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ABSTRACT

Within a stream, changes in flow rate and local environment can affect the total organic content (TOC) concentrations in the stream water and TOC delivery downstream to water supply reservoirs. Disinfection by-products (DBPs) result from various chemical reactions between chlorine, bromine, and organic carbon in raw water during the drinking water treatment process; DBPs are potential carcinogens and are regulated by the U.S. Environmental Protection Agency. In this project, we measured the TOC concentrations in two streams in the Beaver Lake Watershed: Town Branch and Brush Creek. We then compared TOC concentrations between the two streams and to that observed in streams draining in forested areas to determine if differences in mean concentrations might be related to the streams' catchment. Finally, using instantaneous discharge at the time of sampling, we determined if TOC concentrations were significantly correlated to the volumetric flow of a stream. The data suggest that there is a positive linear relationship between the TOC concentration and the flow rate of a stream. While TOC concentrations did not vary between sites, TOC flux and yield were significantly different between the two streams.

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MEET THE STUDENT-AUTHORS

Abigail Washispack

I am from Conway, Arkansas, and graduated with honors from Conway High School in the spring of 2008. After being named a Bodenhamer fellow, I decided to attend the University of Arkansas for my undergraduate degree. I am currently pursuing a B.S. degree with a major in Biological Engineering and an emphasis in Biomedical Engineering. As a rising junior I am very involved in the campus ministry Campus Crusade for Christ and enjoy competing on various intramural teams, including soccer, softball, and ultimate Frisbee. I have also had the pleasure of being an Honors College Ambassador for the last two years.

I began this undergraduate research project with Dr. Brian Haggard in the spring of 2009 as part of the University of Arkansas Freshman Engineering Program's Honors Research Symposium. Upon graduation from the University of Arkansas, I plan to attend graduate school. After earning a doctoral degree in Biomedical Engineering, I hope to pursue a career in tissue engineering research.

I would like to thank Dr. Brian Haggard for all of his guidance and support throughout this project and give a special thanks to all the faculty of the Freshman Engineering Program. Finally, thank you to my wonderful family for all your love and support.

Jason McGinnis

I grew up in Tomball, Texas, and graduated from Tomball High School in 2008. I came to the University of Arkansas to pursue an engineering degree, unsure which field to pursue. I participated in the Freshman Engineering Program's Honors Research Symposium and began this research with Abby. After completing this project I switched to Civil Engineering and went to the Community Development in Belize summer program where we constructed a 100,000 gal/day filtration system to provide clean water for the village of Steadfast. Now I have finally found my place in the Mechanical Engineering Department. This project showed me how stimulating research and interpreting data can be so I plan to pursue engineering research in the future.

INTRODUCTION

Disinfection by-products (DBPs) are the result of various treatment processes used to produce drinking water. The first DBPs identified were trihalomethanes (THMs), where presence of THMs was related to the concentration of total organic carbon (TOC) in source water. Shortly after, in 1976, the National Cancer Institute declared chloroform a carcinogen. Chloroform is a THM, so this discovery implied that the consumption of drinking water containing high concentrations of THMs could be correlated to the development of certain types of cancer (Singer, 1994). These findings led to various EPA regulations on DBPs and even TOC concentrations in source water.

The most common water treatment process today is chlorine disinfection, which produces DBPs when chlorine and bromide ions react with organic substances; the various DBPs produced include THMs and haloacetic acids (HAAs). In response to the discovery of different kinds of DBPs and the health risks associated with their presence in drinking water, new regulations on water quality have been passed in recent years. In 1996, amendments were made to the Safe Drinking Water Act (SDWA) of 1974 that required the EPA to set standards for harmful microorganisms and DBP concentrations in drinking water based on the risks associated with each (EPA, 2010). In response to the amendments, the EPA created Stage 1 and Stage 2 of the Disinfectants and Disinfection Byproducts Rule (EPA, 2010). Stage 1 sets regulations on maximum concentrations of three disinfectants and maximum concentrations of two common DBPs. Stage 2 builds on Stage 1 by first identifying treatment systems with high DBP concentrations and then requiring more stringent testing for THMs and HAAs.

The precursor for DBPs is organic carbon in the source water, which is separated into two categories: dissolved organic carbon (DOC) and particulate organic carbon (POC). Organic carbon can enter a stream through allochthonous inputs or autochthonous production; allochthonous inputs originate outside the fluvial channel and include land applied fertilizers, animal manure, and plant material. Leaf litter is the one of the main allochthonous inputs, particularly in forested catchments (Meyer et al., 1998). According to Meyer et al. (1998), up to 30% of DOC produced daily in a forested stream is generated from leaf litter stored in the fluvial channel. Autochthonous production occurs within the fluvial channel through autotrophs including macrophytes, phytoplankton, and periphyton.

Local and watershed scale land use also influences the delivery of organic carbon to streams, and the production of organic carbon within the stream. For example, catchments with more urban and/or agricultural area often have greater concentrations of TOC, as well as the potential to produce more autochthonous inputs. According to Goonetilleke et al. (2005), "catchment characteristics play the most significant role in urban stormwater runoff quality." Water chemistry is significantly impacted by land use and land cover and often catchment characteristics are used to predict water chemistry (Gergel et al., 1999).

Variation in TOC concentration occurs with both seasonal changes and discharge variation. Studies have shown that concentrations of organic carbon are greatest during autumn, mostly due to an influx of leaf litter (Meyer et al., 1998). Generally changes in fluvial channel discharge are related to storm events and coincide with higher organic carbon concentrations (Giovannetti, 2007). Storm events cause an increase in allochthonous inputs, particularly in urban catchments where increased runoff volume and peak discharge occur. Several studies show that there are higher concentrations of pollutants and, thus, organic carbon early in a storm event and preceding peak flow (Goonetilleke et al., 2005). Particulate organic carbon concentrations have also been recorded to be much higher during increasing flow rates than during the receding limb of the hydrograph (Meyer and Tate,1983).

In order to limit the presence of DBPs in public drinking water, the amount of organic carbon in the raw water supplies needs to be minimal. The sources of organic carbon within drinking water supply reservoirs must be understood and measured. Then, management practices can be implemented to reduce the influx of organic carbon into the water supply. The first objective of this research was to determine the concentration of TOC in two streams located in the Beaver Lake Watershed: Town Branch and Brush Creek. Town Branch drains an urban area, whereas Brush Creek drains an agricultural and forested catchment. We compared TOC concentrations in the two streams to determine if there was a significant difference in mean concentrations that might be related to the streams' catchment. We also compared the TOC concentrations in these two streams to that observed in streams draining in forested areas that were sampled by Giovannetti (2007). The final objective was to determine if TOC concentrations were correlated to the volumetric flow of a stream using instantaneous discharge at the time of sampling.

MATERIALS AND METHODS

We selected sites at two streams within the Beaver Lake Watershed: Town Branch 62 (USGS station ID 07048480), located at the bridge on Highway 62 and Brush Creek 45 (USGS station ID 07048890), located near the bridge on Highway 45. Town Branch has a catchment with 60% urban development and an area of 1.22 km^2, whereas Brush Creek has a catchment with 54% forest and 46% pasture land use with an area of 46.8 km^2 (Haggard et al., 2007).

Over a seventy day period from February 4th, 2009 to April 10th, 2009, we collected a total of twenty 250 mL water samples, nine at Brush Creek and eleven at Town Branch. Each sample was collected from the side of the fluvial channel, and the sampling equipment and bottles were field rinsed before each water sample was collected. The samples were then taken to the Arkansas Water Resources Center Water Quality Lab at the University of Arkansas Engineering Research Center in Fayetteville, Ark. where TOC concentration in the collected water samples was measured using a Skalar Wet Chemistry Autoanalyzer (Skalar Analytical B.V., The Netherlands).

The method used to measure TOC concentration was EPA Test Method 415.2 for Total Organic Carbon. This method is intended for samples with TOC concentrations between 0.05 mg/L and 10 mg/L and uses persulfate oxidation and ultraviolet illumination. In this method, 1 mL of acidified persulfate reagent is added to the sample, which is then placed in a sparger. The sample is then purged with helium and sent to a scrubber, which removes approximately 99.9% of CO_2 in the sample. Purgeable organics then progress through a reduction system. Hydrogen is added to the gas stream, which then passes over a nickel catalyst. This catalyst converts the purgeable organic carbon to methane. A flame ionization detector then measures the concentration of purgeable organic carbon.

The sample is then moved to a quartz ultraviolet reaction coil. In the presence of the acidified persulfate reagent, the nonpurgeable organics are exposed to ultraviolet illumination. This process converts the nonpurgeable organics to CO_2, which progresses to a second sparger where it is purged with helium and transferred to the reduction system and then the methane detector. The measured concentration of nonpurgeable organic carbon is then added to the concentration of purgeable organic carbon. This sum is the TOC concentration of the sample (EPA, 1982).

The discharge of the water at each site is available on the World Wide Web through the United States Geological Survey (USGS) real-time stream flow-monitoring program. The discharge and gage height (i.e., depth of water) at the time of sampling was recorded from the USGS website (http://waterdata.usgs.gov/nwis/rt). The gage height (m), volumetric discharge (m^3/s), and the TOC concentration (mg/L) at the time of sampling were recorded for each sample taken at Town Branch and Brush Creek (Tables 1 and 2). The flux (mg/sec) of each sample was calculated by multiplying the discharge and TOC concentration. The yield ($mg/sec/km^2$) of each sample was calculated by multiplying the flux and the catchment area. Statistical analysis was performed for the TOC concentration (mg/L), TOC flux (mg/second), and TOC yield ($mg/sec/km^2$) at each site (Table 3) using Microsoft Excel® 2007 software (Microsoft Corporation, Redmond, Wash.).

RESULTS AND DISCUSSION

A Student's *t*-test with unequal variances on log-transformed data showed that TOC concentrations were not significantly different at the two sites, where geometric means were 2.18 mg/L at Brush Creek and 2.73 mg/L at Town Branch. Nine sampling dates overlapped between the two sites, and a paired T-test also showed that TOC concentrations were not significantly different between sites. Overall, the range in TOC concentrations was similar between sites, except that one sampling date at Town Branch had a concentration over 15 mg/L. Unfortunately, Brush Creek was not sampled on this date because of logistical constraints.

The water samples generally had lower TOC concentrations (<2 mg/L), when it had not rained for a few days. The water samples taken during or right after a rainstorm had TOC concentrations higher than those measured during periods of low flow. For example, the last three samples collected at Town Branch were taken before, at the beginning of (i.e., first flush), and after a single storm (i.e., receding limb of the hydrograph). The TOC concentrations for these samples were 1.58 mg/L, 15.8 mg/L, and 3.70 mg/L, respectively (Table 1). This suggests that TOC concentrations increased during storm events relative to the concentrations measured [prior to the rain] during periods of low flow.

TOC concentrations were graphed as a function of volumetric discharge at the time of sampling at Brush Creek and Town Branch (Fig. 1). Both graphs showed a positive linear relationship between TOC concentration and flow rate ($r^2 = 0.80$ and 0.94, respectively). The linear relationship remained strong ($r^2 = 0.74$) for the Town Branch site even without the data point where TOC concentration was 15.8 mg/L. This indicated that TOC concentrations increase with increasing flow rate, and that storm events can significantly increase TOC concentrations in these streams.

The average TOC concentration for sites in different catchment types were computed based on data collected by Giovannetti (2007), which sampled twenty different streams throughout Northwest Arkansas including the two streams in this study. Forest watersheds were defined as a catchment with greater than 80% forested land use; agricultural watersheds were defined as a catchment with greater than 30% pasture land area; mixed forest watersheds were defined as a catchment that had less than 2% urban-suburban land use and did not fit into the forest on agricultural classifications; and, mixed urban watersheds were defined as a catchment that had 2% or more urban-suburban land use and did not fit into other categories (Giovannetti, 2007). The TOC concentration for agriculture, forest, mixed forest, and mixed urban catchments were compared to that measured in this study at

Brush Creek and Town Branch. This study had geomean TOC concentrations numerically higher than the forested streams (0.84-1.33 mg/L) sampled by Giovannetti (2007), whereas the other streams (agricultural and mixed land use catchments) had geomean TOC concentrations ranging from 0.84 to 3.45 mg/L (Fig. 2).

The data we have collected showed that the TOC concentrations for Town Branch draining an urban catchment was statistically not different than that from Brush Creek draining the mixed agricultural and forested catchment. However, there were significant differences between the streams based on flux and yield (Table 3). The TOC flux was greatest at Brush Creek (Student's *t*-test for unequal variances on log-transformed data, $P < 0.03$), likely because stream discharge was greatest at this site. On the other hand, TOC yield for Town Branch was significantly higher than that from Brush Creek ($P < 0.08$), indicating that the urban landscape of the Town Branch catchment produced more organic carbon per unit area than the agricultural catchment of Brush Creek. Thus, it is best to look at more than just concentration when trying to understand TOC transport from different catchments.

This study shows that TOC concentration was similar between streams draining agricultural and urban catchments, whereas transport on a unit area basis was greater from the urban stream. This supports the conclusion of previous papers (Goonetilleke et al., 2005; Gergel et al., 1999), which indicated that urban catchments had higher TOC concentrations and transport than other catchment types. However, the urban stream in this study had concentrations similar to Brush Creek and within the range of that measured in streams draining agricultural and mixed land use catchments (data from Giovannetti, 2007).

Our sampling data showed that there was a positive linear relationship between TOC concentrations and flow rates at these two streams ($P < 0.05$). However, previous research indicates that TOC might be lost as a first flush during storm events. Since most of our high flow rate TOC samples were taken after the peak flow rate, we might not have adequately characterized this relation. In order to confirm this conclusion, more samples need to be taken at the beginning of peak flow events. Other research studies (Goonetilleke et al., 2005; Meyer et al., 1983) and the one sample taken during these conditions indicate that the TOC concentration may be considerably higher prior to peak flow rate. The overall TOC data displayed as a function of flow rate shows that first flush of organic carbon might occur in these watersheds, because the slope of the linear relation was steep for Town Brach compared to Brush Creek. Future studies should conduct an in-depth assessment of TOC concentrations during storm events to determine if a specific trend is followed and if the trend is the same for different catchment types.

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Table 1. Measured Gage Height, Volumetric Discharge, and TOC Concentration for Water Samples Collected at Town Branch.

Date	Time	Gage Height (m)	Discharge (m^3/s)	TOC (mg/L)
2/4/09	16:05	0.532	0.008	1.67
2/11/09	17:20	0.537	0.037	3.69
2/18/09	16:00	0.536	0.014	1.51
3/4/09	16:05	0.536	0.014	1.65
3/11/09	16:45	0.533	0.008	1.96
3/25/09	14:50	0.543	0.028	3.3
3/27/09	14:50	0.539	0.022	3.39
4/1/09	16:50	0.539	0.022	2.03
4/8/09	17:35	0.536	0.014	1.58
4/9/09	16:20	0.536	0.088	15.8
4/10/09	12:50	0.543	0.028	3.7

Table 2. Measured Gage Height, Volumetric Discharge, and TOC Concentration for Water Samples Collected at Brush Creek.

Date	Time	Gage Height (m)	Discharge (m^3/s)	TOC (mg/L)
2/4/09	16:45	0.884	0.272	1.47
2/11/09	16:45	1.073	2.152	5.41
2/18/09	16:45	0.872	0.207	1.92
3/4/09	15:45	0.835	0.062	1.20
3/11/09	16:15	0.826	0.040	1.51
3/25/09	16:00	0.975	0.991	5.41
4/1/09	17:45	0.911	0.453	2.70
4/8/09	16:30	0.856	0.136	1.51
4/10/09	14:00	0.878	0.238	1.83

Table 3. Number of samples (n), Minimum, Median, Maximum, Mean, Standard Deviation (S), and Geometric Mean (GeoMean) for TOC Concentration, Flux, and Yield at Brush Creek and Town Branch.

				TOC Concentration (mg/L)			
Site	n	Minimum	Median	Maximum	Mean	S	GeoMean
Brush Creek	9	1.20	1.83	5.41	2.55	1.68	2.18
Town Branch	11	1.51	2.03	15.8	3.66	4.12	2.73
				TOC Flux (mg/s)			
Site	n	Minimum	Median	Maximum	Mean	S	GeoMean
Brush Creek	9	59.8	399	11600	2200	3910	553
Town Branch	11	13.7	43.7	1380	176	403	55.5
				TOC Yield (mg/s*km^2)			
Site	n	Minimum	Median	Maximum	Mean	S	GeoMean
Brush Creek	9	1.28	8.53	248	47.0	83.6	11.8
Town Branch	11	11.2	35.8	1130	144	83.6	45.5

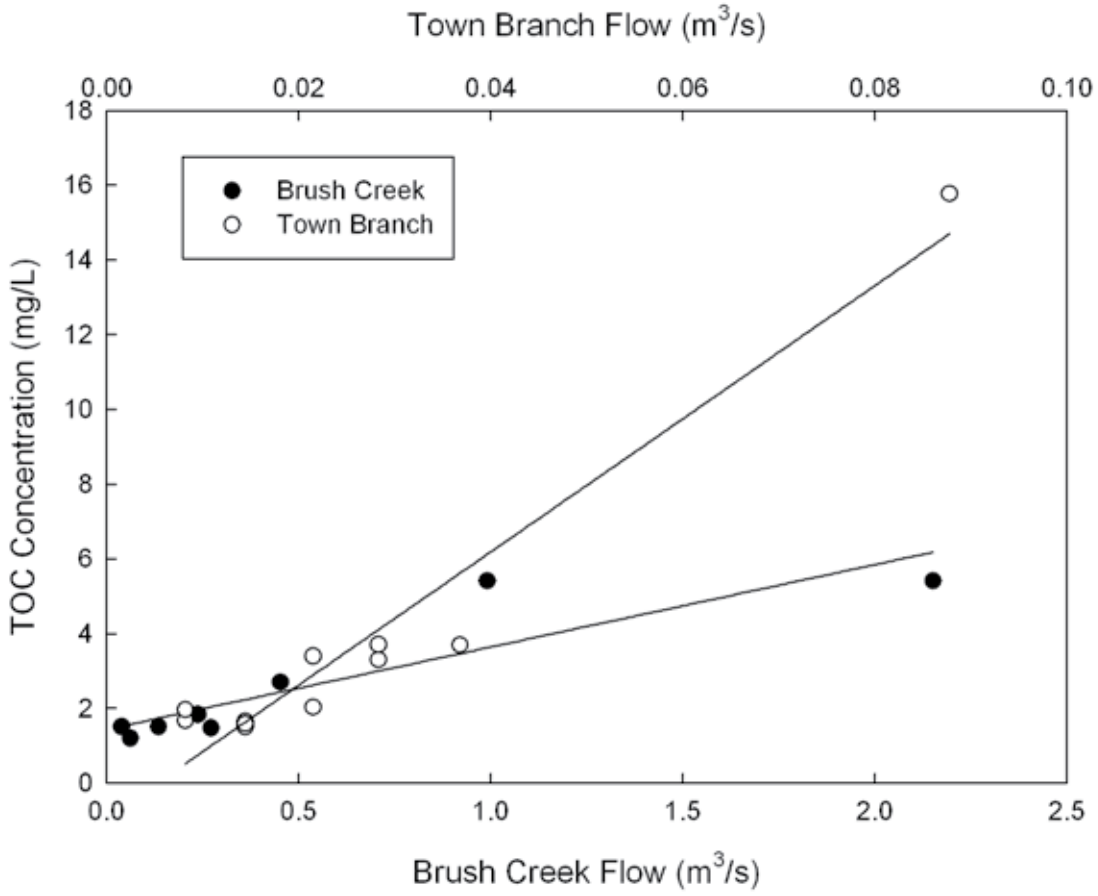

Fig. 1. Total organic carbon concentrations (mg/L) as a function of flow rate (m^3/s) for samples taken at Town Branch and Brush Creek.

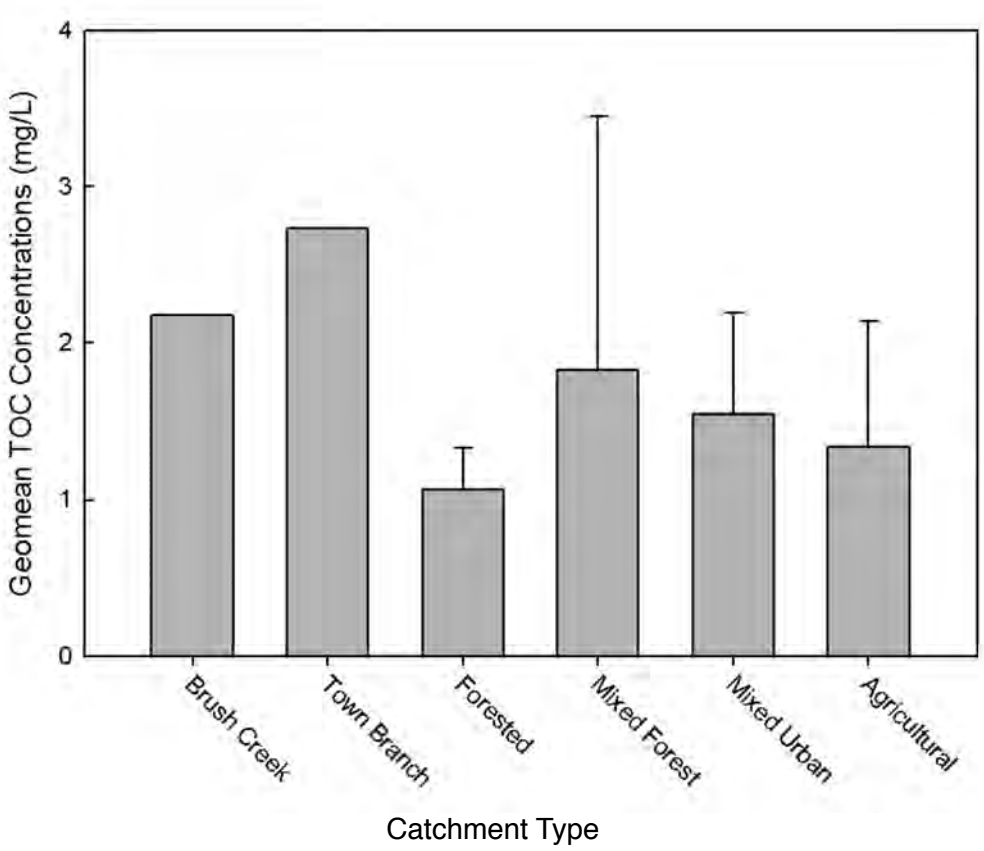

Fig. 2. Comparison of average TOC concentrations for different catchment types. Stream from this study or catchment type from Giovannetti (2007).