

## Control of Precipitation Events on Dynamics of Disinfection Byproduct Formation Potential

### Introduction

Chlorination, one of the major steps of treating our drinking water, is known to produce carcinogenic and mutagenic disinfection byproducts such as trihalomethanes (THM), haloaceticacids (HHA) in the presence of dissolved organic carbon (DOC). Recognizing their adverse effects, the US Environmental Protection Agency mandated regulation of these two DBP groups in the late 1970's (U.S. EPA, 1979), and the latest promulgation of the Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 DBPR) is expected to further reduce the production of the regulated DBPs by targeting higher risk utilities (U.S. EPA, 2005).

DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
DBP	Disinfection byproduct
C-DBP	Carbonaceous disinfection byproduct
N-DBP	Nitrogenous disinfection byproduct
THM	Trihalomethane
HAA	Haloaceticacids
HAN	Haloacetonitrile
DBPFP	Disinfection byproduct formation potential

Table 1- List of acronyms

However, the two groups of currently regulated DBPs are not the only groups of DBPs found in chlorinated water. Nitrogenous disinfection byproducts (N-DBP), a specialized subset of carbonaceous DBP (C-DBP) where a functional group is nitrogen-based, is a good example of unregulated DBP group whose significance for the drinking water industry is increasing for several reasons (Water Research Foundation, 2009). First, although found in much smaller concentrations, N-DBPs show higher toxicity than the regulated DBPs (Plewa et al, 2000, 2004, 2008; Muellner 2007). Secondly, some utilities are considering switching to chloramine disinfection to reduce the production of the regulated DBPs in order to comply with the Stage 2 DBPR, which may lead to higher forming potential for some N-DBP species (Water Research Foundation, 2009; Lee et al, 2007). Lastly, many water utilities are showing increased levels of dissolved organic nitrogen concentrations in their raw waters due to wastewater discharges and algal activities, and such an increase in dissolved organic nitrogen is believed to promote the formation of N-DBPs (Woo et al, 2002). This problem is expected to be further exacerbated in municipalities whose growing demand for drinking water will inevitably increase their dependence on such impacted water sources (Water Research Foundation, 2009). In considering all of the above

reasons, the U.S. EPA cited N-DBPs as one of research priorities (Weinberg et al, 2002; Chowdhury et al, 2009), but our current understanding of their formation dynamics or predictability is very limited in comparison to our understanding of the regulated DBPs.

**Knowledge Gaps:** While recent developments have increased our understanding of the nature and formation of DBPs, our management strategy regarding DBPs is far from perfect, with considerable knowledge gaps that need to be addressed. First, a vast majority of published research on DBPs has focused on the two groups of regulated DBPs. As stated in the earlier section, many water utilities are switching to chloramine disinfection to comply with the Stage 2 DBPR, which may lead to greater concentration of the unregulated, more toxic DBPs such as N-DBPs. Therefore, the need to advance our knowledge in N-DBP formation dynamics is of immediate importance. Secondly, our increasing dependence on non-pristine water sources requires more comprehensive research that covers various land uses and their associated DBPFP. Surface water or stormwater runoff that travel through urban or pasture land, for example, could exhibit markedly different concentration and quality in their DOCs and may show much higher load of both organic and inorganic nitrogen. Under such an environment, the composition of DBPs will significantly differ from pristine water sources and may lead to higher concentration of N-DBPs. Lastly, there needs to be a better predictive model that can explain the temporal variability of DBPFP at a regional scale. Despite the fact that there have been more than 100 models presented in scientific journals (Kraus et al, 2010), only a limited number of models incorporates the seasonality or the impact of precipitation. Also, most of the models require analytical measurements of chemical parameters in their raw or treated water sample to predict DBPFP or concentrations, thus showing limited strength in forecasting a long-term trend.

**Study Goal:** The central goal of this study focuses on these knowledge gaps, and bases its methods and ideas on two recent journal articles. A recent study by Kraus et al. (Kraus et al, 2010) revealed that the formation potential for THMs and HAAs was highest after the first major rain event of the season in the McKenzie River watershed in Oregon. This was due to the fact that the first major storm flushes a large amount of DOC with high aromatic carbon content into streams. This finding clearly demonstrates the significance of precipitation events on the dynamics of DBP formation. The impact of precipitation events on the biogeochemistry of surface water, especially regarding DOC, has been an important subject for research in recent years. A recent publication by Raymond and Saiers (Raymond and Saiers, 2010) demonstrated that 86% of annual DOC export from forests occurs during precipitation events. Furthermore, Raymond and Saiers showed that large precipitation events ( $>1.38 \text{ cm day}^{-1}$ ), which make

up only 4.8% of annual hydrograph, were responsible for 57% of annual DOC flux. These two correlations, between DOC concentration and DBPFP, and between precipitation events and DOC export, underscore the importance of precipitation events in understanding the temporal variability of DBPFP dynamics. Furthermore, studying the control of precipitation events of DBPFP has the potential to provide valuable insights for generating a model that can predict when the peak DBP concentration will occur and what water sources will contribute to such increase in DBP concentration.

To examine the importance of precipitation events on DBPFP, this study investigates 1) how change in quality and quantity of DOC under precipitation events correspond to formation potential of trihalomethanes (THMs) and haloacetonitriles (HANs) during storm events; 2) how seasonal change affects the dynamics of DOC-DBPFP correlation; 3) how these dynamics differ in forested and urban watersheds.

## Methods

**Study Areas- Forested Watershed:** The forested watershed examined for this study is situated in Allaben, NY where Esopus Creek drains 16,500 ha of the Catskill Mountains (Figure 1). The watershed is predominantly composed of forest cover (97.3%, NLCD, 2007) with deciduous tree species such as sugar maple (*Acer saccharum*), beech (*Fagus grandifolia*), and red oak (*Quercus borealis*) (McIntosh, 1972). As a primary source of drinking water for New York City, much of the Catskill Mountain is designated as forest preserve, and roughly 62.5 % of the study watershed is protected by the state (NYS DEC, 2011). General climate of the region can be characterized as humid continental with cool summer and cold winters, and relatively uniform precipitation throughout the year ([www.nrcc.cornell.edu](http://www.nrcc.cornell.edu)). Data from Slide Mountain weather station, located within the watershed, indicates that the region receives average precipitation of 160 cm with average temperature of 5.5° C ([www.nrcc.cornell.edu](http://www.nrcc.cornell.edu)). General geology of the watershed can be described as layers of glacial till overlaid on top of bedrocks composed of sandstones and shale (Stoddard and Murdoch, 1991).

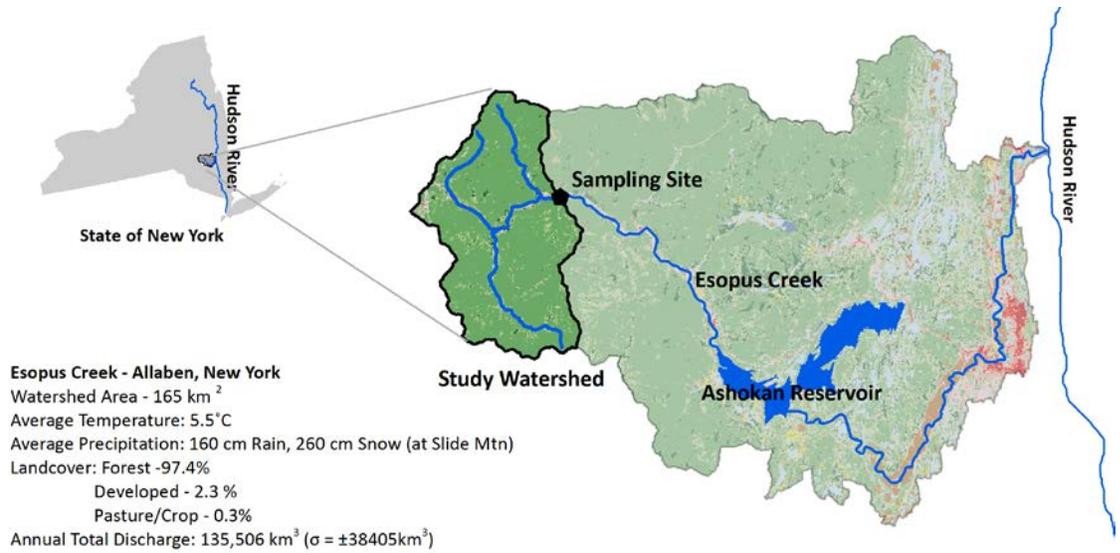


Figure 1 - Study Watershed (Forested) - Esopus Creek, NY

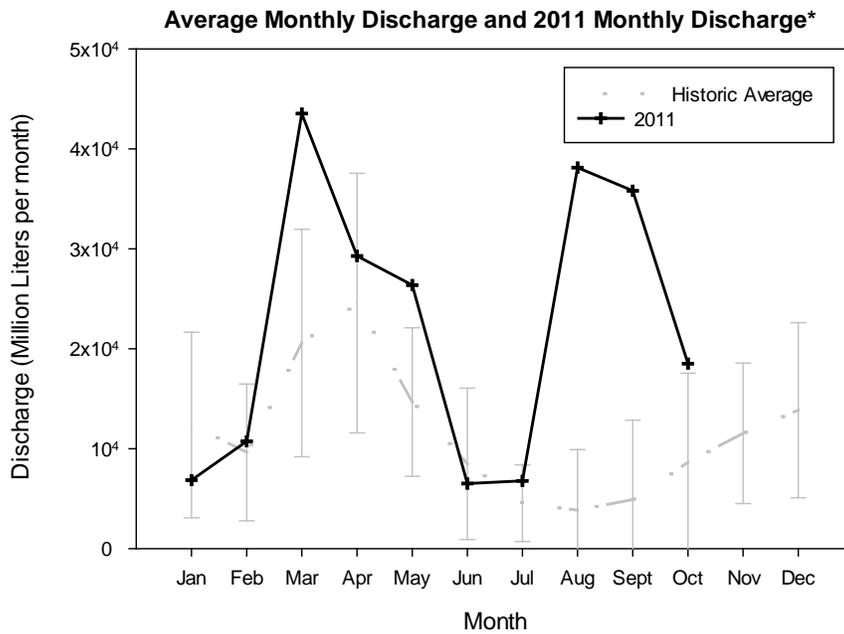


Figure 2 - Historic hydrograph of the forested watershed and 2011 data

The sampling point for this watershed is located on Esopus Creek and a USGS gauging station has been monitoring the discharge of the stream at this location since 1963 (USGS 01362200, 42°07'01", 74°22'50" NAD27). The gauging station is upstream from the effluent of Shandaken Tunnel, and allows for collection of samples unaffected by the water transported from Schoharie Reservoir through the tunnel. Average annual total discharge recorded by the USGS gaging station is 135 billion L yr<sup>-1</sup> (± 38)

over the 46 year period. Discharge volume of the stream shows strong seasonality with high flows during spring snowmelt and significantly lower values during the summer months (Figure 2, grey dashed line). Hydrograph of the Esopus creek for year 2011 reflects the large snowfall of the previous winter and the effect of Hurricane Irene (Figure 2, bold line).

**Study Area -Urban Watershed:** A watershed in Still River basin in Connecticut was selected as the urban watershed for this study (Figure 3). The watershed area is roughly 161km<sup>2</sup>, and consists of urban development, mixed forests, and some pasture land. Although this watershed is not completely urbanized, its proximity to the forested watershed, similar size and discharge rate, and the presence of USGS gauging station made it an ideal counterpart for the forested watershed. In fact, this is the only urbanized watershed monitored by USGS in the surrounding area. The climate of the watershed is similar to the forested watershed, but shows moderately less precipitation (120.4 cm, NCDC, 2011) and higher average temperature (10.4° C) due to lower lever elevation and the closer proximity to the coast. General geology of the region can be described as loamy and sandy soil overlaid on glacial till (USDA, 1981). The sampling site for this watershed is also located adjacent to a USGS gauging station (USGS 01201487 41°27'58", 73°24'13" NAD27), and historic discharge data (from 2001 to 2009) shows similar trend as the forested watershed where snowmelt and fall storms lead to noticeably increased discharge rate during spring month and late fall (Figure 4).

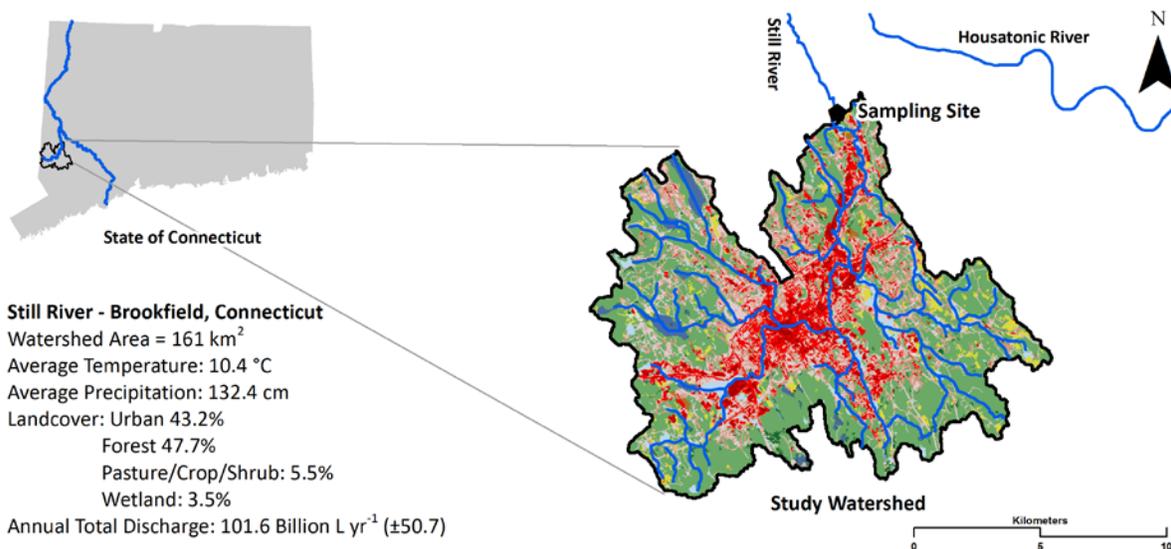


Figure 3 - Study watershed (Urban) - Still River, CT

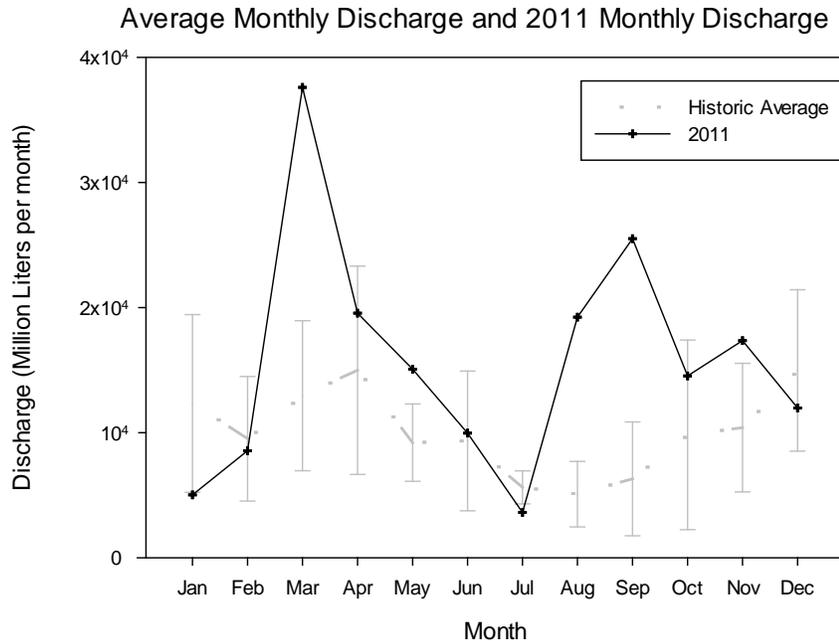


Figure 4 - Historic hydrograph of the forested watershed and 2011 data

**Sampling Method:** Two sites, each representing forested and urban watersheds, were sampled during base flows and precipitation events from April 2011 to November 2011 (Figure 1, 3). To examine the full extent of seasonality and precipitation intensity, I sampled during 6 storm events throughout the year at both sites. Both of the sites are equipped with USGS gauging stations where continuous measurements of stream discharge are recorded. In order to achieve high-resolution sample series that reflects the rapidly changing hydrograph, autosamplers (Sigma 900 MAX) were programmed to collect samples at varying intervals. Sampling frequency varied from every 2 hours to 8 hours depending on the size of the storm. In general, more samples were collected during rising and peak hydrograph rather than the slowly falling hydrograph since compositional change of solutes in streams occurs more rapidly when water level quickly rises. Both samplers were filled with ice at the onset of sampling program to minimize the microbial degradation of organic matters in the samples. Most samples were retrieved within two days and all samples were filtered with 0.2  $\mu\text{m}$  polycarbonate membrane to ensure that samples can be preserved without freezing.

**DOC, TDN, and SUVA Analysis:** Prior to testing the formation potential of disinfection byproducts, it is crucial to measure the amount of chlorine dosage required to disinfect all organic materials and leave a positive residual at the end of the test. This study applied a standard formation potential test method that determines the total chlorine dosages based on concentration of DOC and  $\text{NH}_4\text{-N}$  on reactivity basis.

Thus, all samples were analyzed in duplicates for [DOC] and [TDN] using a Shimadzu TOC-VCSH analyzer. As a quality control measurement, each duplicate was measured in three aliquots, and two aliquot measurements with the smallest CV were selected for further analysis. A spectrophotometric method (Hach DR2700 with Method 8155) was used for measurement of ammonia-nitrogen and all samples were measured in duplicates.

In addition to the quantitative measurement of dissolved substances, compositional characteristics of samples were also analyzed. Stream water experiences more than just quantitative chemical change during a storm, but also experiences qualitative change since rising hydrograph transports more aromatic organic matter from soil surface during an event. Ultraviolet absorbance(UVA) measured at 256nm normalized by [DOC], also known as SUVA, is a good indicator for such variation and known to represent the amount of aromatic carbon in dissolved organic matter.

***DBP Formation Potential Test: Dosing*** -Since the main goal of this project focuses on understanding the temporal variation in DBPFP during events and between seasons, it is imperative that the method used for calculating DBPFP realistically mimics the chlorination process used in treatment plants. In other words, the dosage should be enough to disinfect all organic materials in samples and have moderate amount of residual chlorine that is commonly found in processed water. The following reactivity-based formula was used for determining the dosage volume for each sample:

$$\text{Cl}_2 \text{ (mg)} = 3 \times [\text{DOC}] + 7.6 \times [\text{NH}_3\text{-N}]$$

Using the above formula, triplicates of samples were dosed with appropriate amount of chlorine and buffered at pH 8 using a boric buffer solution. The dosed samples were then incubated at room temperature in dark for 24 hours. At the end of the incubation period, one of the triplicates for each sample were analyzed for its pH and residual chlorine, and any sample that showed pH value outside 7.8-8.2 range or negative residual chlorine concentration was discarded.

***DBP Formation Potential Test: Measurement***: All samples that passed the pH and residual chlorine test after 24 hours of incubation were then quenched with ascorbic acid to remove all residual chlorine. Following the quenching process, MTBE solution was mixed with the samples and vigorously shaken for 5 minutes to extract the disinfection byproducts. The extracted DBP solutions were analyzed by a Gas-Chromatographer equipped with an electron-capture detector. Four different types of THMs and two different types of HANs were measured during the analysis (Table 2), and their total concentrations

were summed and normalized by DOC concentrations to represent formation potential for each DBP types (DBPFP). Thus, DBP formation potential (DBPFP) serves as an index for DBP precursor in each sample and reflects its compositional characteristics of organic matter, rather than concentration.

Trihalomethane (THM)				Haloacetocnitrile (HAN)	
CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	CNCl <sub>2</sub>	CCl <sub>3</sub> NO <sub>2</sub>

Table 2- List of DBPs analyzed in this study

## Preliminary Results and Discussion

As of December 2011, a total of 207 samples from 11 storm events have been collected from the two sites. All samples have been measured for concentration of DOC, TDN, ammonium, and SUVA (Table 3). Based on these values and hydrographs of the streams, 43 samples were chosen to be tested for DBPFP.

	Forested Watershed			Urban Watershed		
	[DOC] in mg C L <sup>-1</sup>	[TDN] in mg N L <sup>-1</sup>	SUVA	[DOC] in mg C L <sup>-1</sup>	[TDN] in mg N L <sup>-1</sup>	SUVA
All samples	1.66 (±0.72)	0.29 (±0.10)	2.89 (±1.4)	6.86 (±2.19)	0.85 (±0.45)	2.52 (±0.80)
Baseflow Samples	1.19 (±0.28)	0.34 (±0.18)	2.18 (±0.54)	5.81 (±2.88)	1.29 (±0.58)	2.39 (±0.98)
Rising Limb Samples	1.92 (±0.89)	0.28 (±0.05)	2.97 (±0.66)	6.02 (±1.44)	0.97 (±0.45)	2.55 (±0.75)
Peak Samples	2.42 (±0.61)	0.33 (±0.05)	3.19 (±0.42)	5.82 (±1.13)	0.81 (±0.31)	2.69 (±0.71)
Falling Limb	1.67 (±0.59)	0.27 (±0.04)	3.14 (±1.88)	7.91 (±1.84)	0.61 (±0.11)	2.54 (±0.78)

Table 3- Summary table for measured [DOC], [TDN] and SUVA

**Forested Watershed** – Baseflow samples from the forested site had relatively minor variation in DOC concentration, ranging from 0.85 mg C L<sup>-1</sup> to 1.21 mg C L<sup>-1</sup>. During precipitation events, the concentration rose up to 5.04 mg C L<sup>-1</sup> with varying degrees of increase ratio. Out of the 6 events studied for this watershed, 5 events showed a typical DOC-Discharge relationship where [DOC] is strongly controlled by discharge rate (Figure 5,6,7). During these events, DOC concentration rapidly rose during

the rising limb of the hydrograph and reached its maximum before the discharge rate reached its peak. The [DOC] following the peak also showed a strong control of discharge during its steady decrease.

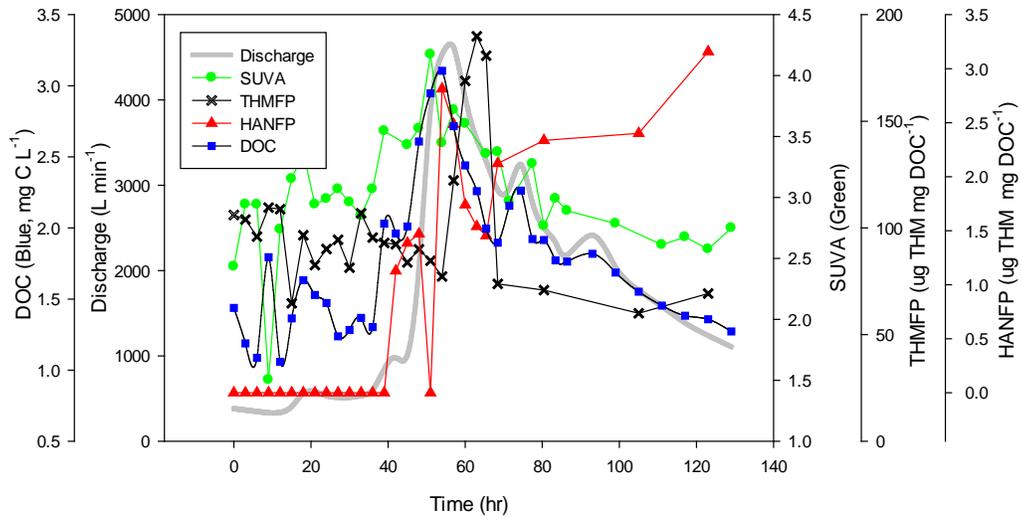


Figure 5 - A spring (May 2011) event hydrograph with DOC, SUVA, THMFP, and HANFP values

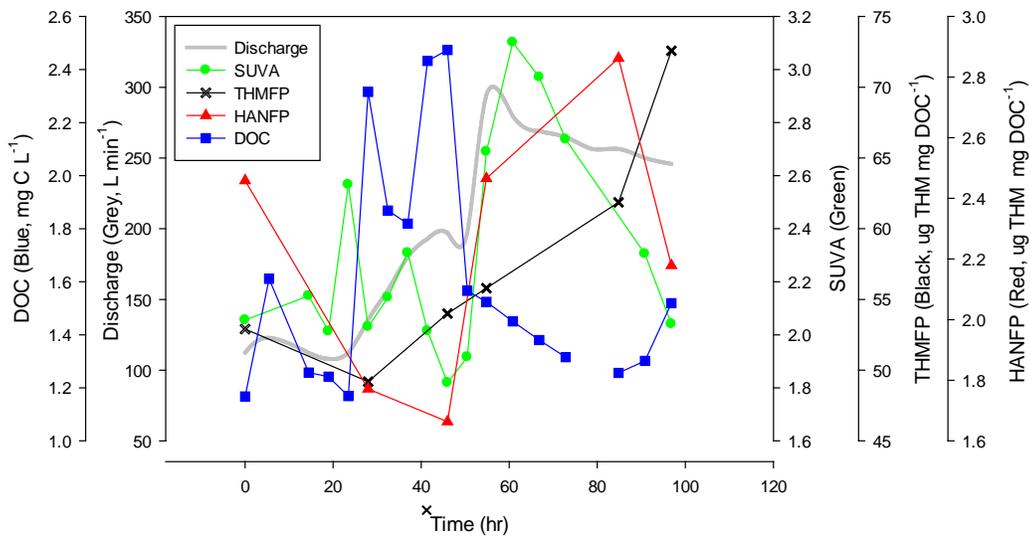
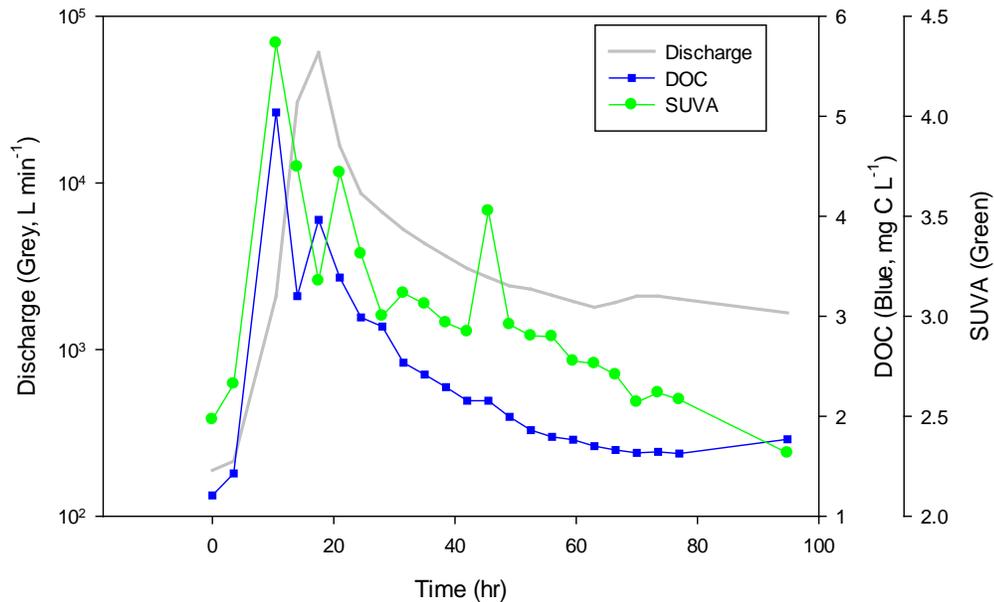


Figure 6 – An early summer (June 2011) event hydrograph with DOC, SUVA, THMFP, and HANFP values



**Figure 7 - A late summer (Aug. 2011) event hydrograph and measured DOC concentration and SUVA for the forested watershed**

The concentration of TDN also showed a similar pattern where discharge rate dictates its variation (Data not shown). However, the range of [TDN] during events was not as wide as [DOC], and its increase ratio was significantly smaller as well. The common pattern shared by [DOC] and [TDN] indicates that precipitation events transport dissolved matter from soil surface via runoff and provides additional dissolved organic matter to the stream. The input of terrigenous dissolved matter is also indicated by SUVA values during events. The high SUVA values observed near the hydrograph peak is a sign that organic matters with more aromatic carbon are being transported (Figure 5,6,7 ). This indicates that terrigenous materials that have not been fully metabolized by microbes become the source of organic matter in the stream as precipitation event progresses. After hydrograph passes its peak, the source of organic matter returns to ground water and lotic organism, and leads to steady reduction in SUVA values.

Judging from the DOC and SUVA patterns observed in this watershed, it is logical to predict that samples collected near the hydrograph peak or the samples with the highest SUVA values would result in forming the greatest amount of disinfection byproduct. However, the highest formation potential values were observed in post-peak samples for both THM and HAN (Figure 5,6 ). The maximum THMFP and HANFP both occurred after SUVA reached their peaks. The weak correlation observed between SUVA and DBPFP is somewhat different from the conventional belief that SUVA is a good indicator for

DBPFP. In fact the, highest DBPFP values were seen when SUVA values were rapidly declining after the hydrographic peak. Further analysis will assess if this pattern is a temporal summer trend or a common pattern for this watershed throughout the year. While it is yet difficult to determine if the lower THMFP seen in June event is due to smaller storm size, comparing base flow values indicate that seasonal change from spring to summer was accompanied by lower THMFP. The observed reduction is logical when considering natural watershed cycle of organic matter. In forested watersheds, the major input of organic matter occurs in fall and microbial activities metabolize fresh labile organic matter as season progresses. Thus, dissolved organic matter present in June samples should be more degraded than May samples, and result in less formation of DBPs. Further analysis will examine this seasonal trend holds true for late summer and fall precipitation events.

***Urban Watershed*** - The studied urban watershed showed markedly different quantitative and temporal DOC pattern from its forested counterpart. As expected, the [DOC] during base flow and precipitations events were both much higher, and the [TDN] also displayed a similar quantitative pattern (Table 3, Figure 8,9,10). Such high DOC and TDN values result from the extent of urban land cover in this watershed. Anthropogenic modification of land cover and export of wastewater, storm water, and other organic pollutants all lead to increased DOC in streams. Another noticeable difference seen in the urban watershed is the delayed [DOC] peak that occurred after the peak of hydrograph (Figure 8,9,10). Contrary to the forested study site, the highest concentration of DOC occurred during the falling limb of the hydrograph. While it is difficult to determine if this delayed peak is an indication for altered solute transport mechanism or manifestation of a unique hydrological characteristic of the watershed, it should also be noted that SUVA did not correlate well with [DOC] as well.

As expected, DBPFP of the samples collected from the urban watershed did show higher values when same month samples were compared (Figure 6 and Figure 8). The comparison again, proves that the compositional characteristic of dissolved organic matter is as important as its concentration in formation dynamics of disinfection byproducts.

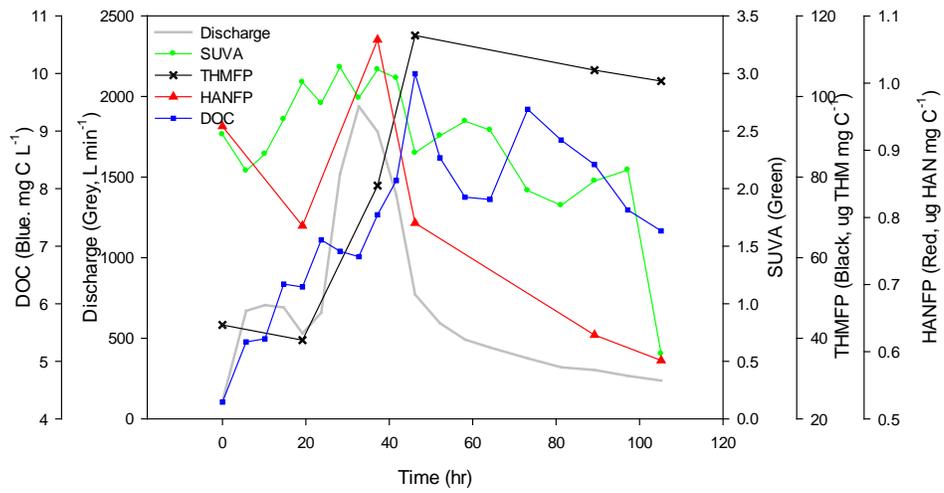


Figure 8 - An early summer (June 2011) event hydrograph with DOC, SUVA, THMFP, and HANFP values

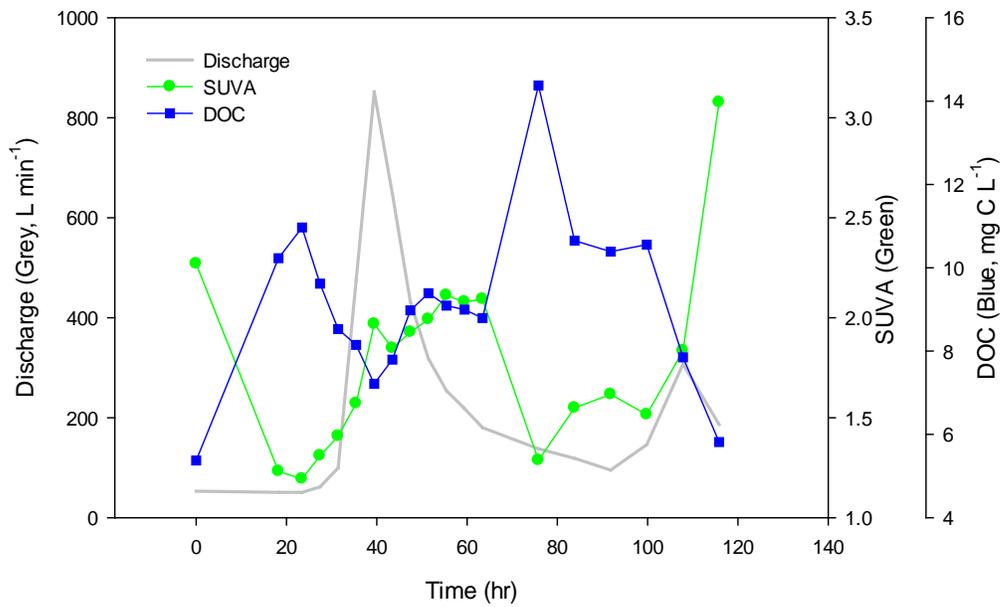


Figure 9 - An early Aug event hydrograph and measured DOC concentration and SUVA for the urban watershed

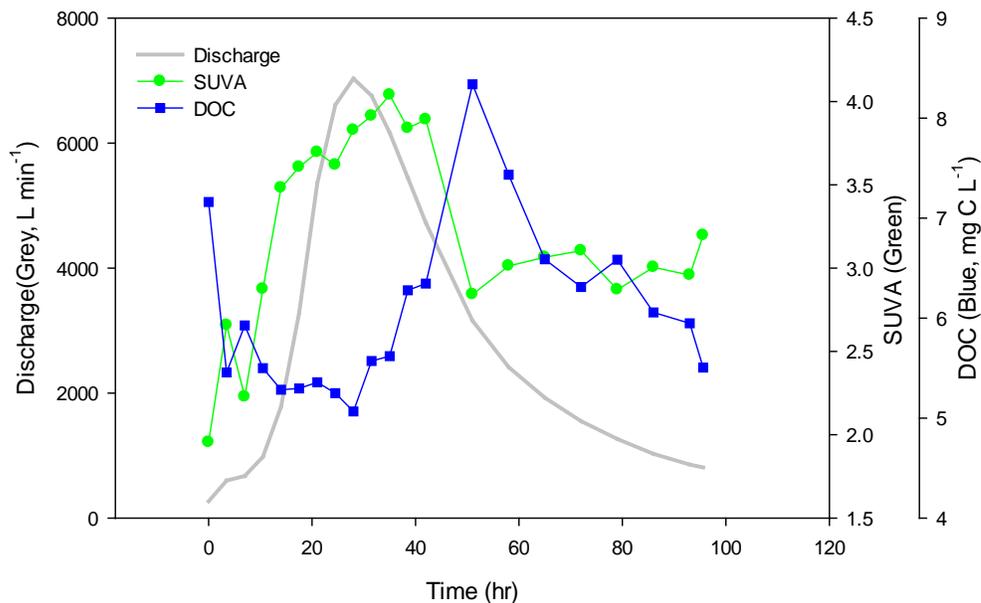


Figure 10 – A late Aug event hydrograph and measured DOC concentration and SUVA for the urban watershed

## Future Study

This study will continue until April 2012 and assess the formation potential dynamics for the two watersheds, especially focusing on how their respective patterns change in fall. Remaining works consist of dosing select samples for DBPFP tests, inclusion of excitation emission matrix data, and more in-depth analysis.

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