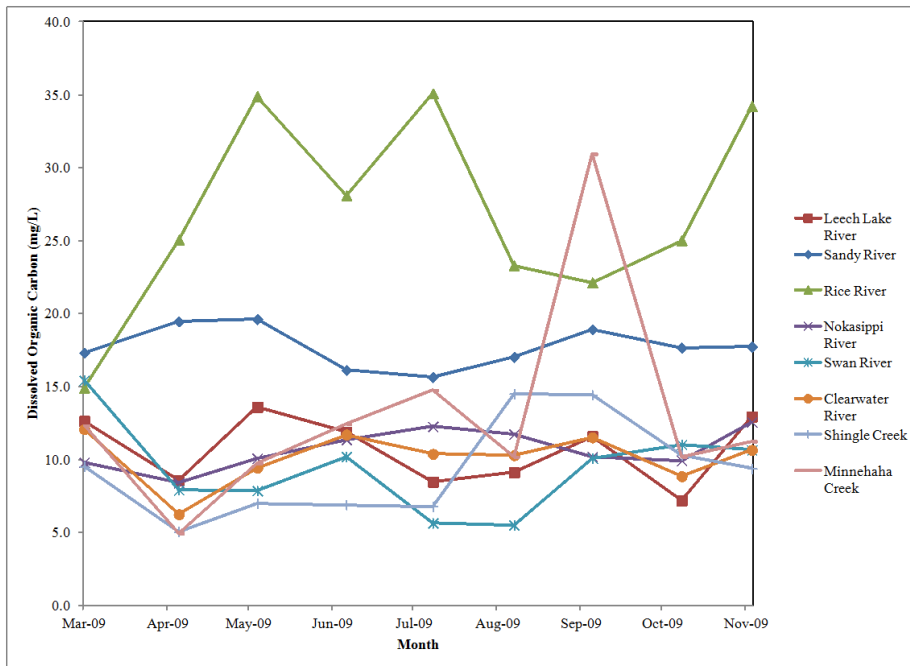


Figure 5-4. Dissolved organic carbon concentrations (mg/L) from monthly samples for eight tributaries of the upper Mississippi River

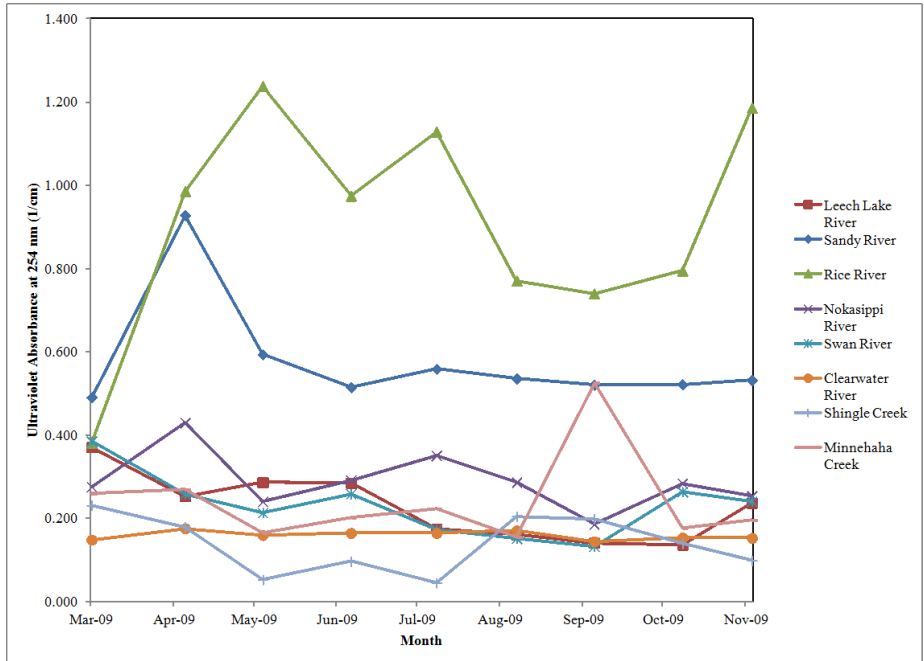


Figure 5-5. Ultraviolet absorbance at 254 nm values (1/cm) from monthly samples for eight tributaries of the upper Mississippi River

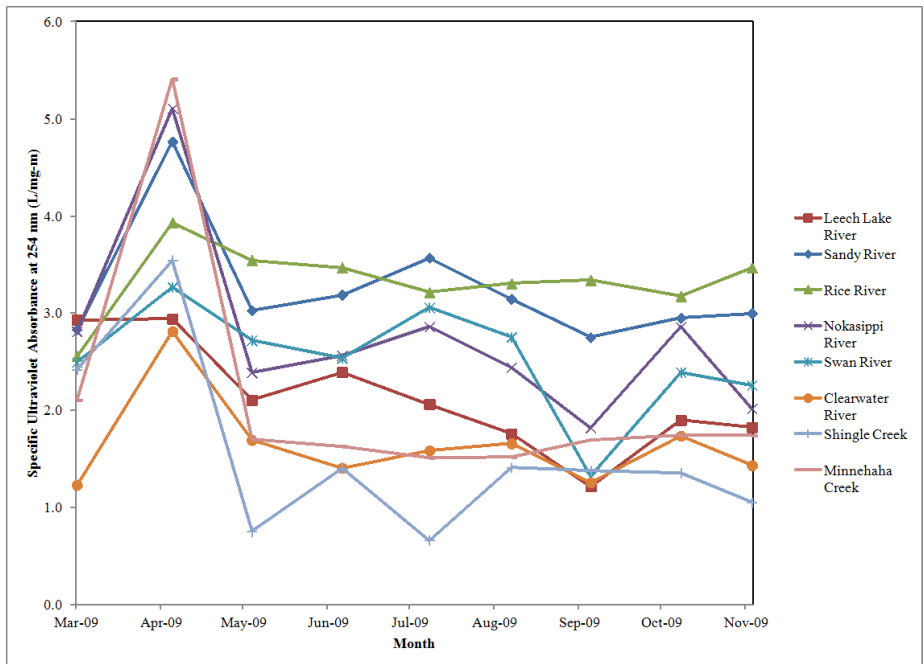


Figure 5-6. Specific ultraviolet absorbance values (L/mg-m) from monthly samples for eight tributaries of the upper Mississippi River

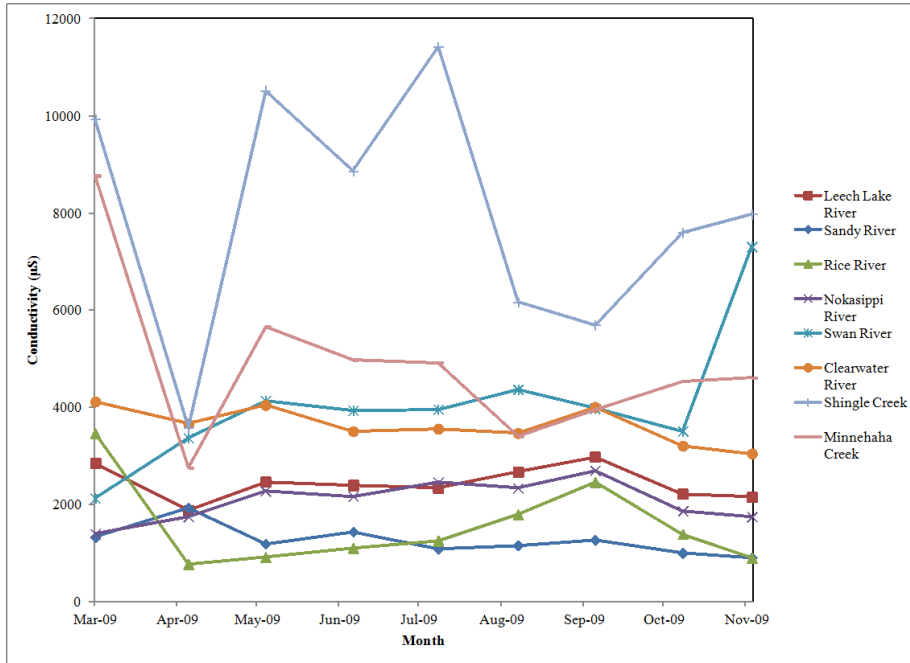


Figure 5-7. Conductivity values (μS) from monthly samples for eight tributaries of the upper Mississippi River

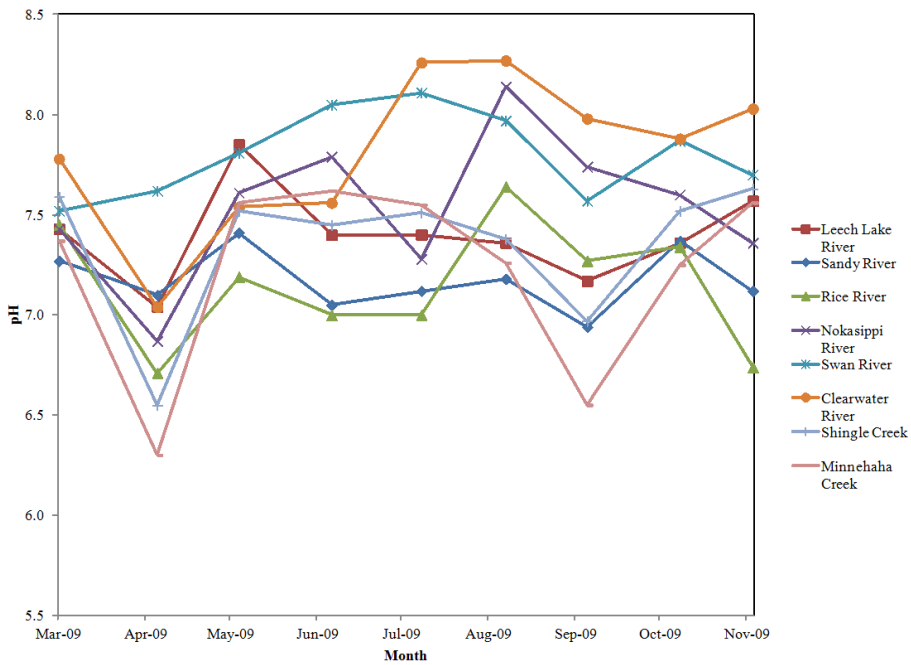


Figure 5-8. pH values from monthly samples for eight tributaries of the upper Mississippi River

Excitation-emission matrices (EEMs) were created for four of the tributaries (Leech Lake, Rice, and Clearwater Rivers, and Shingle Creek) from samples taken in April, July, and September to further analyze the composition of dissolved organic matter (DOM) and how it changed with time and land use (Figures 5-8, 5-9, 5-10, and 5-11). EEMs can often be used to distinguish between water sources based on the location and magnitude (intensity) of the resulting Raman peaks in the three-dimensional graphs (Her et al., 2003). For all of the samples, broad peaks at (450 - 500, 300), (450 - 500, 240), and (540, 295) indicated that the NOM could be characterized as both humic and fulvic acid-like (Table 5-3).

Another peak at approximately (302, 265) denoted the presence of soluble microbial by-products (SMPs) (Chen et al., 2003). Seasonal differences in the composition of NOM in the tributaries were exhibited in the EEMs. For Leech Lake River, Clearwater River, and Shingle Creek, the relative intensity of the SMP-like peak increased in the July sample. The highly colored Rice River, in contrast, had a more intense peak at (450 - 500, 240) in July, indicative of an increase in fulvic acid-like NOM with lower molecular weight and higher aromaticity (Chen et al., 2003; Thurman, 1985). Variations in peak intensity are similar to those observed for SUVA because the fluorophores within NOM are typically aromatic ring structures (Skoog et al., 2007). FIs for the samples ranged from 1.21 (Rice River, April) to 1.60 (Shingle Creek, July), indicating that the organic matter was derived from both terrestrial (~1.4) and microbial (~1.9) sources (McKnight et al., 2001).

Table 5-3. Water quality parameters for seasonal water samples from four tributaries of the upper Mississippi River

Sample		UV ₂₅₄ (1/cm)	TOC (mg/L)	DOC (mg/L)	SUVA (L/mg-m)	Conductivity (uS)	pH	Fluorescent Index	Maximum Intensity (Raman)	Peak Location ¹ (nm)
Leech Lake River	April	0.253	9.75	8.60	2.94	1880	7.04	1.33	1.80	(302,265)
	July	0.175	8.41	8.49	2.06	2350	7.40	1.41	2.47	(304, 265)
	September	0.141	28.7	11.6	1.22	2980	7.17	1.45	1.80	(302, 265)
Rice River	April	0.986	26.1	25.1	3.93	775	6.71	1.21	5.46	(460, 240)
	July	1.129	35.1	32.8	3.44	1258	7.00	1.22	11.17	(462, 240)
	September	0.740	24.0	22.1	3.34	2460	7.27	1.27	4.91	(458, 240)
Clearwater River	April	0.176	6.63	6.25	2.81	3670	7.04	1.46	2.15	(302,265)
	July	0.165	12.6	10.4	1.59	3560	8.26	1.48	2.35	(302, 265)
	September	0.145	15.6	11.5	1.26	4010	7.98	1.47	1.92	(302, 265)
Shingle Creek	April	0.180	6.46	5.08	3.55	3590	6.55	1.41	1.70	(520, 290)
	July	0.045	8.58	6.79	0.66	11420	7.51	1.60	2.17	(302, 265)
	September	0.199	15.1	14.4	1.38	5700	6.97	1.43	1.82	(470, 265)

1. Peak location is given in EEM coordinates: (emission, excitation)

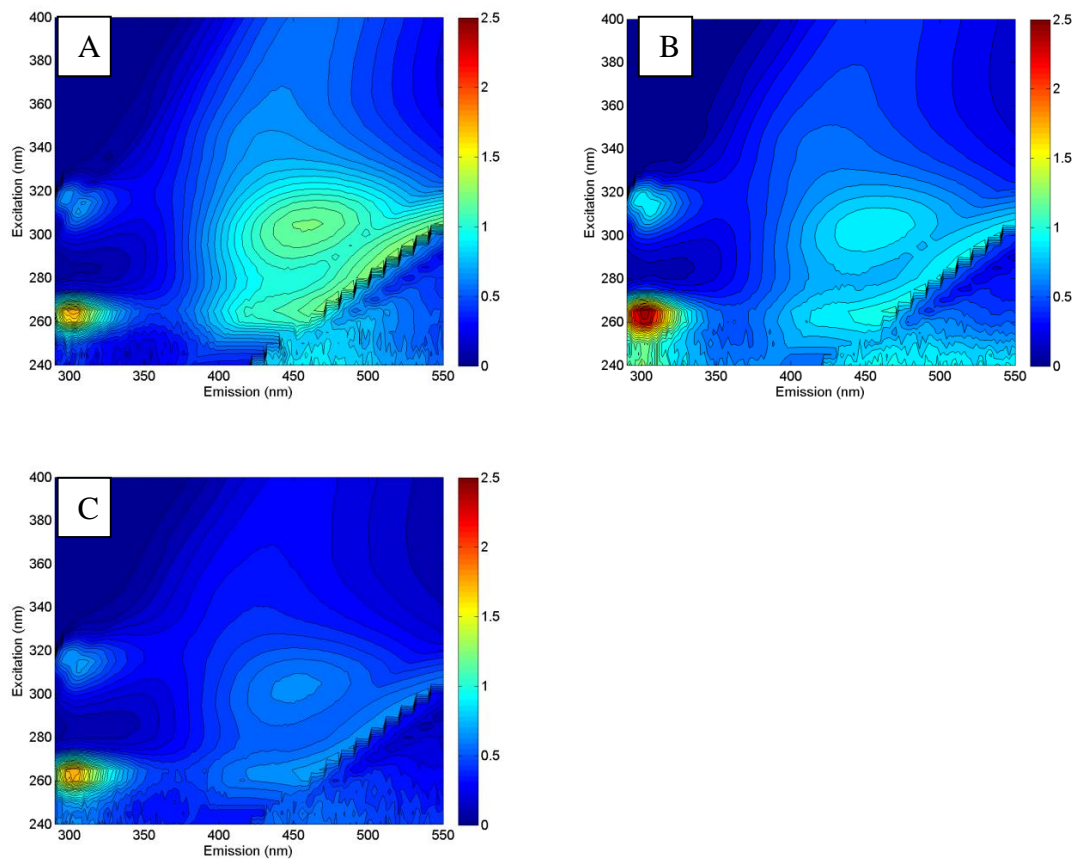


Figure 5-9. Excitation-Emission Matrices in units of relative intensity of Leech Lake River in April, FI = 1.33 (A), July, FI = 1.41 (B), and September 2009, FI = 1.45 (C)

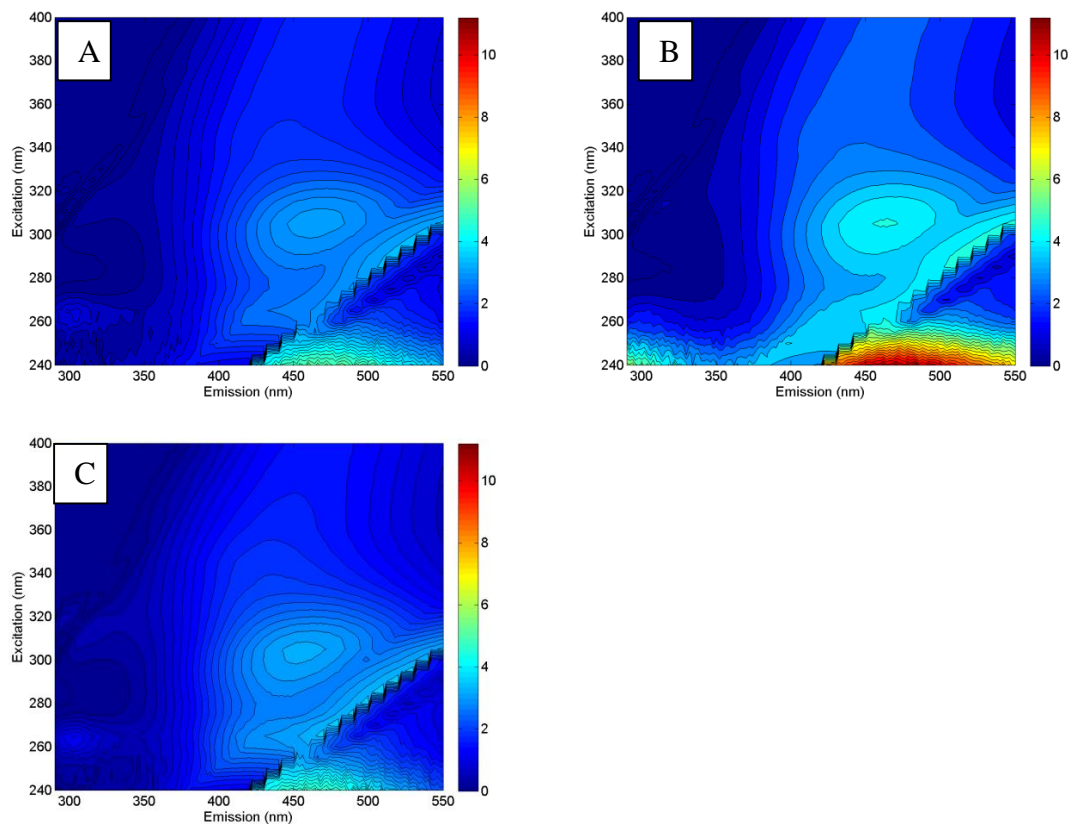


Figure 5-10. Excitation-Emission Matrices in units of relative intensity of Rice River in April, FI = 1.21 (A), July, FI = 1.22 (B), and September 2009, FI = 1.27 (C)

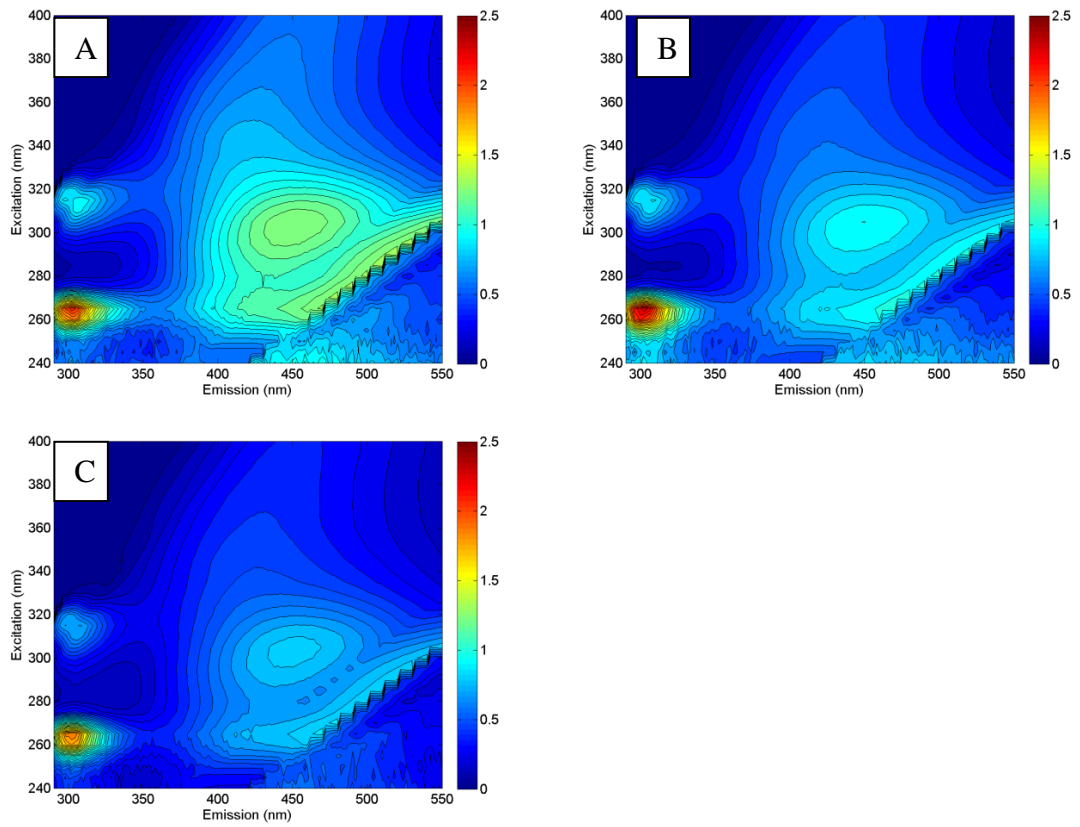


Figure 5-11. Excitation-Emission Matrices in units of relative intensity of Clearwater River in April, FI = 1.46 (A), July, FI = 1.48 (B), and September 2009, FI = 1.47 (C)

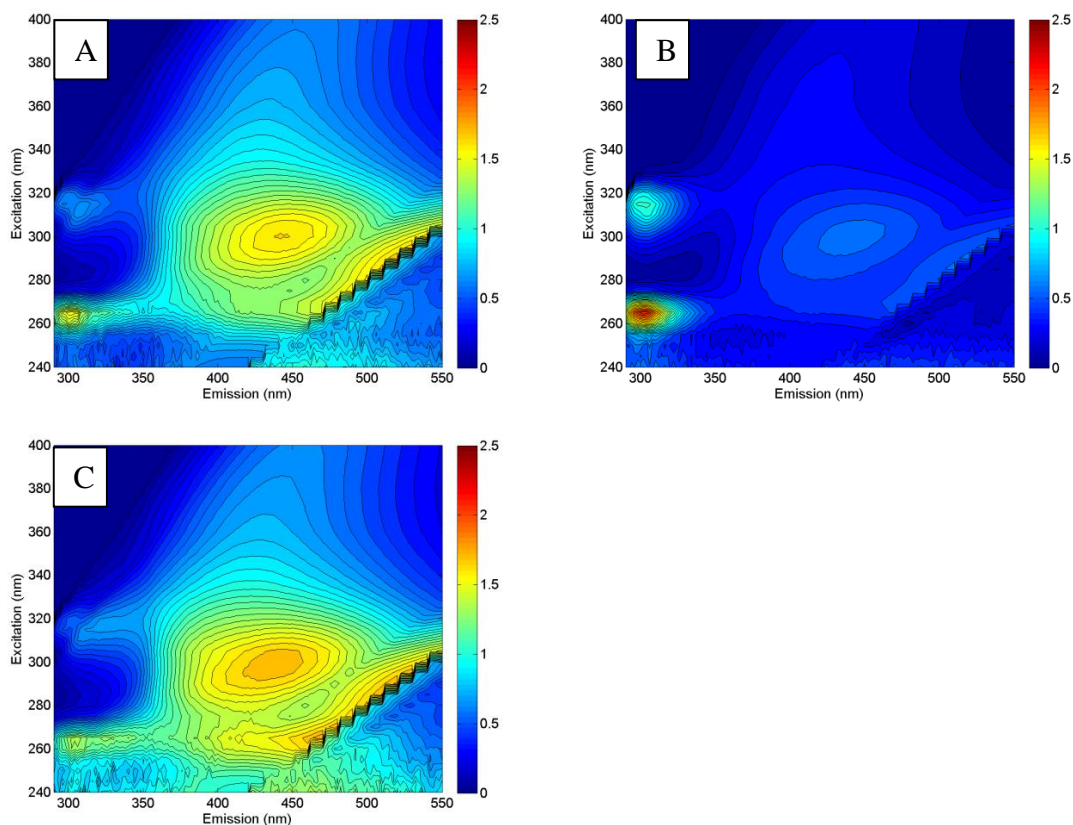


Figure 5-12. Excitation-Emission Matrices in units of relative intensity of Shingle Creek in April, FI = 1.41 (A), July, FI = 1.60 (B), and September 2009, FI = 1.43 (C)

5.4.2 Membrane performance

All tested membranes experienced fouling from the seasonal tributary waters (Figure 5-13). The PM30 membrane, which was more hydrophobic than the YM30 membrane, typically had the highest declines in permeability for watersheds with forest, wetland, and agricultural land uses. The two membranes experienced similar fouling for Shingle Creek, a small urban watershed. The gel polarization layer typically forms more slowly on hydrophilic membranes due to weaker interactions between functional groups in the NOM and those on the membrane surface (Cherkasov et al., 1995). Hydrophilic membranes have therefore been suggested as a means of treating waters with high concentrations of hydrophobic NOM (Kabsch-Korbutowicz et al, 1999; Schäfer et al.,

2000). Seasonal variations for each membrane and tributary were usually within one standard deviation of the average. Exceptions were July for Clearwater River and Shingle Creek. These watersheds had more alkaline pH values at that sampling time. High hardness concentrations and alkaline pH may reduce the effectiveness of membranes and cause serious fouling (Kabsch-Korbutovicz et al, 1999). When normalized for carbon loading on the surface, the average relative rate of fouling of the membranes across all seasons and tributaries did not change (PM30 > YM30) (Table 5-4). Among the tributaries, Rice River had the lowest carbon loading normalized average permeability decline, an indication that fouling was due to high concentrations of DOC rather than unique land use characteristics of the NOM. Seasonal differences based on loading remained consistent compared to non-normalized permeability declines (July > April > September) emphasizing that autochthonous production and NOM of lower molecular weight may play an important role in membrane fouling.

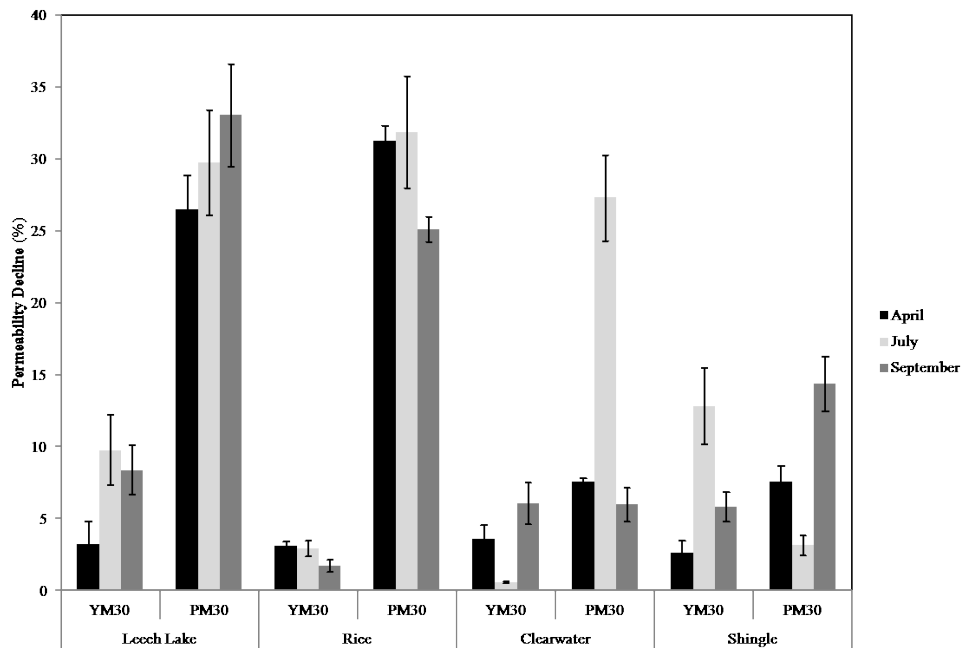


Figure 5-13. Percent permeability decline (\pm standard deviation) for two membranes filtering four tributaries of the Mississippi River in April, July, and September 2009

Table 5-4. Average percent permeability decline normalized per mg/L carbon load for two membranes filtering seasonal water samples from four tributaries of the upper Mississippi River

	Leech Lake River		Rice River		Clearwater River		Shingle Creek		Average	
Membrane	YM30	PM30	YM30	PM30	YM30	PM30	YM30	PM30	YM30	PM30
April	0.38	3.08	0.13	1.24	0.57	1.21	0.52	1.49	0.40	1.76
June	1.15	3.50	0.09	0.97	0.06	2.62	1.89	0.47	0.80	1.89
September	0.72	2.85	0.08	1.14	0.53	0.52	0.41	1.00	0.43	1.38
Average	0.75	3.14	0.10	1.12	0.39	1.45	0.94	0.99	0.54	1.67
Average	1.95		0.61		0.92		0.96		1.11	

DOC removal was consistent across membrane type, but varied seasonally (Figure 5-14). For all tributaries and membranes, July removals of DOC were outside of one standard deviation from the April and September sampling times. More DOC was removed in July for the Rice River sample (64.3 and 65.2%), but less in the other tributaries (3.1 - 27.9%). The maximum Raman intensity for the Rice River, as determined by fluorescent spectroscopy (Table 5-3), indicated that the NOM had more aromatic ring structures, which may have contributed to its better removal by both the hydrophobic and hydrophilic membranes. Similar to the DOC results, UV₂₅₄ removal was consistent across membrane type, but varied seasonally (Figure 5-15). All tributaries removed the most UV₂₅₄ from the April water, which had low SUVA values, indicating NOM of lower molecular weight and aromaticity compared to the other waters. Low SUVA molecules are typically small, neutral, and aliphatic and have been implicated in irreversible membrane fouling due to their tendency to absorb within the pores (Kimura et al., 2004; Fan et al., 2001; Cho et al., 2000). No absorbance was removed from the July Leech Lake sample.

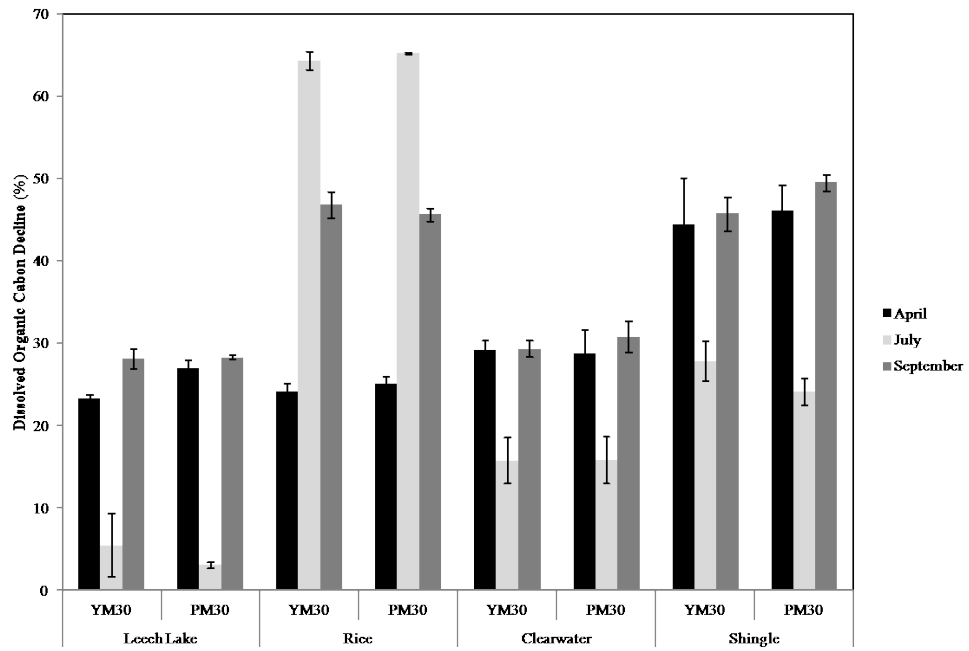


Figure 5-14. Percent DOC Removal (\pm standard deviation) for two membranes filtering four tributaries of the Mississippi River in April, July, and September 2009

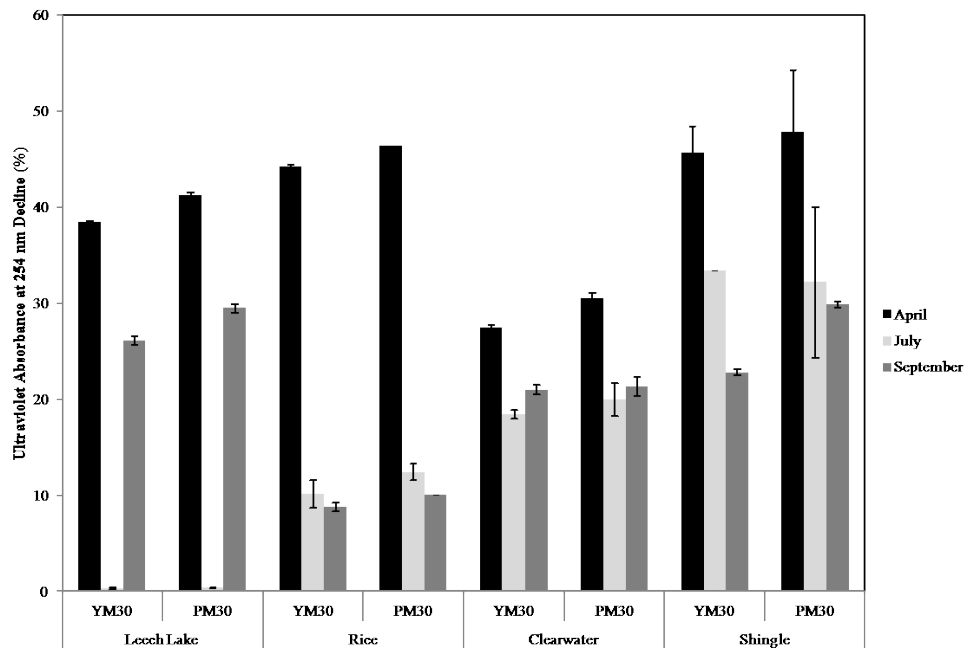


Figure 5-15. Percent UV₂₅₄ removal (\pm standard deviation) for two membranes filtering four tributaries of the Mississippi River in April, July, and September 2009

5.5 Conclusion

Tributaries of the upper Mississippi River representing a range of land uses were sampled for nine months to determine the impact of temporal and spatial variation in NOM concentration and composition with respect to membrane filtration. The water quality of the tributaries was responsive to seasonal events, such as flooding after the spring snow melt, individual storm events, and primary production in the summer. Distinct spatial NOM signatures were not observed due to the mix of land uses within the large watersheds. The two urban streams, however, could be differentiated from the others by their response or 'flashiness' to storm and flood events. The hydrophilic membrane had the least permeability decline from the temporal and spatial waters. In particular, the tributaries draining watersheds dominated by forests and wetlands fouled the hydrophobic membrane at a much greater relative degree when compared to tributaries draining watersheds dominated by agriculture and urban land uses. Removal of DOC and UV₂₅₄ in the seasonal waters was consistent by membrane hydrophobicity, but not consistent by season. These factors suggest that membrane treatment of waters fouled by NOM may be affected by both land use (influencing NOM removal) as well as membrane hydrophobicity and temporal events (influencing the rate of membrane fouling) in a complex synergy. Additional research is needed to elucidate the specific roles of these governing parameters.

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Chapter 6

Conclusions

6.1 Summary and Conclusions

The results of this research suggest that the potential benefits derived from the increased data provided by an on-line monitoring system should outweigh the maintenance requirements for such instrumentation. Such data potentially could be used for real-time control of chemical dosing rates as well as membrane backwash and cleaning schedules.

The permeability of full-scale hydrophilic ultrafiltration membranes was negatively correlated with river flow and raw water specific ultraviolet absorbance. A hydrophilic membrane also showed the least permeability decline for untreated and lime softened seasonal Mississippi River waters. Proper operation of pretreatment systems such as lime softening can decrease the NOM load on water treatment membranes.

NOM concentration and composition were relatively stable along the Mississippi River in Minnesota, despite varying land use. The size of the river mutes many of the NOM contributions by tributaries. In these tributaries, TOC, DOC, and SUVA were negatively correlated with percent of agricultural land use in the watershed. TOC and DOC concentration and export were positively correlated with the percent of shrubland area in the watershed even though this land use is minimal. In a nine month study of both temporal and land use impacts, membrane fouling did not obviously vary between land uses, but was highly influenced by both membrane hydrophobicity and seasonal events, such as spring snow melt.

This survey of the upper Mississippi River and its tributaries could help inform policy and engineering decisions regarding watershed and surface water quality management and treatment plant design. More specifically, the results of this research encourage extensive near real-time monitoring and membrane pilot studies as well as pretreatment and large-scale watershed assessments for utilities considering membrane filtration systems for surface water treatment. In

addition, this work could aid in the formulation of policies and regulations governing land use, land development, stormwater management, and wastewater discharges.

6.2 Contributions

The main contributions of this research include:

1. Determination that near real-time monitoring of NOM concentration and composition is feasible and furthermore, is beneficial to understand the performance of water treatment plants utilizing membrane filtration.
2. Generation of a correlation between land use (shrubland and agriculture) and TOC and DOC concentrations in the upper Mississippi River watershed.
3. Calculation of DOC export in the upper Mississippi River watershed during a late summer through early fall period.
4. Determination that a hydrophilic membrane in conjunction with lime softening experienced the least fouling from upper Mississippi River seasonal waters.
5. Observation that membrane fouling is more influenced by membrane hydrophobicity and temporal changes rather than watershed land uses.

6.3 Research Needs

As water utilities install membranes to meet drinking water quality regulations, the role of membrane and NOM hydrophobicity in relation to the character and degree of NOM fouling has significant implications. The variation in surface waters, watersheds, available membranes, and treatment processes encourages more study of this topic from biomes to molecular interactions.

Mississippi River and tributary sampling sites were often chosen for ease of access. For a more comprehensive picture of a water body, sampling stations with flow and precipitation monitoring and automatic grab samplers should be established.

The filtration experiments performed for this research were done in a small, stirred cell system. Full-scale membrane plants have rigorous cleaning schedules of backwashes, chemicals, and air scouring that are critical to maintaining the constant production of safe drinking water. It would be useful to perform filtration experiments on spatially and temporally variable waters in a larger system that could mimic some full-scale cleaning processes. Differences between the portions of NOM responsible for reversible and irreversible fouling could then be better understood.

The larger permeability declines observed with natural waters as opposed to model NOM components indicate the need to study membrane fouling from a holistic rather than a 'splitter' standpoint. Unfortunately, the complexity of NOM precludes this, so modeling of seasonal Mississippi River water is suggested as a means to better understand the fouling mechanisms involved.

Chapter 7

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Appendix A

Membrane Filtration Results of Individual Runs

Figure A-1. IHSS Suwannee River Humic Acid in Carbonate Buffer K131 Membrane

Membrane	K-131	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Suwannee River Humic Acid in Carbonate Buffer	
Temperature	21.2 - 21.5	degC
Pressure	24	psi
Time Interval	10	sec
Stirring Rate	1	level

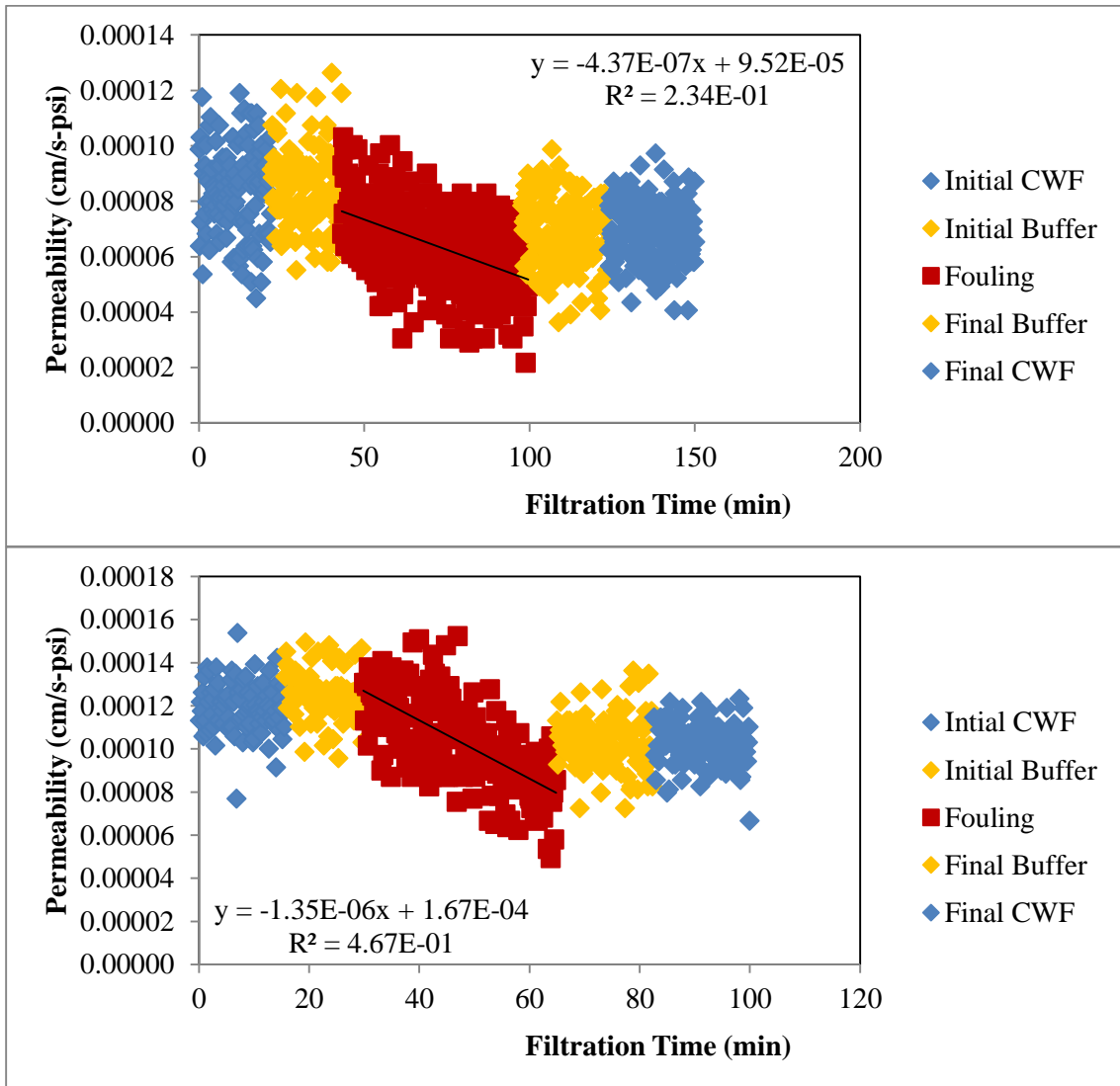


Figure A-2. IHSS Suwannee River Humic Acid in Carbonate Buffer M100 Membrane

Membrane	M-100	
MWCO	75	kDa
Material	PVDF	
Area	28.7	cm ²
Water	Suwannee River Humic Acid in Carbonate Buffer	
Temperature	20.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

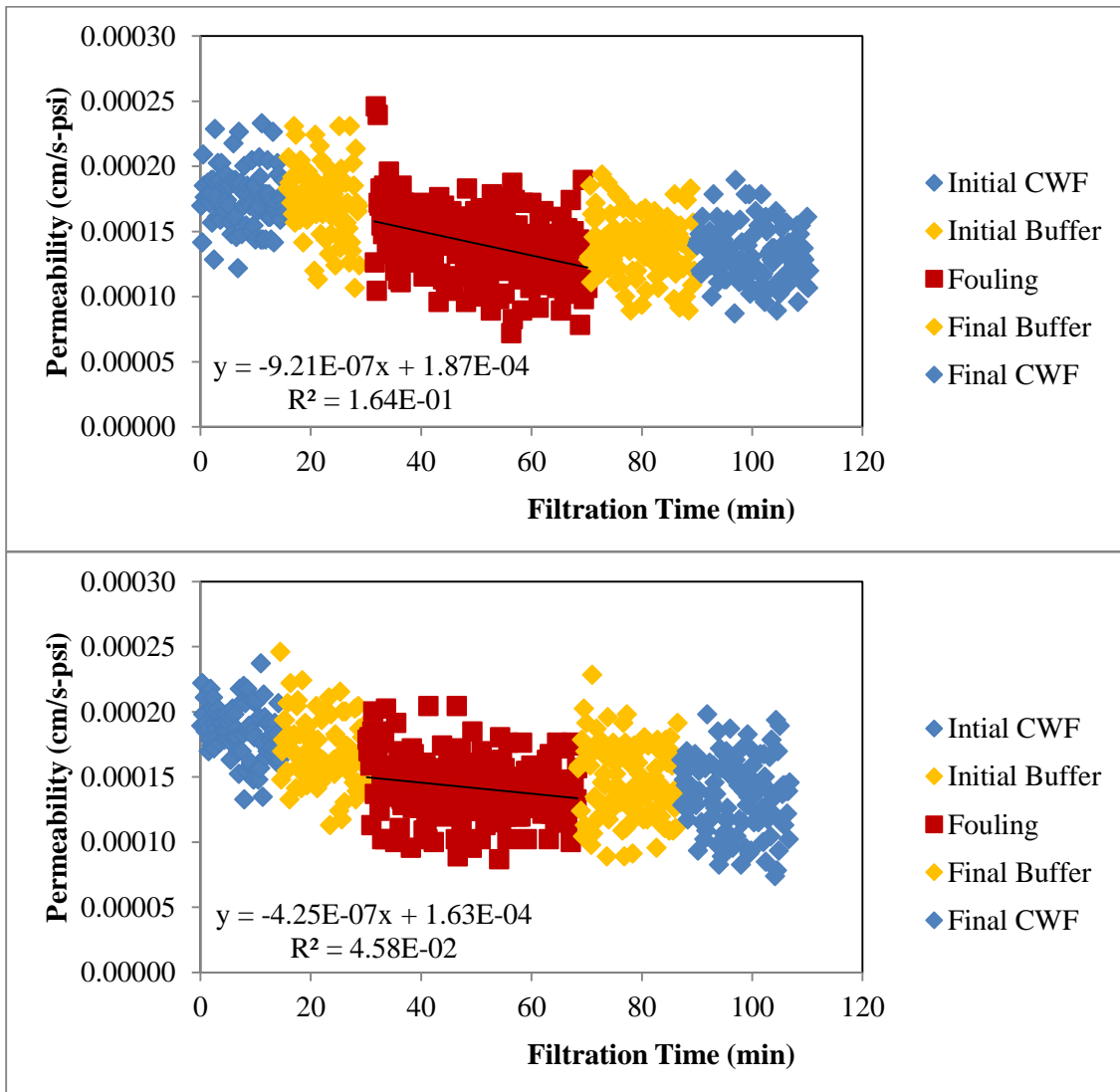


Figure A-3. IHSS Suwannee River Humic Acid in Carbonate Buffer YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	Suwannee River Humic Acid in Carbonate Buffer	
Temperature	20.7 - 20.9	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

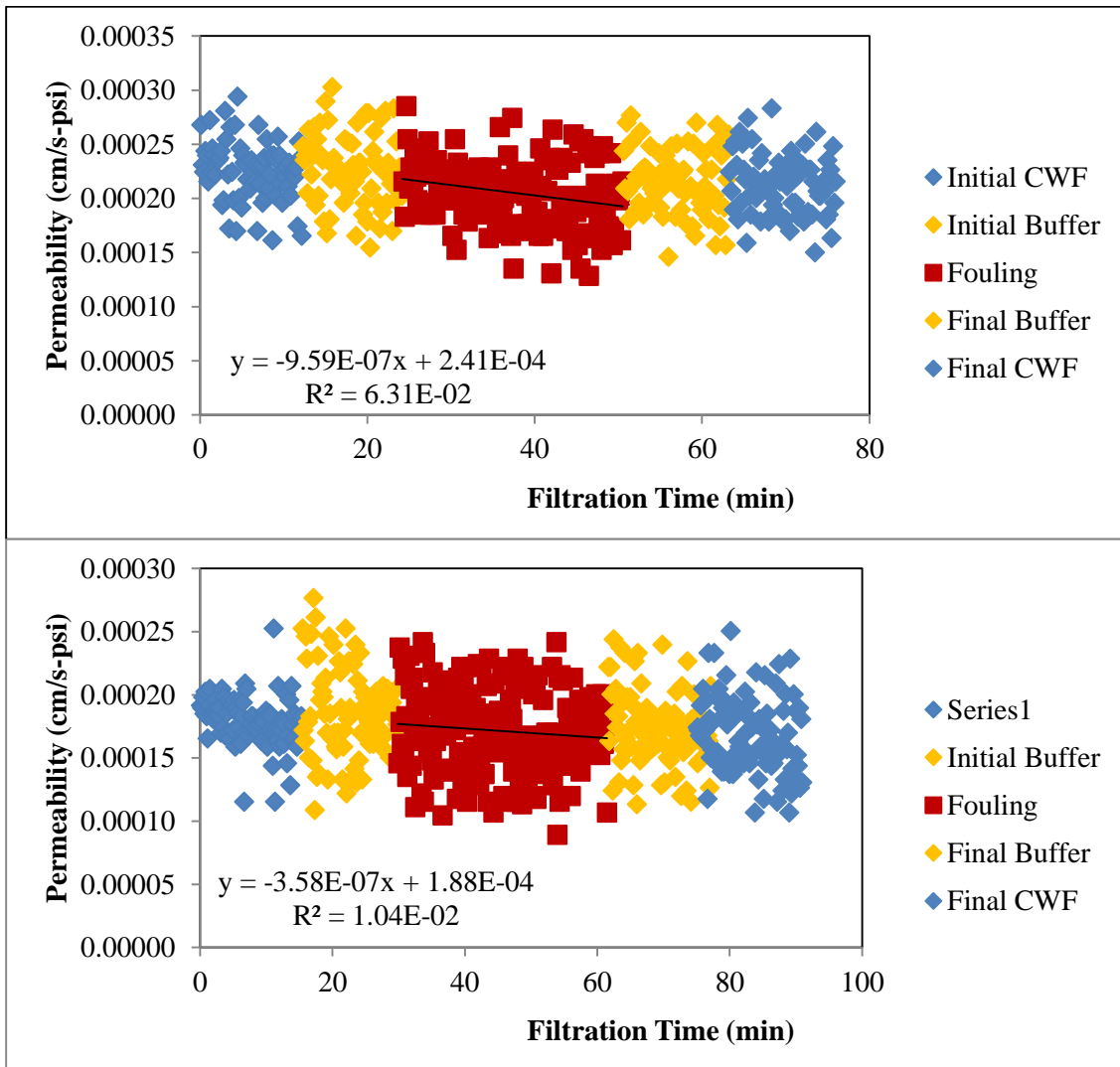


Figure A-4. IHSS Suwannee River Humic Acid in Carbonate Buffer PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Suwannee River Humic Acid in Carbonate Buffer	
Temperature	20.4 - 20.5	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

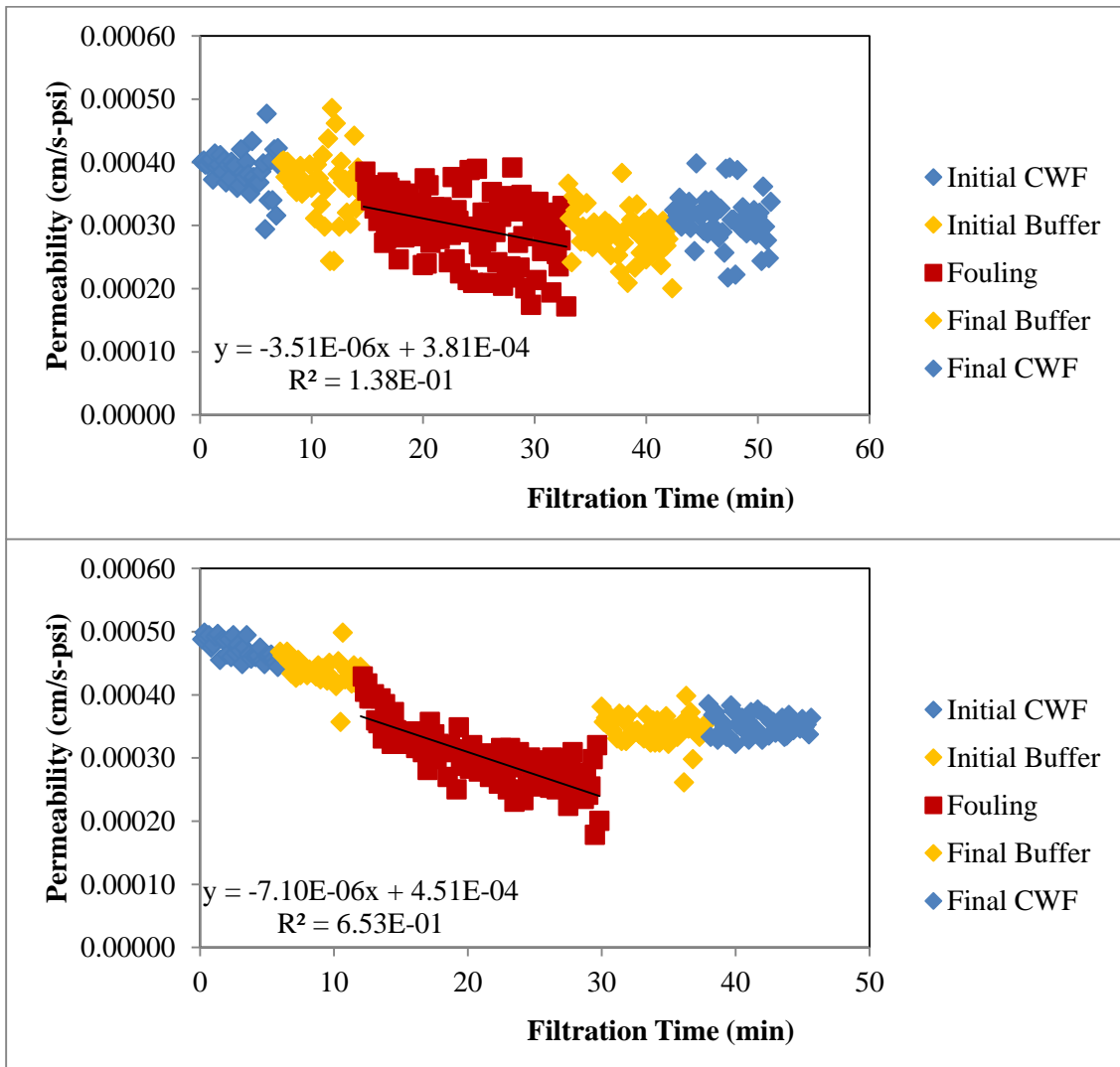


Figure A-5. IHSS Suwannee River Fulvic Acid in Carbonate Buffer K131 Membrane

Membrane	K-131	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Suwannee River Fulvic Acid in Carbonate Buffer	
Temperature	21.2 - 21.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

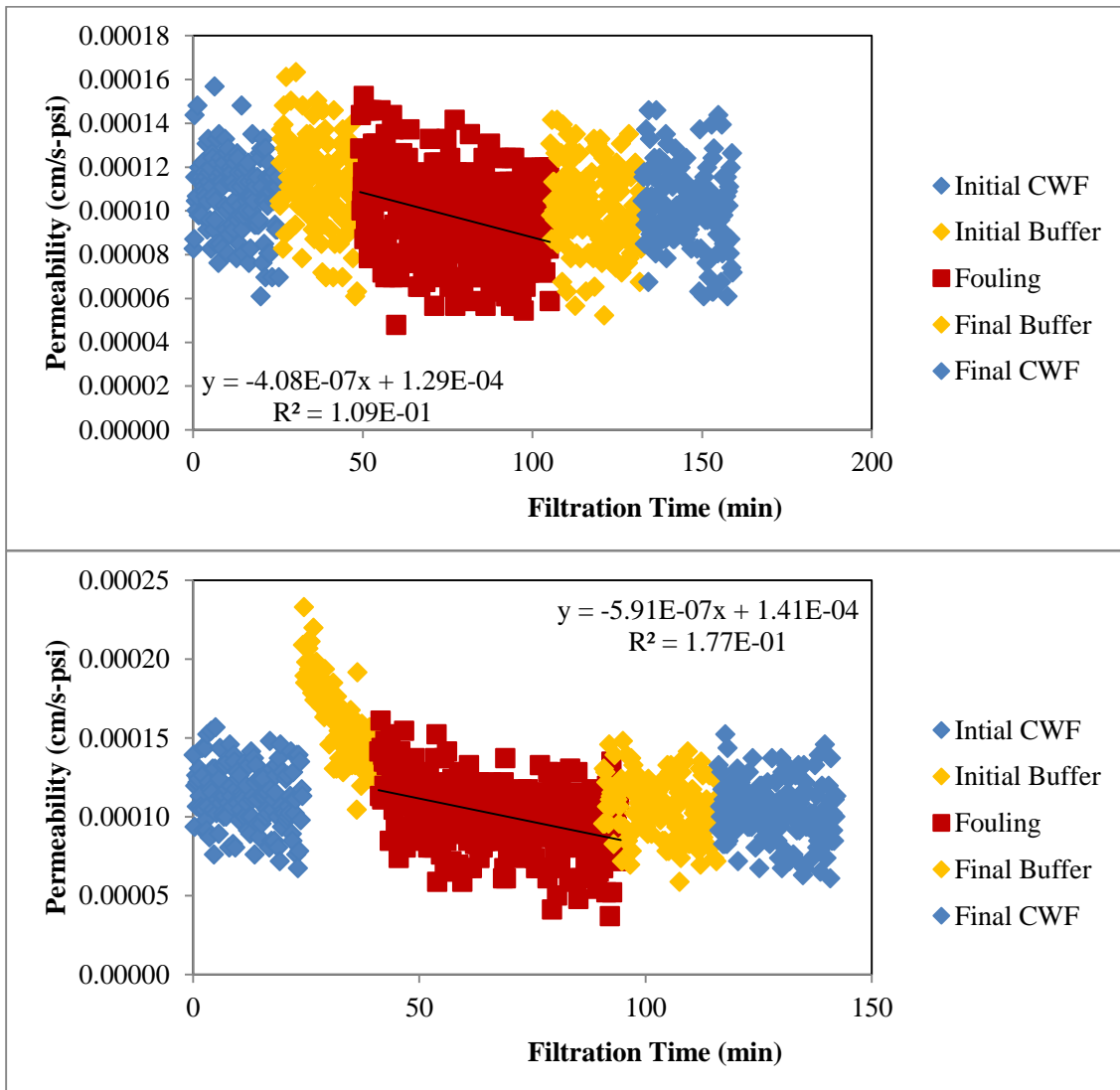


Figure A-6. IHSS Suwannee River Fulvic Acid in Carbonate Buffer M100 Membrane

Membrane	M-100	
MWCO	75	kDa
Material	PVDF	
Area	28.7	cm ²
Water	Suwannee River Fulvic Acid in Carbonate Buffer	
Temperature	22.6 - 25.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

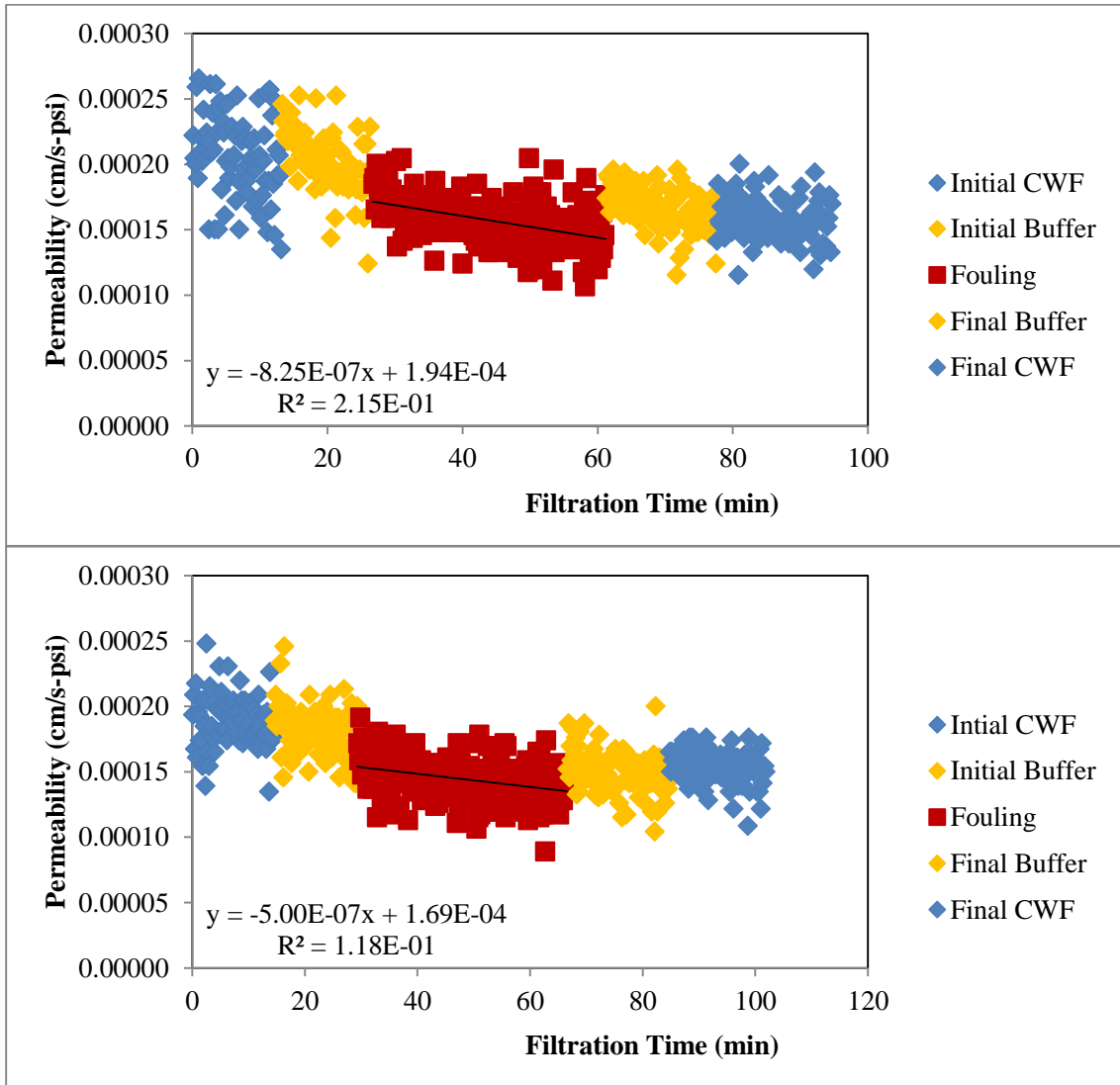


Figure A-7. IHSS Suwannee River Fulvic Acid in Carbonate Buffer YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	Suwannee River Fulvic Acid in Carbonate Buffer	
Temperature	20.9	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

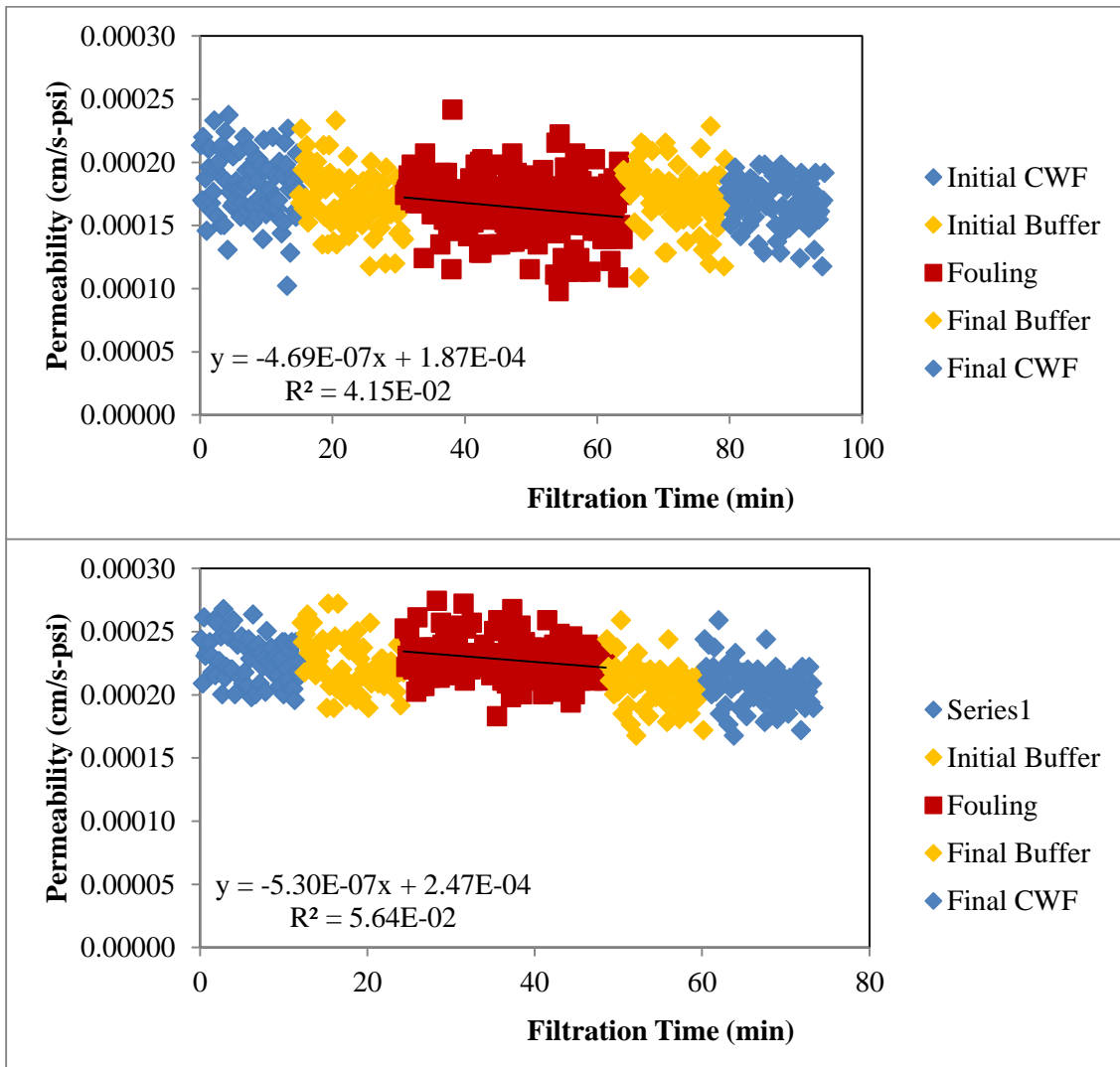


Figure A-8. IHSS Suwannee River Fulvic Acid in Carbonate Buffer PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Suwannee River Fulvic Acid in Carbonate Buffer	
Temperature	20.5 - 20.6	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

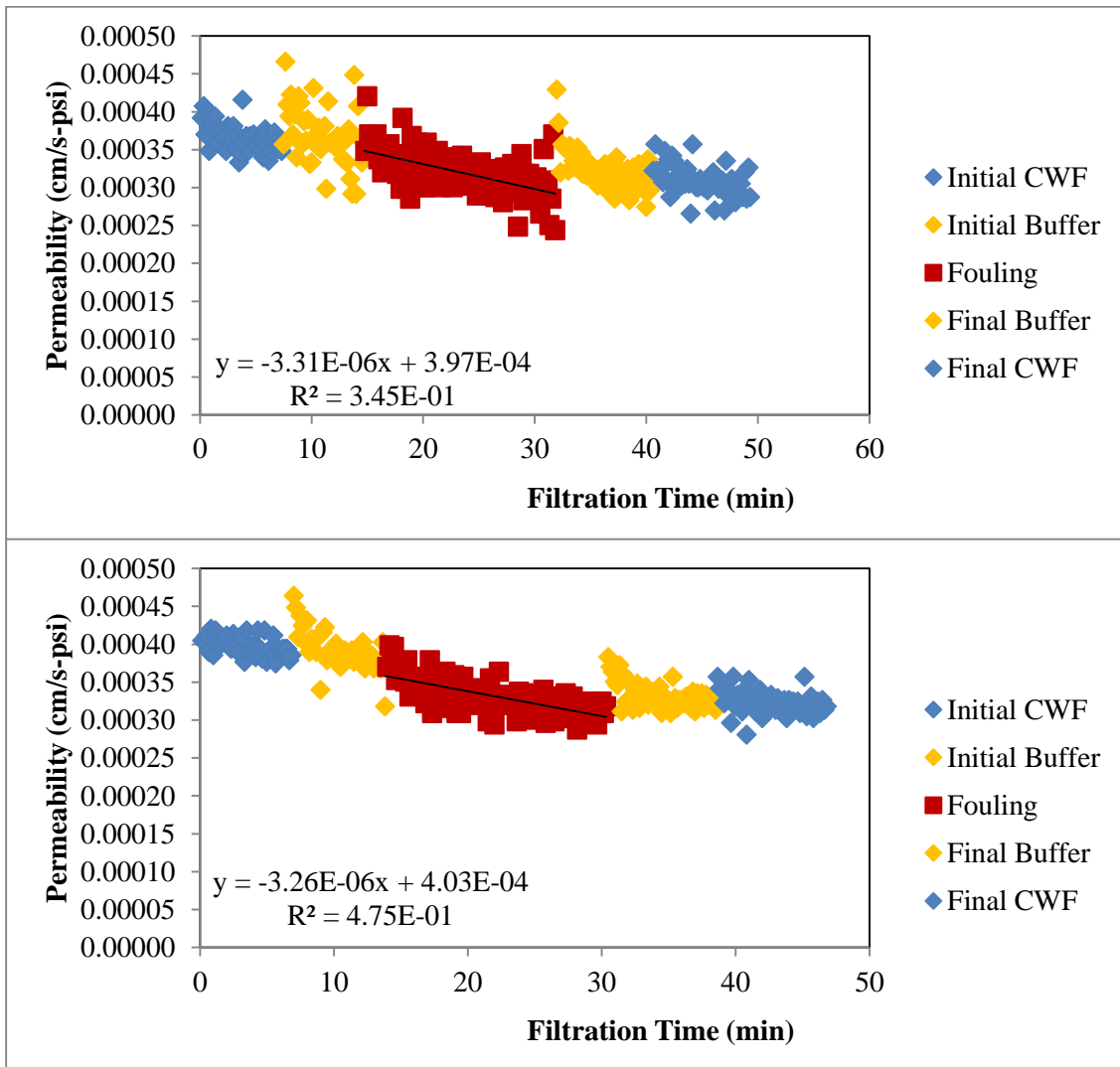


Figure A-9. IHSS Suwannee River Whole NOM in Carbonate Buffer K131 Membrane

Membrane	K-131	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Suwannee River Whole NOM in Carbonate Buffer	
Temperature	22.3 - 22.8	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

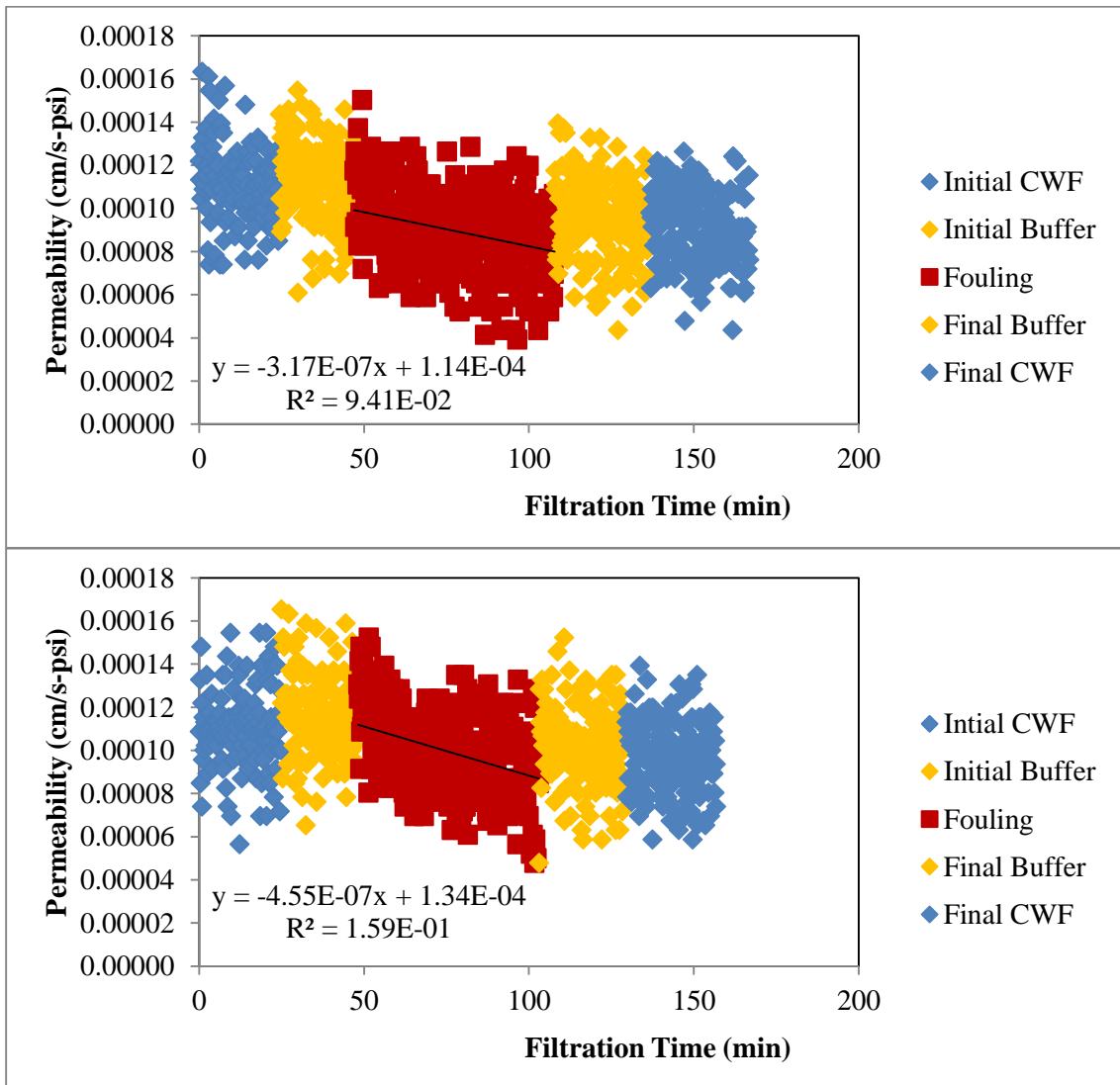


Figure A-10. IHSS Suwannee River Whole NOM in Carbonate Buffer M100 Membrane

Membrane	M-100	
MWCO	75	kDa
Material	PVDF	
Area	28.7	cm ²
Water	Suwannee River Whole NOM in Carbonate Buffer	
Temperature	19.9 - 20.4	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

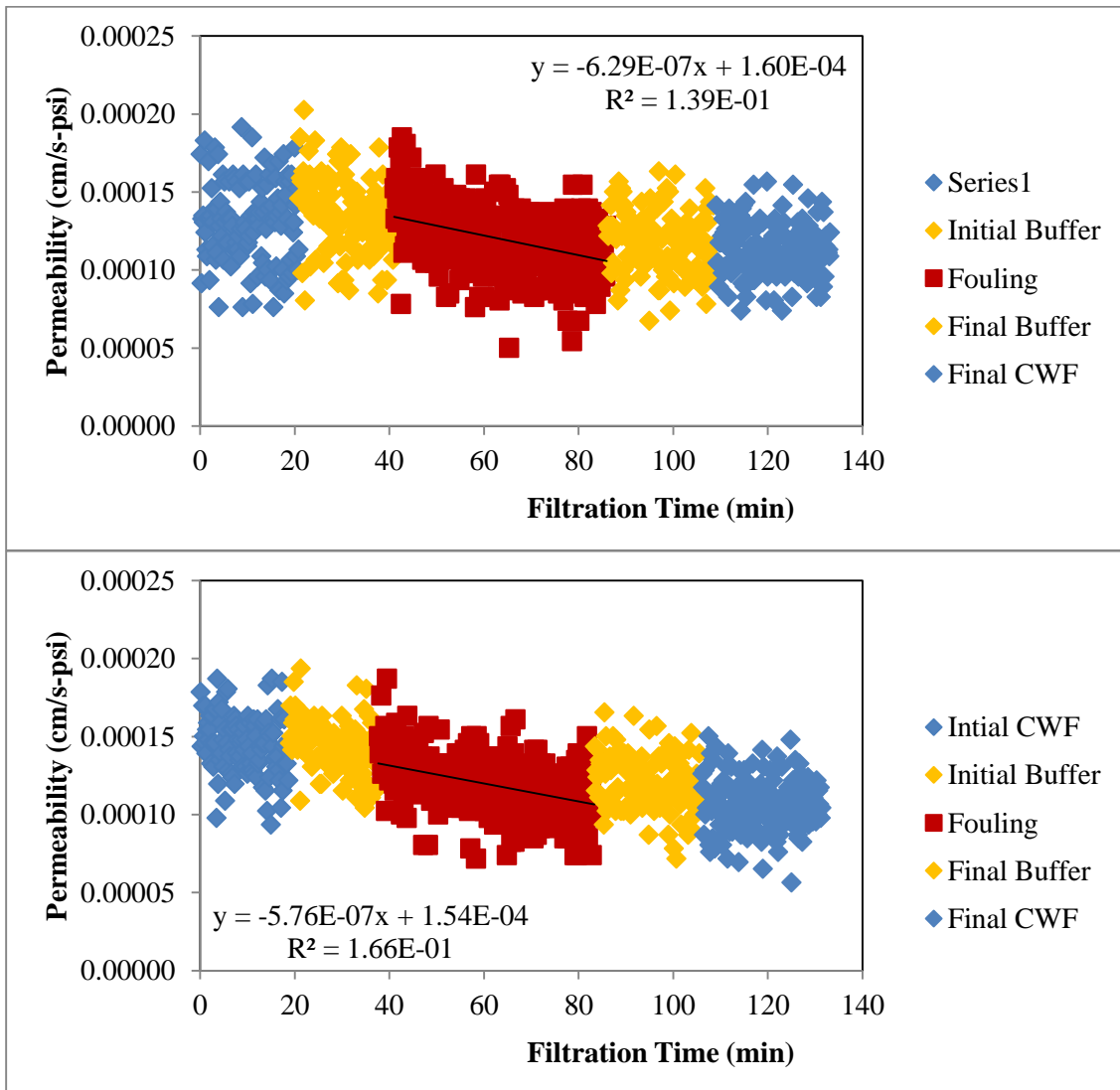


Figure A-11. IHSS Suwannee River Whole NOM in Carbonate Buffer YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	Suwannee River Whole NOM in Carbonate Buffer	
Temperature	18.5 - 19.0	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

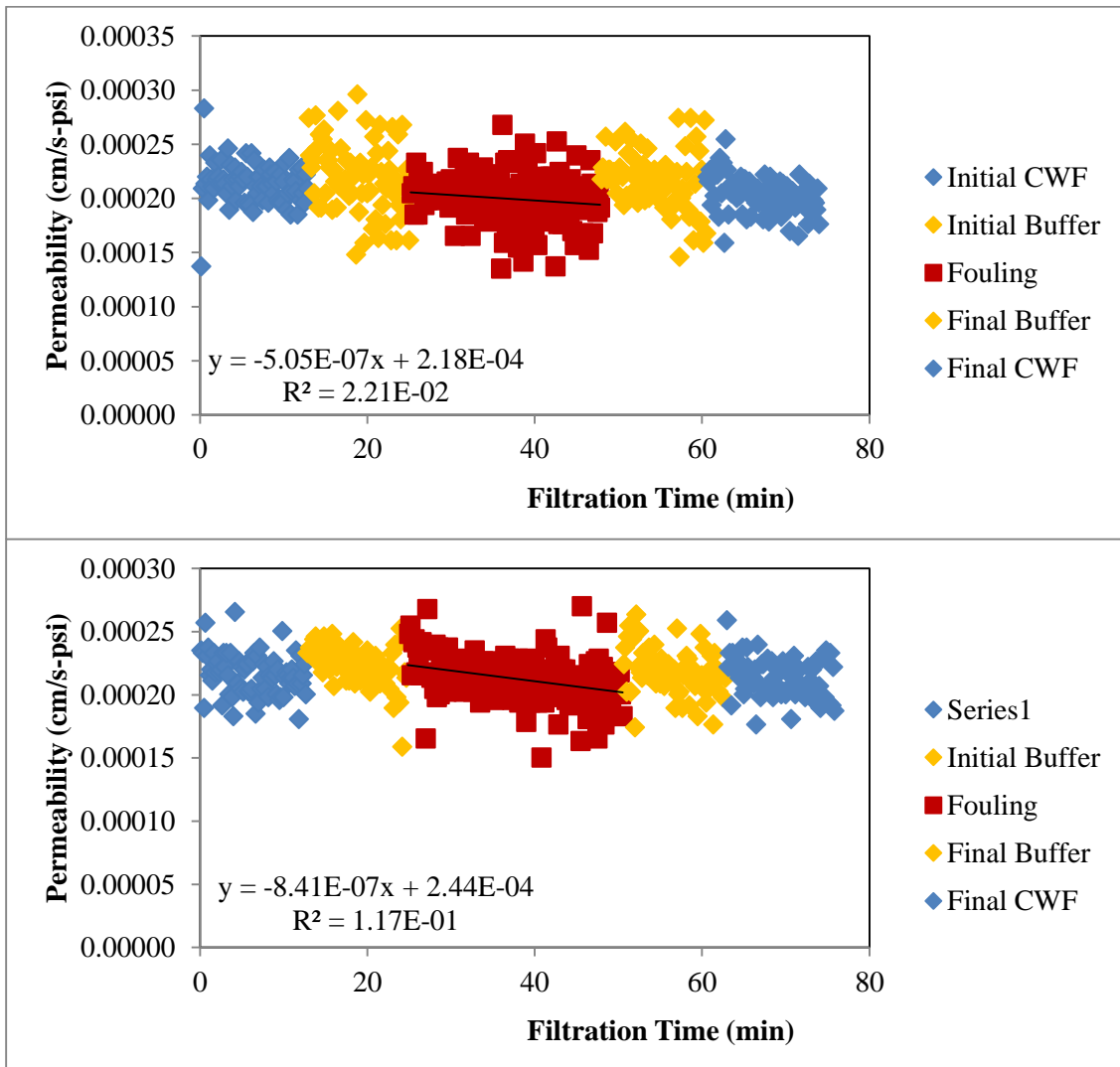


Figure A-12. IHSS Suwannee River Whole NOM in Carbonate Buffer PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Suwannee River Whole NOM in Carbonate Buffer	
Temperature	21.4	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

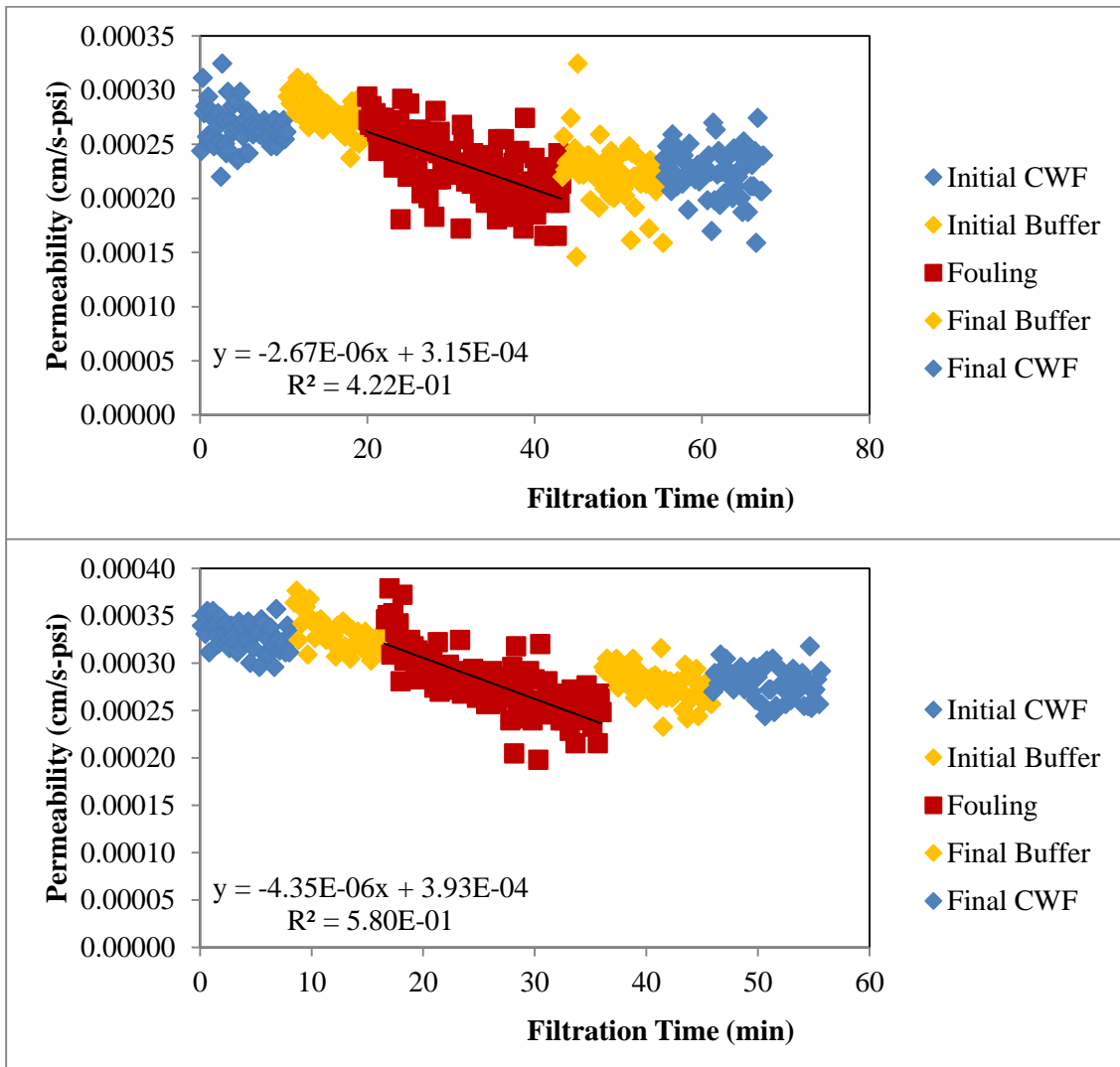


Figure A-13. IHSS Pony Lake Fulvic Acid in Carbonate Buffer K131 Membrane

Membrane	K-131	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Pony Lake Fulvic Acid in Carbonate Buffer	
Temperature	18.3 - 19.2	degC
Pressure	22	psi
Time Interval	10	sec
Stirring Rate	1	level

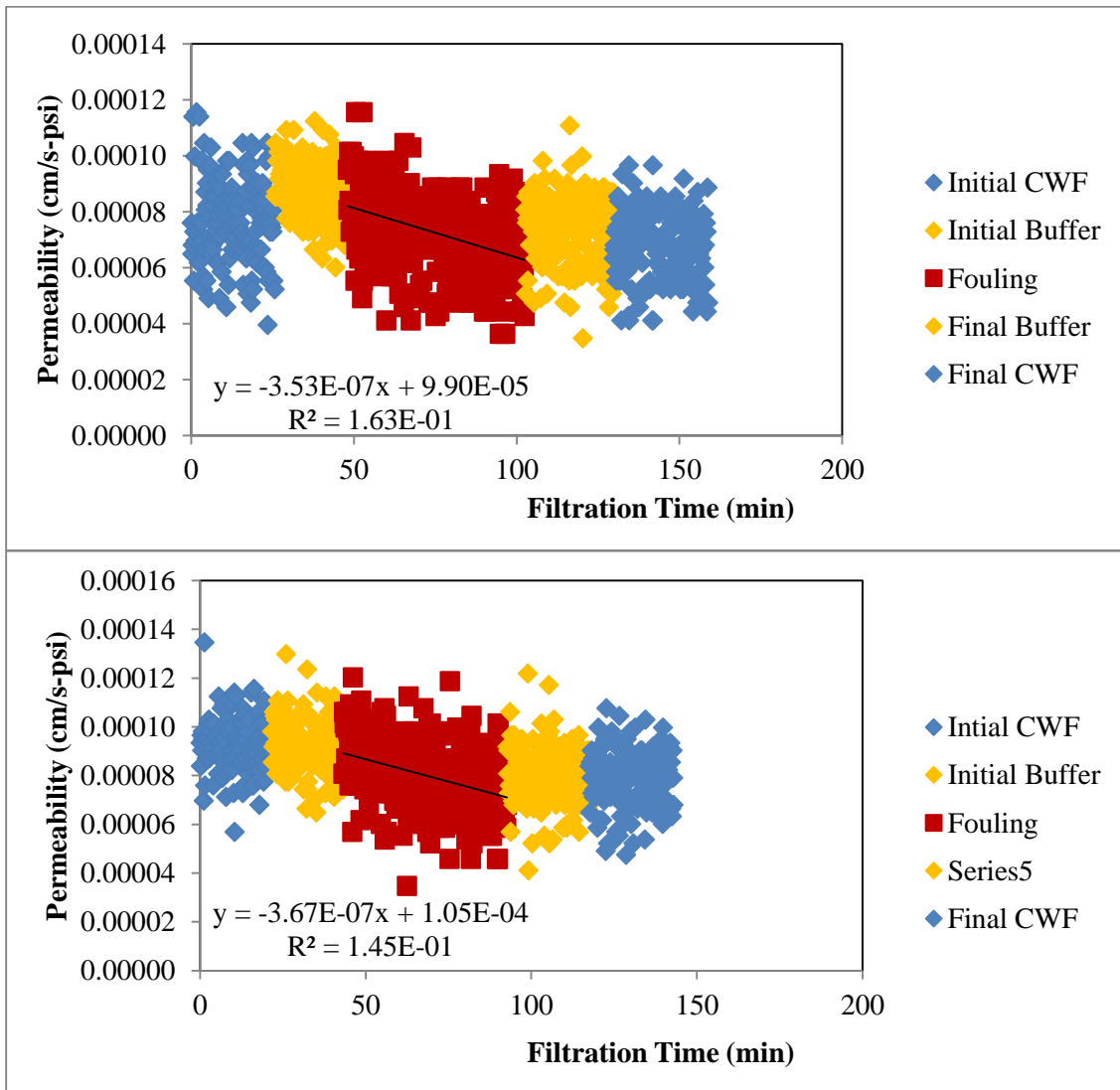


Figure A-14. IHSS Pony Lake Fulvic Acid in Carbonate Buffer M100 Membrane

Membrane	M-100	
MWCO	75	kDa
Material	PVDF	
Area	28.7	cm ²
Water	Pony Lake Fulvic Acid in Carbonate Buffer	
Temperature	19.4 - 19.5	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

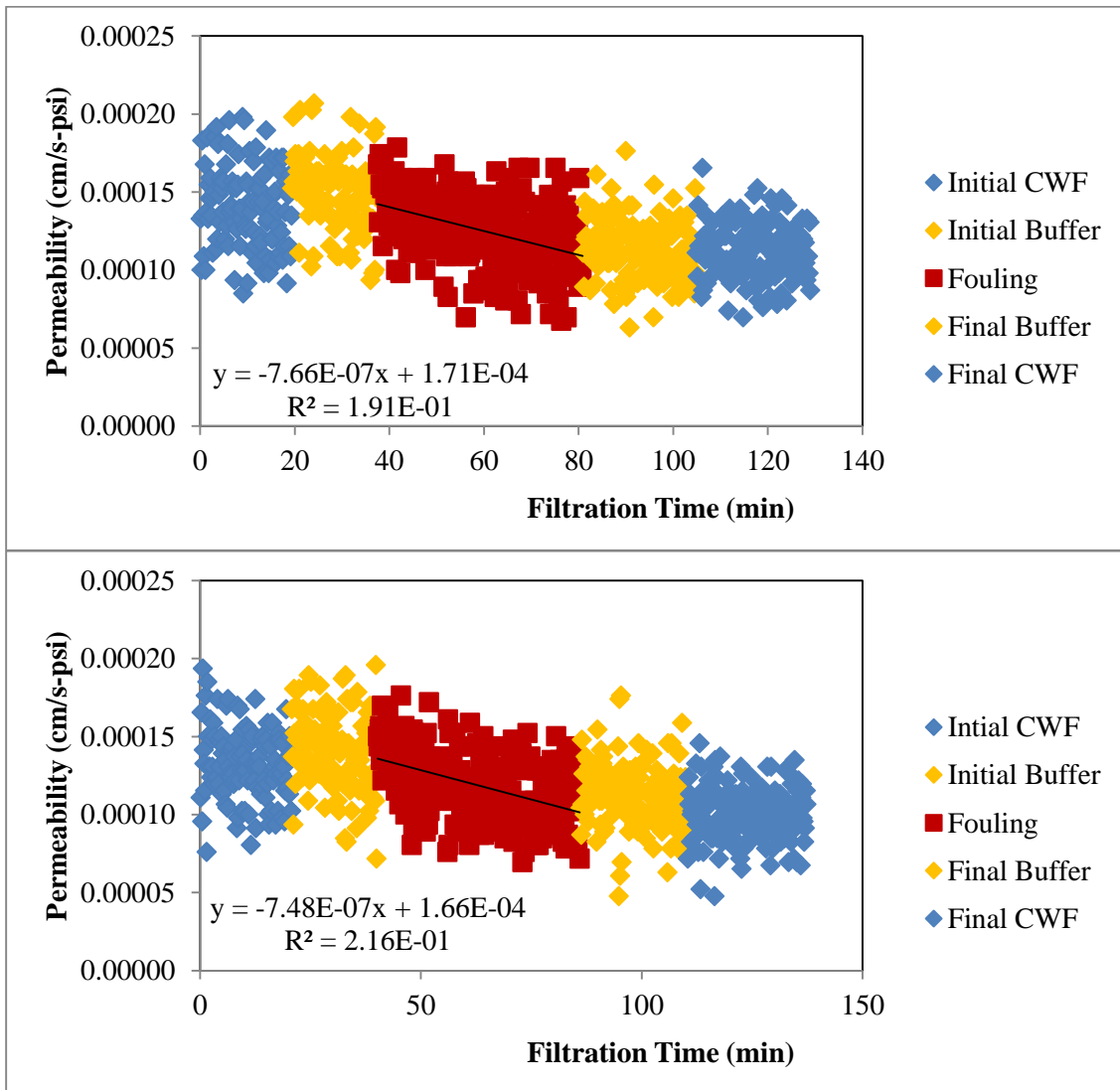


Figure A-15. IHSS Pony Lake Fulvic Acid in Carbonate Buffer YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	Pony Lake Fulvic Acid in Carbonate Buffer	
Temperature	19.7 - 20.2	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

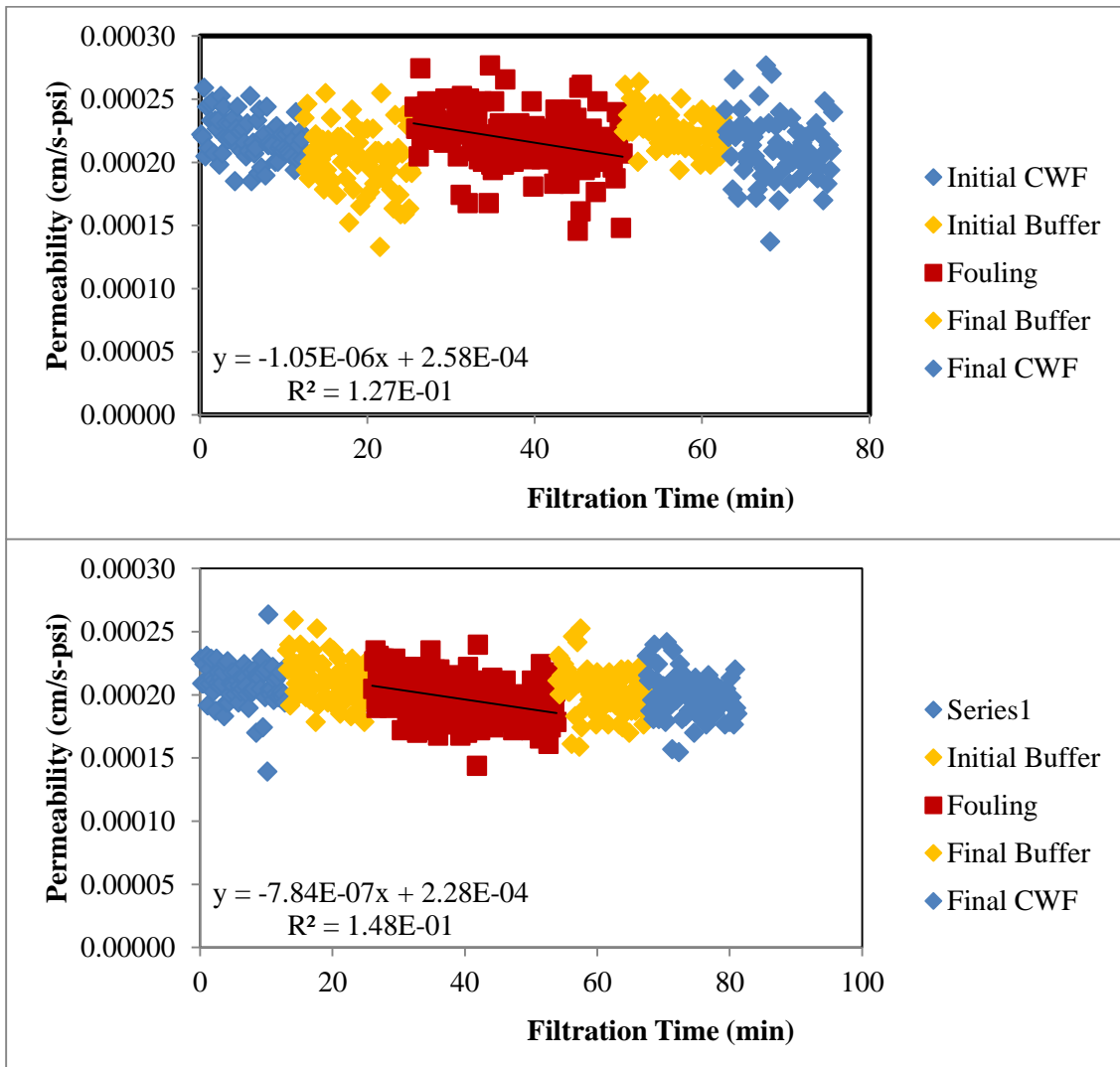


Figure A-16. IHSS Pony Lake Fulvic Acid in Carbonate Buffer PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Pony Lake Fulvic Acid in Carbonate Buffer	
Temperature	19.4 - 20.9	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

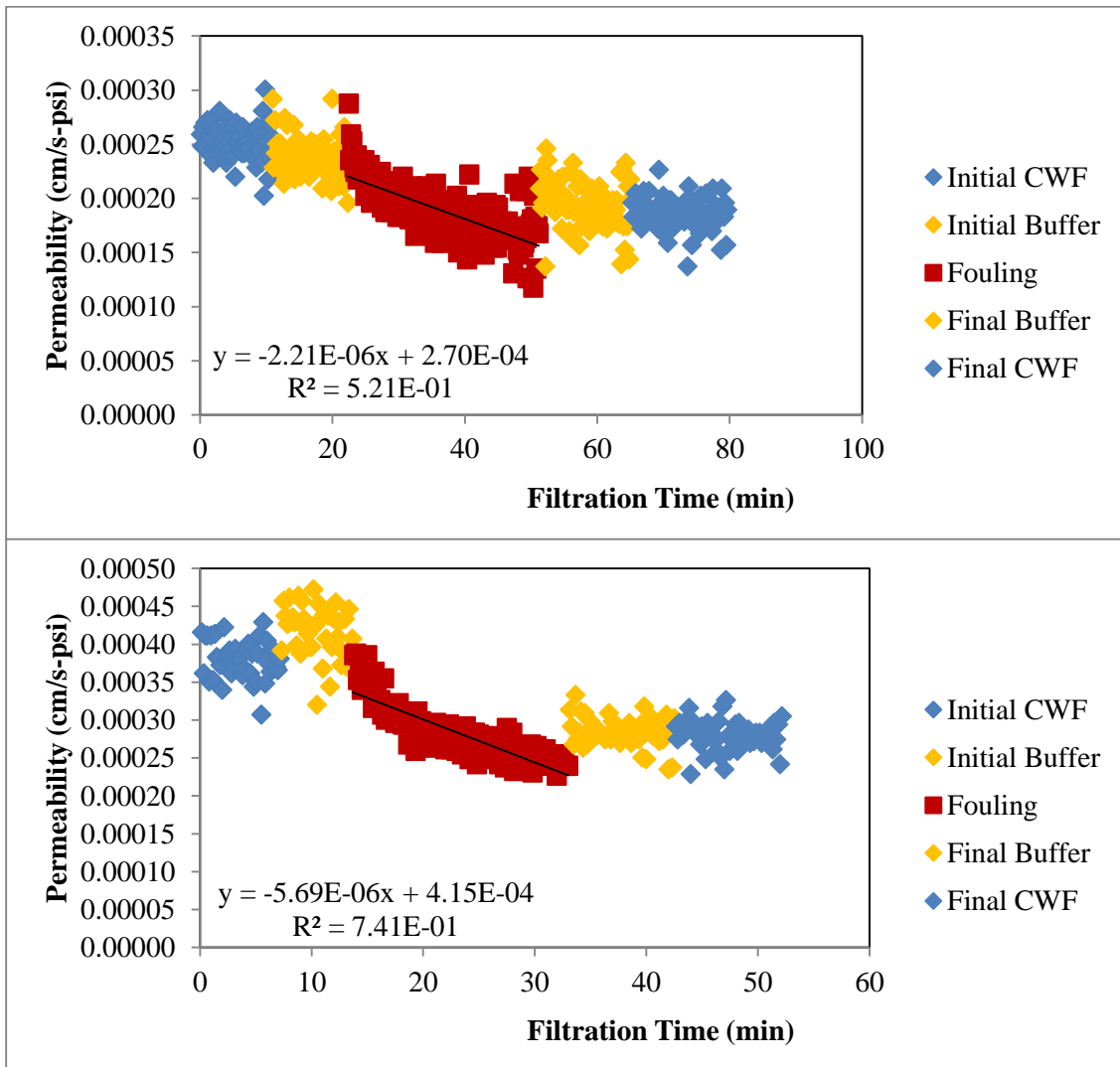
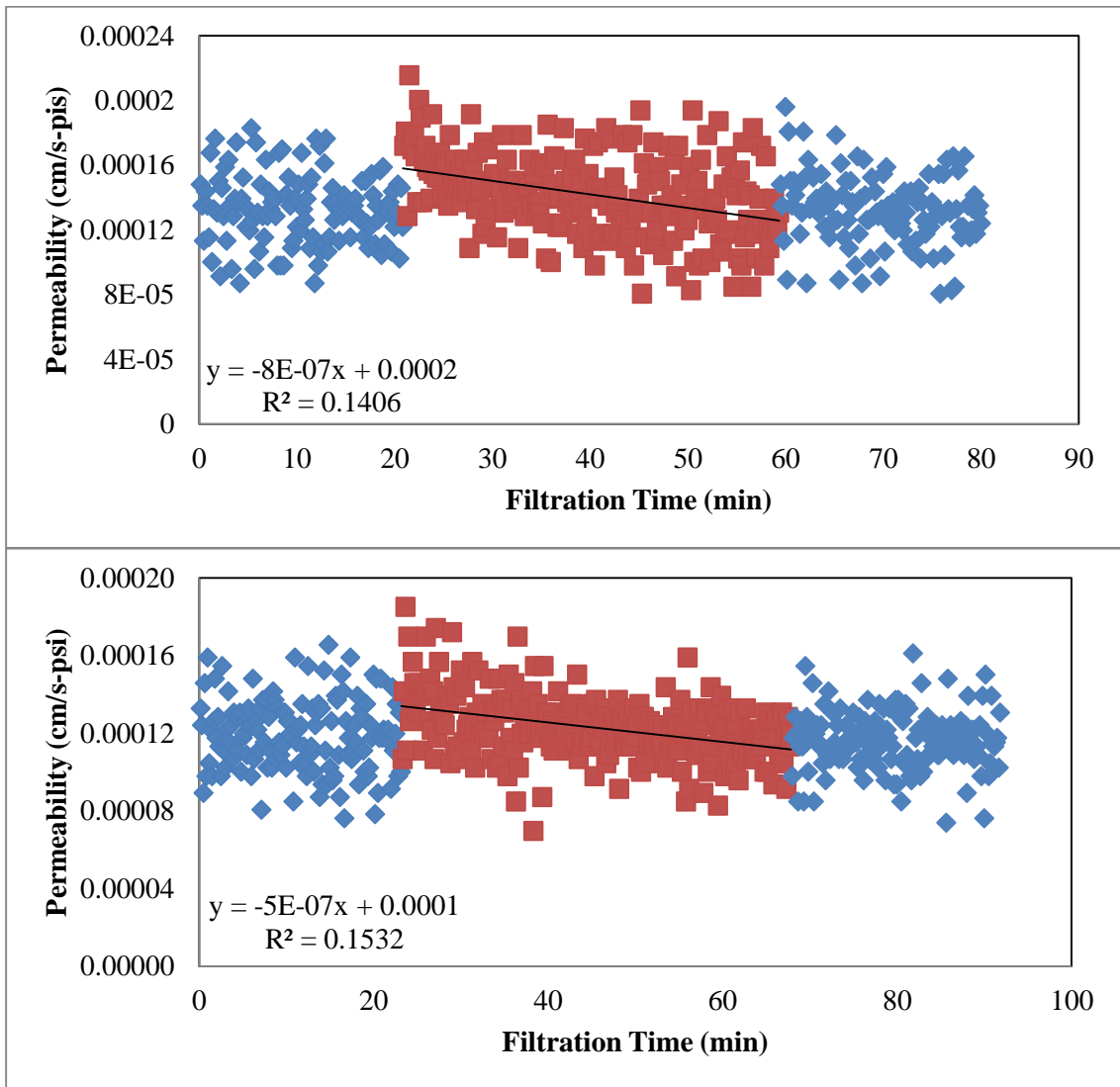


Figure A-17. Mississippi River Winter Raw K131 Membrane

Membrane	K-131	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Winter Raw Filtered	
Temperature	22.3-22.6	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level



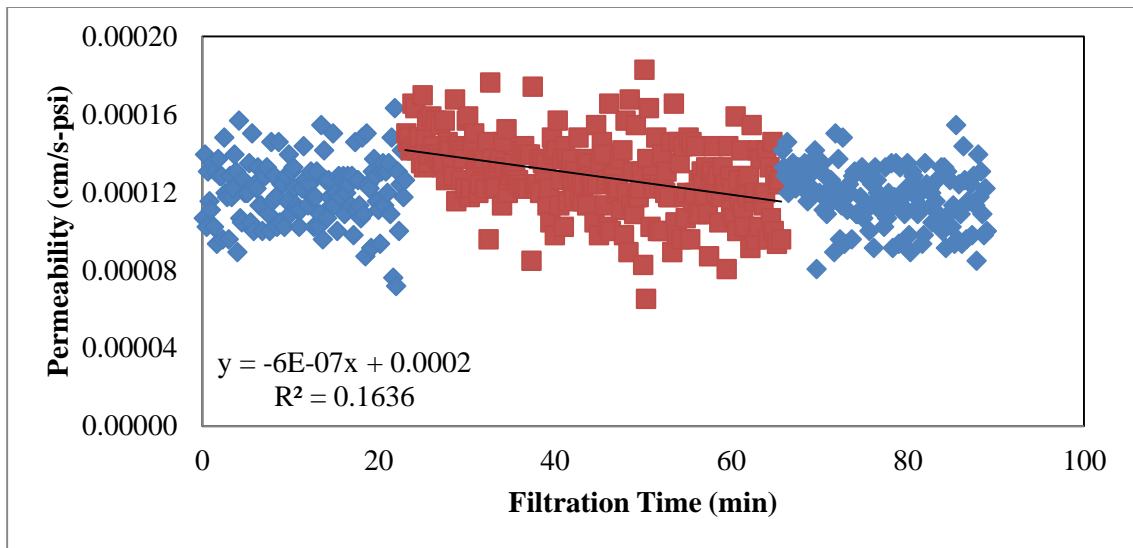
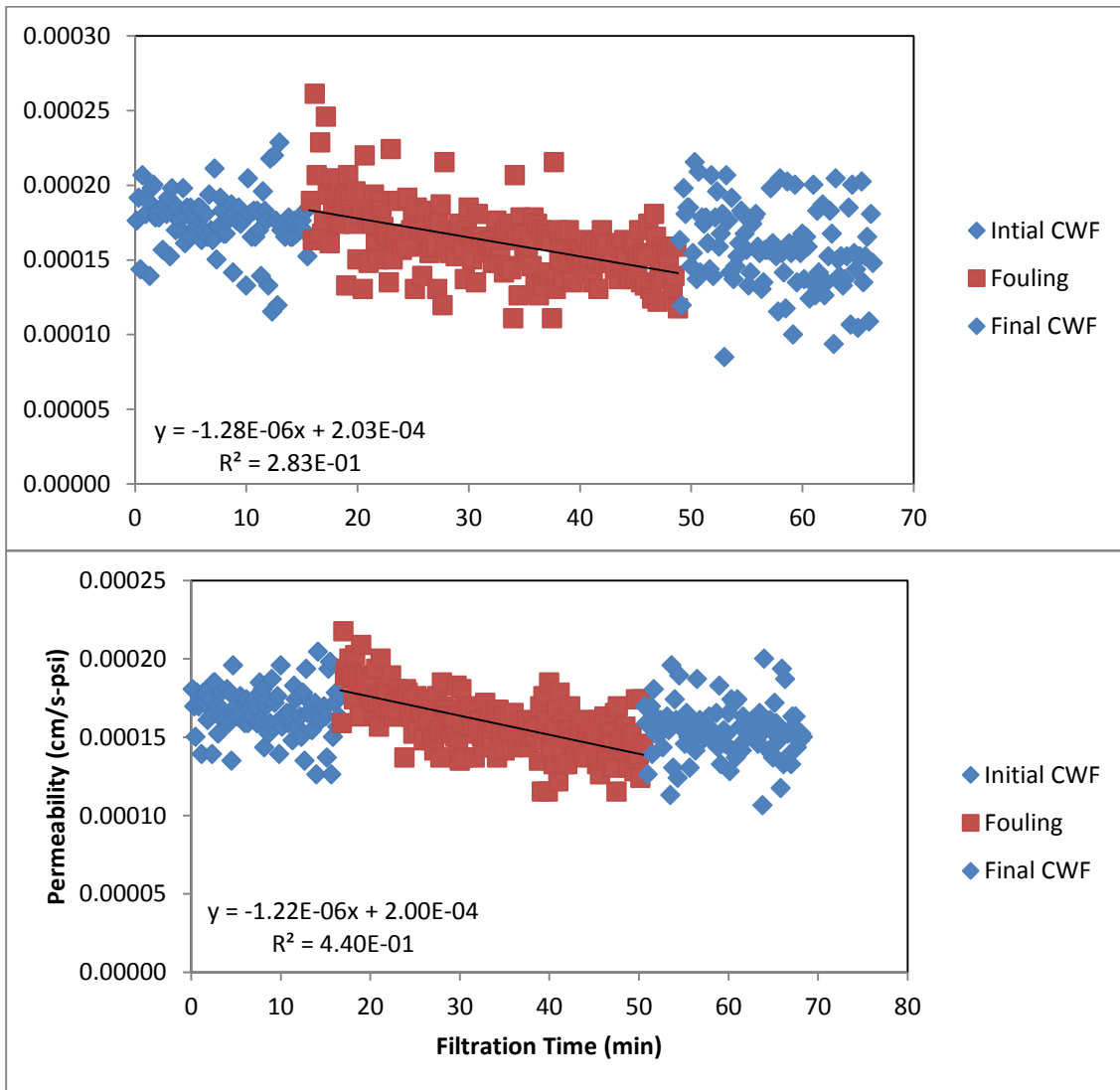


Figure A-18. Mississippi River Winter Raw M100 Membrane

Membrane	M-100	
MWCO	75	kDa
Material	PVDF	
Area	28.7	cm ²
Water	Winter Raw Filtered	
Temperature	22.7 - 23.0	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level



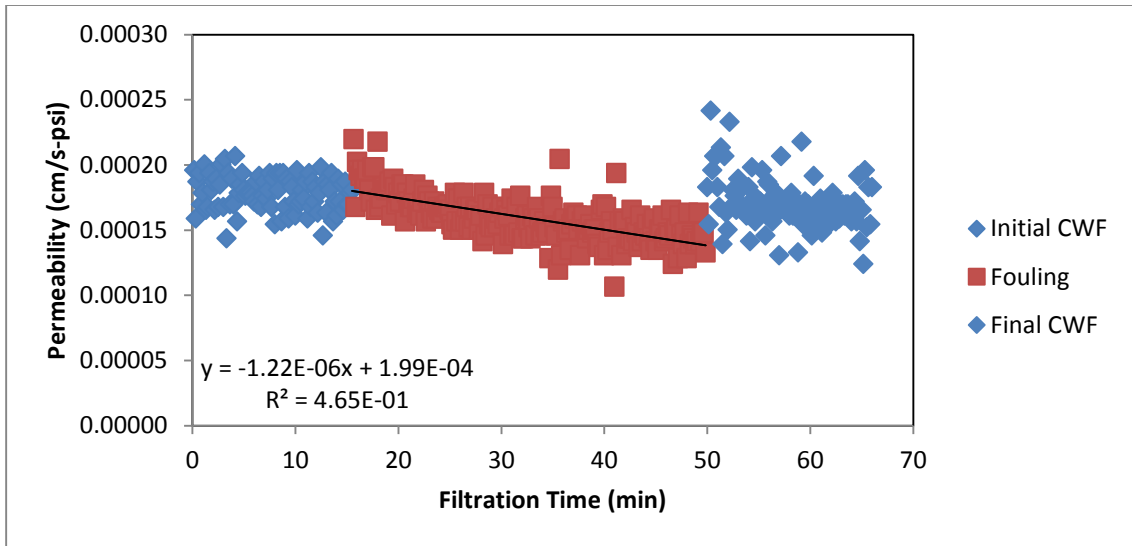


Figure A-19. Mississippi River Winter Raw YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	Winter Raw Filtered	
Temperature	23.3 - 23.5	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

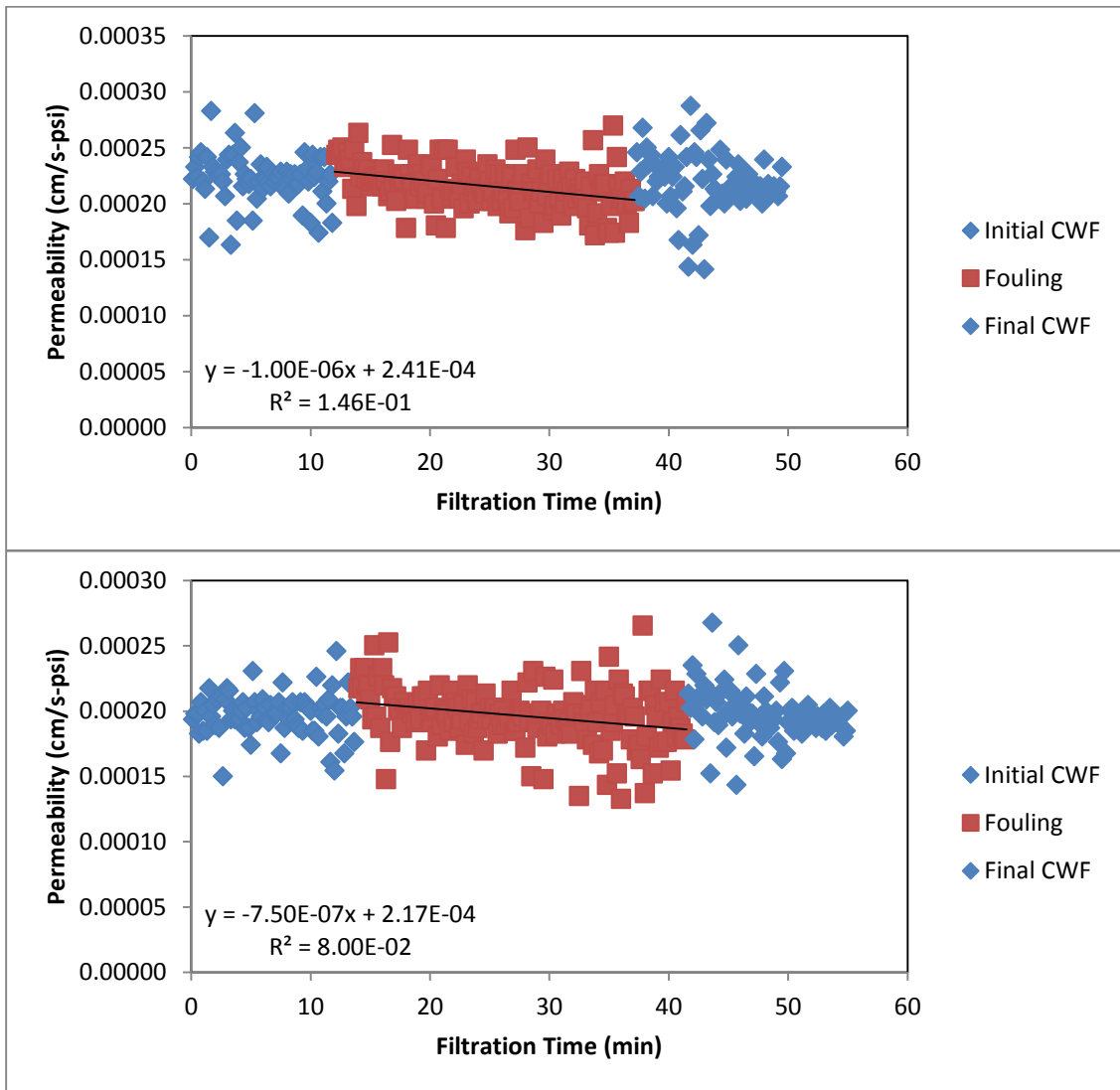


Figure A-20. Mississippi River Winter Raw PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Winter Raw Filtered	
Temperature	22.8	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

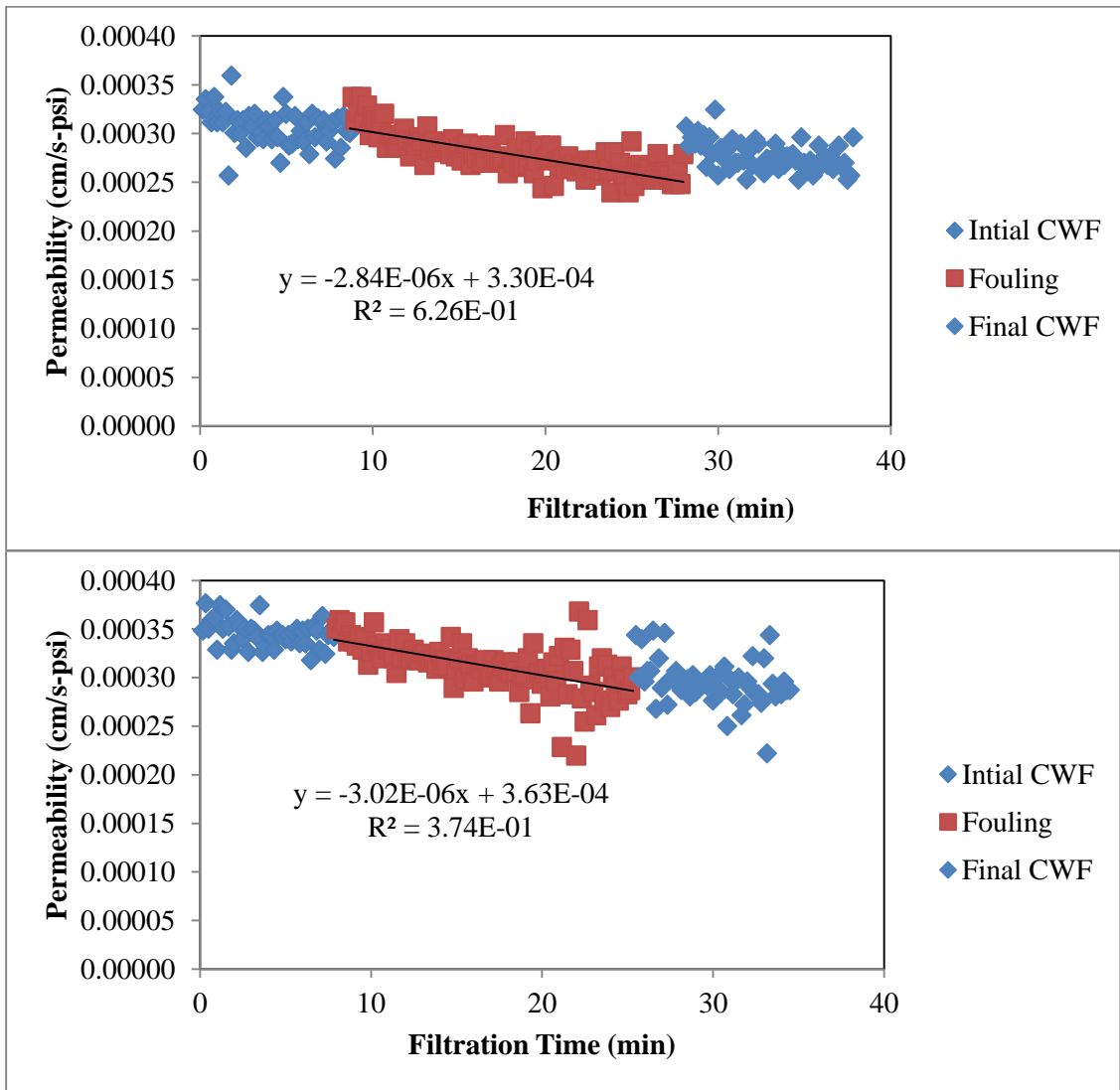
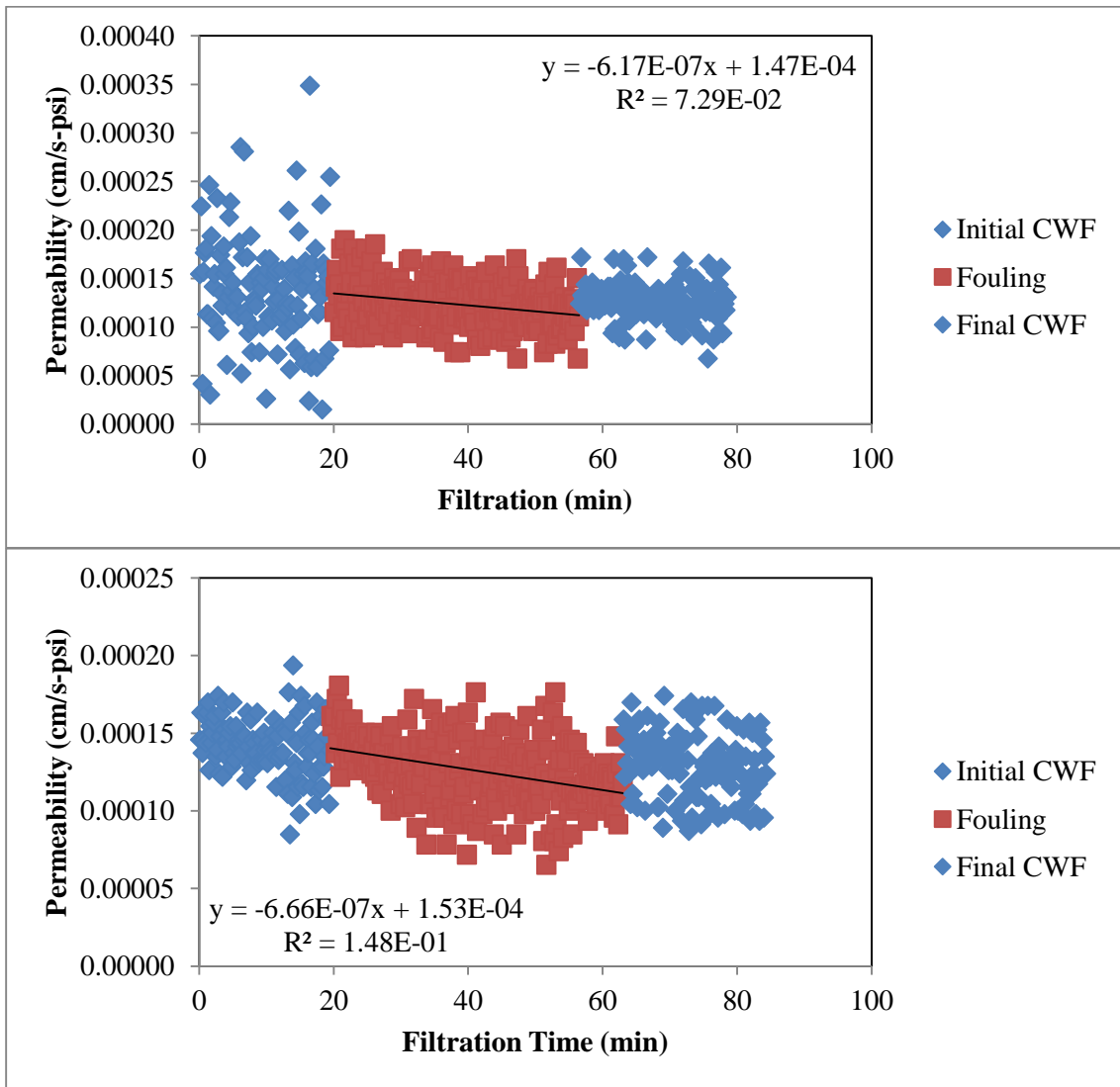


Figure A-21. Mississippi River Spring Raw K131 Membrane

Membrane	K-131	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Spring Raw Filtered	
Temperature	22.6-22.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level



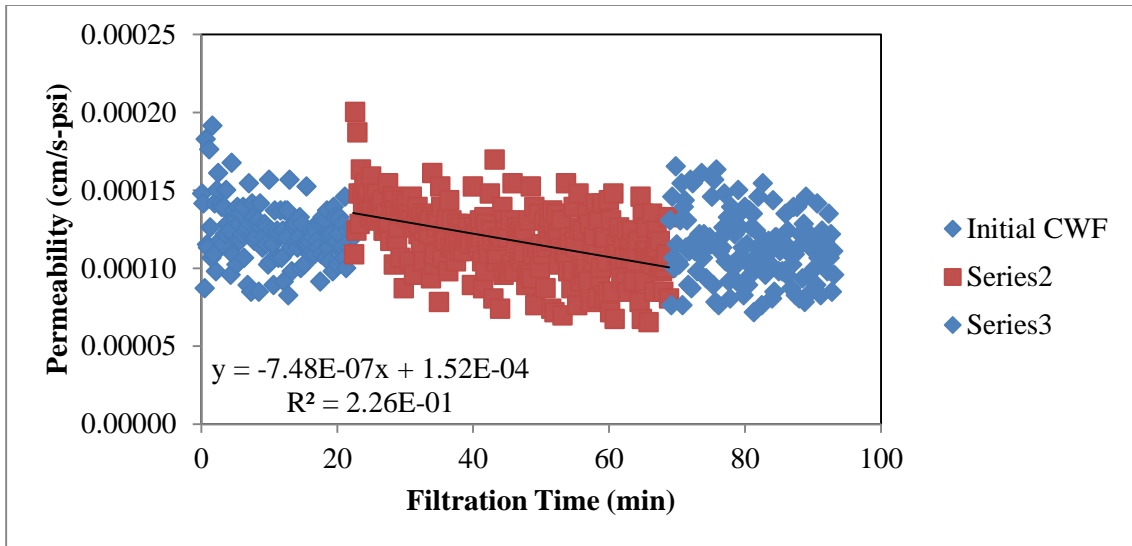
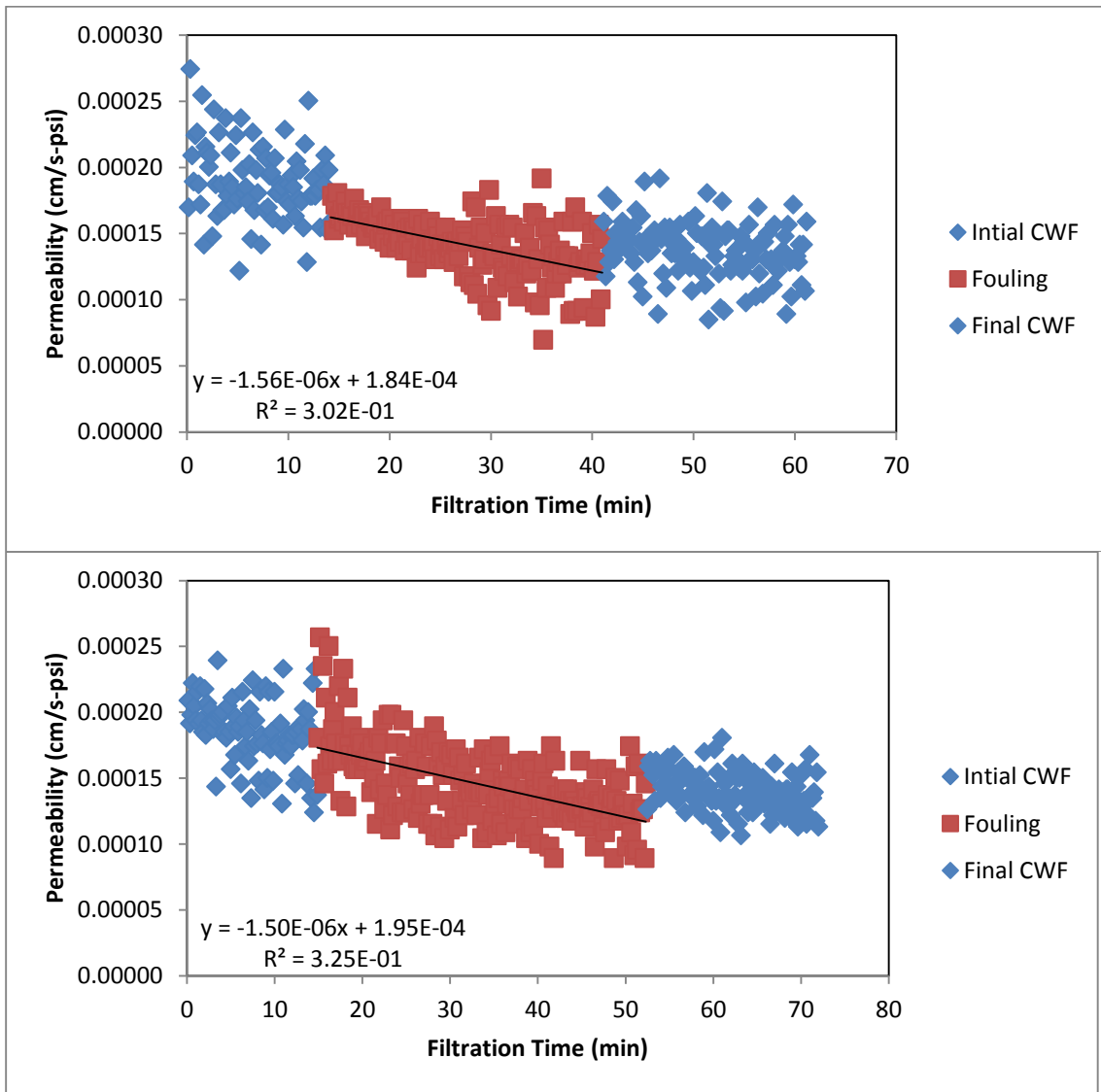


Figure A-22. Mississippi River Spring Raw M100 Membrane

Membrane	M-100	
MWCO	75	kDa
Material	PVDF	
Area	28.7	cm ²
Water	Spring Raw Filtered	
Temperature	22.7 - 23.0	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level



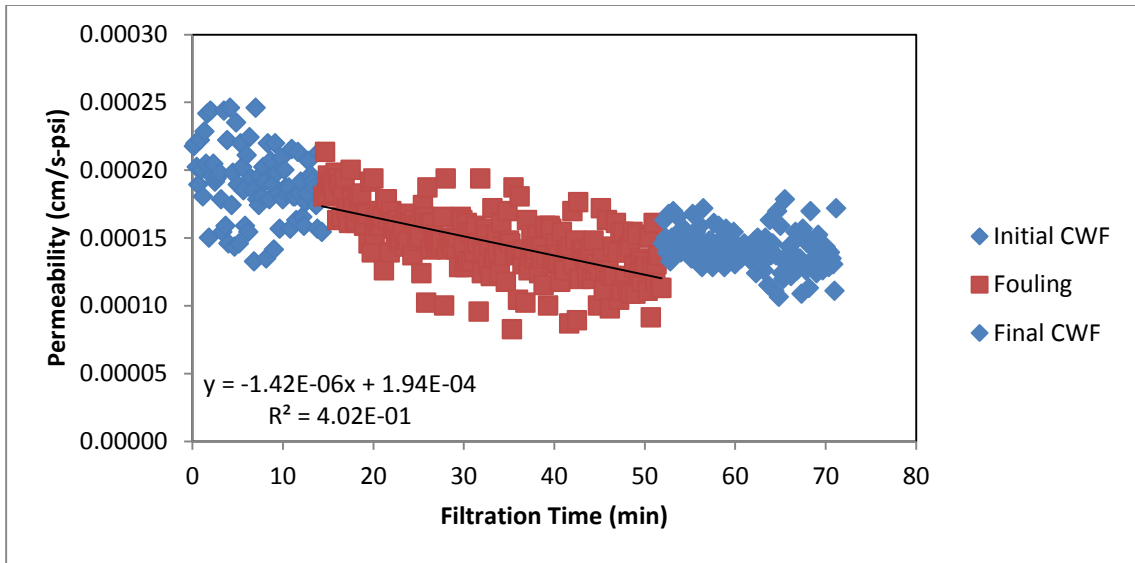


Figure A-23. Mississippi River Spring Raw YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	Spring Raw Filtered	
Temperature	22.9 - 23.0	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

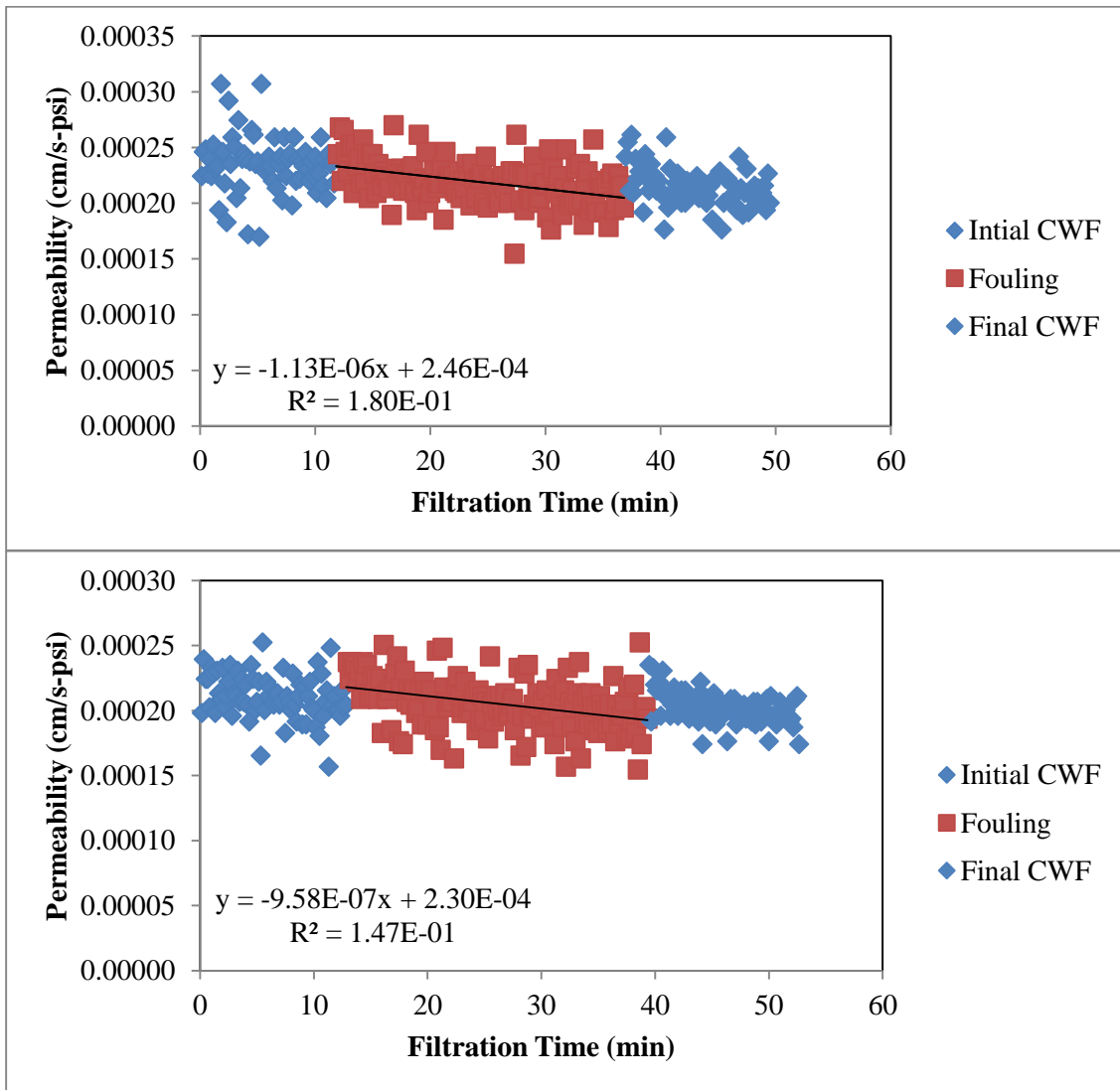


Figure A-24. Mississippi River Spring Raw PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Spring Raw Filtered	
Temperature	22.8 - 22.9	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

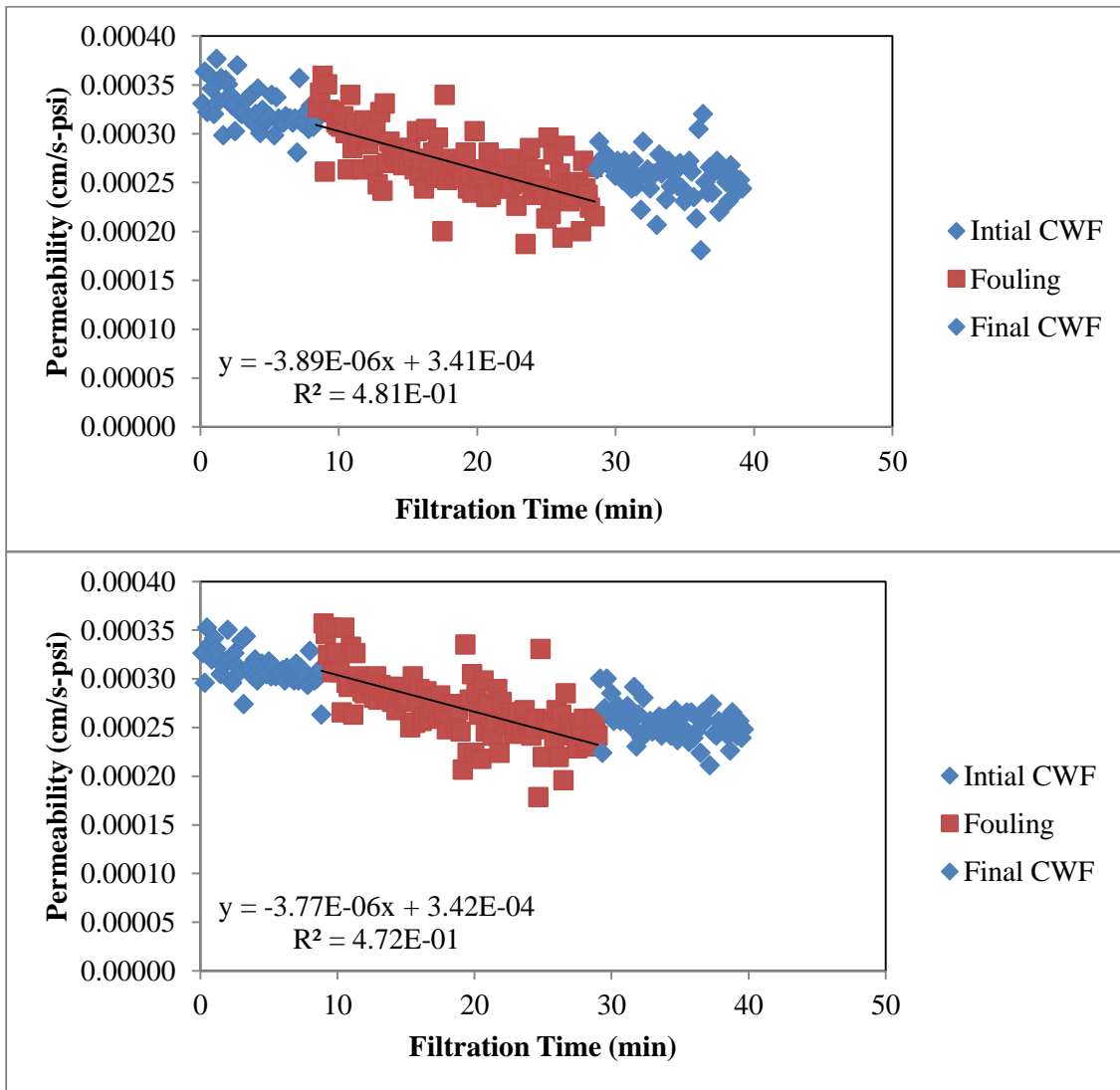


Figure A-25. Mississippi River Spring Settled K131 Membrane

Membrane	K-131	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Spring Settled Filtered	
Temperature	22.6 - 22.9	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

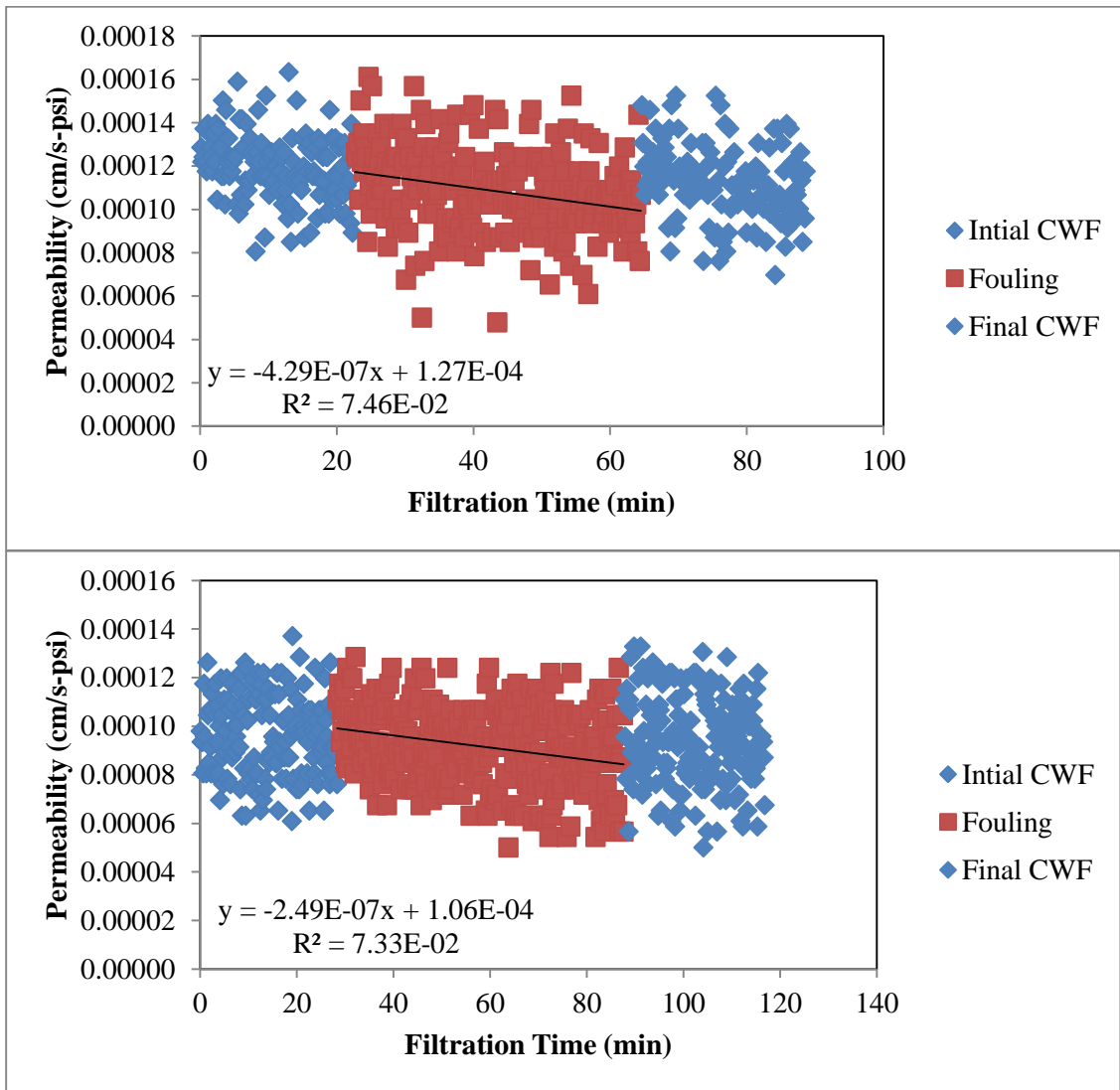
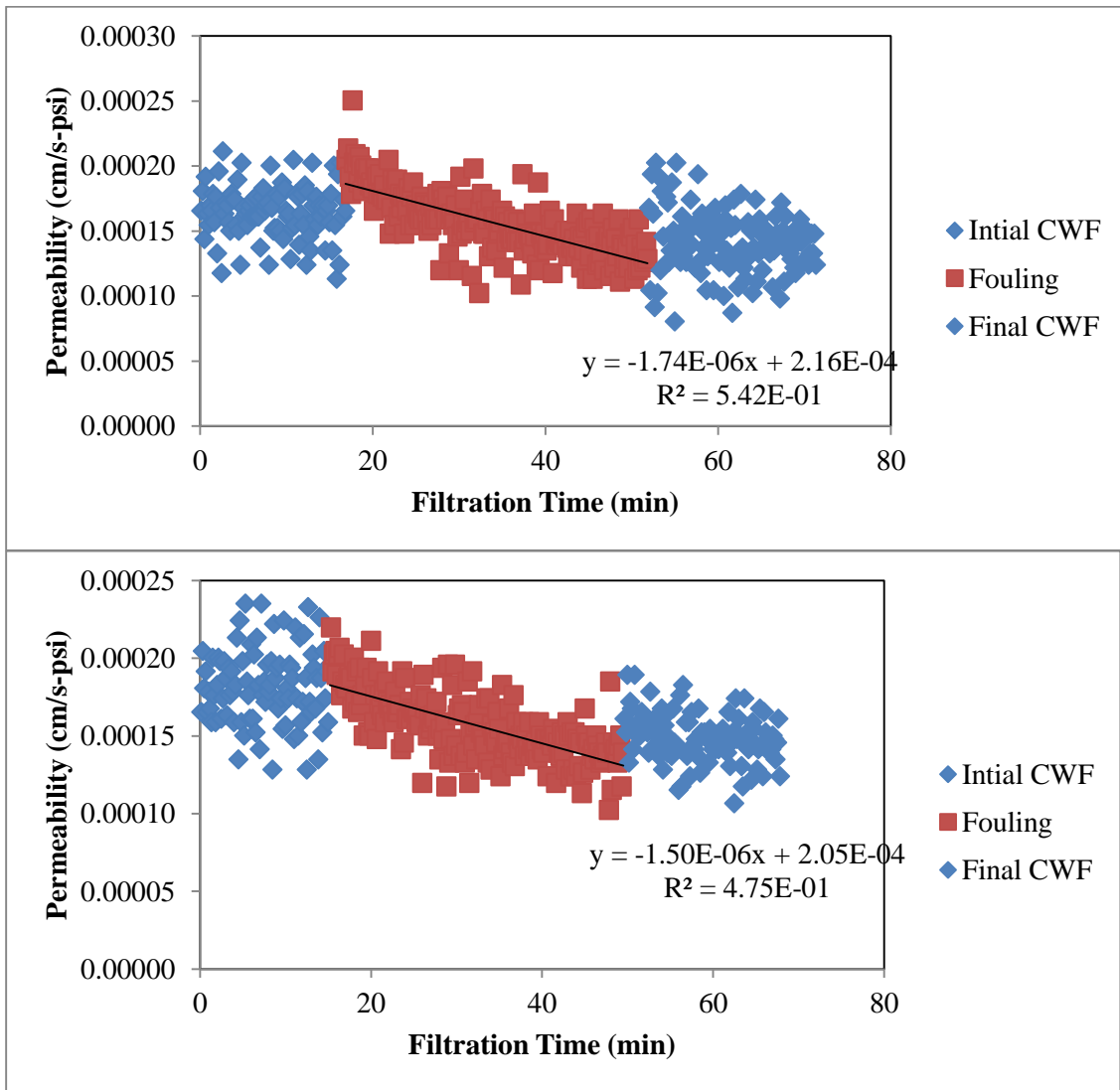


Figure A-26. Mississippi River Spring Settled M100 Membrane

Membrane	M-100	
MWCO	75	kDa
Material	PVDF	
Area	28.7	cm ²
Water	Spring Settled Filtered	
Temperature	22.4-22.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level



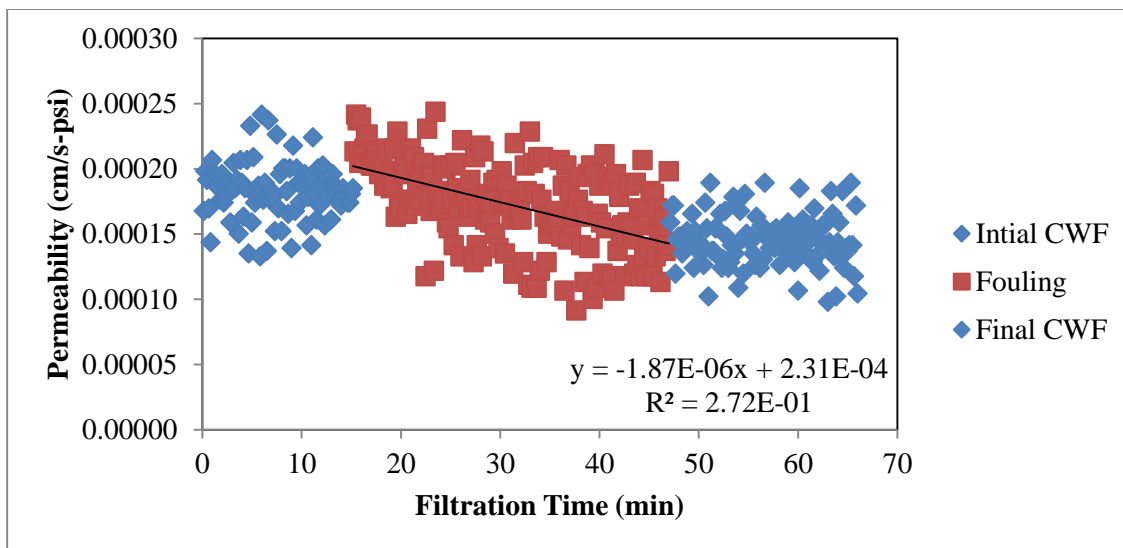


Figure A-27. Mississippi River Spring Settled YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	Spring Settled Filtered	
Temperature	23.0 - 23.1	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

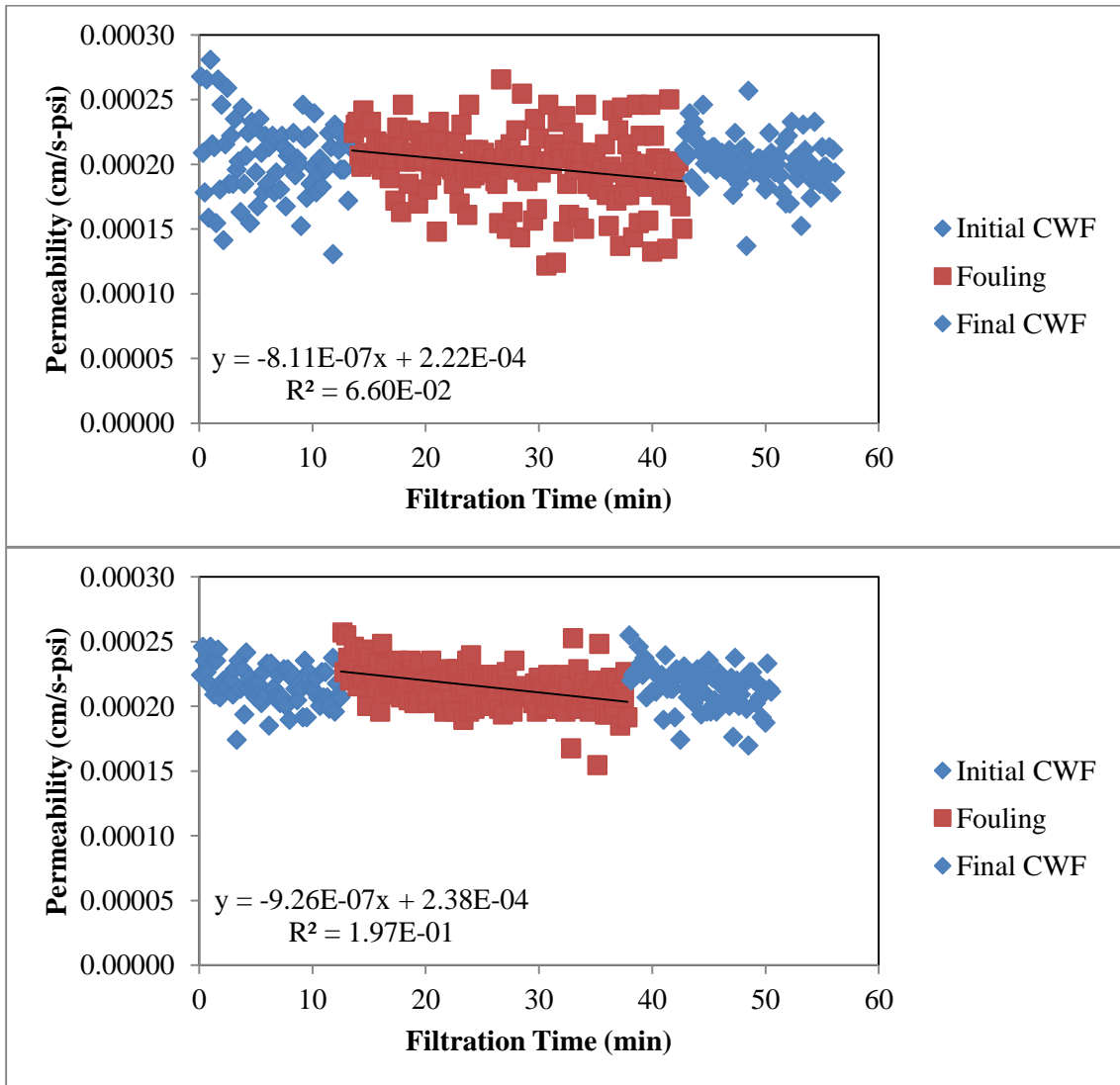


Figure A-28. Mississippi River Spring Settled PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Spring Settled Filtered	
Temperature	23.4	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

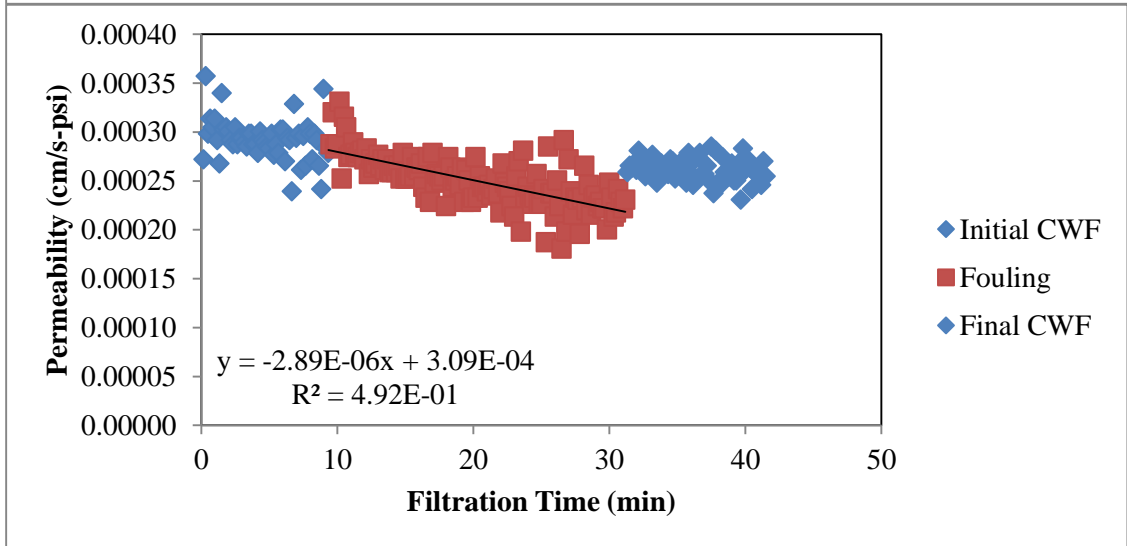
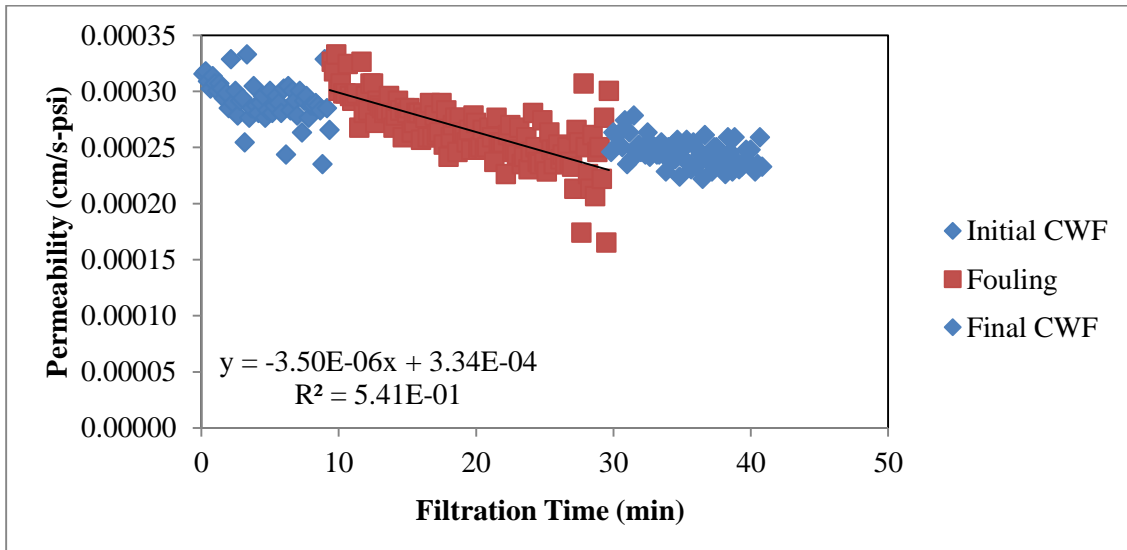


Figure A-29. Mississippi River Summer Raw K131 Membrane

Membrane	K-131	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Summer Raw Filtered	
Temperature	23.1 - 23.6	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

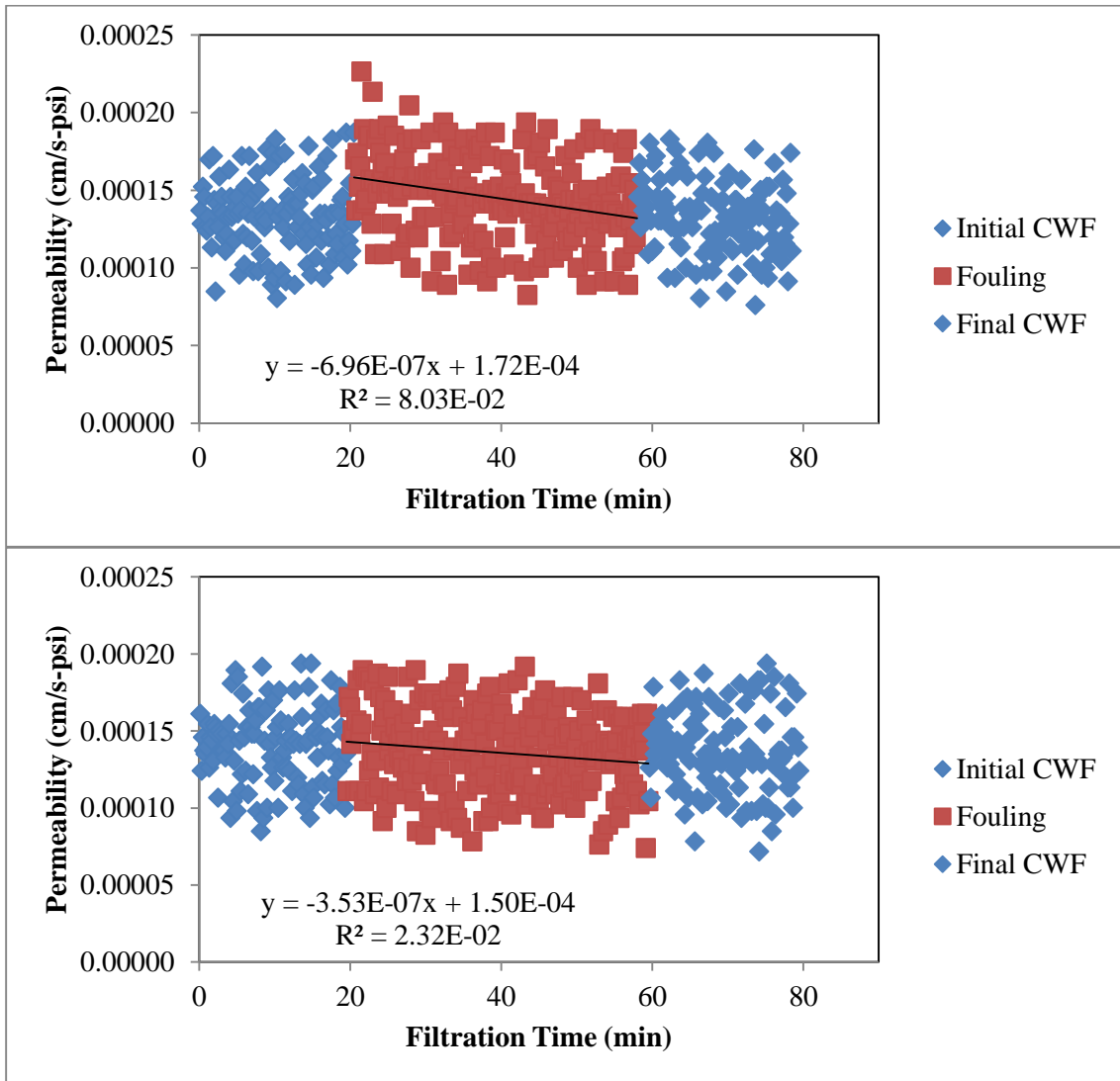


Figure A-30. Mississippi River Summer Raw M100 Membrane

Membrane	M-100	
MWCO	75	kDa
Material	PVDF	
Area	28.7	cm ²
Water	Summer Raw Filtered	
Temperature	22.6 - 23.1	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

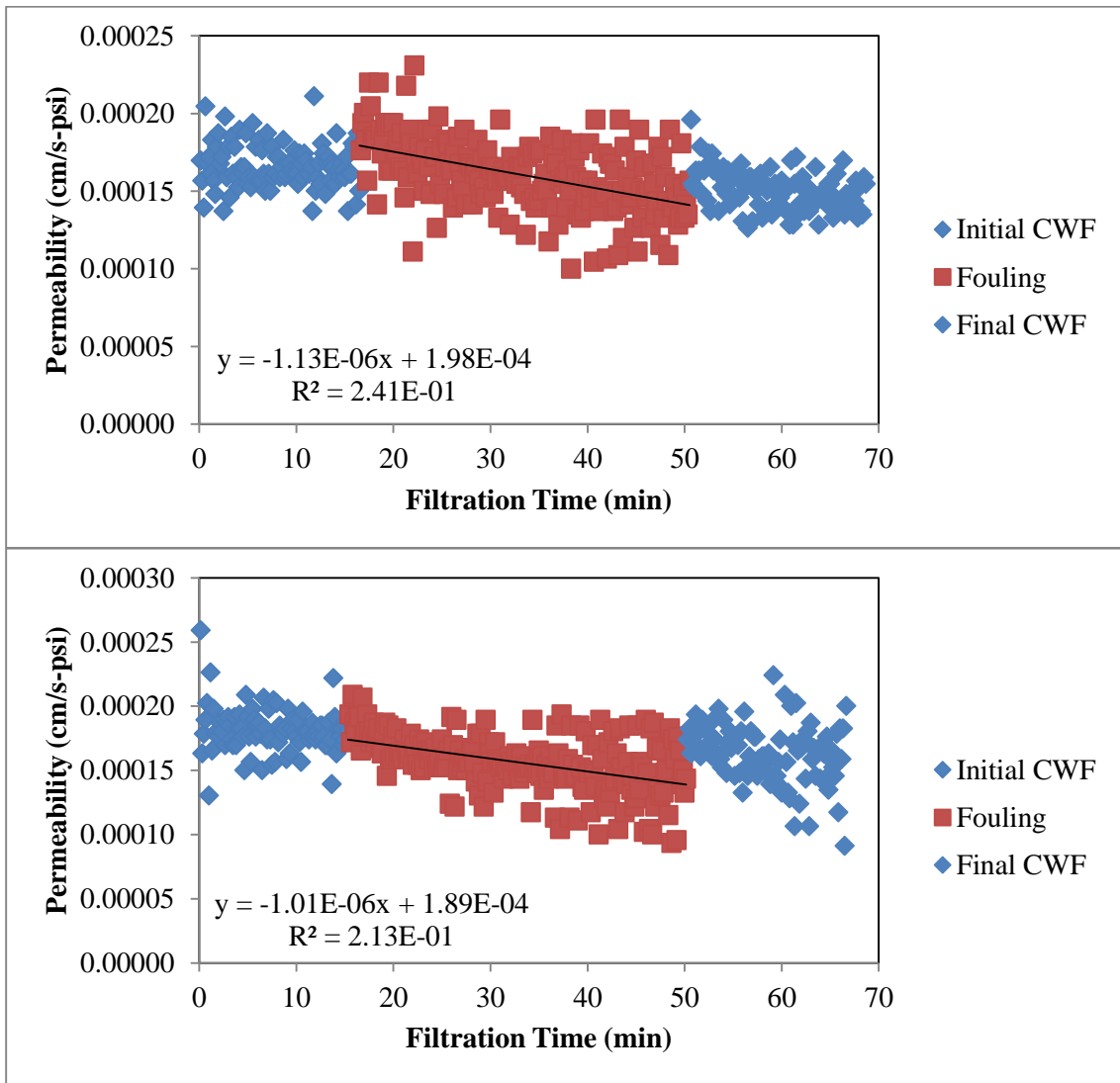


Figure A-31. Mississippi River Summer Raw YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	Summer Raw Filtered	
Temperature	21.4	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

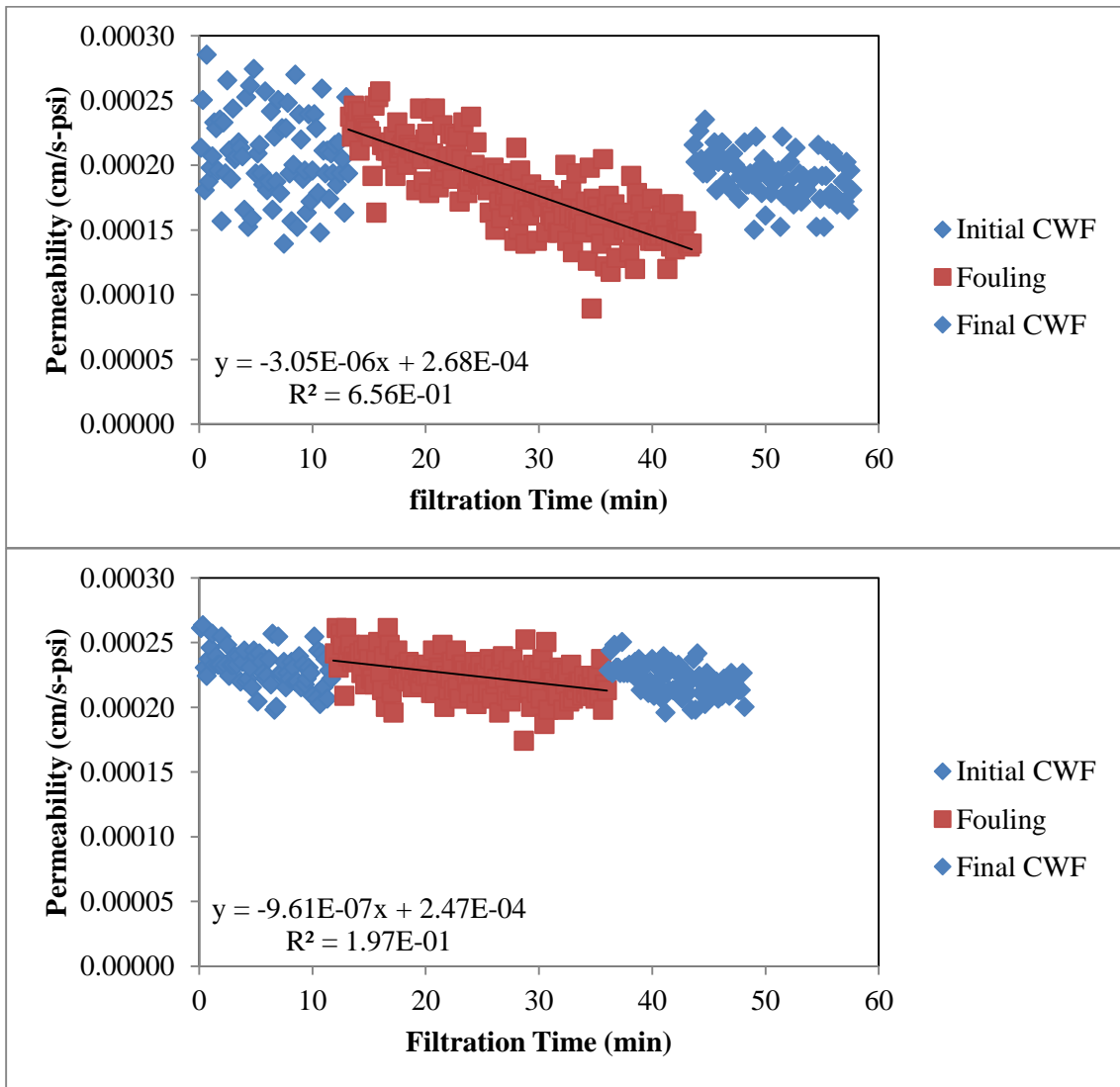
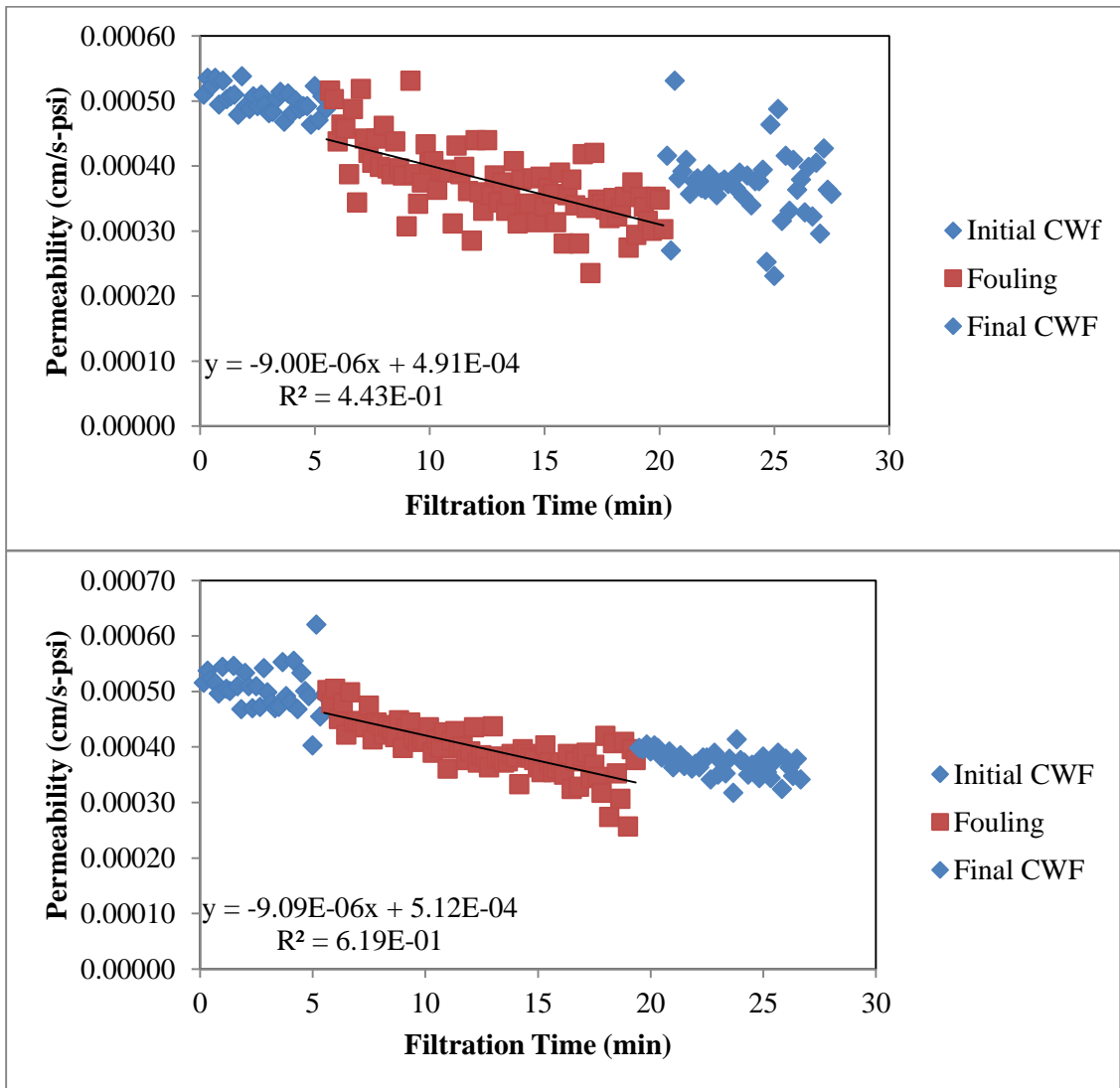


Figure A-32. Mississippi River Summer Raw PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Summer Raw Filtered	
Temperature	22.5 - 23.1	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level



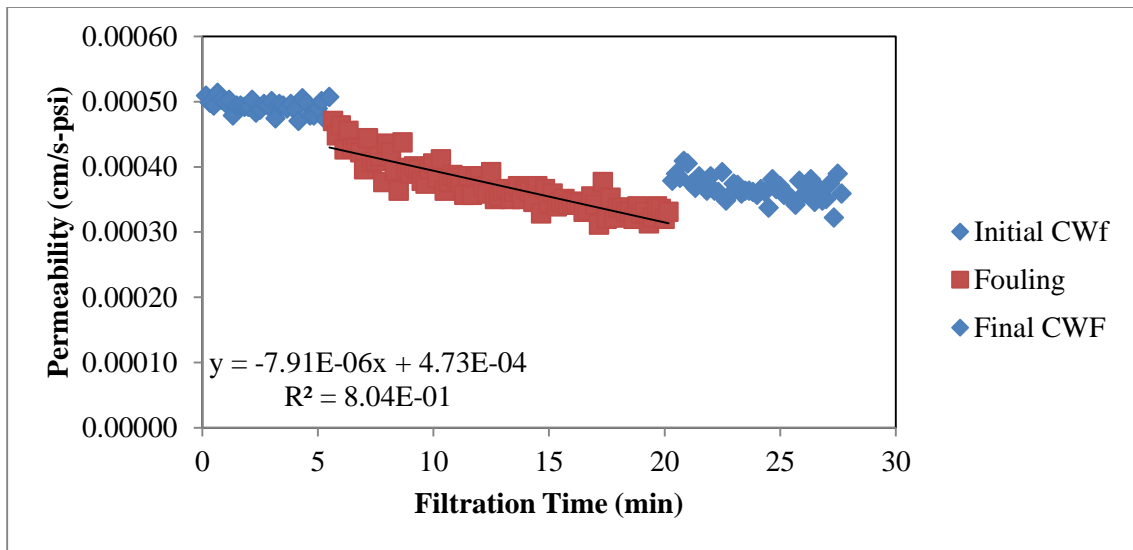


Figure A-33. Mississippi River Summer Settled K131 Membrane

Membrane	K-131	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Summer Settled Filtered	
Temperature	23.1 - 23.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

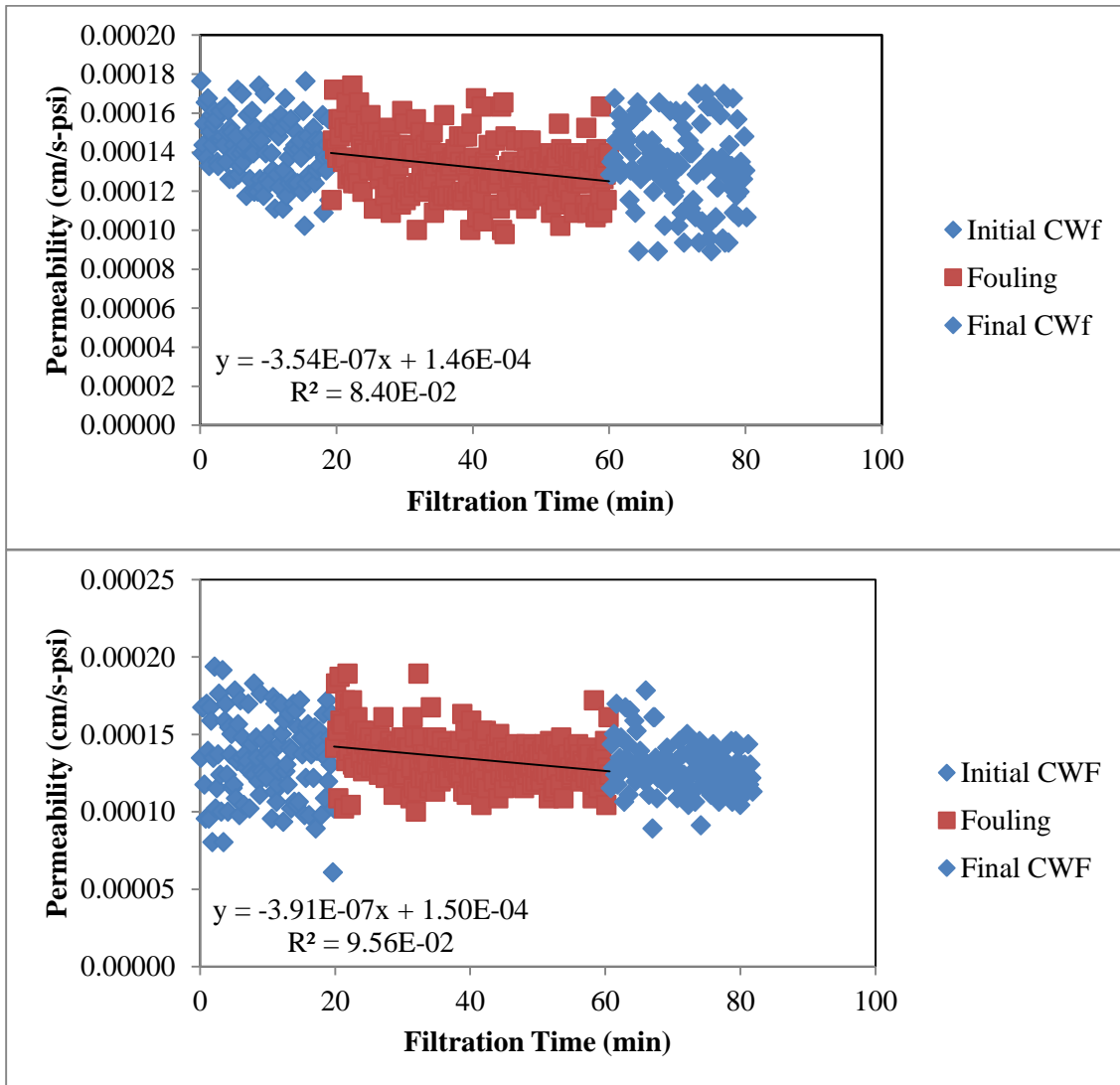


Figure A-34. Mississippi River Summer Settled M100 Membrane

Membrane	M-100	
MWCO	75	kDa
Material	PVDF	
Area	28.7	cm ²
Water	Summer Settled Filtered	
Temperature	22.9 - 23.4	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

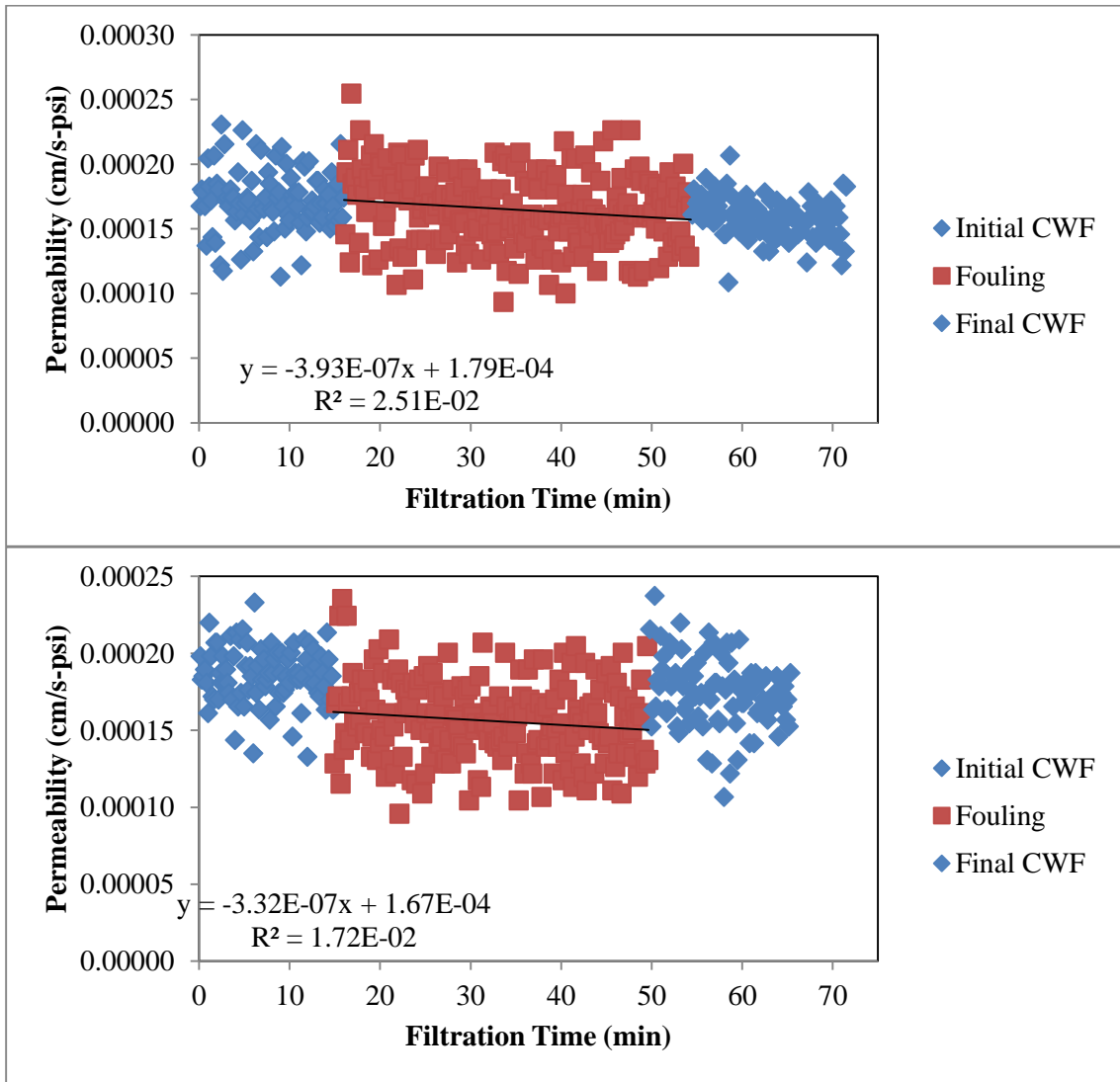


Figure A-35. Mississippi River Summer Settled YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	Summer Settled Filtered	
Temperature	23.3 - 23.5	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

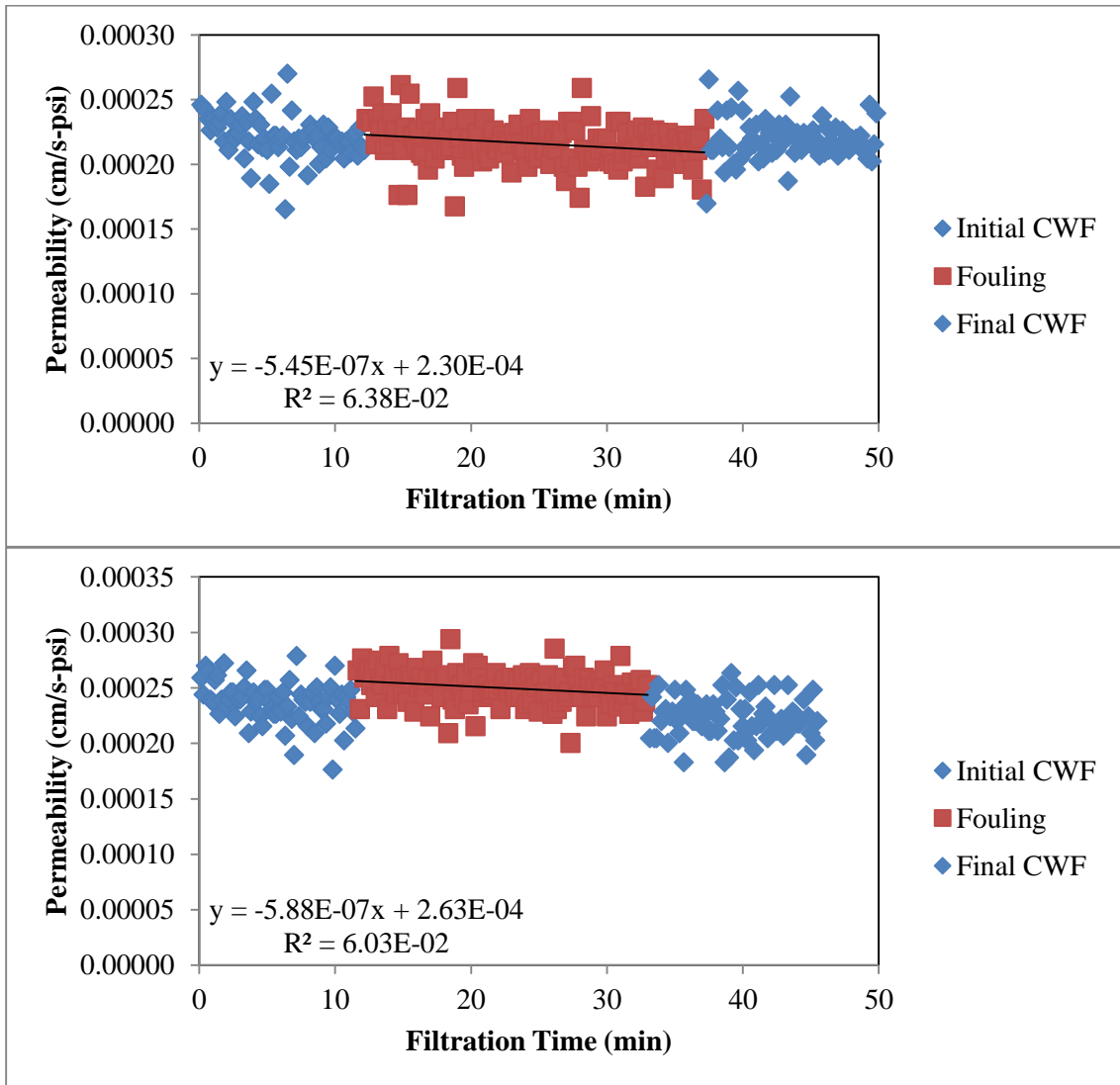


Figure A-36. Mississippi River Summer Settled PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Summer Settled Filtered	
Temperature	23.6 - 23.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

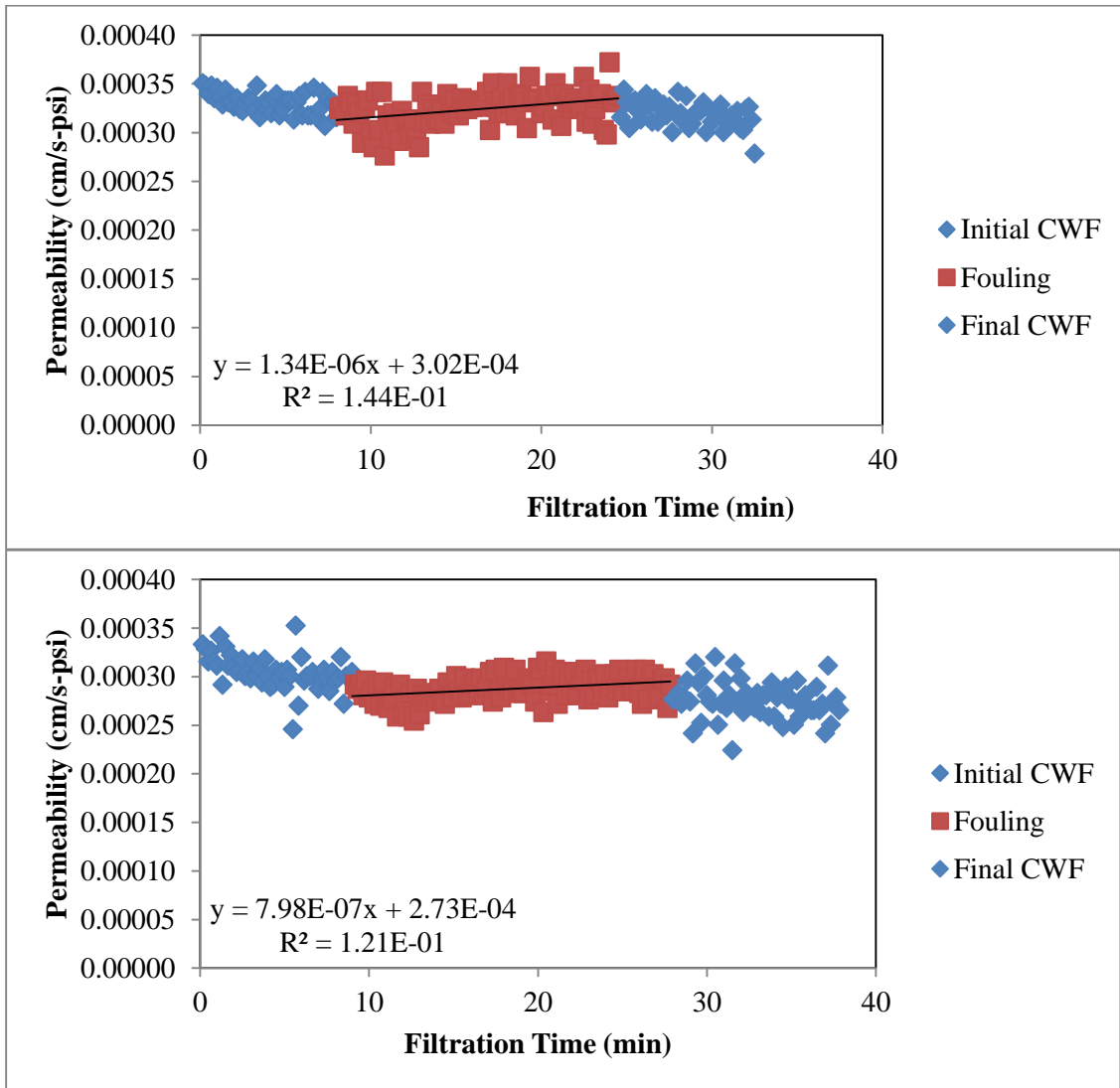
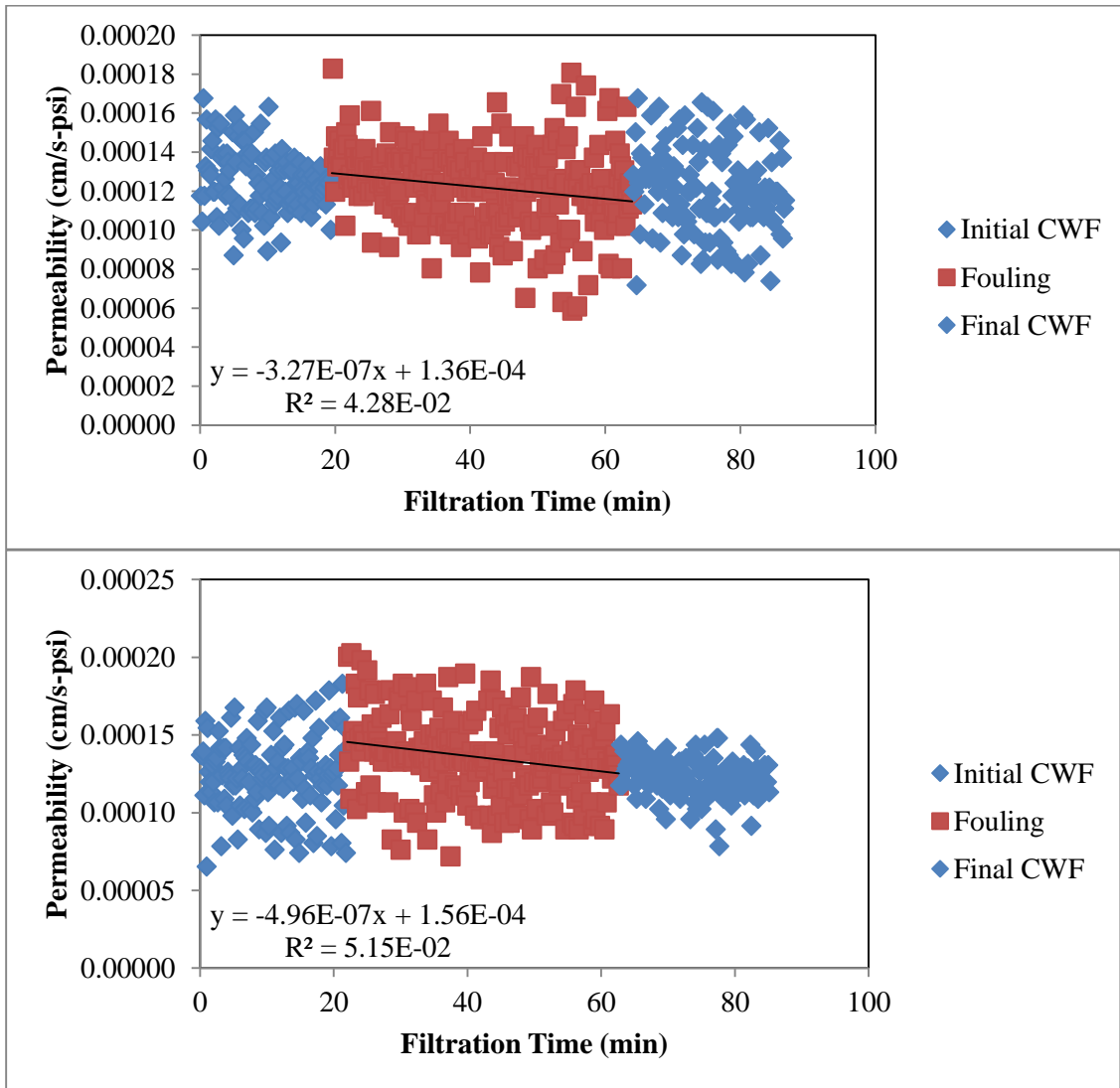


Figure A-37. Mississippi River Autumn Raw K131 Membrane

Membrane	K-131	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Fall Raw Filtered	
Temperature	16.8 - 18.0	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level



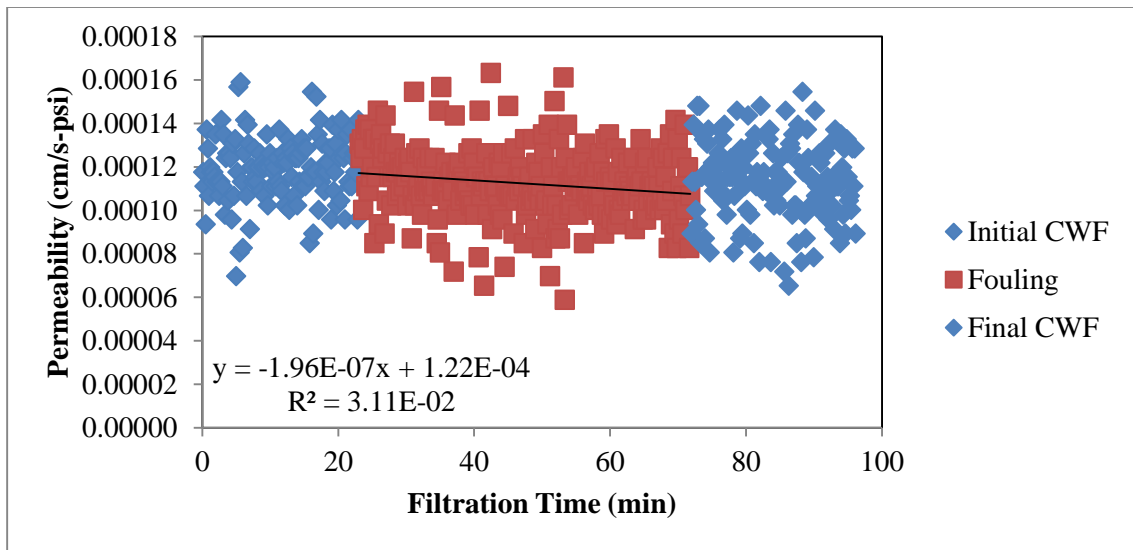


Figure A-38. Mississippi River Autumn Raw M100 Membrane

Membrane	M-100	
MWCO	75	kDa
Material	PVDF	
Area	28.7	cm ²
Water	Fall Raw Filtered	
Temperature	23.2 - 23.6	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

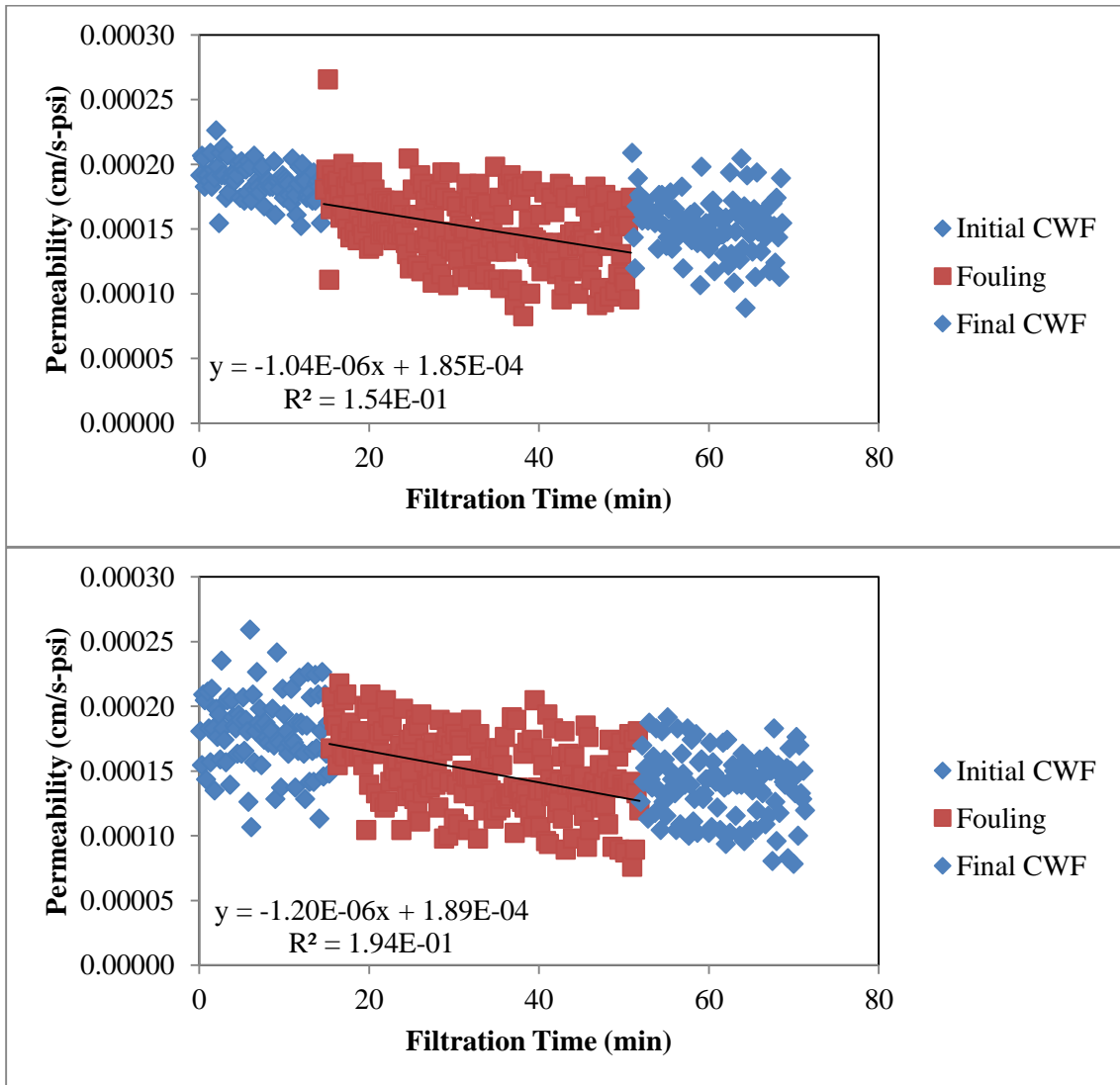


Figure A-39. Mississippi River Autumn Raw YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	Fall Raw Filtered	
Temperature	22.6 - 23.5	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

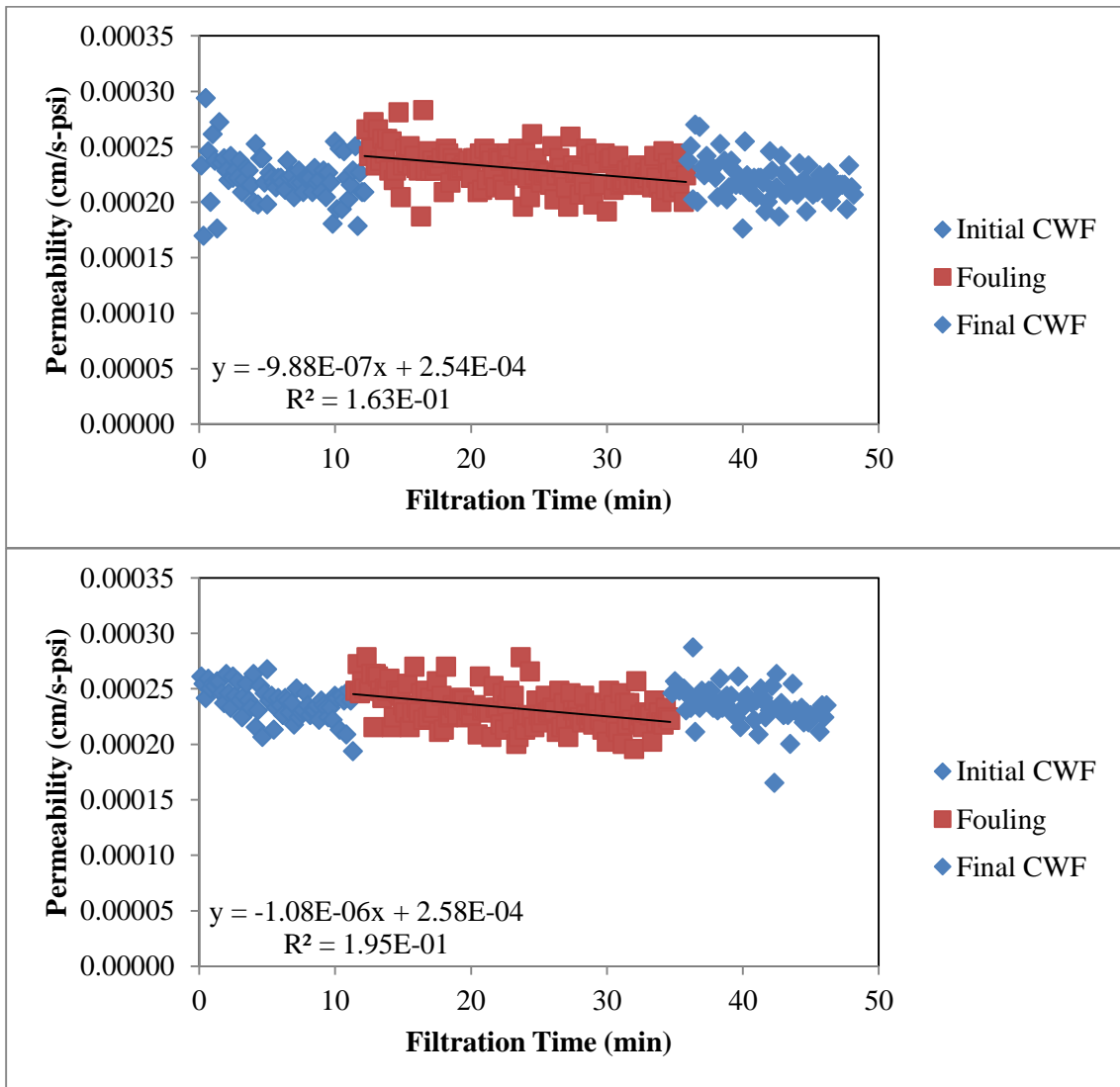


Figure A-40. Mississippi River Autumn Raw PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Fall Raw Filtered	
Temperature	23.7 - 23.9	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

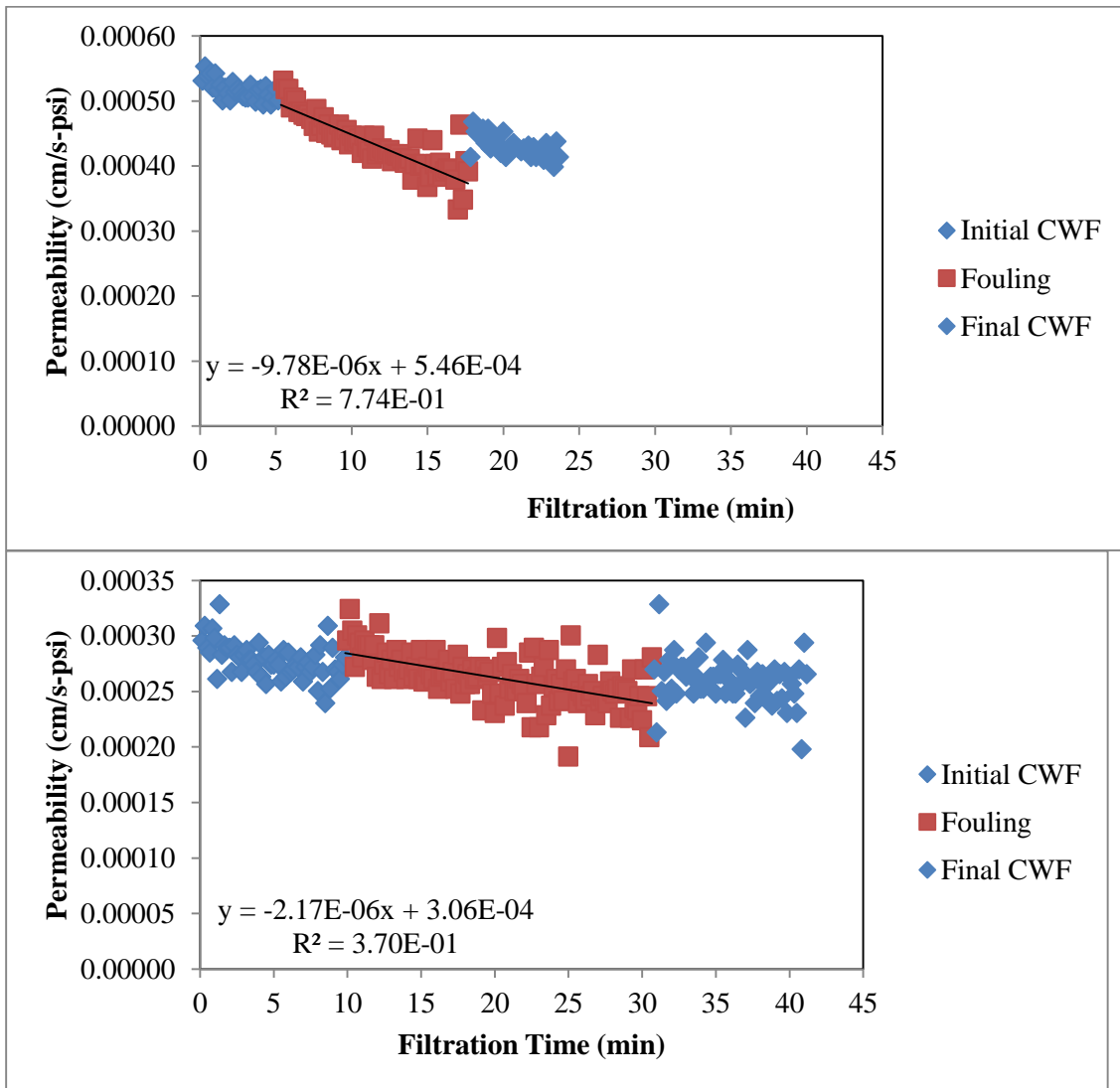
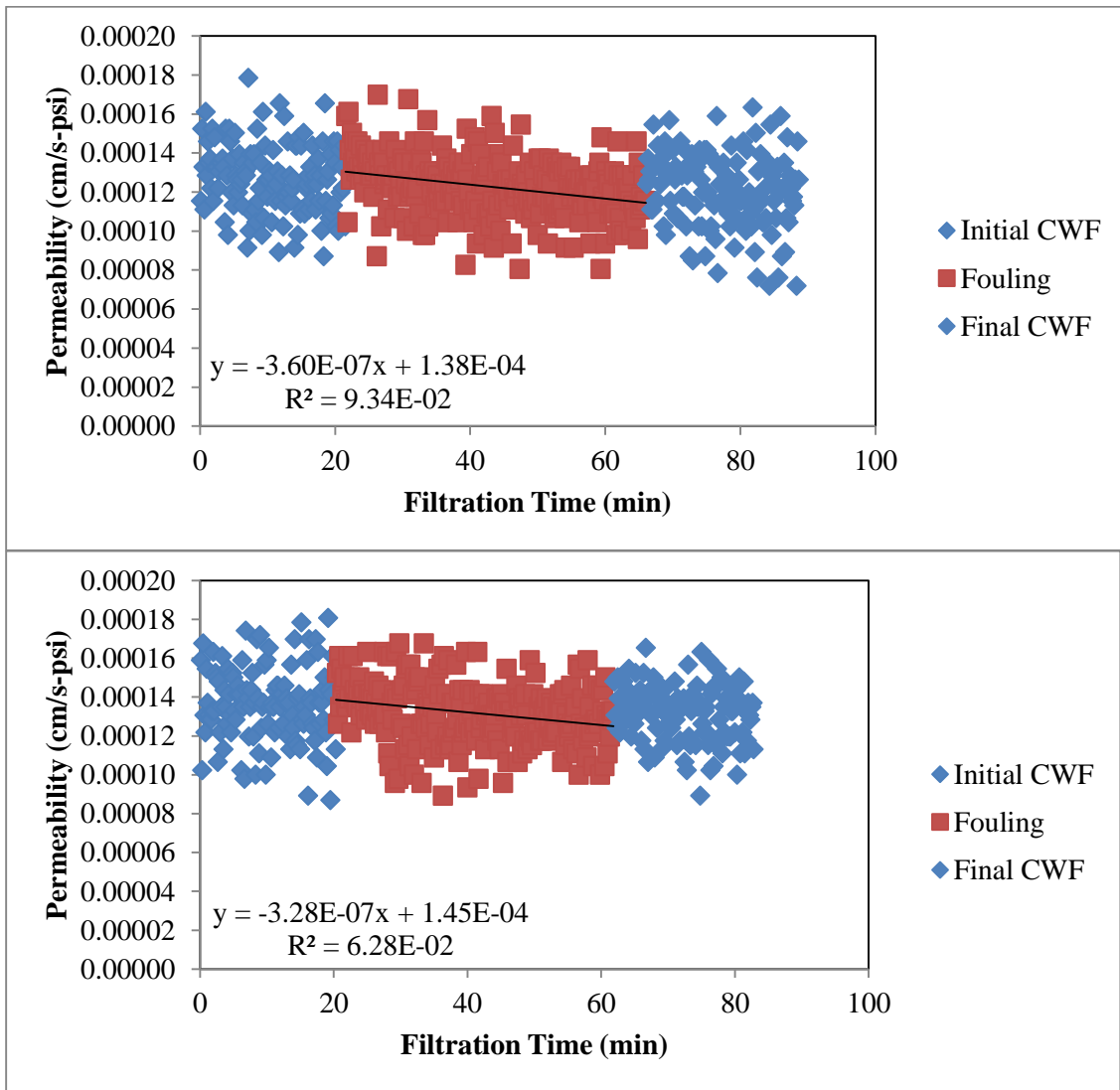


Figure A-41. Mississippi River Autumn Settled K131 Membrane

Membrane	K-131	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Fall Settled Filtered	
Temperature	20.9 - 23.4	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level



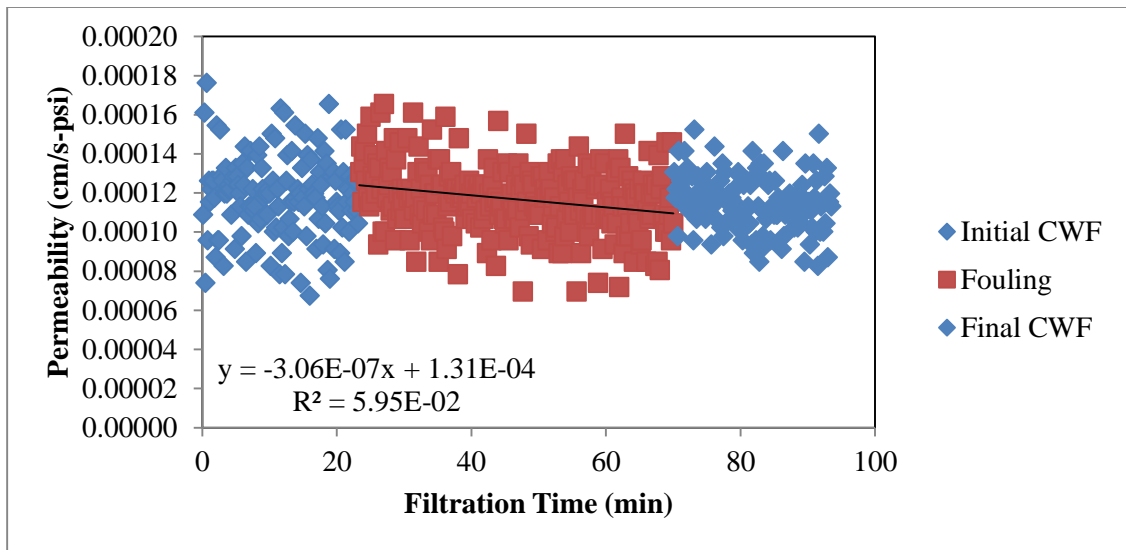


Figure A-42. Mississippi River Autumn Settled M100 Membrane

Membrane	M-100	
MWCO	75	kDa
Material	PVDF	
Area	28.7	cm ²
Water	Fall Settled Filtered	
Temperature	23.2 - 23.9	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

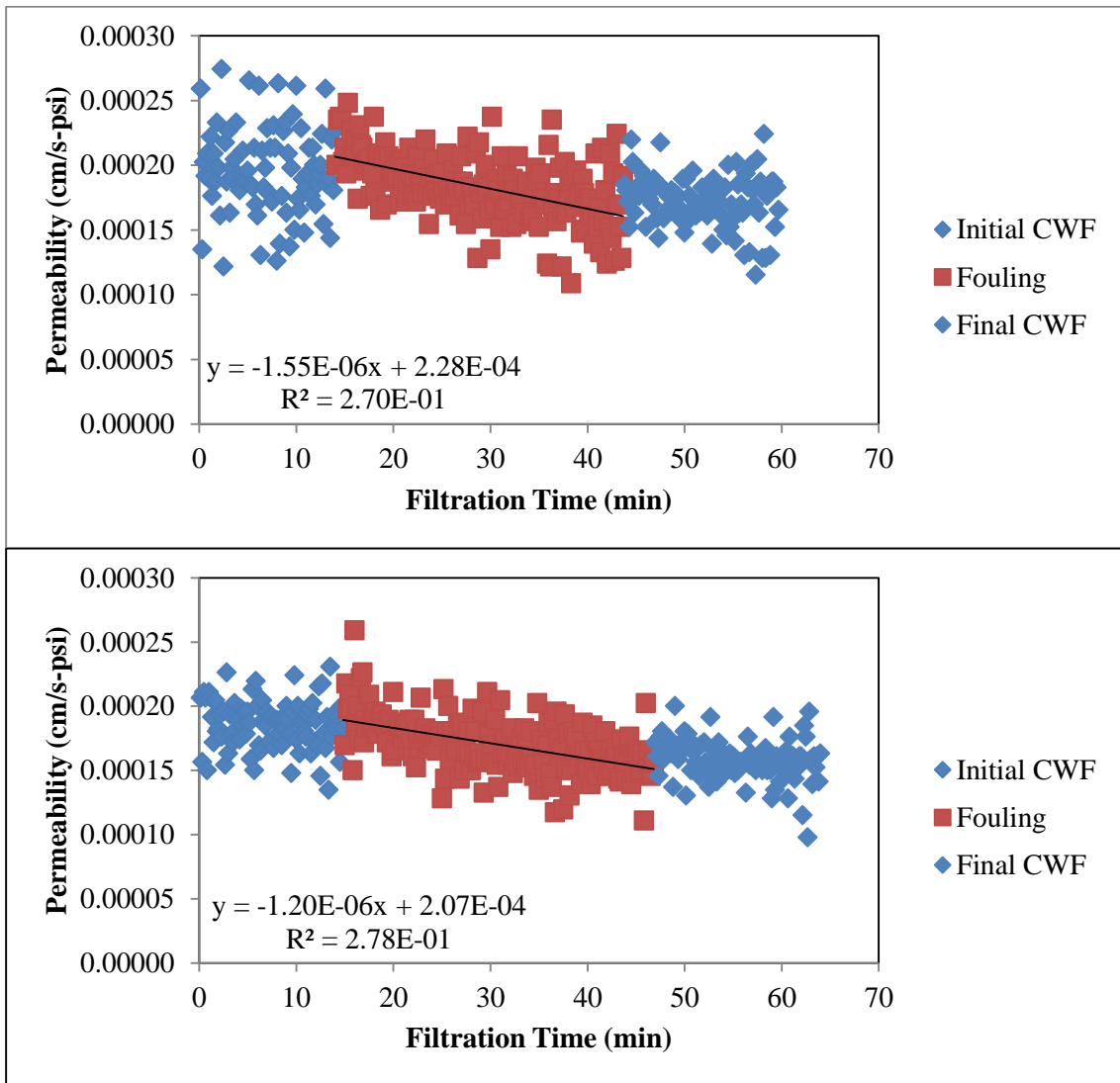


Figure A-43. Mississippi River Autumn Settled YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	Fall Settled Filtered	
Temperature	25.7 - 26.1	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

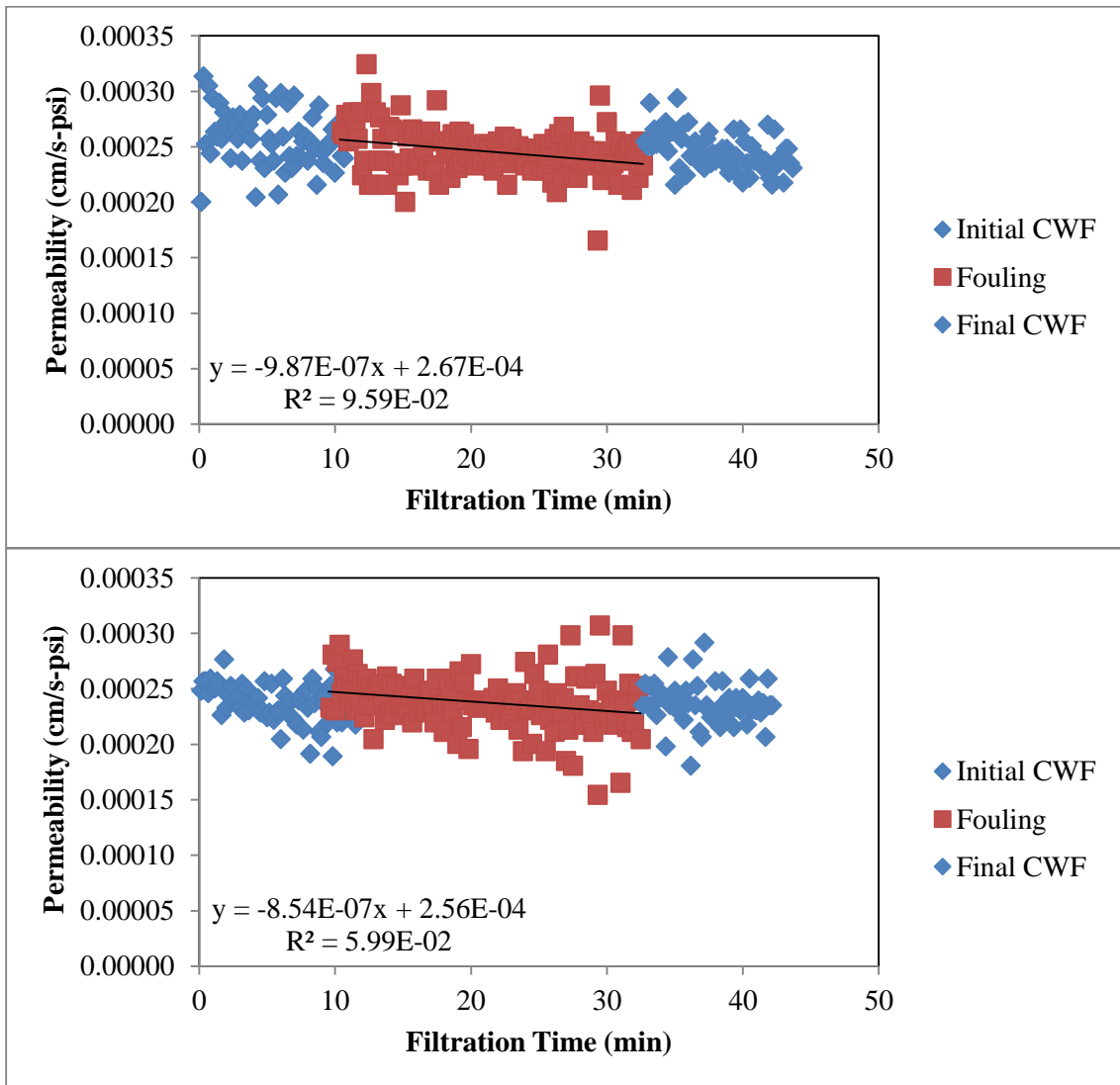


Figure A-44. Mississippi River Autumn Settled PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	Fall Settled Filtered	
Temperature	22.9 - 23.1	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

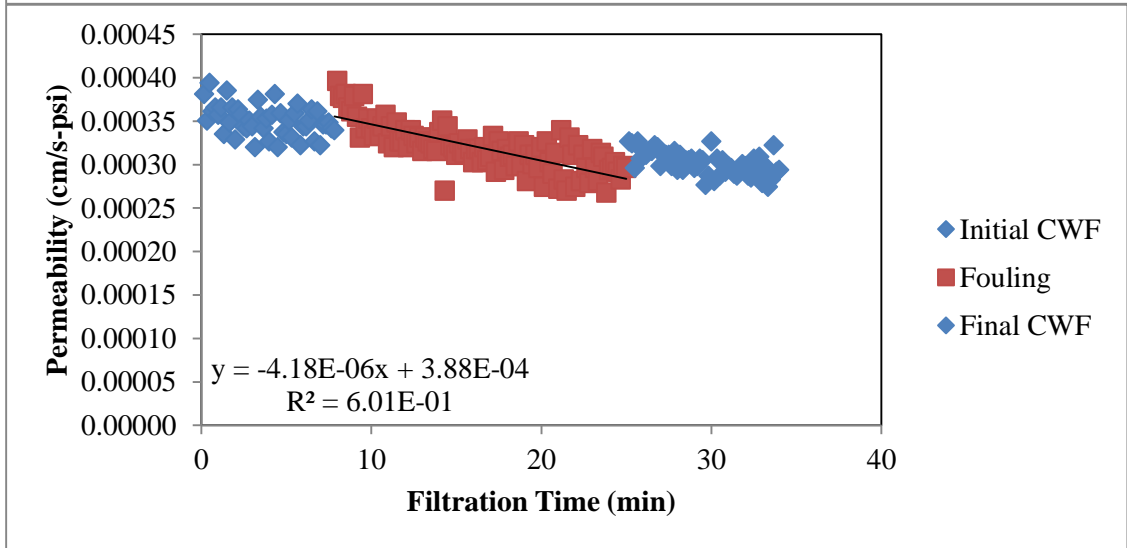
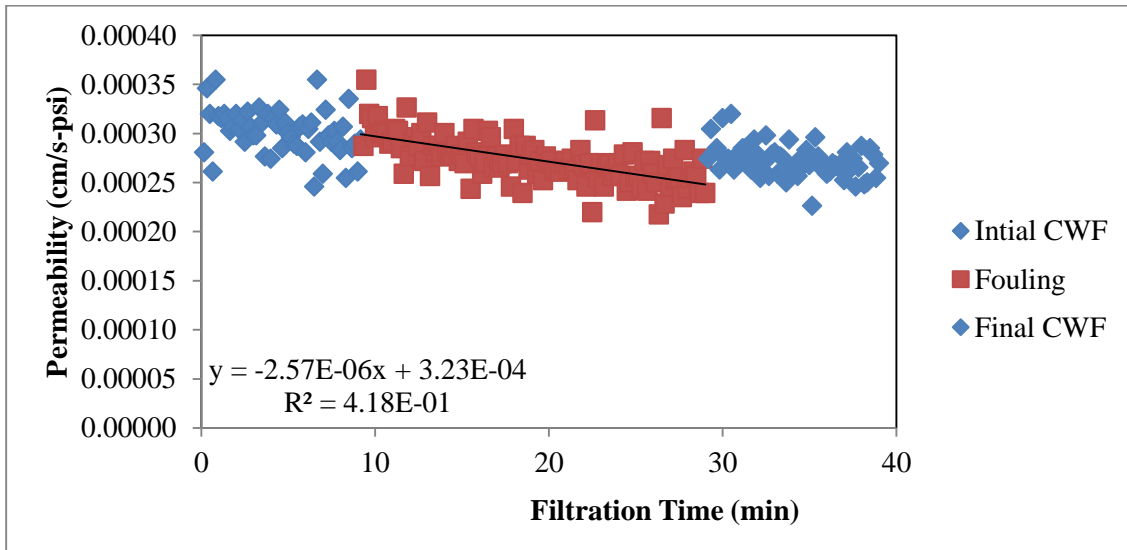


Figure A-45. Leech Lake River April YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	April Leech Filtered	
Temperature	20.6 - 20.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

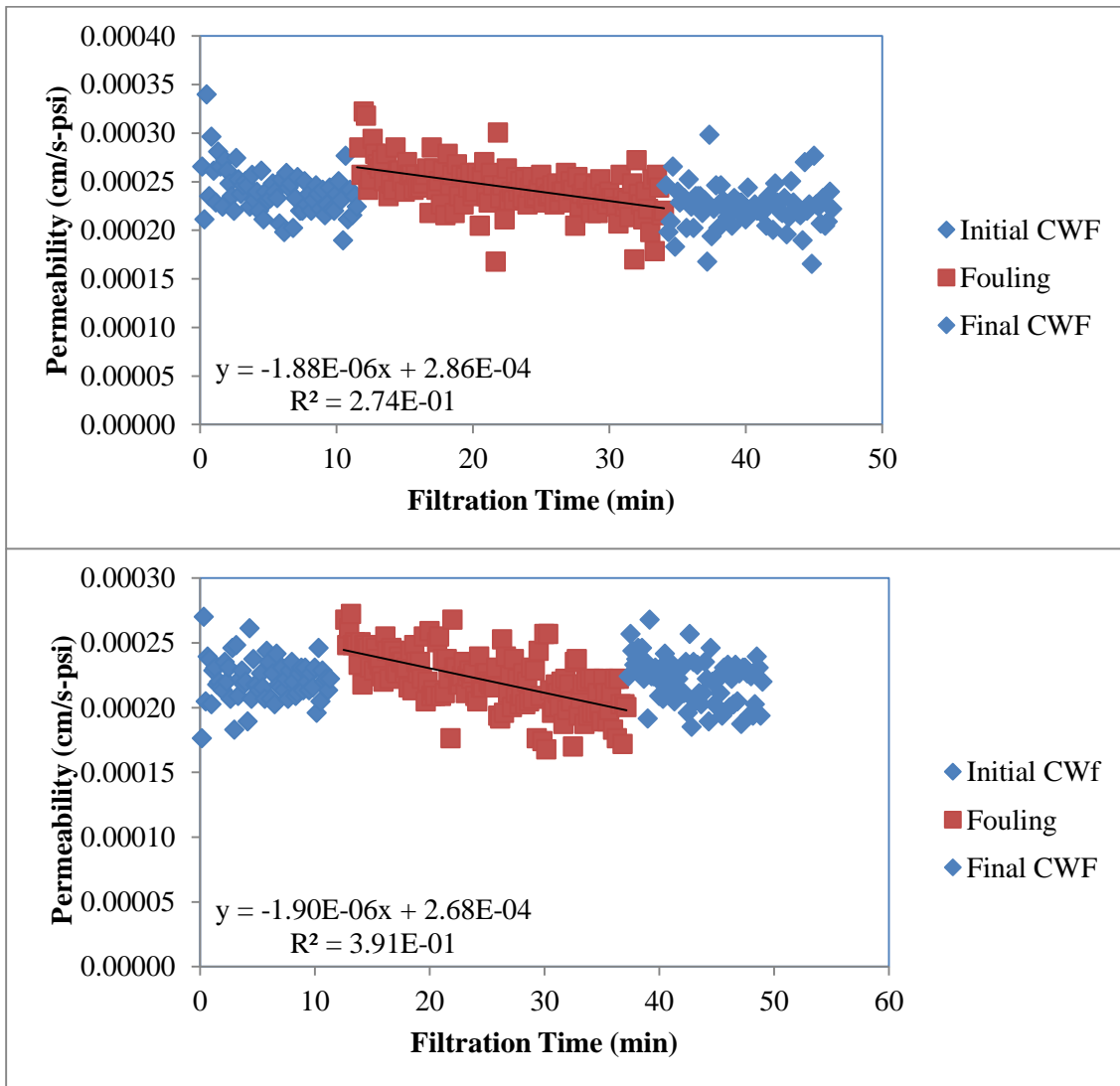


Figure A-46. Leech Lake River April PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	April Leech Filtered	
Temperature	20.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

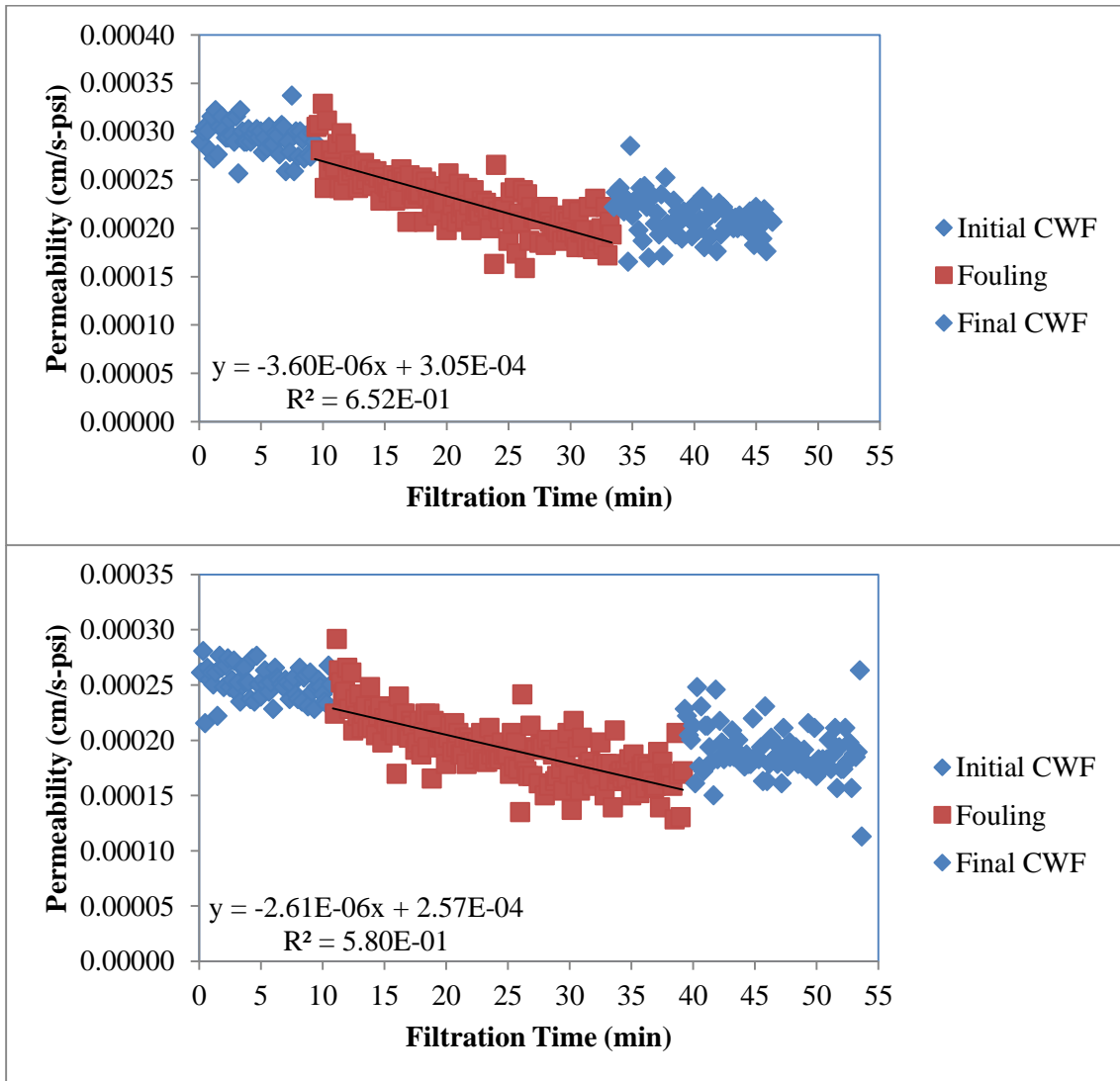


Figure A-47. Rice River April YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	April Rice Filtered	
Temperature	22.4 - 22.5	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

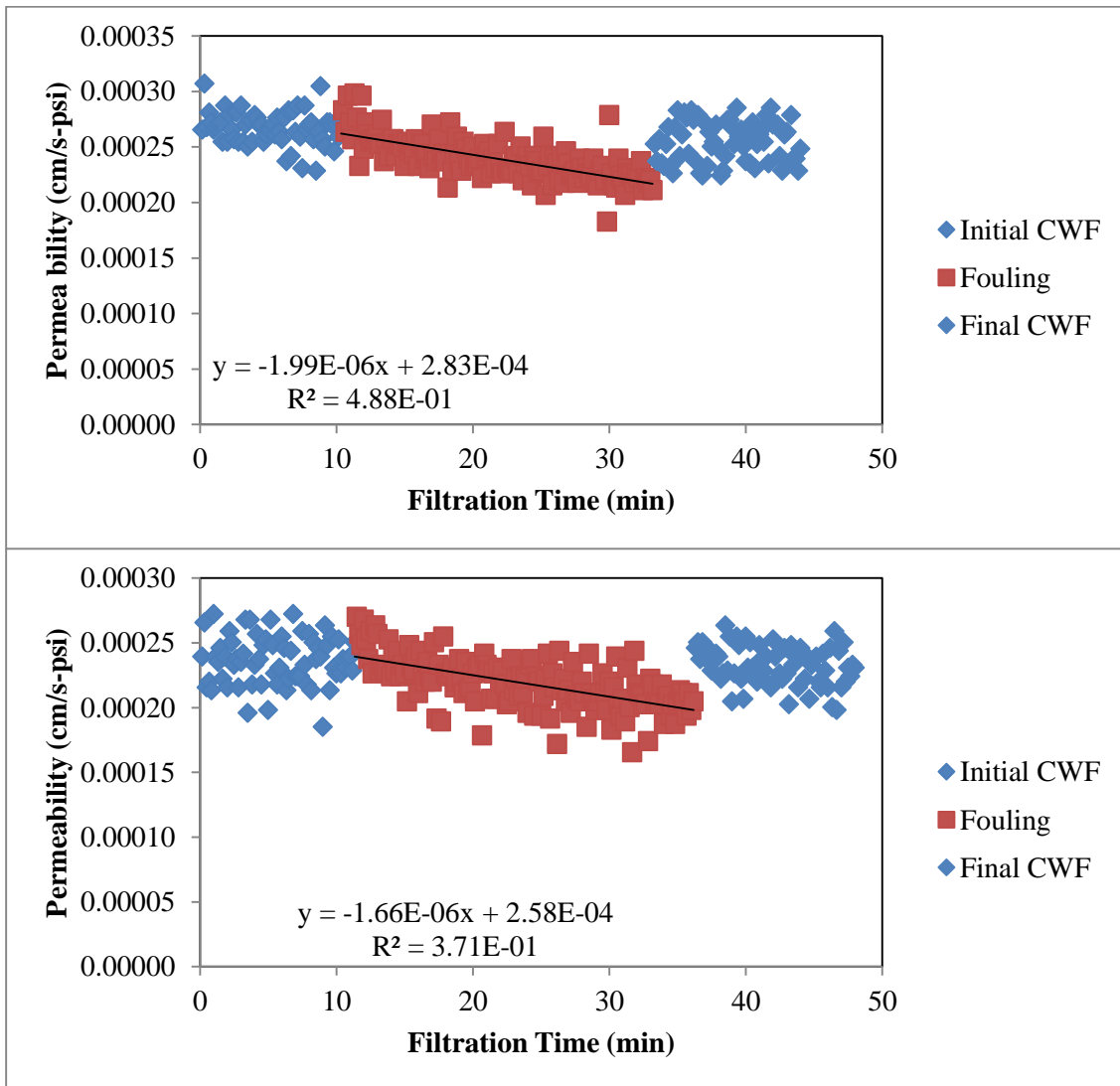


Figure A-48. Rice River April PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	April Rice Filtered	
Temperature	22.4 - 22.5	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

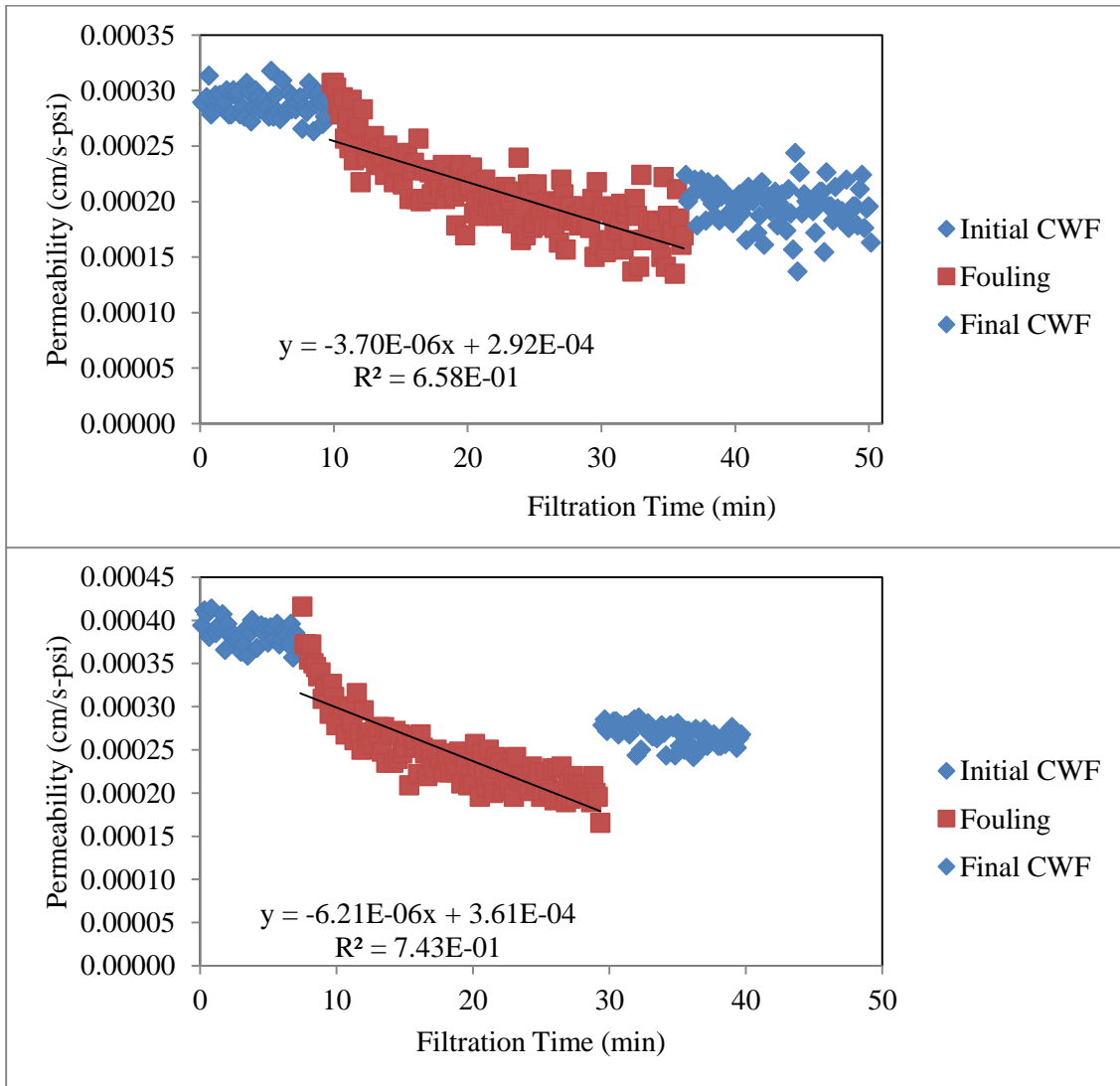


Figure A-49. Clearwater River April YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	April Clearwater Filtered	
Temperature	21.0 - 21.2	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

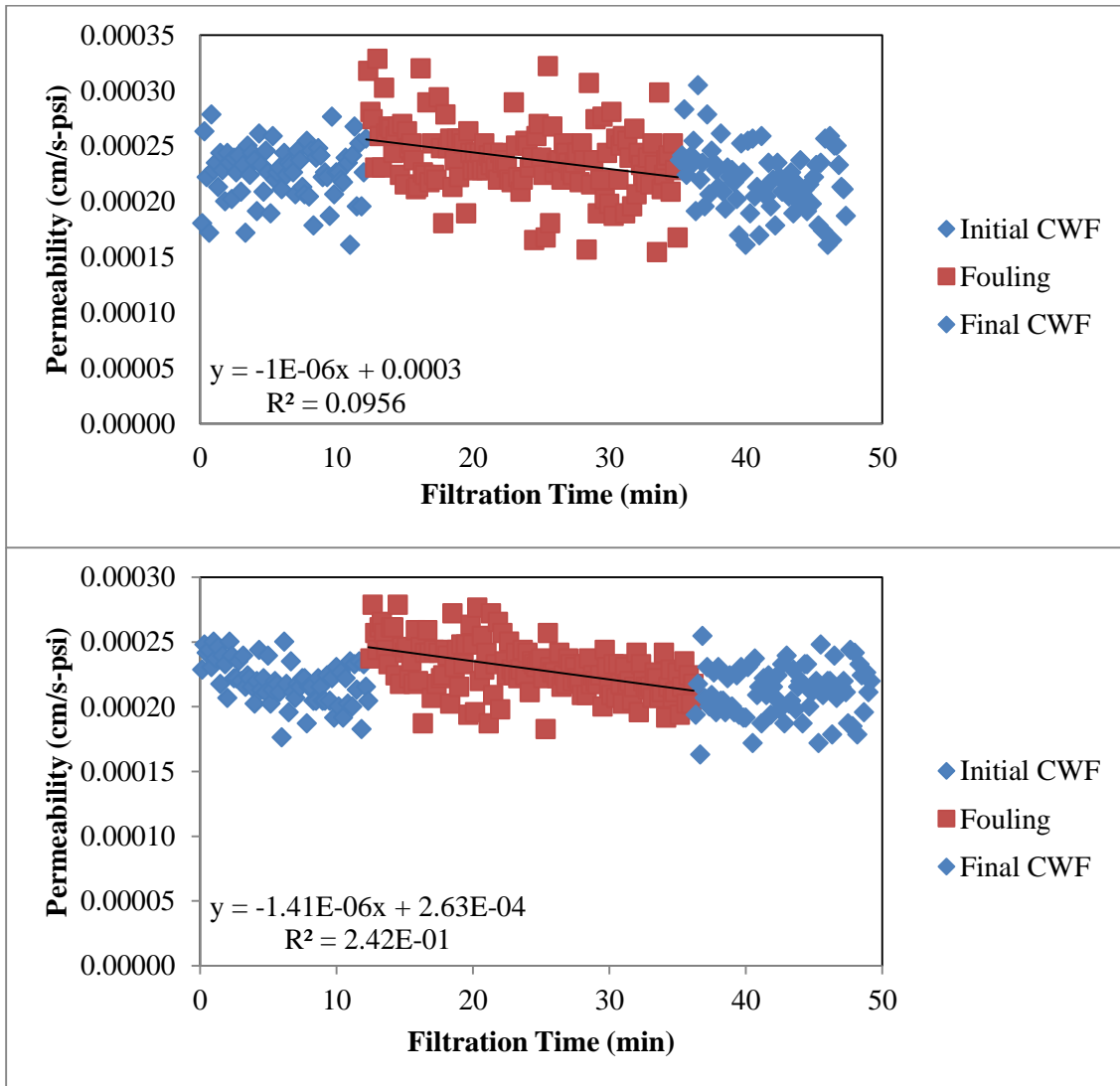


Figure A-50. Clearwater River April PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	April Clearwater Filtered	
Temperature	21.7 - 21.9	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

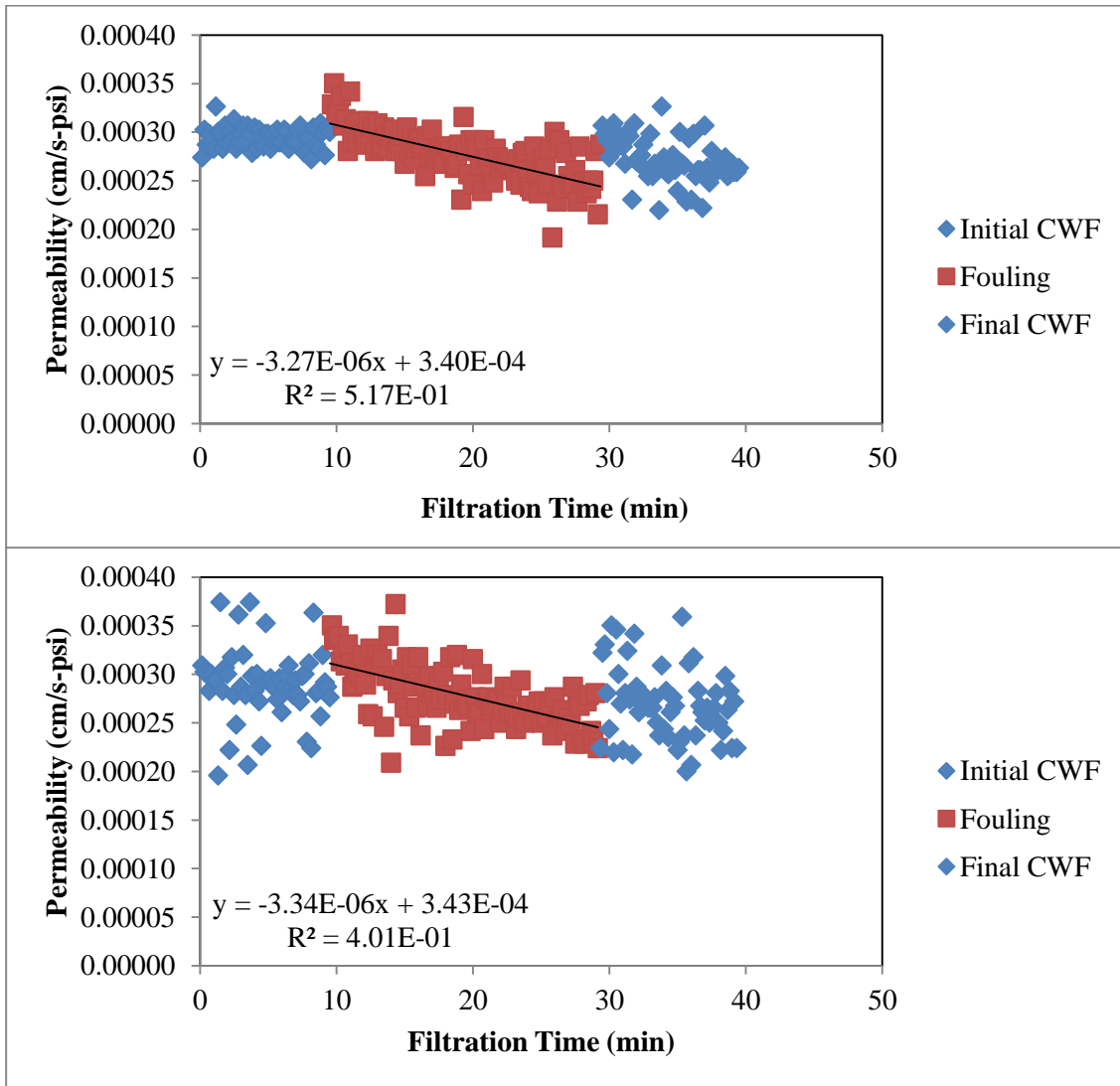


Figure A-51. Shingle Creek April YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	April Shingle Filtered	
Temperature	20.9 - 21.3	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

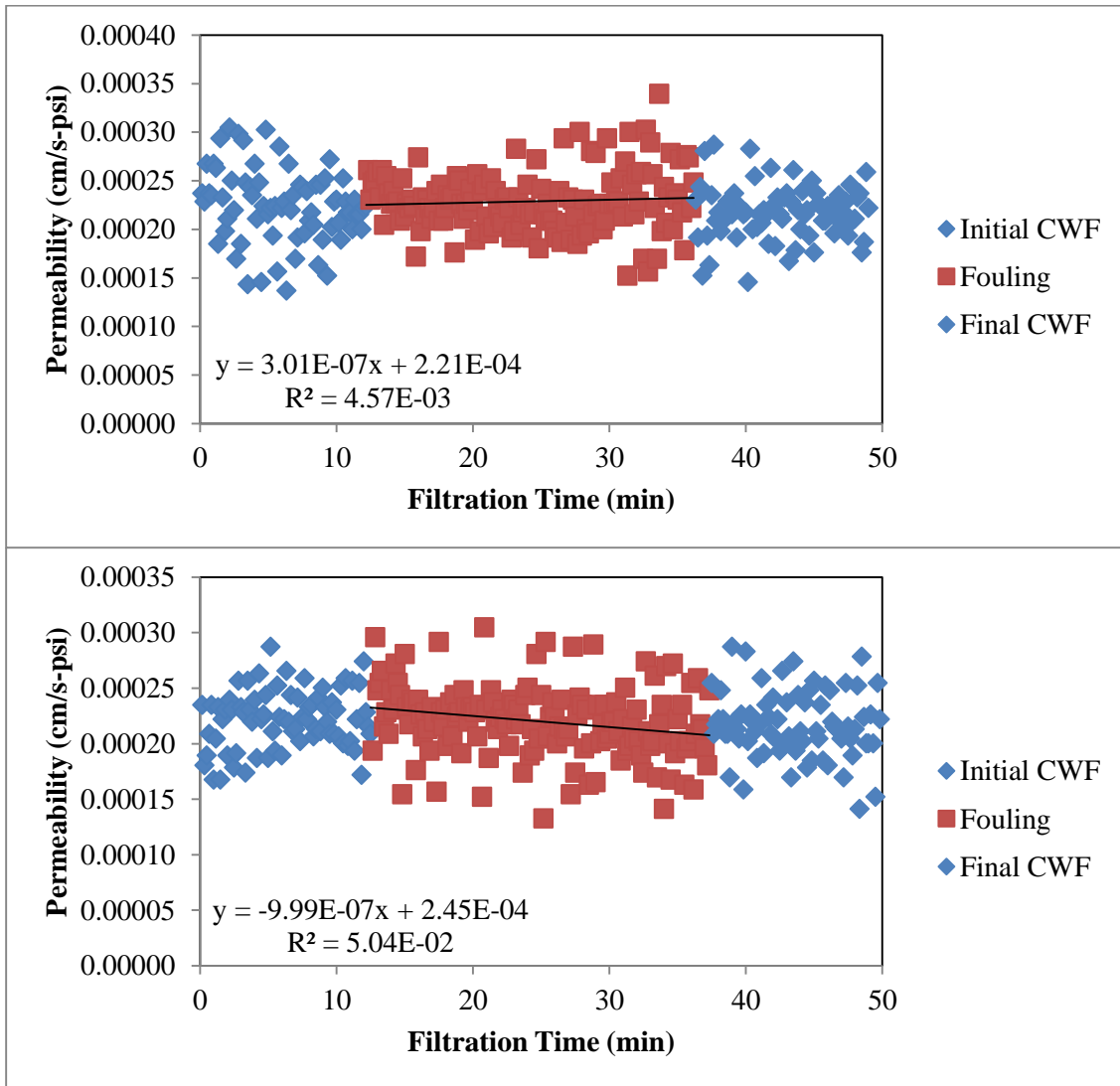


Figure A-52. Shingle Creek April PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	April Shingle Filtered	
Temperature	21.4	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

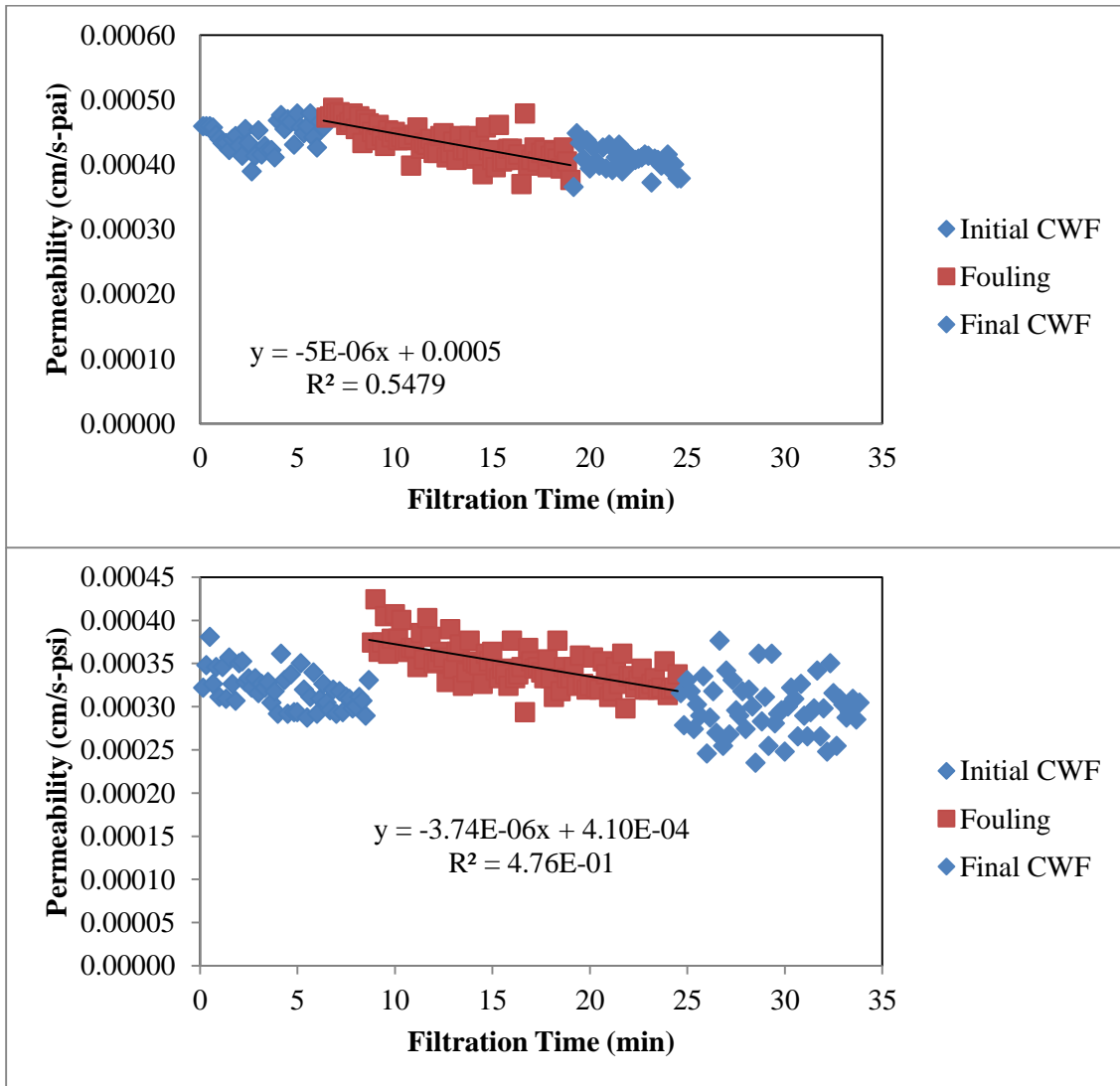


Figure A-53. Leech Lake River July YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	July Leech Filtered	
Temperature	20.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

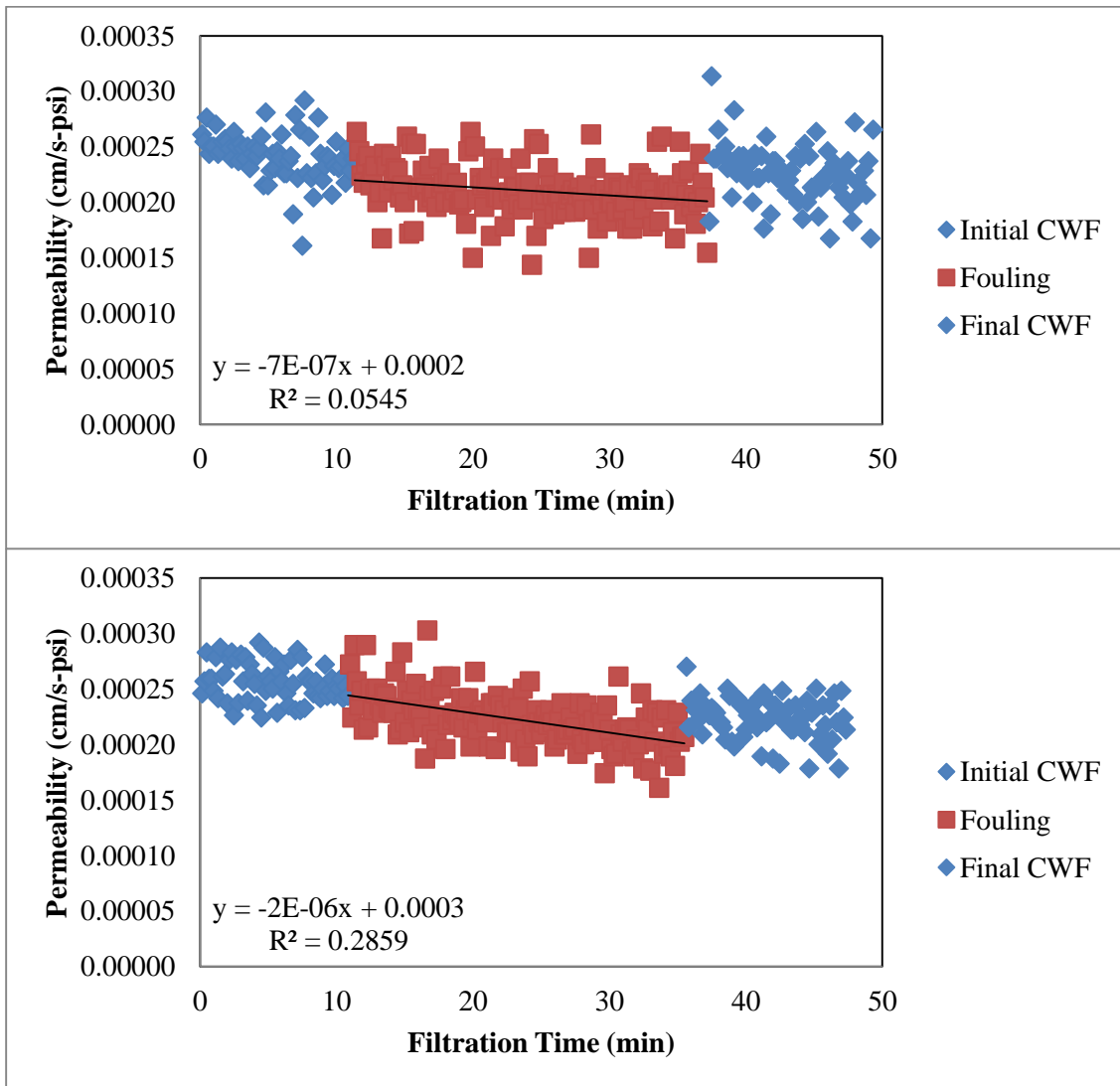


Figure A-54. Leech Lake River July PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	July Leech Filtered	
Temperature	20.7 - 20.9	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

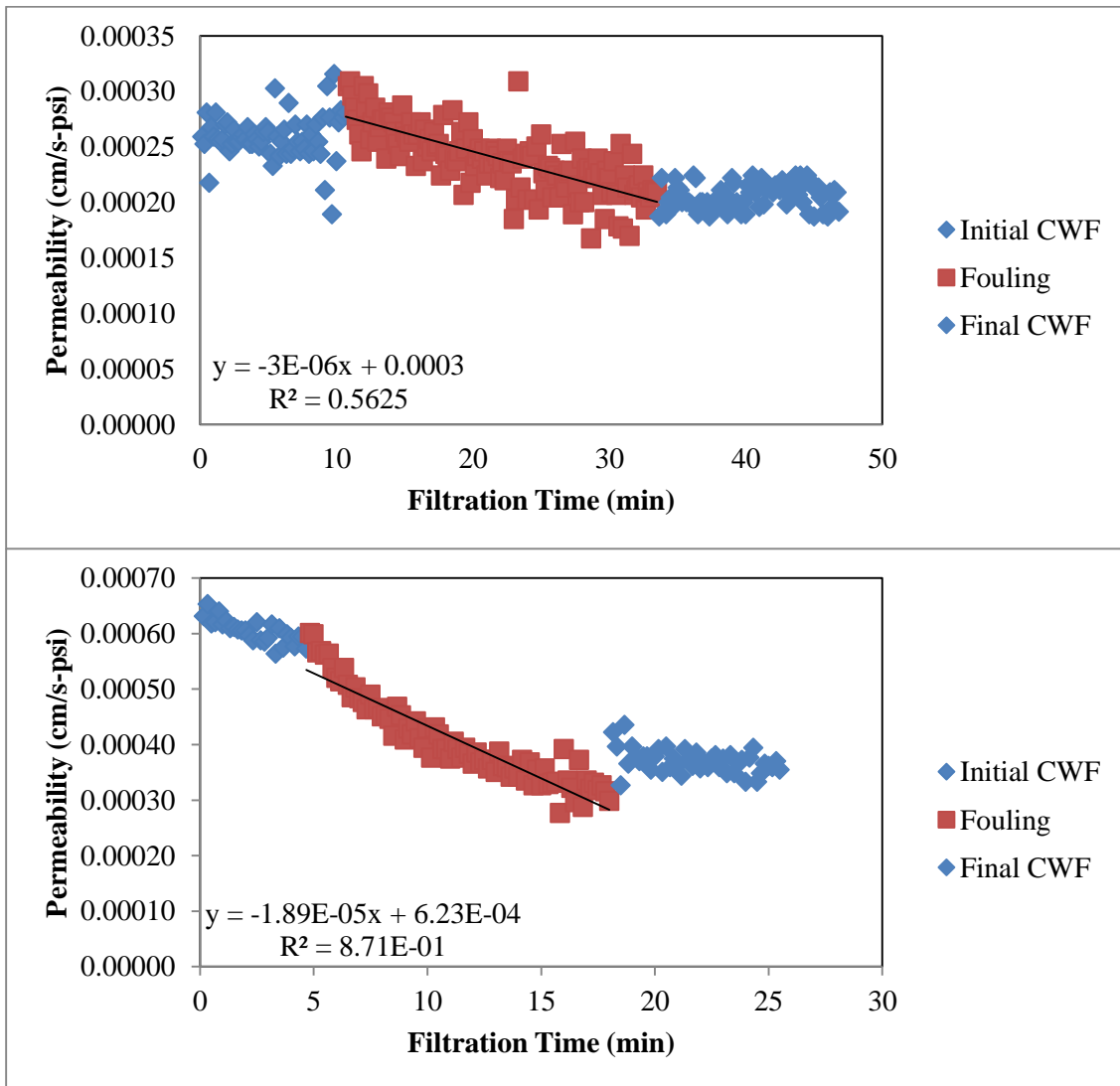


Figure A-55. Rice River July YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	July Rice Filtered	
Temperature	20.9 - 21.0	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

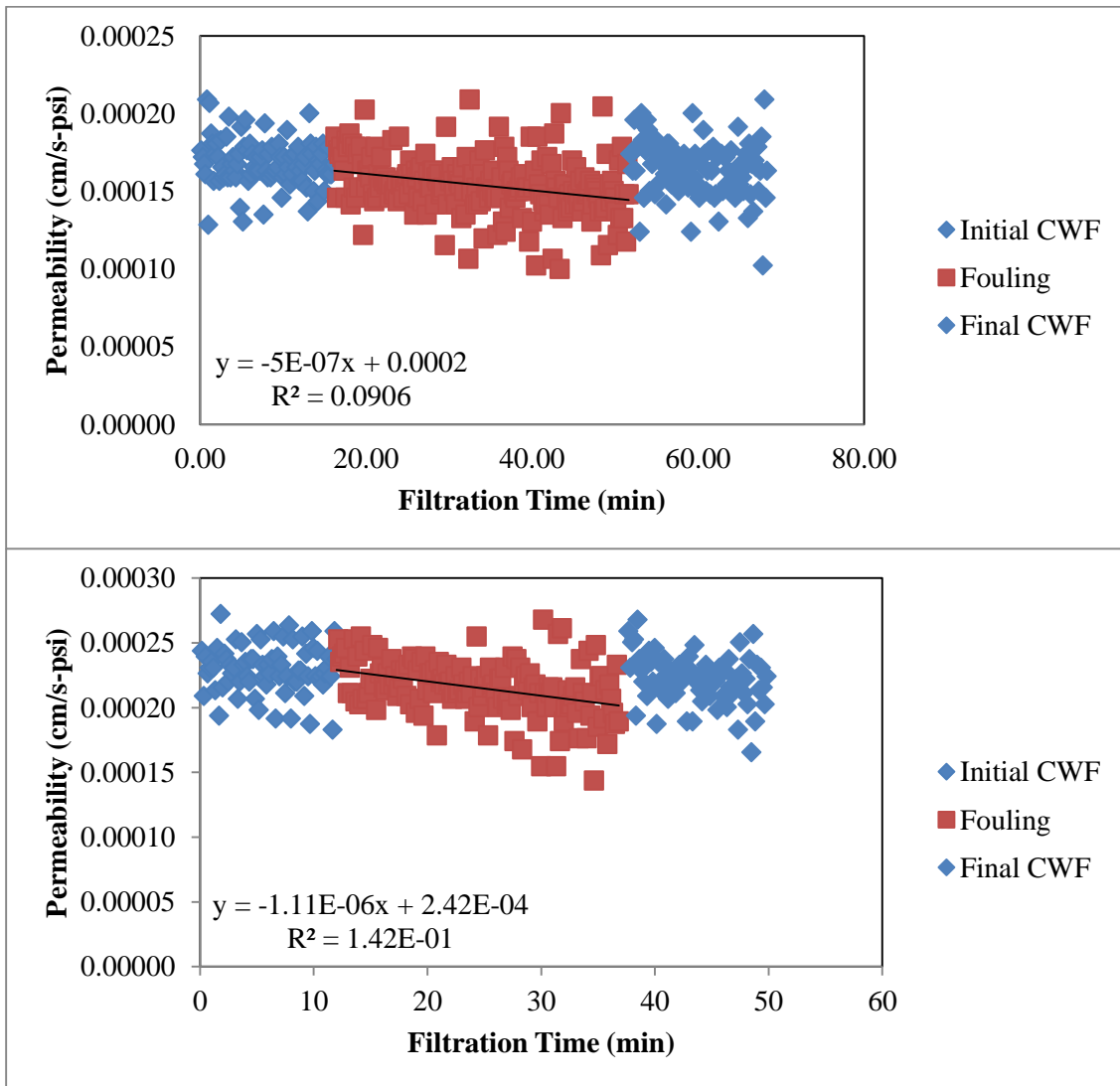


Figure A-56. Rice River July PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	July Rice Filtered	
Temperature	21.0 - 21.1	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

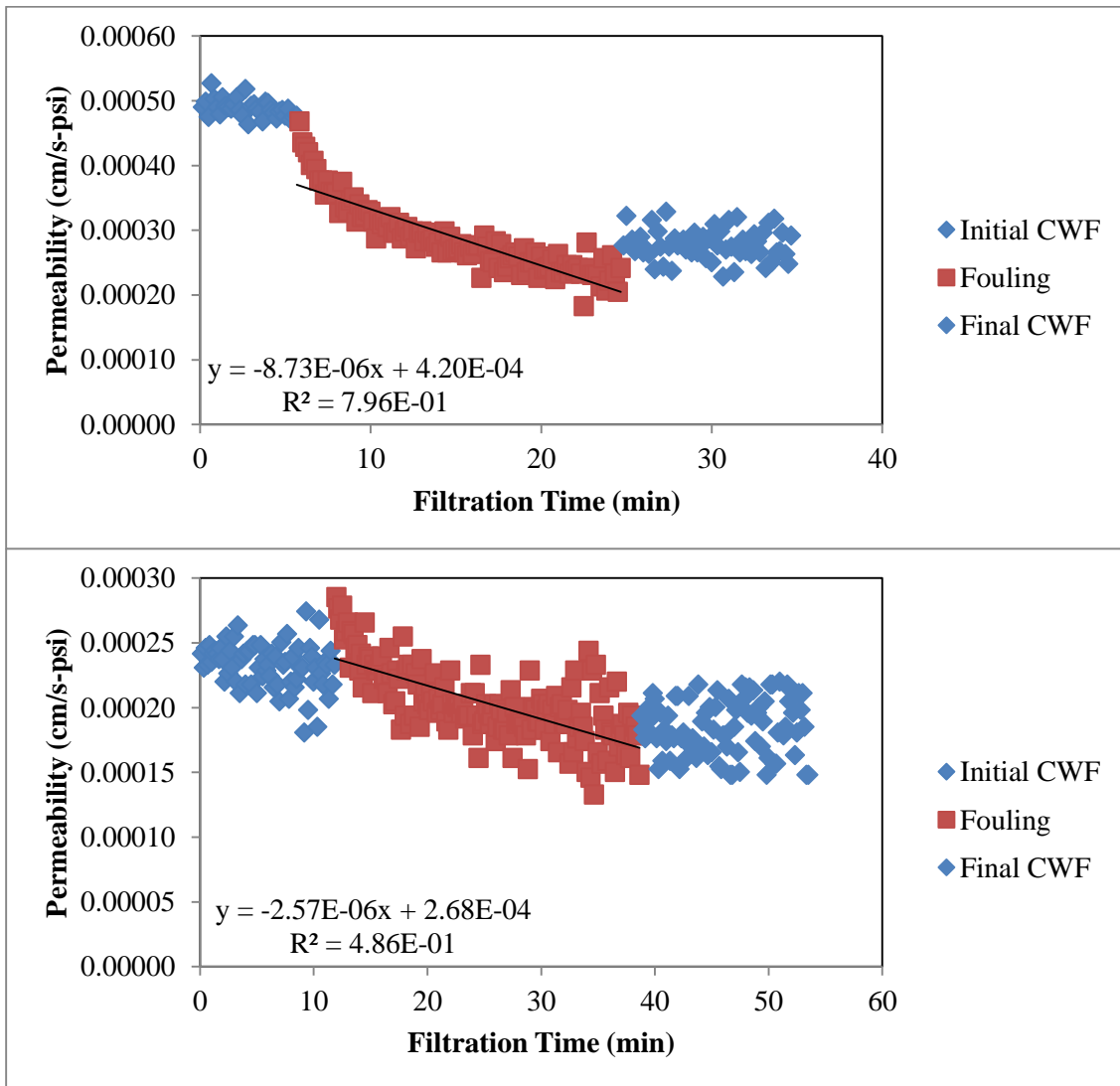


Figure A-57. Clearwater River July YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	July Clearwater Filtered	
Temperature	20.4 - 20.6	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

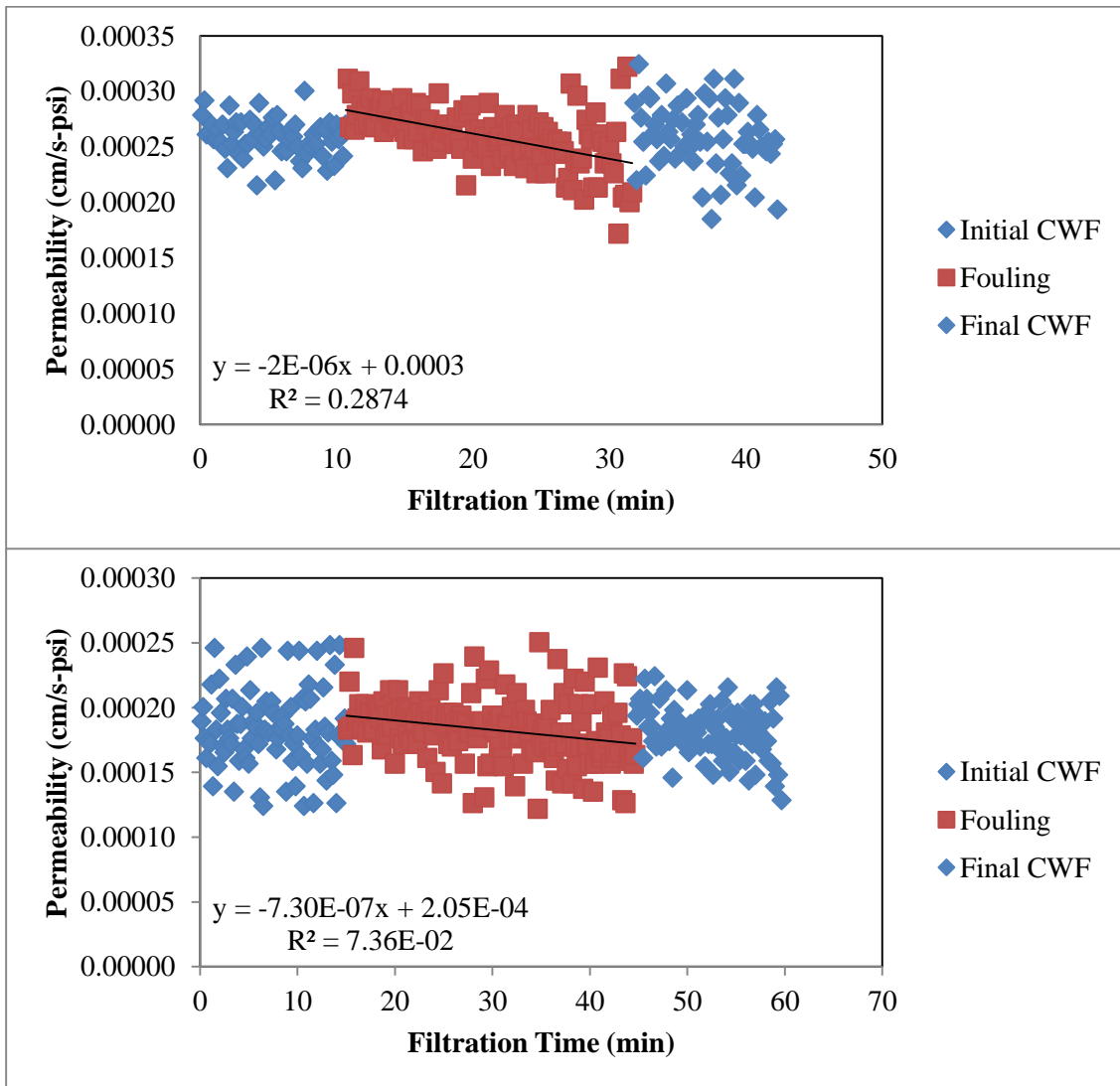


Figure A-58. Clearwater River July PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	July Clearwater Filtered	
Temperature	20.6	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

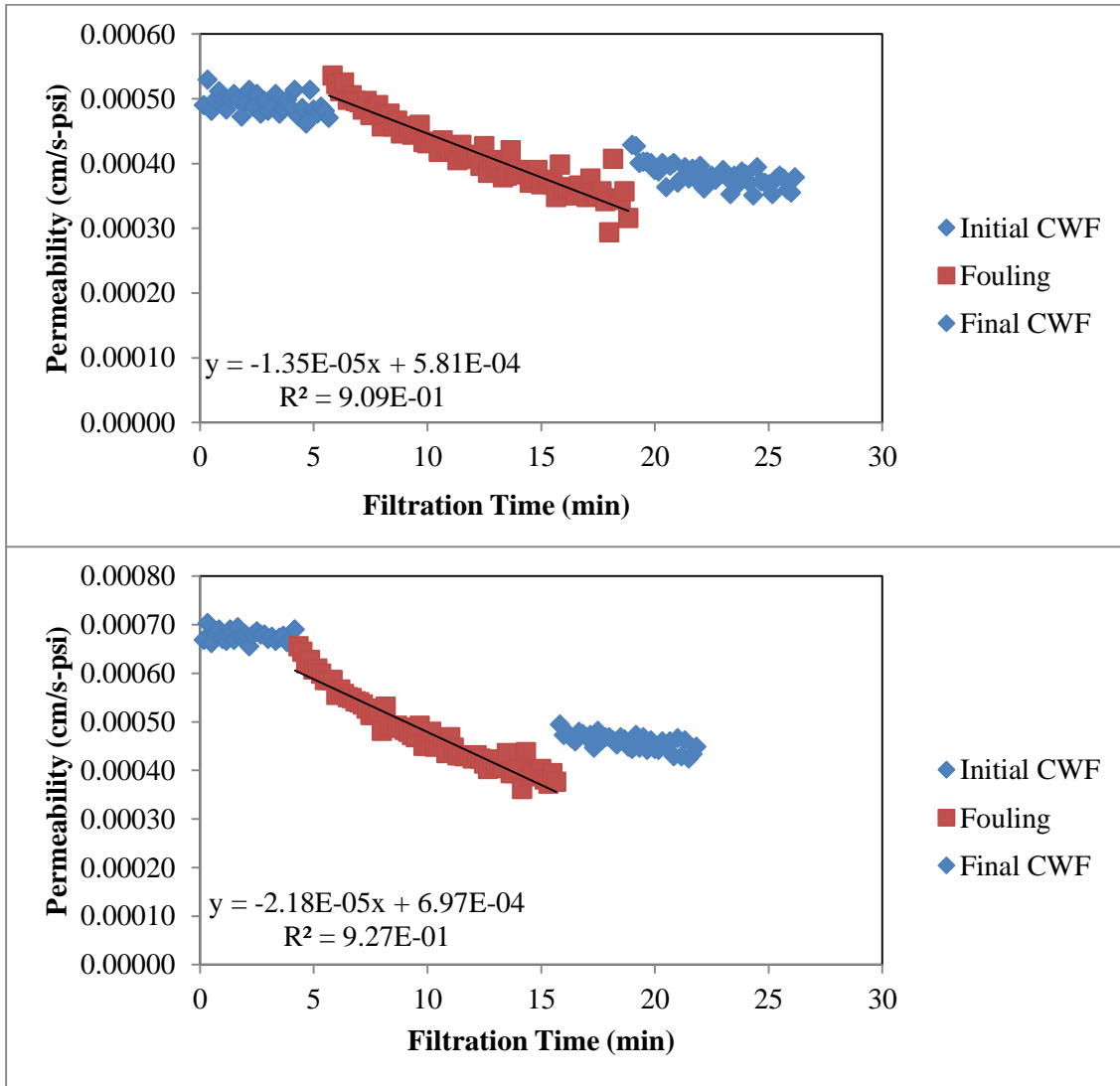


Figure A-59. Shingle Creek July YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	July Shingle Filtered	
Temperature	20.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

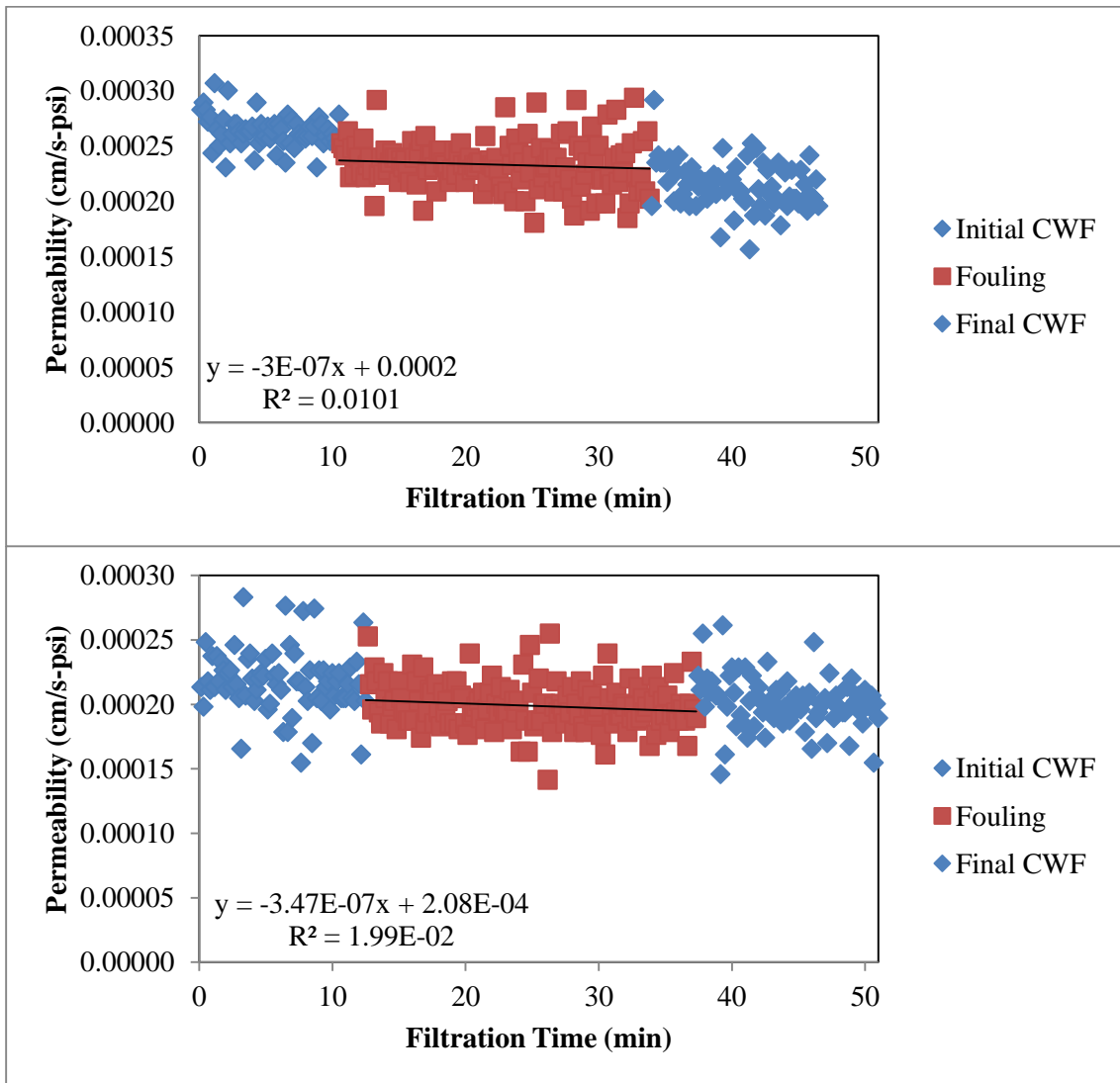


Figure A-60. Shingle Creek July PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	July Shingle Filtered	
Temperature	20.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

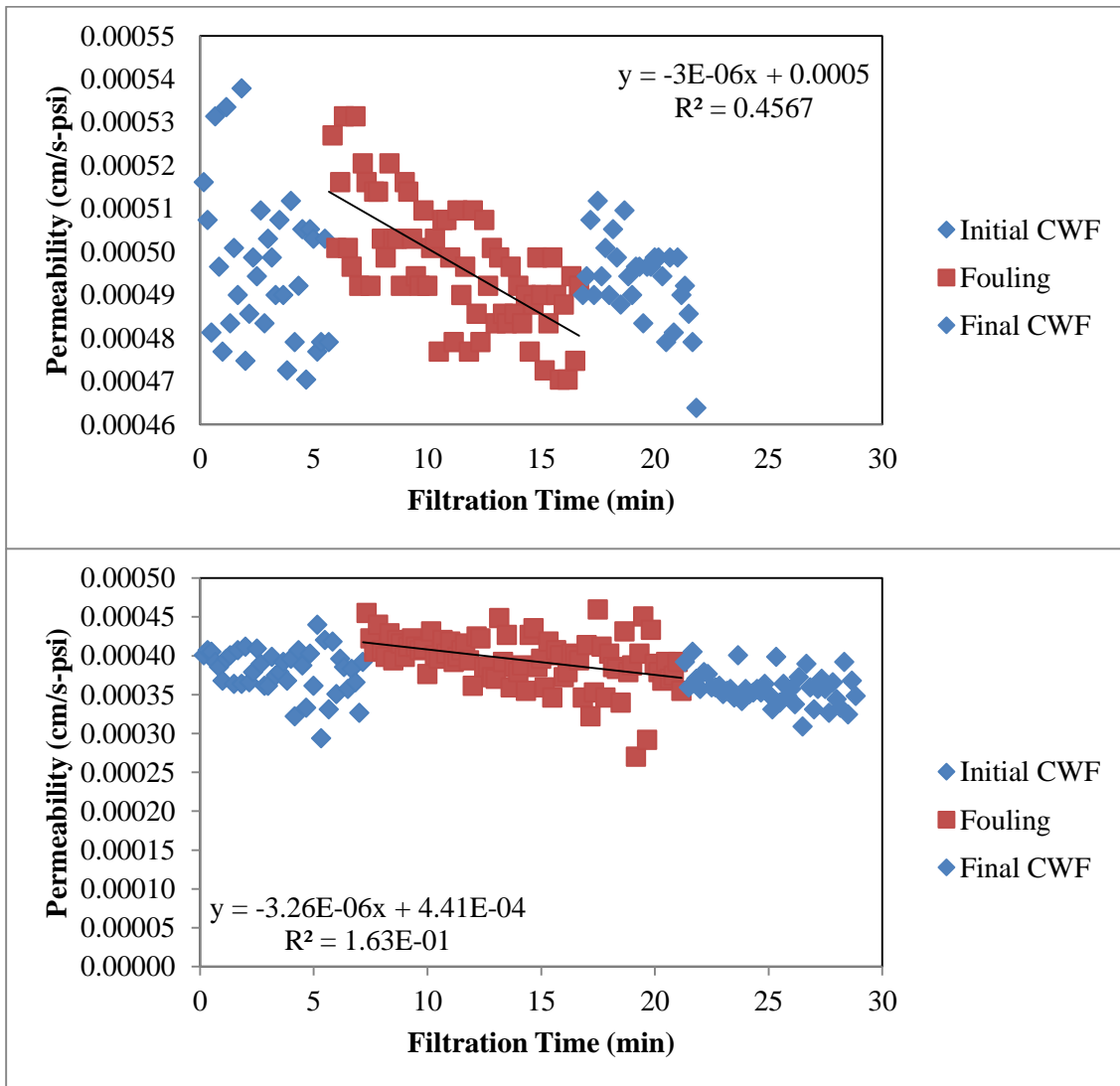


Figure A-61. Leech Lake River September YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	September Leech Filtered	
Temperature	20.8 - 20.9	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

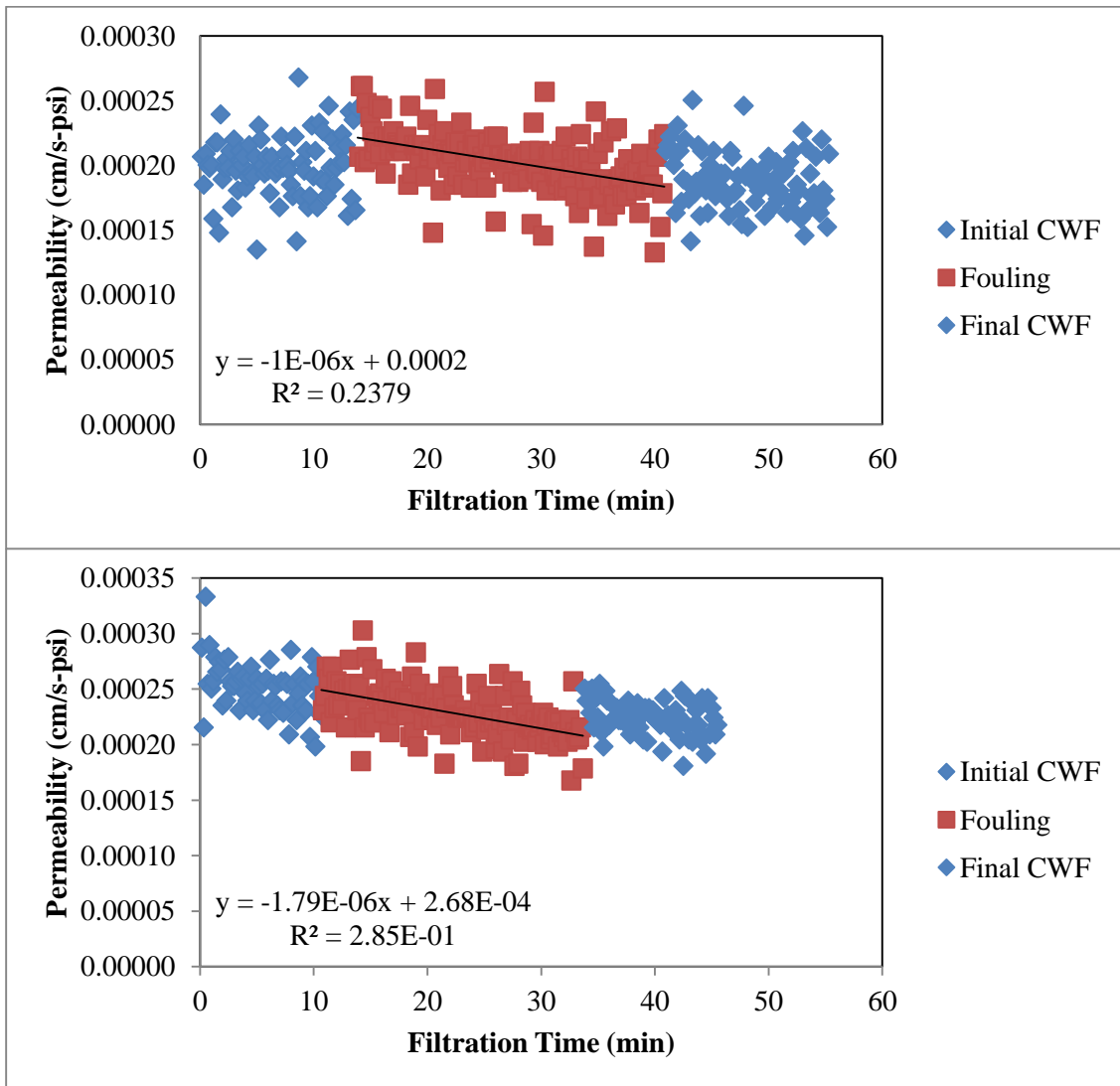


Figure A-62. Leech Lake River September PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	September Leech Filtered	
Temperature	20.9 - 21.0	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

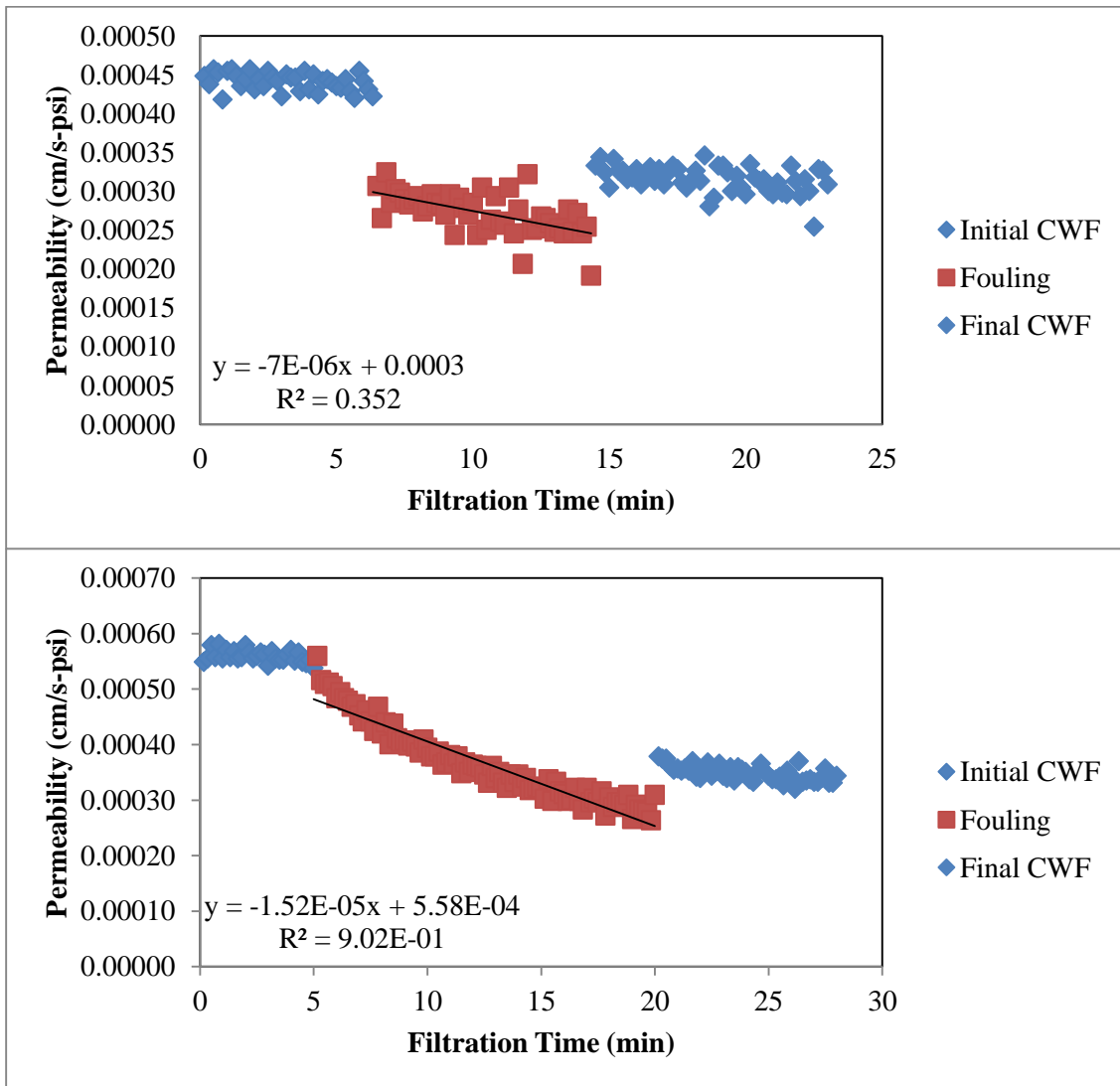


Figure A-63. Rice River September YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
	Regenerated	
Material	Cellulose	
Area	28.7	cm ²
Water	September Rice Filtered	
Temperature	20.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

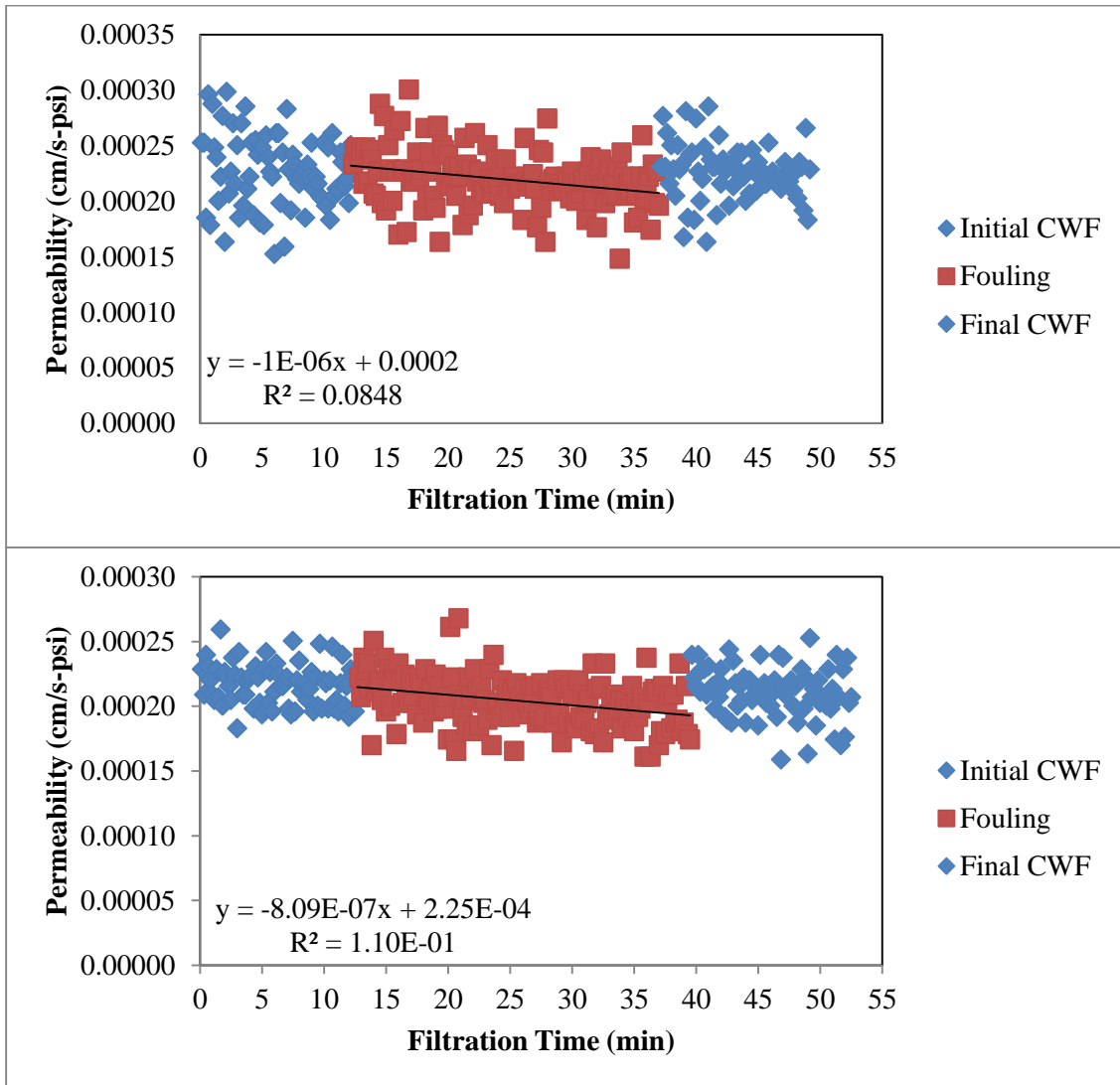


Figure A-64. Rice River September PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	September Rice Filtered	
Temperature	20.8 - 21.4	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

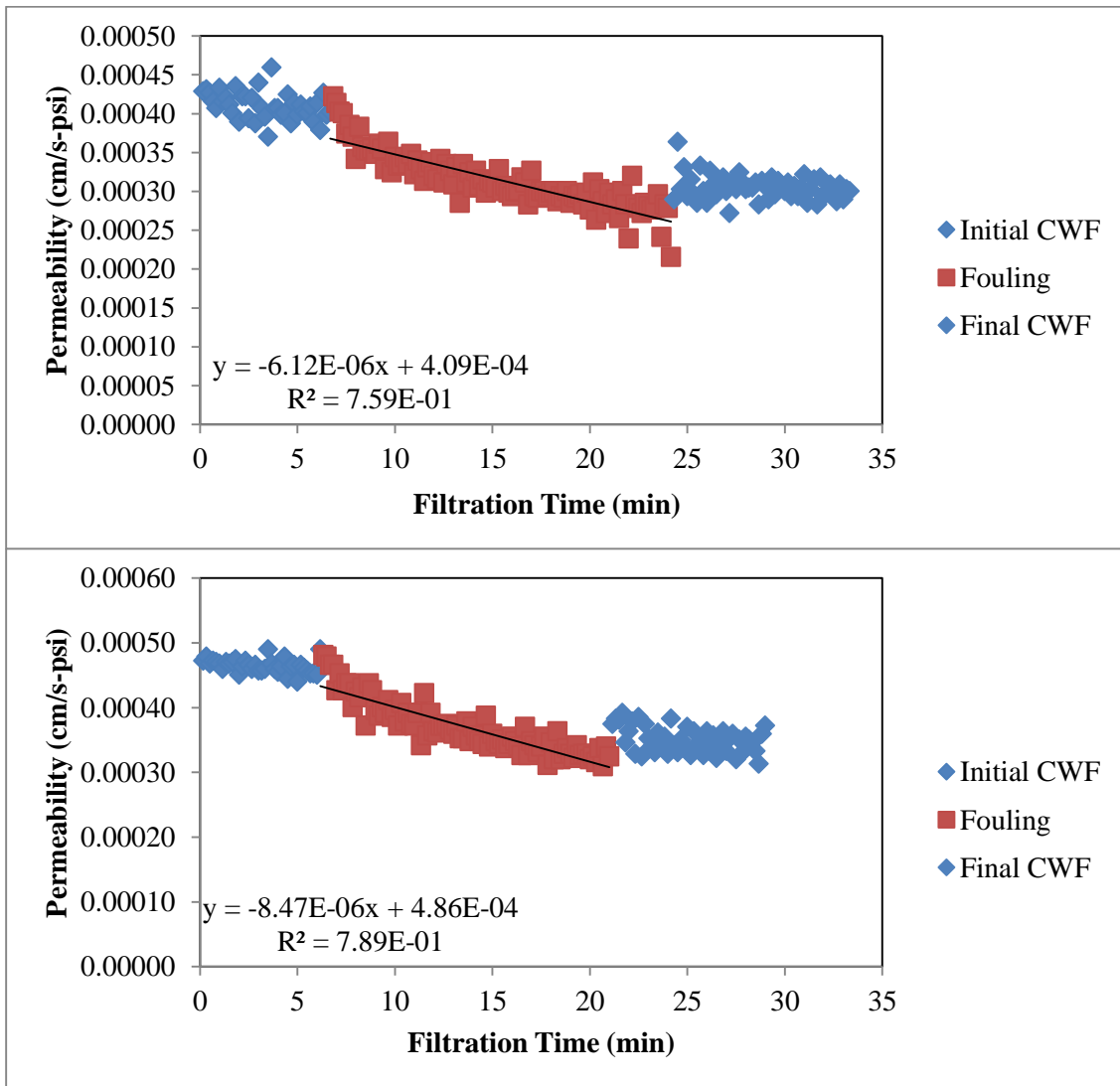


Figure A-65. Clearwater River September YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	September Clearwater Filtered	
Temperature	21.4	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

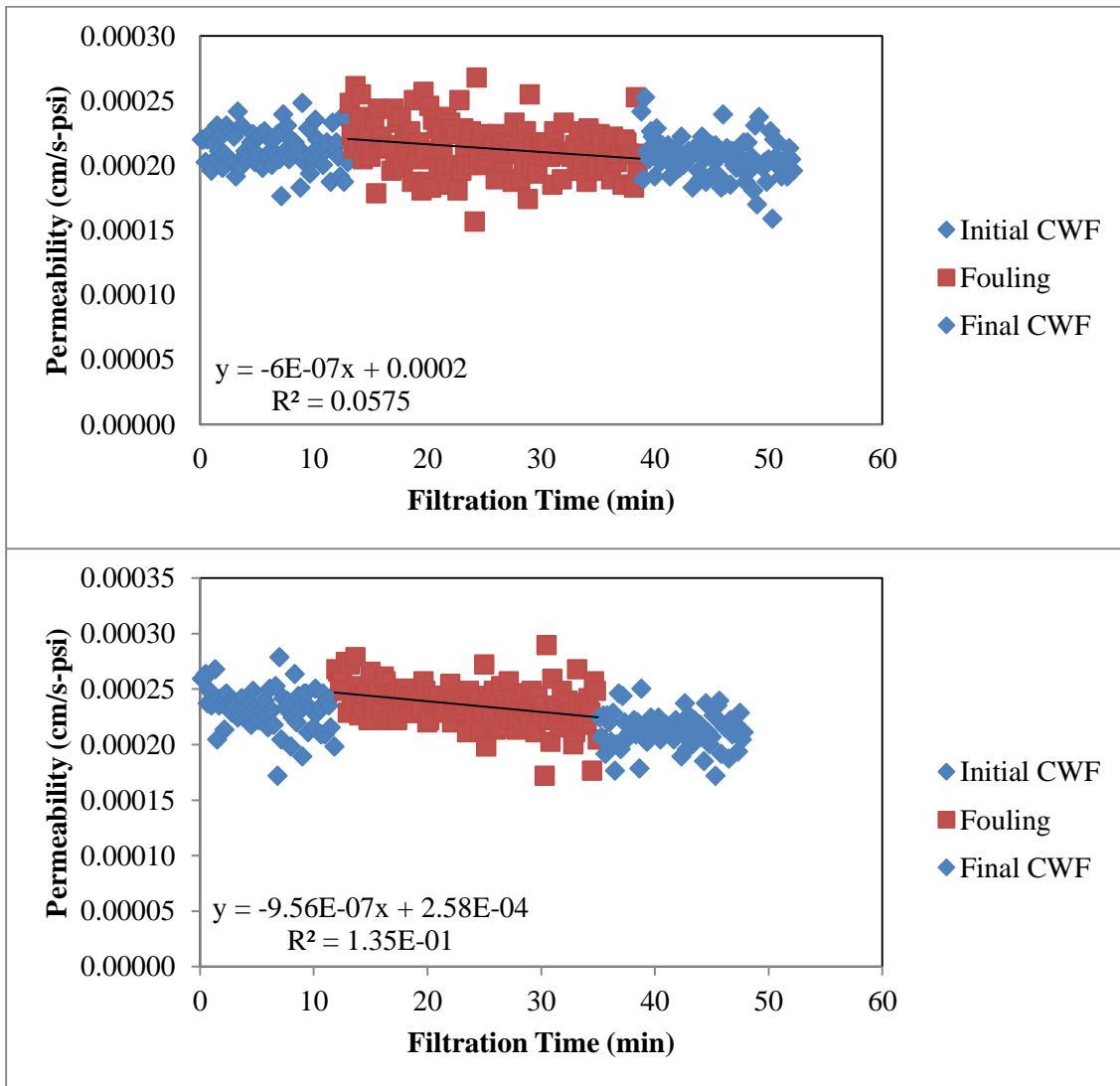


Figure A-66. Clearwater River September PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	September Clearwater Filtered	
Temperature	21.1 - 21.2	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

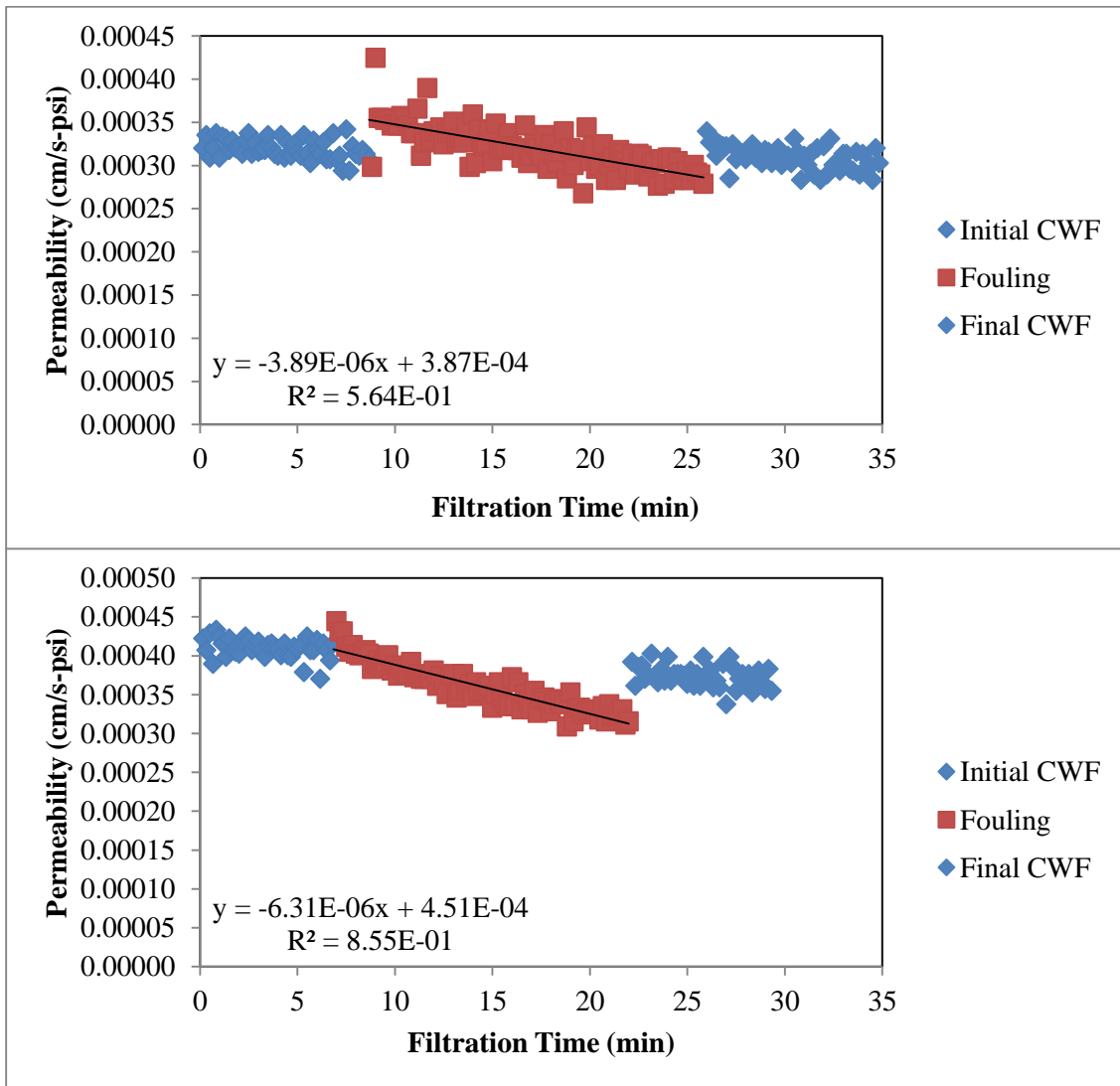


Figure A-67. Shingle Creek September YM30 Membrane

Membrane	YM30	
MWCO	30	kDa
Material	Regenerated Cellulose	
Area	28.7	cm ²
Water	September Shingle Filtered	
Temperature	21.4 - 21.7	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level

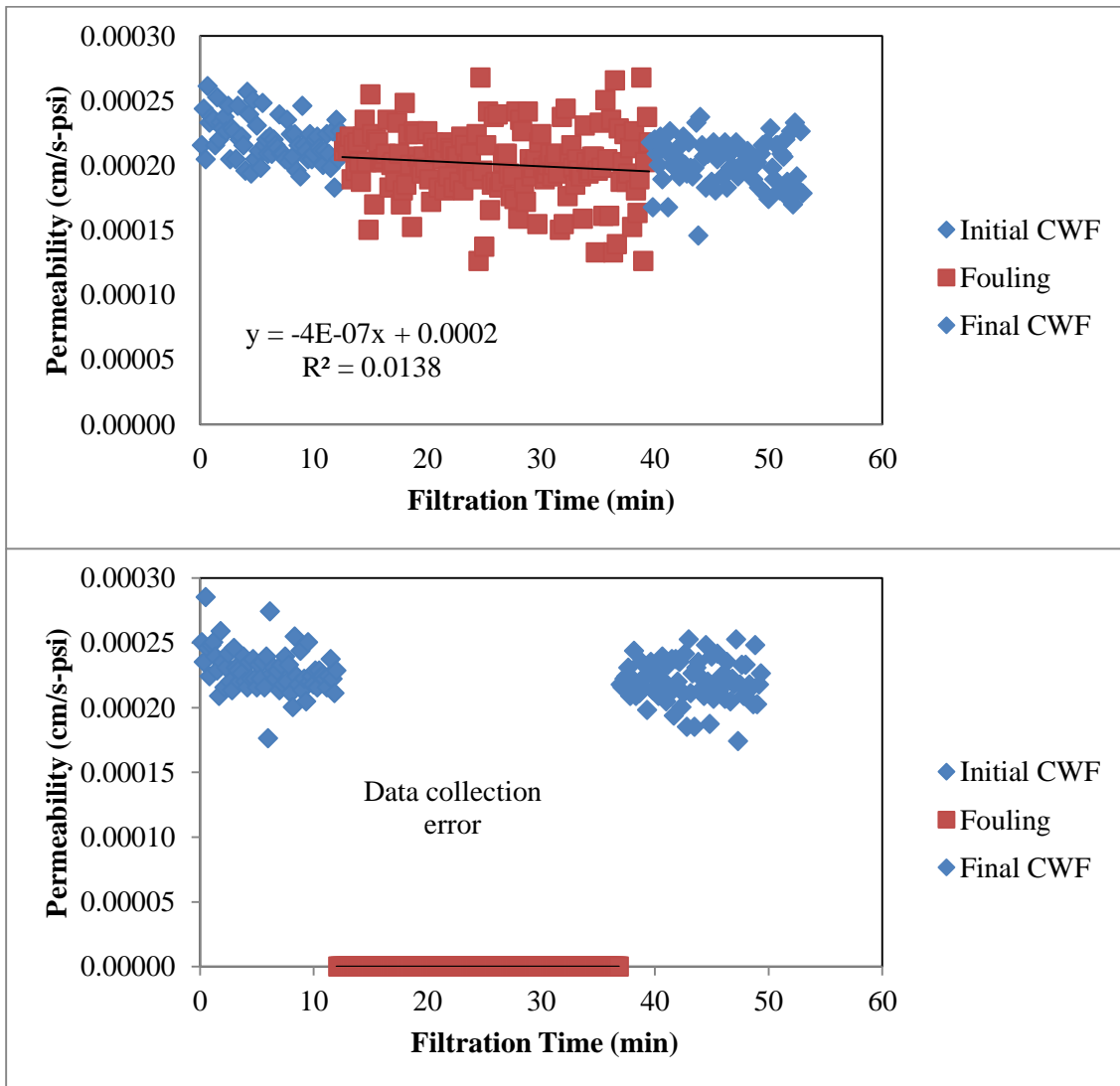
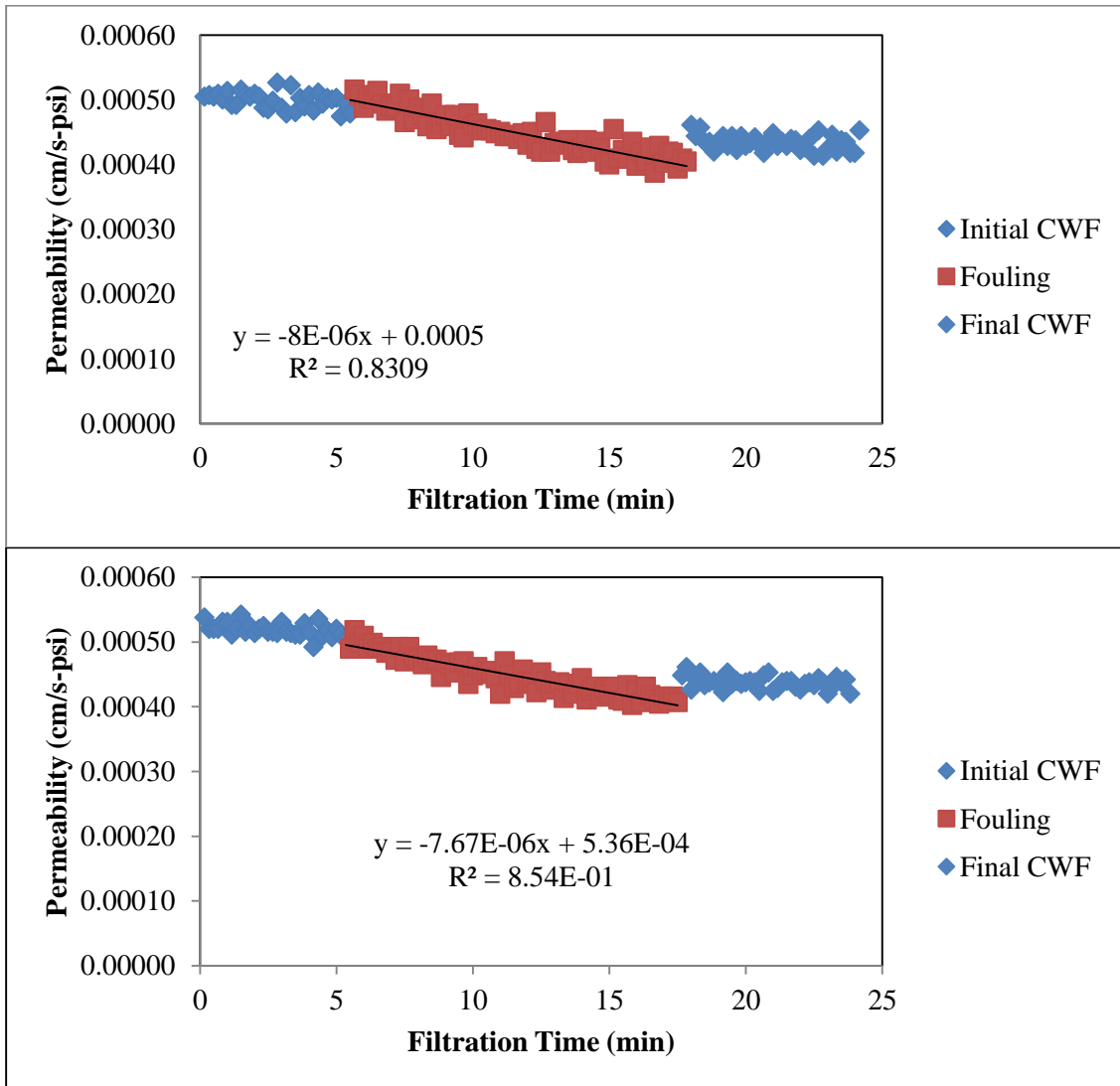


Figure A-68. Shingle Creek September PM30 Membrane

Membrane	PM30	
MWCO	30	kDa
Material	PES	
Area	28.7	cm ²
Water	September Shingle Filtered	
Temperature	21.8 - 22.0	degC
Pressure	16	psi
Time Interval	10	sec
Stirring Rate	1	level



Appendix B
MatLAB Programs

MatLAB code to perform multi-variant regression between land use and NOM

characteristics

```
b1=zeros(7,7);
se1=zeros(7,7);
pval1=zeros(7,7);
inm1=zeros(7,7);
rsquare=zeros(7,1);
for i=1:7
    flag=0;
    [b,se,pval,inm]=stepwisefit(X(:,1:7),Y(:,i));
    b1(:,i)=b;
    se1(:,i)=se;
    pval1(:,i)=pval;
    inm1(:,i)=inm;
    ind=find(inm);
    for j=1:length(ind)
        E(:,j)=X(:,ind(j));
        flag=1;
    end
    if (flag==1)
        b2=regstats(Y(:,i),E);
        rsquare(i,1)=b2.rsquare;
        clear E;
    end
end
```


MatLAB code to correct for inner-filter and blank readings of the spectrofluorometer, produce 3D EEMs, and calculate fluorescent index

```
% Code written by Rose M. Cory
% Minor revisions by Meghan Funke
% Additional revisions by Bethany Brinkman for extended range, figure labels, revised FI
calculation

% Original MF program runs em 350-550 (increments of 2, total of 101) and ex 240-400
(increments of 5, total of 33)
% BMB program runs em 290-550 (increments of 2, total of 131) and ex 240-400 (increments of
5, total of 33)

% Purpose of this code is to:
% 1. Correct EEM data for instrument response
% 2. Normalize EEM data to raman area (corrects for changes in instrument output over time
% 3. Creates a figure of the corrected EEM
% 4. Calculates the Fluorescence Index (FI)

% Corrected EEMs and figures are saved to folder defined in this code.

% Create an excel file (do not include headers), with the following information entered
respectively for each EEM sample:

% Column 1: Complete filepath of .xls EEM scan location on computer
% Column 2: Complete filepath of .xls blank scan location on computer
% Column 3: Complete filepath of .csv abs scan location on computer
% Column 4: Raman area
% Column 5: Correct sample ID, all samples must be numbered consecutively by adding "_##" to
the end of the ID.
% Column 6: Complete filepath of emission correction file
% Column 7: Complete filepath of excitation correction file

% Import the previous excel file by going to: File-Import Data
% Import both the data file and the textdata file
% Rename the textdata file as "test"
% Confirm that "test" has 7 columns

% Be sure to enter the correct filepaths later in code

% Defines the qq matrix, or, which EEM scan is currently being corrected

prompt = {'Enter the number of samples'};
samples = str2num(char(inputdlg(prompt)));
for qq=1:samples

A = xlsread(char(test(qq,1)), 'Sheet1'); % Column 1 of test file
ifile = char(test(qq,5)); % Column 5 of test file
blank = xlsread(char(test(qq,2)), 'Sheet1'); % Column 2 of test file
```

```

abs = csvread(char(test(qq,3)), 2,0);      % Column 3 of test file, reads absorbances starting
after headings
raman_area = (data(qq,1));                % Only data column from import file

A = A(2:132,2:34); % Selects for all em (290-550, 131 samples) and ex (240-400, 33 samples)
nm
blank = blank(2:132,2:34);
A = A - blank; % Subtracts the water blank from the sample

Asize = size(A);
emissionLen = Asize(1);
excitation = (240:5:400);
emission = A(1:emissionLen, 1); % may need to change this part depending on em increment

% Read in correction files (make sure correction files are correctly formatted)

MC = xlsread(char(test(qq,6)), 'Sheet1');
XC = xlsread(char(test(qq,7)), 'Sheet1');

% EMISSION AND EXCITATION corrections using matrix algebra:
% Note wavelengths and xcorrect must be inverted or change the eqn to divide by Y

X=diag(XC);
Y=diag(MC);

zi=A;
zi=((zi/X)*Y)';

zir=zi/raman_area; % Normalizes corrected matrix intensities to raman area

% Inner filter correction:

x=abs(:,1:1); % Absorbance wavelengths
y=abs(:,2:2); % Absorbance intensities
abs_1nm = interp1(x, y, 200:1:600, 'linear', 'extrap');
abs_1nm = abs_1nm';
ex_abs=abs_1nm(41:5:201,:); % Creates list of ex abs (240-400)
em_abs=abs_1nm(91:2:351,:); % Creates list of em abs (290-550)
ex_abs=ex_abs';
for i=1:length(em_abs)
    for j=1:length(ex_abs)
        IFC(i,j)=ex_abs(j)+em_abs(i);
    end
end
czir=zir.*10.^(0.5*IFC);

% Saves the raman normalized and ex, em and inner filtered corrected EEM matrix

```

```

pathname = 'C:\Users\bbrinkman\Desktop\EEM\';

for i=1:length(ifile)

    pathname(length(pathname) + 1) = ifile(i);

end

pathnamelength = length(pathname);

pathname(pathnamelength + 1: pathnamelength + 4) = '.xls';

save(pathname, 'czir', '-ascii', '-double', '-tabs');

% Creates a 3D contour figure of the corrected EEM
% You may need to adjust the range in line

% Figure x- y- axis range:

em = 290:2:550;
ex = 240:5:400;

% Transposes corrected matrix for plotting
% zipr=zir(51:251,:);

A=czir';

figure('visible', 'off'); % Remove if you want to see all the figures as they are created
contourf(em,ex,A,30); % with 30 contour lines - ON
handle = gca;
set(handle,'fontsize', 14);
xlabel('Emission (nm)')
ylabel('Excitation (nm)')
% mesh(em,ex,I');
% surf(em,ex,I');
% colormap(hsv);
caxis([0, 2]); % sets min and max intensity values
% caxis('manual'); % prevents auto-setting of caxis
H = colorbar('vert');
set(H,'fontsize',14);

% Saves current object only (this won't work if you close the figure first)

pathname = 'C:\Users\bbrinkman\Desktop\EEM\';

for i=1:length(ifile)
    pathname(length(pathname) + 1) = ifile(i);
end

```

```
pathnamelength = length(pathname);  
pathname(pathnamelength + 1: pathnamelength + 4) = '.tif';  
saveas(gcf, pathname, 'tif');
```

```
% Creates one excel file that includes all FI values for all EEM samples
```

```
FI_IF(qq,1) = czir(81,27)/czir(106,27); % Calculates FI, ratio between intensity at ex=370nm and  
em=450nm/em=500nm
```

```
end
```

```
pathname = 'C:\Users\bbrinkman\Desktop\EEM\FI_Test.xls';  
save(pathname, 'FI_IF', '-ascii', '-double', '-tabs');
```

Appendix C

Field Notes

Spatial Mississippi River Sampling Trip

Lake Itasca outlet (start of river)

- Date: August 18, 2008
- Time: 1700
- Width: 16 feet
- Depth: 6 inches (consistent)
- Velocity: 2 feet in 4.22 seconds (1.2 m/s DNR)
- Flow: 3.79 cfs (6 cfs DNR)
- Description: ~85°F, warm, sunny day, lots of tourists, sampled upstream of rock dam, few visible particles in water and fingerling fish, edge of lake as reeds, watershed is northern forest (red and white pine, poplar) and swampland

Sucker Brook

- Date: August 18, 2008
- Time: 1900
- Width: 7.5 feet
- Depth: 9 inches (consistent)
- Velocity: 4 feet in 2.85 seconds
- Flow: 7.89 cfs
- River Mile: 1344 (1.2 miles upstream of confluence)
- Coordinates: 47°14'59" N 95°14'40" W, Sucker Brook at State Highway 200
- Description: Sucker Brook is a trout stream draining Iron Springs Bog SNA, spruce forests, and Sucker Lake, water is fast moving, clear, bottom is rocky with lots of submerged plant growth, watershed is northern forest, mostly shaded with wildflowers on bank

Mississippi River after LaSalle wetlands

- Date: August 19, 2008
- Time: 800
- Width: 66 feet (Google Earth)
- Depth: 3 feet, 6 feet from shore
- Velocity: 4 feet in 29.33 seconds
- Flow: 27.0 cfs
- River Mile: 1315
- Coordinates: 47°26'0" N 95°7'49" W, Mississippi River at County Route 5
- Description: Large wetland expanse - mainly reeds and grasses (no cattails), northern woods, some ag - mostly hay with some cows and corn, water is sluggish and more turbid, thick (> 2 ft) organic mat

Hennepin Creek

- Date: August 19, 2008
- Time: 900
- Width: 8 feet
- Depth: 8 inches in thalweg, 3-4 inches elsewhere, 6 inches average
- Velocity: 5 feet in 3.28 seconds

- Flow: 6.10 cfs
- River Mile: 1310 (1.31 miles upstream of confluence)
- Coordinates: 47°23'52" N 95°5'13" W, Hennepin Creek at Wildfire Road
- Description: Trout stream in Mississippi Headwater State Forest, many areas logged within last five years, northern forest, sandy soils, some marshy areas surrounding, drain pipes under road have lip but no impoundment

Mississippi River before Bemidji

- Date: August 19, 2008
- Time: 1030
- Width: 63 feet (Google Earth)
- Depth: 31 inches in thalweg, up to 16 inches on sandbar, 2 feet average
- Velocity: 7 feet in 9.43 seconds
- Flow: 93.5 cfs
- River Mile: 1288
- Coordinates: 47°24'4" N 94°54'24" W, Mississippi River at County Route 71
- Description: Slightly more ag (hay), northern forest, marshy around river banks, algal growth on bottom rocks, sandy, colored

Mississippi River after Bemidji

- Date: August 19, 2008
- Time: 1200
- Width: 103 feet (Google Earth)
- Depth: Estimated ~4 feet
- Velocity: 4 feet in 8.65 seconds
- Flow: 143 cfs (135 cfs USGS)
- River Mile: 1282
- Coordinates: 47°29'1" N 94°49'51" W, Mississippi River at County Route 19
- Description: At output of Lake Bemidji, lake has large marshy fringe, cattails surrounding river, bottom is sandy with macrophytes, fine particles suspended

Mississippi River below chain of lakes

- Date: August 24, 2008
- Time: 1430
- Width: 55 feet (Google Earth)
- Depth: Deep!
- Velocity: 4 feet in 18.85 seconds
- Flow: 143 cfs (8/4 437 cfs, 9/12 352 cfs USGS grab)
- River Mile: 1221
- Coordinates: 47°19'29" N 93°57'34" W, Mississippi River at US Highway 2
- Description: After series of lakes, northern forest, marshy banks, river is deep and slow, fairly clear, algal growth on rocks

Leech Lake River

- Date: August 24, 2008
- Time: 1500
- Width: 80 feet (Google Earth)

- Depth:
- Velocity: 3 feet in 8.38 seconds
- Flow:
- River Mile: 1216.5 (1.03 miles upstream of confluence)
- Coordinates: 47°17'27" N 93°54'47" W, Leach Lake River along County Route 139
- Description: Outflow of Leech Lake, primarily marshy fringe, large contribution of well water (Dan and Lisa Fox, residents)

Mississippi River before Grand Rapids

- Date: August 24, 2008
- Time: 1530
- Width: 207 feet (Google Earth)
- Depth:
- Velocity: ~6 feet in 4.59 seconds
- Flow: (273 cfs USGS - station in middle of town)
- River Mile: 1187
- Coordinates: 47°14'0" N 93°35'11" W, Mississippi River at US Highway 2
- Description: Immediately below Pokegama Dam, banks are higher, northern forest, algal growth on bottom, variable bottom depth, reedy sand banks in places

Prairie River

- Date: August 24, 2008
- Time: 1600
- Width: 132 feet (Google Earth)
- Depth: 6-8 inches, average 7 inches
- Velocity: 3 feet in 3.66 seconds
- Flow: 63.1 cfs (37 cfs USGS)
- River Mile: 1181 (1 mile upstream of confluence)
- Coordinates: 47°13'9" N 93°28'42" W, Prairie River at US Highway 2
- Description: Shallow, fast flowing river outside of Grand Rapids, forested banks, gravel bottom with some algae

Mississippi River after Grand Rapids

- Date: August 24, 2008
- Time: 1700
- Width: 146 feet (Google Earth)
- Depth:
- Velocity: ~2 feet in 4.25 seconds
- Flow: (273 cfs USGS - station in middle of town)
- River Mile: 1175
- Coordinates: 47°10'27" N 93°25'15" W, Mississippi River at US Highway 2
- Description: Northern forest banks, colored, muddy and sandy bottom

Swan River

- Date: August 24, 2008
- Time: 1730
- Width: 60 feet (Google Earth)

- Depth: 1 foot, consistent
- Velocity: 3 feet in 2.41 seconds
- Flow: 74.7 cfs
- River Mile: 1142 (0.62 miles upstream of confluence)
- Coordinates: 47°0'44" N 93°15'20" W, Swan River at State Route 65
- Description: Fast flowing, clear, rocky bottom, mostly wooded banks

Two River Springs

- Date: September 15, 2008
- Time: 1200
- Width: 10 feet
- Depth: 5-9 inches, 6 inches average
- Velocity: 4 feet in 8.62 seconds
- Flow: 2.32 cfs
- River Mile: 1122 (0.43 miles upstream of confluence)
- Coordinates: 46°52'36" N 93°21'27" W, Two River Springs at 240th Ave.
- Description: Heavily wooded banks, clear, fast flowing, lots of silt on bottom

Libby Brook

- Date: September 15, 2008
- Time: 1230
- Width: 5 feet
- Depth: 2.5 inches
- Velocity: 4 feet in 3.09 seconds
- Flow: 1.35 cfs
- River Mile: 1116.8 (450 feet upstream of confluence)
- Coordinates: 46°50'47" N 93°20'18" W, Libby Brook at County Highway 65
- Description: Fast, clear, free flowing, high banks with grasses, immediate banks with wetland plants, gravel/sand bottom

Sandy River

- Date: September 15, 2008
- Time: 1245
- Width: 65 feet (Google Earth)
- Depth: ~3-4 feet
- Velocity: 2 feet in 34.75 seconds
- Flow: 13.1 cfs
- River Mile: 1109 (0.5 miles upstream of confluence)
- Coordinates: 46°47'12" N 93°19'29" W, Sandy River at County Highway 65
- Description: Murky, extremely slow flowing outlet of Sandy Lake, silt accumulation on bottom, high banks with grasses, light algal growth floating on top

Willow River

- Date: September 15, 2008
- Time: 1330
- Width: 117 feet (Google Earth)
- Depth: 2 feet

- Velocity: 3 feet in 10.97 seconds
- Flow: 64.0 cfs
- River Mile: 1082 (0.97 miles upstream of confluence)
- Coordinates: 46°40'57" N 93°35'20" W, Willow River at County Road 69
- Description: High banks with grasses and forest, silty on bottom, narrows and speeds up before bridge

Mississippi River before Aitkin

- Date: September 15, 2008
- Time: 1400
- Width: 235 feet (Google Earth)
- Depth: 2 feet about 6 feet from shore, 3 feet estimated average
- Velocity: 10 feet in 4.47 seconds
- Flow: 1577 cfs (8/13 574 cfs, 9/25 694 cfs USGS grab)
- River Mile: 1077.5
- Coordinates: 46°39'5" N 93°36'45" W, Mississippi River at State Highway 169
- Description: High grassy banks with forest, houses lining river but spaced, bottom sandy and silty, water murky

Rice River

- Date: September 15, 2008
- Time: 1415
- Width: 42 feet (Google Earth)
- Depth: 15 inches
- Velocity: 5 feet in 6.75 seconds
- Flow: 370.4 cfs
- River Mile: 1070 (3.86 miles upstream of confluence)
- Coordinates: 46°35'56" N 93°36'46" W, Rice River at State Highway 169
- Description: Deeply colored, forested banks, silty bottom, hay fields, scattered houses

Sisabagamah Creek

- Date: September 15, 2008
- Time: 1430
- Width: 6 feet
- Depth: 4 inches
- Velocity: 2 feet in 3.88 seconds
- Flow: 1.03 cfs
- River Mile: 1061.3 (2.05 miles upstream of confluence)
- Coordinates: 46°32'43" N 93°39'11" W, Sisabagamah Creek at State Highway 169
- Description: Mix of tilled ag/hay and wetlands, reedy, small stream, varied cover, sandy bottom, no picture

Ripple River

- Date: September 15, 2008
- Time: 1445
- Width: 42 feet (Google Earth)
- Depth: 20 inches

- Velocity: 3 feet in 2.75 seconds
- Flow: 80.2 cfs
- River Mile: 1060.5 (0.87 miles upstream of confluence)
- Coordinates: 46°32'0" N 93°42'9" W, Ripple River at State Highway 169/2nd St. NE
- Description: Tree and grass lined but surrounded by businesses, sandy and mucky bottom

Mississippi River in Aitkin

- Date: September 15, 2008
- Time: 1500
- Width: 145 feet (Google Earth)
- Depth: 32 inches 6 feet from shore
- Velocity: 5 feet in 7.28 seconds
- Flow: (699 cfs USGS)
- River Mile: 1095 (0.43 miles upstream of confluence)
- Coordinates: 46°32'33" N 93°42'46" W, Mississippi River at 4th Ave. NW
- Description: Tree lined banks, more turbid, silty bottom

Mississippi River before Brainerd

- Date: September 24, 2008
- Time: 1200
- Width: 617 feet (Google Earth)
- Depth: 4 feet 3 inches 20 feet from shore
- Velocity: N/A in backwater
- Flow: (940 cfs USGS)
- River Mile: 1007
- Coordinates: 46°22'16" N 94°9'56" W, Mississippi River at State Highway 210
- Description: Lum Park in Brainerd, river flows through several wide lake areas, scattered houses, midland forests, some submerged weeds and lily pads

Crow Wing River

- Date: September 24, 2008
- Time: 1245
- Width: 212 feet (Google Earth)
- Depth: 2 feet in middle
- Velocity: 3 feet in 3.19 seconds
- Flow: 399 cfs (474 cfs USGS)
- River Mile: 993 (3.49 miles upstream of confluence)
- Coordinates: 46°18'13" N 94°22'34" W, Crow Wing River off County Road 36
- Description: Right below Sylvan Hydro Station, wide, rocky bottom with some algal growth, limited houses, temperate forest

Mississippi River after Brainerd

- Date: September 24, 2008
- Time: 1315
- Width: 242 feet (Google Earth)
- Depth: 2 feet 20 feet from shore

- Velocity: 3 feet in 2.78 seconds
- Flow: 522 cfs (940 cfs USGS)
- River Mile: 999
- Coordinates: 46°18'45" N 94°15'58" W, Mississippi River at State Highway 371
- Description: Fast flowing, rocky bottom with lots of algal growth, in bit of gorge, temperate forests on bank, sandy banks

Mississippi River at Fort Ripley

- Date: September 24, 2008
- Time: 1345
- Width: 480 feet (Google Earth)
- Depth: 21 inches 40 feet from shore
- Velocity: 10 feet in 8.68 seconds
- Flow: 968 cfs
- River Mile: 986
- Coordinates: 46°10'41" N 94°21'55" W, Mississippi River at State Highway 371
- Description: Wide, very scattered houses, temperate forests, lots of emergent vegetation near banks, sandy bottom with lots of submerged vegetation

Nokasippi River

- Date: September 24, 2008
- Time: 1400
- Width: ~25 feet
- Depth: 19 inches
- Velocity: 3 feet in 1.72 seconds
- Flow: 69 cfs
- River Mile: 1007 (20 feet upstream from confluence)
- Coordinates: 46°10'39" N 94°21'53" W, Nokasippi River at State Highway 371
- Description: Shallow, rocky/sandy bottom with algal growth

Pike Creek

- Date: September 24, 2008
- Time: 1445
- Width: 109 feet (Google Earth)
- Depth: 4 feet 3 inches
- Velocity: 3 feet in 5.53 seconds
- Flow: 251 cfs
- River Mile: 965.7 (100 feet upstream from confluence)
- Coordinates: 45°57'10" N 94°23'28" W, Pike Creek at County Road 52
- Description: Sandy bottom, lots of emergent and submerged vegetation

Mississippi River after Little Falls

- Date: September 24, 2008
- Time: 1500
- Width: 632 feet (Google Earth)
- Depth: 2 feet 5 inches 6 feet from shore
- Velocity:

- Flow:
- River Mile: 965.7
- Coordinates: 45°57'9" N 94°23'26" W, Mississippi River at County Road 52
- Description: River broad, sandy bottom with lots of algae, temperature forest, influence from Pike Creek?

Swan River

- Date: September 24, 2008
- Time: 1515
- Width: 127 feet (Google Earth)
- Depth: 2 feet 7 inches
- Velocity: 1 foot in ~4 seconds
- Flow: 82 cfs
- River Mile: 962 (0.31 miles upstream from confluence)
- Coordinates: 45°55'8" N 94°23'21" W, Swan River at Great River Road
- Description: Reedy sides, bottom sandy, stopwatch soaked

Two Rivers

- Date: September 24, 2008
- Time: 1530
- Width: ~ 30 feet, 12 foot culvert
- Depth: 6 inches in culvert
- Velocity: 3 feet in 2.49 seconds
- Flow: 7.2 cfs
- River Mile: 953.8 (0.84 miles upstream from confluence)
- Coordinates: 45°49'31" N 94°21'35" W, Two Rivers at County Road 25
- Description: Rocky/sandy bottom, limited algae, reedy low banks, cow pastures

Spunk Creek

- Date: October 1, 2008
- Time: 1145
- Width: 26.5 feet
- Depth: 11 inches
- Velocity: 3 feet in 3.28 seconds
- Flow: 7.4 cfs
- River Mile: 950 (1 mile upstream from confluence)
- Coordinates: 45°47'4" N 94°18'56" W, Spunk Creek at County Road 21
- Description: Rocky/sandy bottom, little bit of algal growth, clear and fast flowing, grassy banks with hardwoods, some channelization with riprap upstream

Platte River

- Date: October 1, 2008
- Time: 1215
- Width: 84 feet (Google Earth)
- Depth: 2 feet
- Velocity: 3 feet in 1.91 seconds
- Flow: 204 cfs

- River Mile: 947.6 (2.36 miles upstream from confluence)
- Coordinates: 45°47'50" N 94°17'30" W, Platte River at County Road 40
- Description: Rocky/sandy bottom, little bit of algal growth, clear and fast flowing, grassy banks with hardwoods, some channelization with riprap upstream

Watab River

- Date: October 1, 2008
- Time: 1300
- Width: ~20 feet
- Depth: 16 inches
- Velocity: 3 feet in 2.00 seconds
- Flow: 40 cfs
- River Mile: 947.5 (516 feet upstream from confluence)
- Coordinates: 45°37'50" N 94°12'25" W, Watab River at Watab Park/County Road 1
- Description: Forested banks, light residential and commercial upstream, clear, fast flowing, rocky bottom, lots of ripples

Mississippi River before Sartell

- Date: October 1, 2008
- Time: 1315
- Width: 550 feet (Google Earth)
- Depth: 2.5 feet 10 feet from shore
- Velocity:
- Flow:
- River Mile: 932.5
- Coordinates: 45°37'21" N 94°12'13" W, Mississippi River at County Road 1
- Description: Just above factory dam at abandoned boat launch, wide, light residential, commercial, industrial development, water turbid, gravelly bottom with lots of algal growth

Sauk River

- Date: October 1, 2008
- Time: 1330
- Width: 106 feet (Google Earth)
- Depth: 12 inches
- Velocity: 3 feet in 1.38 seconds
- Flow: 230 cfs (114 cfs USGS)
- River Mile: 929.8 (305 feet upstream from confluence)
- Coordinates: 45°35'29" N 94°10'40" W, Sauk River at County Road 1
- Description: Light development, rapid flow, algal growth on rocky bottom, forested banks, ducks

St. Cloud Wastewater Treatment Plant

- Date: October 1, 2008
- Time: 1430
- Width:
- Depth:

- Velocity:
- Flow: ~10 MGD
- River Mile: 919
- Coordinates: 45°28'29" N 94°7'19" W, Effluent Building/Glen Carlson Drive
- Description: Effluent building of St. Cloud WWTP

Clearwater River

- Date: October 1, 2008
- Time: 1500
- Width: ~20 feet
- Depth: 10"
- Velocity: 3 feet in 1.98 seconds
- Flow: 25.3 cfs
- River Mile: 913.6 (0.19 miles upstream from confluence)
- Coordinates: 45°25'25" N 94°3'10" W, Clearwater River at County Road 75
- Description: Riverside Park in Clearwater, just below dam with stepped outfall, rocky bottom, some submerged vegetation, light development

Mississippi River after St. Cloud

- Date: October 1, 2008
- Time: 1515
- Width: 463 feet (Google Earth)
- Depth: 3 feet 6 feet from shore
- Velocity: 3 feet in 2.56 seconds
- Flow: 1628 cfs (2220 cfs USGS)
- River Mile: 913.2
- Coordinates: 45°25'3" N 94°2'35" W, Mississippi River at State Route 24
- Description: River is wide with sandy shoals, light development, sandy shores with forest

Mississippi River at La Crescent

- Date: October 5, 2008
- Time: 1445
- Width: 1341 feet (Google Earth)
- Depth: 8 feet, channelized
- Velocity:
- Flow: (15400 cfs at Winona USGS)
- River Mile: 700.8
- Coordinates: 43°50'35" N 91°17'41" W, Mississippi River at North Shore Acres Road
- Description: Medium development, sandy bottom, river controlled by series of dams, numerous large islands with permanent trees, forested banks/bluffs

Mississippi River at Wabasha

- Date: October 5, 2008
- Time: 1630
- Width: 936 feet (Google Earth)
- Depth: 8 feet, channelized

- Velocity:
- Flow:
- River Mile: 760.3
- Coordinates: 44°23'7" N 92°2'0" W, Mississippi River at County Road 60
- Description: End of Lake Pepin, moderate development, bluffs decreasing, lots of duck weed in slower spots by shore, some algal growth

Mississippi River at Red Wing

- Date: October 5, 2008
- Time: 1700
- Width: 594 feet (Google Earth)
- Depth: 8 feet, channelized
- Velocity:
- Flow:
- River Mile: 790.9
- Coordinates: 44°34'1" N 92°32'16" W, Mississippi River at Levee Road
- Description: Moderate development, beginning of Lake Pepin, some bluffs, bottom generally sandy with some submergent vegetation, forested banks or houses/industry

Mississippi River at St. Anthony Falls Laboratory

- Date: October 6, 2008
- Time: 1630
- Width: 333 feet (Google Earth)
- Depth: 8 feet, channelized
- Velocity:
- Flow:
- River Mile: 853.3
- Coordinates: 44°58'53" N 93°15'14" W, Mississippi River at SAFL Lab
- Description: Immediately downstream of Lower St. Anthony Falls Lock and Dam, heavily urbanized, with either parkland or urban development on shores, in backwater

Crow River

- Date: October 10, 2008
- Time: 945
- Width: 236 feet (Google Earth)
- Depth: 2 feet 8 feet from shore
- Velocity: 3 feet in 4.41 seconds
- Flow: 321 cfs (132 cfs in Rockford USGS)
- River Mile: 879 (0.11 miles upstream from confluence)
- Coordinates: 44°14'40" N 93°31'20" W, Crow River at County Road 42 in Dayton
- Description: Muddy from rain, few leaves, moderate development, mostly houses in small towns, established sand bar with vegetation, sandy/murky bottom

Rum River

- Date: October 10, 2008
- Time: 1015
- Width: 206 feet (Google Earth)

- Depth: 2 feet 10 feet from shore
- Velocity: 3 feet in 8.35 seconds
- Flow: 148 cfs (299 cfs in St. Francis USGS)
- River Mile: 871.5 (0.08 miles upstream from confluence)
- Coordinates: 45°11'27" N 93°23'26" W, Rum River at Peninsula Park, S Ferry Pkwy
- Description: South of downtown Anoka, medium development, bottom is muddy/sandy with numerous fallen branches decomposing, some litter and leaves

Mississippi River at Anoka

- Date: October 10, 2008
- Time: 1030
- Width: 642 feet (Google Earth)
- Depth: 20 inches 10 feet from shore
- Velocity: 3 feet in 2.73 seconds
- Flow: 1150 cfs (4490 cfs USGS)
- River Mile: 871.5 (0.08 miles upstream from confluence)
- Coordinates: 45°11'25" N 93°23'29" W, Miss. River at Peninsula Park, S Ferry Pkwy
- Description: Just north of Rum River inflow in downtown Anoka, development to edge of river, bottom sandy/mucky with some algal growth, few leaves, also rocky with buried pipes

Shingle Creek

- Date: October 10, 2008
- Time: 1115
- Width: 16 feet
- Depth: 7 inches
- Velocity: 3 feet in 2.35 seconds
- Flow: 11.9 cfs
- River Mile: 857.8 (260 feet upstream from confluence)
- Coordinates: 45°1'57" N 93°17'8" W, Shingle Creek at N Mississippi Regional Park
- Description: Highly developed, rocky/gravel bottom, fast flowing, some trash, leaves, water clear

Minnehaha Creek

- Date: October 11, 2008
- Time: 1115
- Width: 12 feet
- Depth: 4 inches
- Velocity: 3 feet in 4.09 seconds
- Flow: 2.9 cfs (2.4 cfs USGS)
- River Mile: 847.4 (0.74 miles upstream from confluence)
- Coordinates: 44°54'55" N 93°12'37" W, Minnehaha Park at Minnehaha Parkway
- Description: Highly urbanized, managed, occasionally channelized, impounded several times along length, rocky with algal growth prevalent, some iron? rocks beside water have red tinge

Mississippi River before confluence with Minnesota River

- Date: October 11, 2008
- Time: 1245
- Width: 463 feet (Google Earth)
- Depth: 8 feet, channelized
- Velocity:
- Flow:
- River Mile: 845.5
- Coordinates: 44°53'36" N 93°10'42" W, Ft. Snelling State Park
- Description: Sandy/gravelly bottom, some algae, highly urbanized with boat traffic, in gorge with forested banks, turbid

Minnesota River

- Date: October 11, 2008
- Time: 1230
- Width: 398 feet (Google Earth)
- Depth: 8 feet, channelized
- Velocity:
- Flow: (9/19 588 cfs 11/13 1520 cfs USGS grab)
- River Mile: 844 (0.35 miles upstream from confluence)
- Coordinates: 44°53'2" N 93°10'34" W, Ft. Snelling State Park
- Description: Very muddy, in gorge, bottom is light much, forested banks, turbid

Combined Mississippi and Minnesota Rivers

- Date: October 11, 2008
- Time: 1315
- Width: 567 feet (Google Earth)
- Depth: 8 feet, channelized
- Velocity:
- Flow:
- River Mile: 842
- Coordinates: 44°55'5" N 93°7'44" W, Lilydale Regional Park, Lilydale Road
- Description: Gorge with rocky face, highly urbanized, visible storm sewer inputs, boat traffic, sandy/slightly mucky bottom, dead fish smell, turbid

Mississippi River in Hastings

- Date: October 11, 2008
- Time: 1445
- Width: 1001 feet (Google Earth)
- Depth: 8 feet, channelized
- Velocity:
- Flow:
- River Mile: 814.2
- Coordinates: 44°44'51" N 92°51'27" W, Mississippi River at Dam Road
- Description: Dock with water, fat redneck guy with shirt off, heavy development, slight gorge, forested banks, chick with waders and a bottle, need beer, turbid, below Lock and Dam #2

St. Croix River

- Date: October 11, 2008
- Time: 1415
- Width: 2200 feet (Google Earth)
- Depth: 8 feet, channelized
- Velocity:
- Flow: (6210 cfs USGS)
- River Mile: 811.5 (1.48 miles upstream from confluence)
- Coordinates: 44°46'8" N 92°48'35" W, St. Croix Carpenter Nature Center, Hwy 21
- Description: Wide, slight gorge with forested banks, boat traffic, moderate development, rocky with some algal growth

Metropolitan Wastewater Treatment Plant

- Date: October 17, 2008
- Time: 915
- Width:
- Depth:
- Velocity:
- Flow: ~120 MGD
- River Mile: 836.2
- Coordinates: 44°55'12" N 93°2'46" W, Effluent Pumping Station/Childs Road
- Description: Effluent channel of plant, concrete lined, ducks on water, some algal growth on sides

Temporal/Land Use Mississippi River Sampling Trips

March 21-22, 2009

- Leech Lake River: 1215, water is fast moving and non-turbid, ice on shores, sampled at WMA bridge
- Sandy River: 1400, water is colored, bank full with ice on edges
- Rice River: 1430, water is colored, had to break ice to center of stream, sheriff stopped
- Nokasippi River: 1540, colored, banks flooded, sampled from side, ice rim
- Swan River: 1615, swift, ice on banks, colored, fell in
- Clearwater River: 1715, swift, slightly colored, lots of foam
- Shingle Creek: 1230, rapid, bottom slightly scummy
- Minnehaha Creek: 1130, bank full, somewhat sluggish

April 25-26, 2009

- Leech Lake River: 1315, clear fast moving water, two dudes fishing, high water
- Sandy River: 1445, highly colored, flood stage
- Rice River: 1515, highly colored, flood stage
- Nokasippi River: 1615, Mississippi and Nokasippi both high, moderately colored
- Swan River: 1700, full, lightly colored, dead fish smell
- Clearwater River: 1800, full, lightly colored
- Shingle Creek: 1300, fast, slightly turbid, foam, dead fish smell, light rain

- Minnehaha Creek: 1330, full, slow, lots of tree seeds floating, steady rain

May 24 and 26, 2009

- Leech Lake River: 920, water still high, slightly colored, low grasses on show emergent, boat traffic
- Sandy River: 1100, water still high, moderately colored
- Rice River: 1200, water seems at normal level, highly colored
- Nokasippi River: 1245, water not in flood plain, lightly colored, boat traffic, minnows
- Swan River: 1330, full but some mud flat exposed, crops emerging from tilled fields
- Clearwater River: 1430, full, small rock dam visible, kids disturbing sediment
- Shingle Creek: 845, low flow, lots of brown filamentous algae growth on bottom and rocks, strong sewage smell
- Minnehaha Creek: 930, moderate flow, no algal growth, slight musty smell

June 26, 2009

- Leech Lake River: 1200, fast flowing, bank full, some algal growth on rocks, limpid, banks of emergent vegetation
- Sandy River: 1315, sluggish, colored, emergent vegetation but forested banks, high particulates
- Rice River: 1415, highly colored, slow moving, forested banks, muck on bottom
- Nokasippi River: 1530, clear, fast moving, sandy bottom with some muck, shore grasses
- Swan River: 1615, mucky bottom, moderate speed with some turbidity
- Clearwater River: 1700, rapid, some foam, wooded/mown banks, sandy/rocky bottom
- Shingle Creek: 1815, rocky bottom, some muck, no fish smell, water fast flowing, but level much lower than previous times this year
- Minnehaha Creek: 1830, sluggish, emergent vegetation, very mucky, natural banks but urban

July 28, 2009

- Leech Lake River: 1215, clear, fast, sedges/cattails on banks, long strands submergent vegetation
- Sandy River: 1330, sluggish, grasses/forest on banks, silty bottom
- Rice River: 1430, highly colored, slow moving, silty bottom, forested banks
- Nokasippi River: 1600, clear, fast, sandy bottom, grassy/forested banks, ~2 feet deep
- Swan River: 1630, clear, moderate speed, sandy/mucky bottom, cattails/forested banks
- Clearwater River: 1730, clear, well moving, sandy/rocky bottom grass/forested banks, ~8 inches deep
- Shingle Creek: 1815, low flow, clear, not colored, mucky/sandy bottom, forested banks
- Minnehaha Creek: 1845, stagnant, clear, lightly colored, sandy/mucky bottom, lots of submerged and floating vegetation, weedy banks

August 27, 2009

- Leech Lake River: 1230, clear, wetland banks, sandy/gravelly bottom with algal growth on rocks
- Sandy River: 1400, sluggish, silty bottom, suspended algae, grass/forest
- Rice River: 1430, highly colored, quick moving, silty bottom
- Nokasippi River: 1600, sandy bottom, clear, fast flowing
- Swan River: 1630, sandy bottom with some algal growth, clear, slow moving

- Clearwater River: 1730, clear fast moving, 8 inches deep, sandy/rocky bottom, some emergent vegetation
- Shingle Creek: 1830, clear, quick moving, algal growth on rocks, weird red band on vegetation above water line, not oily or foul smelling
- Minnehaha Creek: 1900, slow, lots of algal growth, mucky

September 25, 2009

- Leech Lake River: 1200, vegetation dying back, clear water, lots of algal growth on bottom rocks, slower than usual
- Sandy River: 1330, leaves yellow on trees, murky, slow, lots of algal growth
- Rice River: 1415, some yellow leaves floating, extremely low, depth 0.5 feet, width 10 feet, velocity 1 ft/s, colored, mucky bottom
- Nokasippi River: 1515, slightly damp, sandy, trees starting to yellow, algae on bottom sides, depth 1.5 ft, velocity 2 ft/s, width 20 feet
- Swan River: 1600, slightly damp, slow, weedy
- Clearwater River: 1700, damp, low, depth 0.75 feet, width 20 feet, velocity 5 ft/s
- Shingle Creek: 1815, damp, few leaves, rapid flow compared to last time, no smell, little bit of muck
- Minnehaha Creek: damp, low water, lots and lots and lots of duck weed

October 28, 2009

- Leech Lake River: 1145, all vegetation brown, fast flowing, some decaying vegetation on sandy bottom, murkier than previously
- Sandy River: 1315, all vegetation brown, decaying leaves on bottom, seems low, construction upstream - boat launch but no obvious turbidity from it
- Rice River: 1345, highly colored, little bit of green vegetation
- Nokasippi River: 1500, very fast flowing, little bit of green vegetation, no leaves on rocky bottom
- Swan River: 1600, some green vegetation, leaves on mucky bottom
- Clearwater River: 1645, fast flowing, high, grass green, no leaves on gravelly bottom
- Shingle Creek: 1745, fast flowing, small bushes still green, leaves on banks and in eddies, no smell
- Minnehaha Creek: 1830, sluggish, small bushes green, leaves on surface and bottom, no duck weed

November 23, 2009

- Leech Lake River: 1030, light rain, all vegetation dead, water clear, some decaying organic matter on bottom
- Sandy River: 1145, light rain, dead vegetation, water semi-clear but colored, visible movement for once
- Rice River: 1215, light rain, dead vegetation, silty bottom, fast flowing, highly colored
- Nokasippi River: 1345, damp, dead vegetation, high and fast, decaying vegetation on sandy/silty bottom
- Swan River: 1445, damp, dead vegetation, high, decaying vegetation on silty bottom
- Clearwater River: 1515, light rain, dead vegetation, high, fast, bottom sandy with a little bit of muck in parts
- Shingle Creek: 1615, light rain, dead vegetation, lots of leaves on bottom
- Minnehaha Creek: 1645, light rain, leaves in water, mucky, a bit low

Appendix D

Description and Parameters of the Mississippi River and Tributaries

Table D-1. Description of sampled watersheds (upper Mississippi River and selected tributaries) and their dominant land use and water quality parameters

Sampling Location	Latitude	Longitude	River Mile	Area	Percent Land Use							TOC	DOC	UV254	UV280	SUVA	Molecular Weight	Aromaticity
				m ²	urban	agriculture	grass	forest	water	wetland	shrub	mg/L	mg/L	l/cm	l/cm	L/mg-m	g/mol	%
Mississippi River at Itasca Headwaters	47.24	-95.21	1347	91.1	1.9	0.9	0.0	83.0	10.7	3.4	0.1	7.80	5.81	0.112	0.078	1.93	1133	15
Sucker Brook	47.25	-95.25	1344	164.5	2.9	1.6	0.0	83.0	7.8	4.6	0.1	10.16	2.84	0.081	0.059	2.86	1478	19
Mississippi River at La Salle Wetlands	47.43	-95.13	1315	499.0	2.4	6.8	0.1	79.0	5.5	5.9	0.3	4.07	4.58	0.139	0.097	3.04	1498	19
Hennepin Creek	47.40	-95.09	1310	101.9	2.7	17.4	0.2	68.2	2.1	8.4	1.0	6.01	5.18	0.185	0.128	3.57	1675	22
Mississippi River before Bemidji	47.45	-94.89	1288	1487.8	3.1	15.5	0.3	67.1	4.3	8.9	0.8	8.51	3.46	0.117	0.073	3.39	1507	19
Mississippi River after Bemidji	47.49	-94.83	1282	1686.6	4.3	16.5	0.3	63.2	5.7	9.3	0.8	6.98	6.92	0.147	0.087	2.12	1093	14
Mississippi River after Lake Winnibigosh	47.32	-93.96	1221	3976.4	3.1	10.0	0.2	60.5	14.5	10.9	0.8	9.85	7.51	0.154	0.085	2.04	1034	14
Leech Lake River	47.27	-93.95	1216.5	3415.1	2.3	5.8	0.1	58.5	18.9	14.1	0.2	8.12	8.47	0.176	0.110	2.08	1112	15
Mississippi River before Grand Rapids	47.25	-93.59	1187	8544.2	2.8	7.9	0.2	60.2	15.8	12.5	0.6	9.32	8.87	0.156	0.104	1.76	1053	14
Prairie River	47.22	-93.48	1181	1326.9	3.2	3.2	0.1	70.8	7.6	11.6	3.6	14.48	14.14	0.410	0.295	2.90	1489	19
Mississippi River after Grand Rapids	47.17	-93.42	1175	9971.8	3.0	7.3	0.2	61.6	14.6	12.4	1.0	10.91	10.40	0.257	0.165	2.47	1250	16
Swan River	47.01	-93.26	1142	836.2	7.2	5.7	0.2	64.3	7.2	12.0	3.3	10.12	10.46	0.337	0.222	3.23	1506	19
Two River Spring	46.88	-93.36	1122	15.2	0.9	1.2	0.0	85.2	2.0	10.7	0.1	4.31	4.87	0.139	0.106	2.86	1530	20
Libby Brook	46.85	-93.34	1116.8	13.6	3.8	2.4	0.0	72.1	1.4	20.2	0.3	7.82	7.95	0.278	0.204	3.50	1716	22
Sandy River	46.79	-93.32	1109	1072.4	4.2	6.8	0.2	61.0	6.2	19.6	2.0	19.69	19.49	0.677	0.463	3.47	1628	21
Willow River	46.68	-93.59	1082	1355.5	2.1	3.8	0.2	67.6	2.5	22.0	1.8	8.39	8.83	0.226	0.156	2.56	1334	17
Mississippi River before Aitkin	46.65	-93.61	1077.5	13926.5	3.2	6.9	0.2	62.8	11.7	13.9	1.3	8.95	9.06	0.216	0.140	2.38	1230	16
Rice River	46.60	-93.61	1070	774.3	2.9	7.6	0.5	65.2	3.9	18.1	1.6	21.00	20.81	0.617	0.414	2.97	1442	19
Sisabagamah Creek	46.55	-93.65	1061.3	81.8	5.3	17.5	0.5	51.7	6.8	16.5	1.5	22.63	23.29	0.733	0.484	3.15	1485	19
Ripple River	46.53	-93.70	1060.5	306.9	5.1	9.5	0.4	53.1	13.7	16.4	1.8	10.60	10.86	0.287	0.182	2.65	1294	17
Mississippi River at Aitkin	46.54	-93.71	1059	15198.7	3.3	7.2	0.3	62.5	11.2	14.2	1.3	9.32	9.49	0.251	0.160	2.64	1296	17
Mississippi River before Brainerd	46.37	-94.17	1007									10.20	10.12	0.240	0.158	2.37	1238	16
Mississippi River after Brainerd	46.31	-94.27	999	18339.0	3.4	7.3	0.3	62.4	11.0	14.4	1.2	9.12	9.43	0.220	0.146	2.33	1231	16
Crow Wing River	46.30	-94.38	993	5026.9	4.3	27.9	0.6	49.3	6.3	10.4	1.1	5.59	5.78	0.096	0.068	1.67	1053	14
Mississippi River at Fort Ripley	46.18	-94.36	986	28205.8	4.0	19.0	0.4	53.1	9.0	13.1	1.3	7.49	7.42	0.178	0.111	2.40	1206	16
Nokasippi River	46.18	-94.36	986	570.5	4.2	25.7	0.3	41.6	4.2	22.7	1.4	7.68	7.20	0.213	0.138	2.96	1407	18
Pike Creek	45.95	-94.39	965.7	88.4	5.7	45.1	1.0	12.7	0.2	31.0	4.1	7.61	7.00	0.196	0.126	2.80	1355	18
Mississippi River after Little Falls	45.95	-94.39	965.7	29516.1	4.1	19.4	0.4	52.4	8.7	13.6	1.3	7.70	7.42	0.193	0.123	2.60	1286	17
Swan River (2)	45.92	-94.39	962	473.2	5.7	35.7	1.2	24.6	3.0	27.7	2.2	5.90	5.81	0.181	0.117	3.11	1453	19
Two Rivers	45.83	-94.36	953.8	377.6	7.7	56.9	2.0	11.0	2.2	18.9	1.3	8.86	8.78	0.227	0.151	2.58	1316	17
Spunk Creek	45.78	-94.32	950	212.5	8.2	45.8	2.8	14.8	3.4	23.9	1.2	7.73	7.75	0.180	0.136	2.32	1328	17
Platte River	45.80	-94.29	947.6	1071.6	4.2	41.3	2.3	23.9	1.9	25.1	1.2	7.48	7.8	0.182	0.127	2.33	1267	16
Watab River	45.62	-94.21	947.5	244.3	12.6	27.9	4.8	24.2	2.4	26.6	1.6	7.69	7.27	0.153	0.108	2.10	1203	16

Mississippi River at Sartell	45.62	-94.20	932.5	32619.8	4.4	21.7	0.7	49.3	8.1	14.5	1.3	7.55	7.55	0.178	0.117	2.36	1235	16
Sauk River	45.59	-94.18	929.8	2700.0	8.3	61.3	4.9	10.1	4.1	10.5	0.8	9.26	8.73	0.147	0.101	1.68	1045	14
St. Cloud Wastewater Treatment Plant	45.47	-94.12	919	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	11.74	10.97	0.168	0.121	1.53	1017	13
Clearwater River	45.42	-94.05	913.6	450.1	9.3	45.3	5.9	11.7	7.1	19.4	1.4	8.44	8.18	0.166	0.107	2.03	1114	15
Mississippi River after St. Cloud	45.42	-94.04	913.2	36138.2	4.9	25.1	1.1	45.6	7.8	14.3	1.3	7.99	7.83	0.169	0.114	2.15	1189	15
Crow River	45.24	-93.52	879	7152.9	8.8	61.6	3.5	8.4	4.8	11.8	0.7	5.36	5.28	0.123	0.091	2.33	1319	17
Rum River	45.19	-93.39	871.5	4035.0	6.7	29.4	3.8	30.1	14.5	14.3	1.3	7.39	7.35	0.191	0.134	2.60	1365	18
Mississippi River at Anoka	45.19	-93.39	871.5	49525.7	5.9	31.6	1.9	37.8	7.7	13.8	1.1	6.94	6.84	0.204	0.138	2.98	1455	19
Shingle Creek	45.03	-93.29	857.8	115.3	71.5	14.5	0.0	9.4	4.5	0.0	0.0	4.79	5.03	0.121	0.088	2.42	1324	17
Mississippi River at Minneapolis	44.98	-93.25	853.3	50965.3	6.9	31.1	2.1	37.2	7.6	13.9	1.2	7.15	7.76	0.231	0.218	2.98	1836	24
Minnehaha Creek	44.92	-93.21	847.4	425.4	32.4	9.4	3.2	21.2	18.3	15.0	0.6	9.20	8.68	0.159	0.113	1.83	1111	15
Mississippi River at Fort Snelling	44.89	-93.18	845.5	51449.7	7.2	30.9	2.1	37.0	7.7	13.8	1.2	7.19	6.99	0.172	0.115	2.46	1278	17
Minnesota River	44.88	-93.18	844	43876.0	6.8	65.3	4.6	4.4	2.3	4.1	0.7	7.48	5.30	0.112	0.082	2.11	1230	16
Mississippi River at Lilydale	44.92	-93.13	842	95364.9	7.3	48.3	3.4	22.8	5.3	9.7	1.0	7.16	6.71	0.138	0.096	2.05	1177	15
Metropolitan Wastewater Treatment Plant	44.92	-93.05	836.2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	10.09	9.66	0.176	0.134	1.82	1154	15
Mississippi River at Hastings	44.75	-92.86	814.2	95985.1	7.6	48.0	3.4	22.7	5.4	9.6	1.0	7.39	7.59	0.151	0.108	1.99	1171	15
St Croix River	44.77	-92.81	811.5	2009.8								5.52	5.45	0.160	0.115	2.94	1500	19
Mississippi River at Red Wing	44.57	-92.54	790.9									7.82	6.48	0.213	0.132	3.28	1464	19
Mississippi River at Wabasha	44.39	-92.03	760.3									6.66	7.86	0.236	0.152	3.00	1413	18
Mississippi River at La Crescent	43.84	-91.29	700.8									7.80	7.12	0.177	0.128	2.48	1350	18
Mississippi River												7.99	7.53	0.185	0.124	2.49	1288	17
Average												1.43	1.63	0.043	0.034	0.44	179	2.25
Standard Deviation												4.07	3.46	0.112	0.073	1.76	1034	13.6
Minimum												10.9	10.4	0.257	0.218	3.39	1836	23.6
Maximum												0.18	0.22	0.230	0.271	0.18	0.14	0.13
RSD																		
Tributaries												9.37	8.97	0.237	0.163	2.57	1342	17
Average												4.54	4.75	0.165	0.110	0.57	188	2.35
Standard Deviation												4.31	2.84	0.081	0.059	1.53	1017	13.3
Minimum												22.6	23.3	0.733	0.484	3.57	1716	22.1
Maximum												0.48	0.53	0.695	0.674	0.22	0.14	0.14
RSD																		

Appendix E

Principal Component Analysis of Factors Effecting Membrane Permeability Decline

Principal component analysis (PCA) allows the interpretation of large data sets by reducing the variables to principal components as represented by the eigenvalues and eigenvectors of the original data. Groupings of the original variable categories can then be plotted to determine their relationships to the principal components and thus each other.

For temporal Mississippi River membrane data set, the two main principal components account for 82.3% of the variability within the data. DOC, SUVA, fluorescent index, UV₂₅₄, and UV₂₈₀ have the heaviest loading from the first principal component while membrane contact angle and pore size have the heaviest loading from the second principal component (Figure E-1). Permeability decline has loading from both principal components as expected since both membrane and NOM parameters contribute uniquely to the rate of fouling.

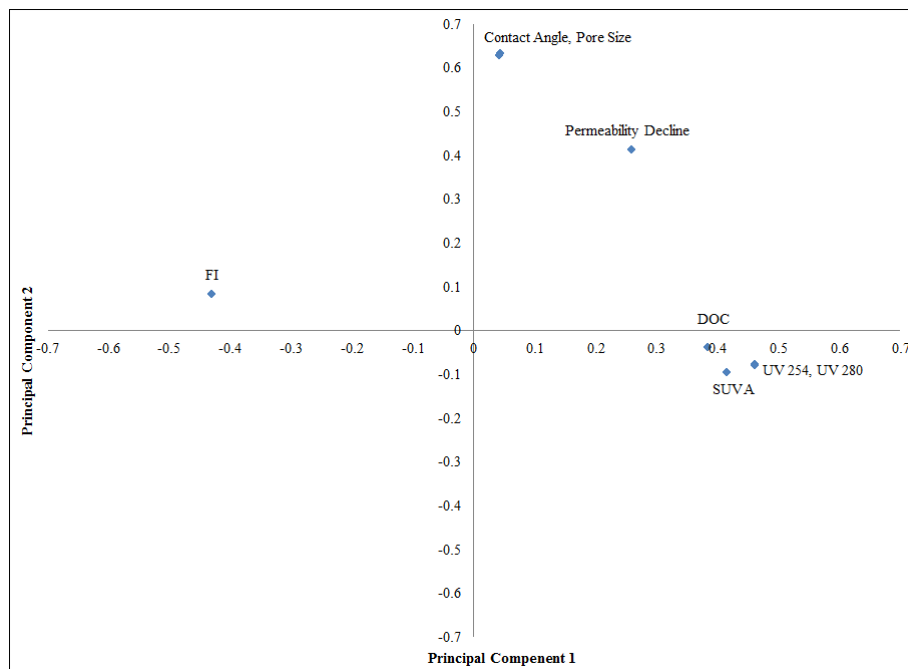


Figure E-1. Principal component analysis loading for four membranes filtering seasonal raw and settled waters from the Mississippi River

For the spatial/temporal Mississippi River tributary membrane data set, the two main principal components account for 64.8% of the variability within the data. DOC, SUVA, UV₂₅₄, UV₂₈₀, and permeability decline have loadings from both principal components while membrane contact angle has no relation to either of the main principal component (Figure E-2).

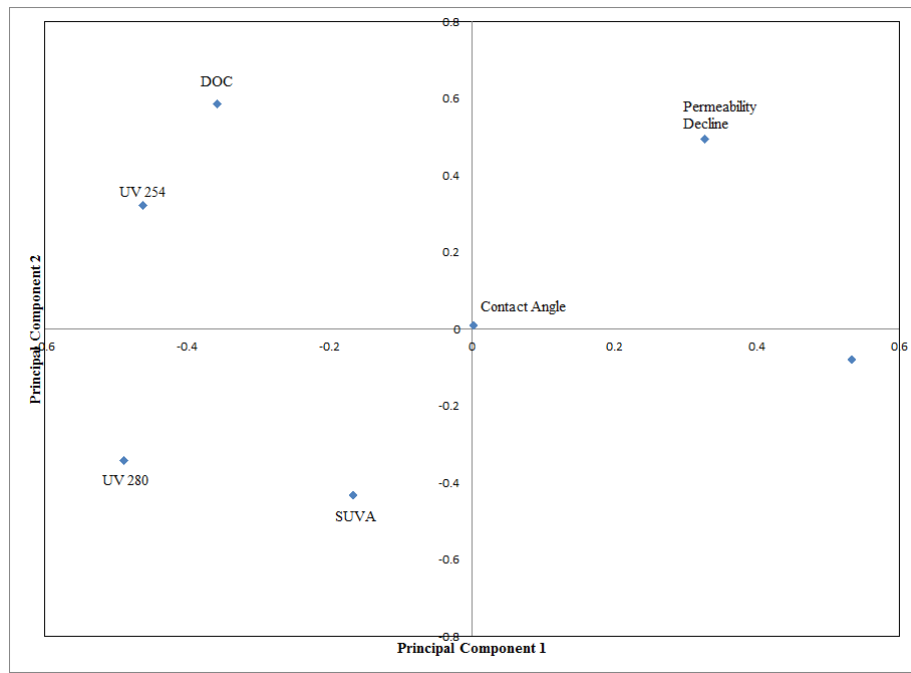


Figure E-2. Principal component analysis loading for two membranes filtering four tributaries of the Mississippi River in April, July, and September 2009

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