Nathan Trimner **UNDERC, Dr. Scott Bridgham** **11-21-01**

DOC in Tenderfoot Creek and Brown Creek: A Preliminary Study

Abstract: The inputs of DOC into streams are important for aquatic ecosystems for several reasons: food web interactions, influences on the transport of heavy metals, and protection of biota from UV radiation. DOC enters a stream in two ways: (1) from the processing of organic material already present in the stream and (2) through the introduction of DOC in soil water. Two streams were studied in northern Wisconsin at the University of Notre Dame Environmental Research Center (UNDERC) for preliminary research regarding DOC inputs and effects on water chemistry. The result of the study was that Tenderfoot Creek has a relatively low concentration of DOC until it becomes associated with wetlands off of the UNDERC property. Brown Creek has a moderate concentration of DOC and experiences a substantial amount of soil water inputs that provide the stream with DOC near the point where it enters into Palmer Lake. Future research should focus on the areas of Tenderfoot north of UNDERC where Tenderfoot Creek shows a dramatic increase in DOC concentration and on the areas of Brown Creek a quarter-mile east of Palmer Lake.

INTRODUCTION

Dissolved organic carbon (DOC) is one of the most important components of the water chemistry of streams. It plays a part in the food web, affects the transport and toxicity of heavy metals, and limits light penetration into streams which protects aquatic organisms from UV radiation (Schiff et al., 1998). The importance of DOC in streams has been studied widely, but much less attention has been placed on the sources of DOC. Louis Kaplan and Denis Newbold explain that stream ecology should be expanded to include the interactions of the terrestrial environment with the aquatic environment, particularly in matters of water flow, which alters the chemistry of streams (Kaplan and Newbold, 1993).

DOC enters streams two distinct ways: (1) through the processing of organic matter that has been directly introduced into the stream upland (leaf litter, branches, animal carcasses, etc.) and (2) through the introduction of water that already contains DOC in solution. In most streams the DOC concentration is greater than the DOC concentration of groundwater, which is normally between 0.5 and 0.7 mgl^{-1} throughout

North America (Kaplan and Newbold, 1993). When streams have a DOC concentration that is greater than 0.5 to 0.7 mgl^{-1}, it is generally because of significant inputs of soil water, which have a high concentration of DOC (Kaplan and Newbold, 1993). The upland introduction of organic matter into a stream is less important further downstream (Kaplan and Newbold, 1993). This is the case at the University of Notre Dame Research Center (UNDERC) in northern Wisconsin. The region is characterized by glacial topography where "riparian wetlands are the dominant source of DOC to streams rather than upland sources which would require longer flow paths and have increased opportunities for sorption (Kaplan and Newbold, 1993)."

As a consequence, wetland hydrology is vital in understanding the inputs of soil water with respect to DOC concentration in the streams of northern Wisconsin. Most wetlands associated with the streams at UNDERC are peatlands, which arise because the decomposition rate of organic matter is lower than productivity in this area. As a consequence, organic matter builds up over the years and forms deep deposits of peat. The hydrology of peatlands is interesting because there are greater groundwater flow rates through the uppermost part of the peat column (Schiff et al., 1998). The greater groundwater flow and subsequent leaching of DOC in the uppermost 0.5m of the peat column explains the lower concentration of DOC in that layer (Schiff et al., 1998). This phenomenon is illustrated in Figure 1.

The hydrology in the uppermost portion of the peat column is especially important for stream chemistry. In areas where wetlands are in close proximity to a stream, the top 0.5m of peat provides most of the soil water to the stream. Figure 2 clearly illustrates how this is important to DOC concentrations in streams. The wet conditions of a nearby wetland expand the surface of the seepage face, which provides the stream with DOC from nearby soils. At UNDERC, the nearby soils of the seepage face consist of the upper layer of peat.

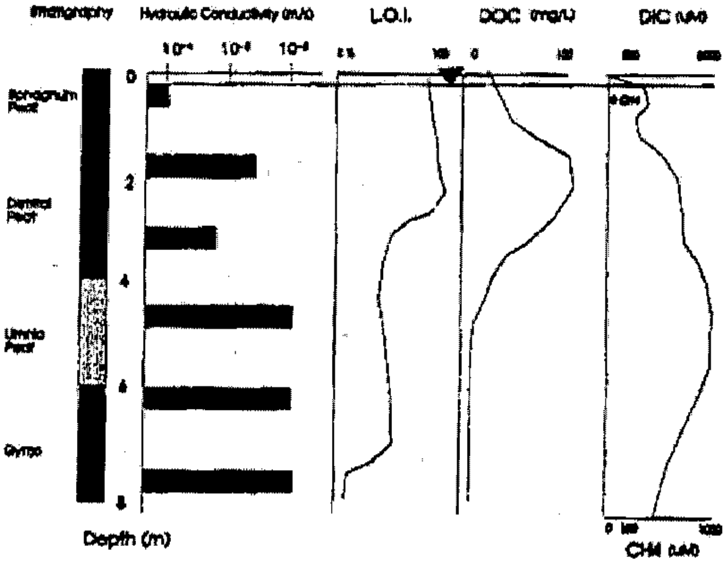


Figure 1. Shows that in the upper 0.5m of peat the higher conductivity is related to lower DOC concentrations. This situation is created by higher water flow in the upper layer of peat, which results in substantial leaching of DOC. (Figure 2 is from Schiff et al., 1998.)

This study contains preliminary research on DOC levels in two streams at the University of Notre Dame Environmental Research Center: (1) Tenderfoot Creek and (2) Brown Creek. It provides limited information on the following characteristics that relate to the interaction between groundwater inputs of DOC and soil water inputs of DOC:

(1) water temperature, which can indicate the amount of groundwater entering a stream even though there are other factors affecting temperature;
(2) conductivity, which has a positive correlation with groundwater inputs;
(3) pH, which should be negatively correlated with DOC concentrations;
(4) the DOC concentration of the water at each site in ppm,
(5) absorbance at 330 nm, which should correlate closely with DOC concentrations;
(6) and absorbance at 280 nm, which reflects the aromaticity of organic compounds.

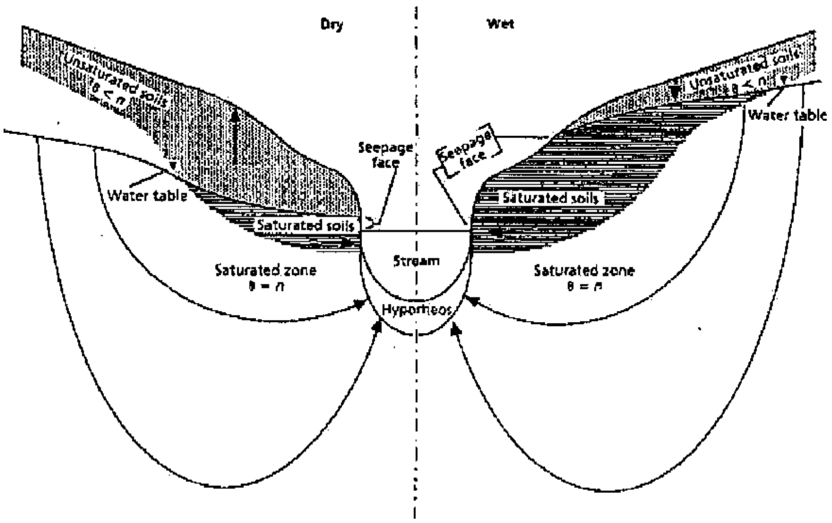


Figure 2. Shows expansion of DOC inputs in wet conditions through the saturated soils of the seepage face. The streams that were studied at UNDERC, Tenderfoot Creek and Brown Creek are associated with wetlands that represent the wet conditions in this figure. (Figure is from Kaplan and Newbold, 1993.)

MATERIALS AND METHODS

Description of the Sites

Sampling was conducted at seven sites chosen for easy access along two streams that flow through the University of Notre Dame's Environmental Research Center (UNDERC). The streams were chosen to show distinct differences in DOC content, pH and conductivity. Tenderfoot Creek is a relatively clear stream flowing north from its source, Tenderfoot Lake. It should reflect the water chemistry of Tenderfoot Lake at its source, but its water chemistry should change as it becomes associated with fens further downstream. Four sites were sampled along Tenderfoot Creek: (1) on Tenderfoot Lake near the wet lab (TFL), (2) at a bridge approximately a quarter-mile downstream from the source of the stream (TFC1), (3) at a bridge approximately three miles further downstream (TFC2), and (4) at another point 10 miles downstream after interactions with wetlands (TFC3).

Brown Creek has a substantial tan color and flows from Kickapoo Lake to the southwest until it reaches Palmer Lake. Kickapoo Lake is a eutrophic lake that has tan water because of moderate DOC concentrations. It would have been interesting to study Brown Creek near its source, but the difficulty of traveling along the stream limited sampling to the last half mile. Despite these limitations, sites were chosen in areas where wetlands could have altered water chemistry. The three sites sampled along Brown Creek were (1) where it flows into Palmer Lake (BC), (2) a small stream emptying into Brown Creek from a Cedar Swamp one quarter mile upstream (BCCS), (3) and at an Alder Swamp further upstream from there (BCAS).

Water Sampling

Each of the seven sites was sampled once in the morning for five consecutive days. Extracting water from the streams was done in a way that limited outside influences on water chemistry and DOC levels. Samples were taken six inches below the surface with a one liter bottle at the end of a five foot pole to prevent contamination and avoid photodegradation of DOC. All samples were transported to filtering equipment in the shade with a six-liter plastic container, which was rinsed with one liter of water from the site and then filled with two liters of sample for filtering. Temperature, pH, and conductivity were measured on-site before filtering. Temperature and conductivity were measured with an Orion conductivity meter (model 122). Temperature was measured in degrees Celsius and conductivity was measured at 199.99 μS/cm. pH was measured with a Orion portable pH meter (model 290 A). When temperature, pH and conductivity were effectively measured, the stream water was filtered through acid-washed GF/F filters into a 125 mL bottle, which was acid-washed and baked before use. Bottles from each site were placed on ice in a sealed cooler to prevent microbial action and photodegradation during transport to a refrigerator in the lab.

DOC Measurements

The samples were kept in the refrigerators at the Jerry Hank laboratory at UNDERC until they could be taken to the University of Notre Dame to measure absorbance at 280 nm, absorbance at 330 nm, and DOC concentrations in ppm.

Absorbance was measured with a Fischer UV-VIS machine and DOC was measured by a Hewlett-Packard TOC Analyzer in ppm.

Data Analysis

All data was analyzed through SYSTAT to create matrixes of pairwise comparison probabilities for each measured characteristic of water chemistry (temperature, conductivity, pH, absorbance at 330 nm, absorbance at 280 nm, and DOC concentration) between the seven sites. SYSTAT was also used to examine the correlation between the six water characteristics through a Pearson correlation matrix.

RESULTS

Water Temperature

Although there were no distinct differences in water temperature between the sites on Tenderfoot Creek and the sites on Brown Creek, there are differences in water temperature between the sites on Brown Creek (Figure 3). The temperature of water at BCCS was significantly lower (19.3 ± 1.87 °C) than the temperature at BC and BCAS (22.08 ± 0.92 °C, $p = 0.01$; 22.17 ± 1.48 °C, $p = 0.008$; respectively). There are also differences in water temperature between the sites on Tenderfoot Creek. The temperature at TFC3 was significantly lower (20.55 ± 0.49 °C) than the temperature at TFC2 (23.6 ± 2.03 °C, $p = 0.038$). If there had been more replicates, the temperature at TFC3 would most likely have been significantly lower than the temperature at TFC1 and TFL (23.3 ± 2.03 °C, $p = 0.056$; 23.1 ± 1.91, $p = 0.083$).

Conductivity

Overall, the sites on Tenderfoot Creek, except for TFC2, are significantly lower in conductivity than the sites on Brown Creek (Figure 4). BC (114.1 ± 6.50 μS/cm) has a conductivity that is significantly lower than the conductivity at TFC1, TFC3, and TFL

(104.5 ± 1.40 µS/cm, p = 0.003; 100.8 ± 2.05 µS/cm, p = 0.003; 104.0 ± 2.33 µS/cm). BCAS (115.8 ± 6.33 µS/cm) has a conductivity that is significantly lower than the conductivity at TFC1, TFC2, TFC3, and TFL (104.5 ± 1.40 µS/cm, p = 0.001; 109.4 ± 2.85 µS/cm, p = 0.040; 100.8 ± 2.05 µS/cm, p = 0.001; 104.0 ± 2.33 µS/cm, p = 0.000). BCCS has a conductivity that is significantly lower than the conductivity at TFC1, TFC3, and TFL (104.5 ± 1.40 µS/cm, p = 0.003; 100.8 ± 2.05 µS/cm, p = 0.003; 104.0 ± 2.33 µS/cm, p = 0.002).

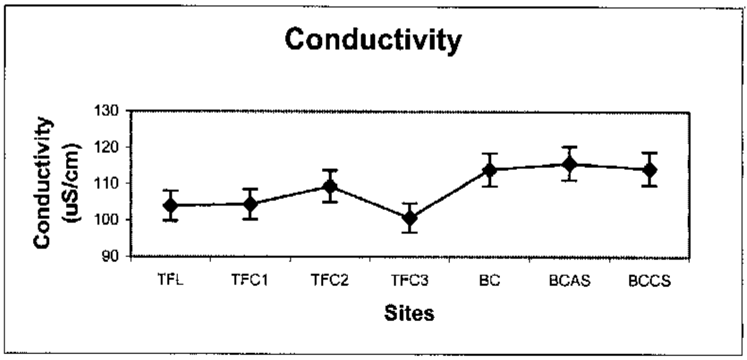


Figure 4. Shows the conductivity for 7 sites along Tenderfoot Creek and Brown Creek.

pH

The sites on Tenderfoot Creek have a significantly higher pH than the sites at Brown Creek (Figure 5). TFC1 (7.6 ± 0.17) has a significantly higher pH than BC, BCAS, and BCCS on Brown Creek (7.2 ± 0.070, p = 0.000; 7.1 ± 0.052, p = 0.000; 7.1 ± 0.16, p = 0.000). TFC2 (7.5 ± 0.15) has a significantly higher pH than BC, BCAS, and BCCS (7.2 ± 0.070, p = 0.000; 7.1 ± 0.052, p = 0.000; 7.1 ± 0.16, p = 0.000). TFC3 (7.6 ± 0.13) has a significantly higher pH than BC, BCAS, and BCCS (7.2 ± 0.070, p = 0.001; 7.1 ± 0.052, p = 0.000; 7.1 ± 0.16, p = 0.000). TFL (8.2 ± 0.19) has a significantly higher pH than BC, BCAS, and BCCS (7.2 ± 0.070, p = 0.000; 7.1 ± 0.052, p = 0.000; 7.1 ± 0.16, p = 0.000). It is interesting that TFL, the Tenderfoot Lake site, has a pH that is significantly higher than the pH at TFC1, TFC2, and TFC3 (7.6 ± 0.17, p = 0.000; 7.5 ± 0.15, p = 0.000; 7.6 ± 0.13, p = 0.000).

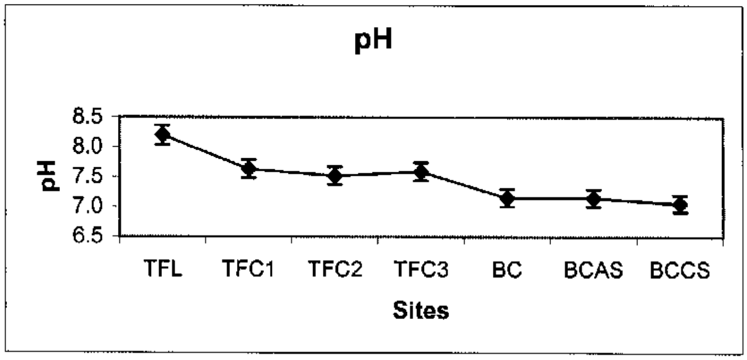


Figure 5. Shows the pH at 7 sites along Tenderfoot Creek and Brown Creek.

Absorbance at 330 nm

The absorbance at 330 nm shows two interesting trends in the data (Figure 6). One is that the sites further downstream on Tenderfoot Creek have a higher absorbance. Although this trend was not shown to be significant in all cases, it was most likely a result of a small number of replicates: TFL (0.080 ± 0.025), TFC1 (0.083 ± 0.017), TFC2 (0.113 ± 0.020), and TFC3 (0.203 ± 0.028). The other trend is that Brown Creek sites have a higher absorbance at 330 nm than Tenderfoot Creek sites. This does not include TFC3, which has the highest absorbance of all sites with 0.203 ± 0.025. BC (0.136 ± 0.19) has a significantly higher absorbance than TFL and TFC1 (0.080 ± 0.025, p = 0.008; 0.083 ± 0.017, p = 0.011). BCAS (0.128 ± 0.030) has a significantly higher absorbance than TFL and TFC1 (0.080 ± 0.025, p = 0.024; 0.083 ± 0.017, p = 0.017). BCCS has a significantly higher absorbance than TFL, TFC1, and TFC2 (0.080 ± 0.025, p = 0.000; 0.083 ± 0.017, p = 0.000; 0.113 ± 0.020, p = 0.007).

It is important to note that there are significant differences in the absorbance at 330 nm between sites along the same stream. The absorbance at 330 nm of BCAS (0.13 ± 0.030) is significantly lower than the absorbance at 330 nm of BCCS (0.17 ± 0.061, p = 0.040). Along Tenderfoot Creek, TFC3 is significantly distinct from TFC1, TFC2, and TFL (0.083 ± 0.017, p = 0.000; 0.11 ± 0.020, p = 0.002; 0.80 ± 0.025, p = 0.000) with an absorbance of 0.20 ± 0.028 at 330 nm.

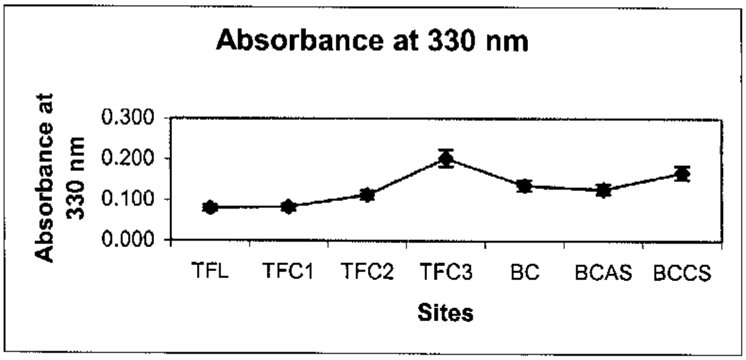


Figure 6. Shows the absorbance at 330 nm for the 7 sites along Tenderfoot Creek and Brown Creek

Absorbance at 280 nm

The data for absorbance at 280 nm is more problematic than the data for absorbance at 330 nm (Figure 7). Despite a low number of replicates, there seems to be a trend of increasing absorbance on Tenderfoot Creek as sites get further downstream: TFC1 (0.194 ± 0.042), TFC2 (0.245 ± 0.050), and TFC3 (0.417 ± 0.031). TFL (0.205 ± 0.040) has a higher absorbance than TFC1, but this difference is not significant. The data for absorbance at 280 nm provides less evidence that Brown Creek has a higher absorbance overall than Tenderfoot Creek.

Although it is difficult to show distinct trends with this data, there are significant differences between sites along the same stream. Along Brown Creek, BCCS has an absorbance at 280 nm (0.39 ± 0.11), which is significantly greater than the absorbance at BC and BCAS (0.25 ± 0.029, $p = 0.000$; 0.29 ± 0.039, $p = 0.008$). Along Tenderfoot Creek, TFC3 has an absorbance at 280 nm (0.42 ± 0.050) that is significantly greater than the absorbance at TFC1, TFC2, and TFL (0.19 ± 0.040, $p = 0.000$; 0.24 ± 0.042, $p = 0.001$; 0.21 ± 0.030, $p = 0.000$).

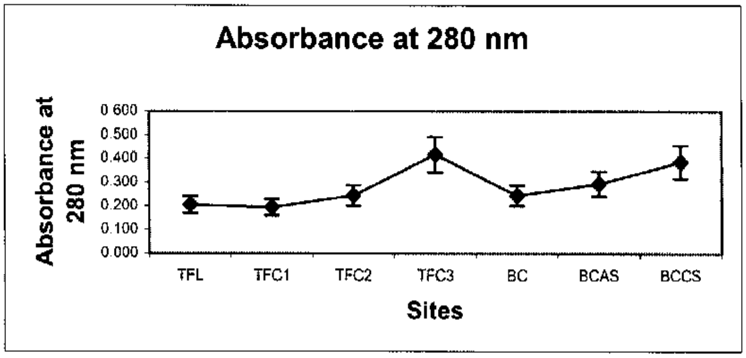


Figure 7. Shows the absorbance at 280 nm for 7 sites along Tenderfoot Creek and Brown Creek.

DOC

The data for DOC shows an increasing concentration of DOC further downstream on Tenderfoot Creek: TFL (11.01 ± 1.74 ppm), TFC1 (13.05 ± 3.43 ppm), TFC2 (13.65 ± 2.61 ppm), and TFC3 (18.30 ± 1.62 ppm). However, this trend was not significant between sites because of a lack of replicates. The lack of replicates created a large problem in determining significant differences between sites along the same creek. There is no significant difference in TOC among the sites at Brown Creek (Figure 8). However, there would most likely be a significant difference between the dissolved organic carbon at BCAS and BCCS if there were more replicates (13.7 ± 1.00; 17.2 ± 4.31, $p = 0.073$). Along Tenderfoot Creek, TFC3 (18.3 ± 2.61) was significantly different from TFC1 and TFL in terms of TOC (13.0 ± 1.74, $p = 0.048$; 11.0 ± 1.62, $p = 0.008$). TFC3 would probably have a significantly greater concentration of TOC than TFC2 if there were more replicates (13.7 ± 3.43, $p = 0.081$).

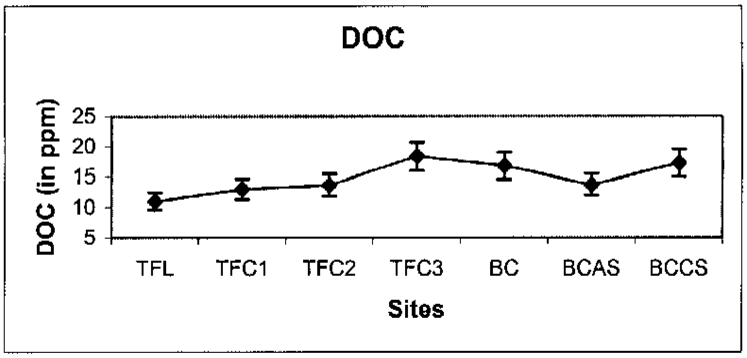


Figure 8. Shows the DOC concentrations for 7 sites along Tenderfoot Creek and Brown Creek.

The Correlation between Water Characteristics

Pearson Correlation Matrix

	Temperature	Conductivity	pH	UV-Vis 330	UV-Vis 280	DOC
Temperature	1.000					
Conductivity	-0.323	1.000				
pH	0.352	-0.565	1.000			
UV-Vis 330	-0.621	0.288	-0.502	1.000		
UV-Vis 280	-0.681	0.234	-0.470	0.887	1.000	
DOC	-0.357	0.194	-0.431	0.722	0.647	1.000

Table 1. This table contains a correlation matrix examining the interactions between 6 different characteristics the two study streams at UNDERC (Brown Creek and Tenderfoot Creek).

Temperature had a strong negative correlation with absorbance at 330 nm and absorbance at 280 nm (R = -0.621, R = -0.681), but only had a weak negative correlation with DOC (R = -0.357) (Table 1). Conductivity had a moderately strong negative correlation with pH (R = -0.565). pH had moderate negative correlation's with absorbance at 330 nm, absorbance at 280 nm, and DOC (R = -0.502, R = -0.470, R = -0.431). Absorbance at 330 nm had a very strong positive correlation with absorbance at 280 nm (R = 0.887). DOC had a strong positive correlation with both absorbance at 330 nm and absorbance at 280 nm (R = 0.722, R = 0.647).

Linear Regressions

The strength of the relationship between temperature and the measurements of DOC was unexpected. DOC and absorbance at 330 nm have a linear regression with an R^2 of 0.3863. DOC and absorbance at 280 nm have a linear regression with an R^2 of 0.4642. The following linear regression illustrates the nature of the negative relationship between temperature and a direct measure of DOC concentration in ppm (Figures 9). This regression only partly explains the variation in the data (R^2 = 0.1274).

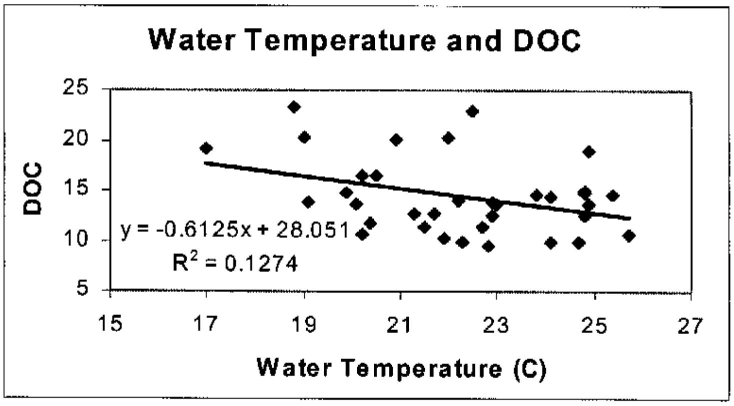


Figure 9. Shows the linear relationship between temperature and DOC concentration (R^2 = 0.1274). Interestingly enough, the linear regressions expressing the relationship between temperature and absorbance at 330 nm and between temperature and absorbance at 280 nm showed that temperature was more closely related to these measures than to DOC directly (R^2 = 0.3863, R^2 = 0.4642).

Conductivity and pH share a unique relationship. Conductivity is positively correlated with groundwater inputs into bodies of water, which are generally low in pH and DOC concentration. The linear regression of conductivity and pH show that it has a negative correlation at the 7 sites along Tenderfoot Creek and Brown Creek (Figure 10).

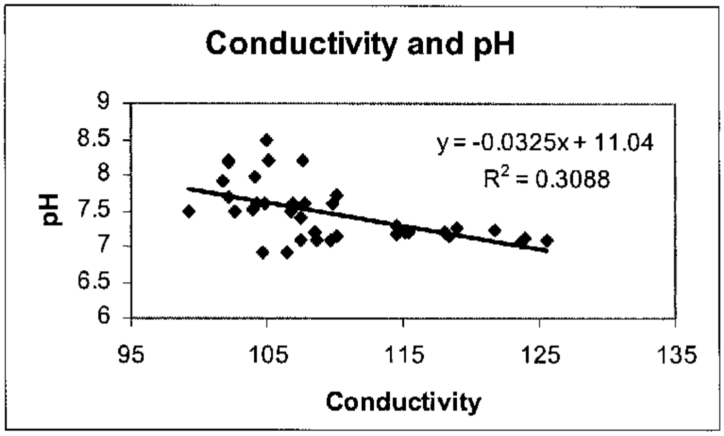


Figure 10. Shows the linear regression, y = -0.0325x + 11.04, and the extent at which the line represents the variation in the data (R^2 = 0.3088).

pH shows an interesting correlation with DOC concentrations. The regression, y = -4.1077x + 45.194, has an R^2 of 0.2065 (Figure 13). The relationship between DOC and absorbance at 330 nm and the relationship between DOC and absorbance at 280 nm are very close (Figures 14 and 15). This was expected because each is a measure of forms of DOC concentrations in solution. The linear regression between DOC and absorbance at 330 explains a majority of the variation in the data ($R^2 = 0.5185$). The linear regression between DOC and absorbance at 280 nm is not much worse than that ($R^2 = 0.4196$)

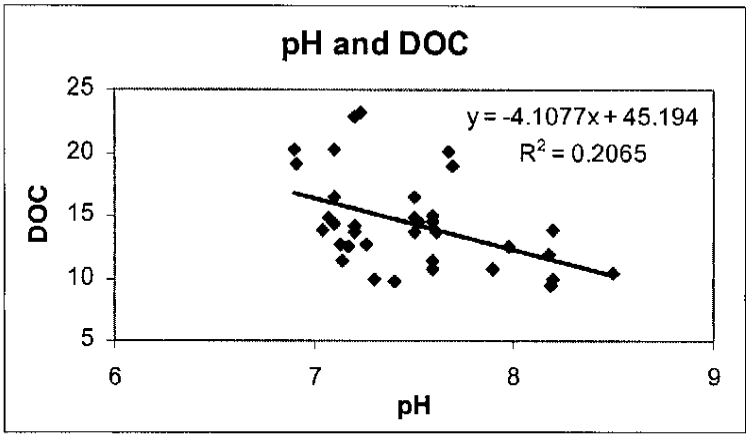
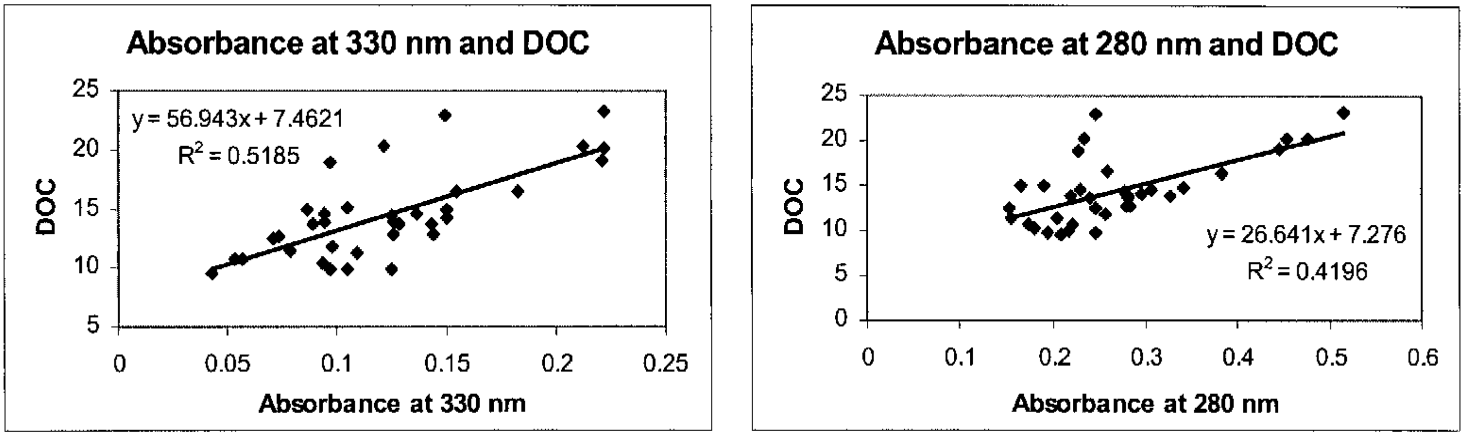


Figure 13. Shows the linear relationship between pH and DOC ($R^2 = 0.2065$).



Figures 14 and 15. Show the linear regression between DOC and absorbance at 330 nm ($R^2 = 0.5185$) and the linear relationship between DOC and absorbance at 280 nm ($R^2 = 0.4196$).

DISCUSSION

Water Characteristics and their Impacts on DOC Concentration

The most unexpected trend in the data was the correlation between water temperature and the various measurements of DOC (absorbance at 330 nm, absorbance at 280 nm, and DOC in ppm). Groundwater could be related to this trend because groundwater generally has a lower temperature than surface water and is correlated with a high conductivity. Conductivity between the two sites is related to pH through a negative correlation and has a weak positive correlation with DOC concentrations (Table 1). So, one would expect a site with a lower temperature to have a higher conductivity, a lower pH, and a higher DOC concentration. This prediction is supported by the data provided by Brown Creek and Tenderfoot Creek. Brown Creek sites have lower temperatures, higher conductivities, lower pHs, and higher DOC concentrations than Tenderfoot Creek sites, except for TFC3.

Despite its support at the site, this prediction is potentially controversial because groundwater is normally low in DOC concentrations (Kaplan and Newbold, 1993). A site with a high amount of groundwater flow should also experience lower DOC concentrations and this is normally true. However, the streams also received water flow from soil water inputs, which have very high concentrations of DOC. If Brown Creek were associated with extensive lengths of wetlands (and it is), soil water inputs could raise DOC concentrations without a significant change in temperature or conductivity.

Description of the Sites and Areas of Interest for Further Studies

Since the purpose of this study was to collect preliminary data for a larger project, a description of the streams will be most beneficial here. Tenderfoot Creek flows out of Tenderfoot Lake, a mesotrophic lake with a pH of 8.2, but has a different water chemistry only a quarter of a mile downstream. There are a few general trends in water chemistry along Tenderfoot Creek: (1) water temperature increased from TFL to TFC2, but decreased at TFC3; (2) conductivity increased from TFL to TFC2, but decreased at

TFC3; (3) pH decreased from TFL to TFC1, but remained relatively constant through TFC3; and (4) DOC concentrations increased through the studied length of Tenderfoot Creek. Although TFC1 and TFC2 are similar in water chemistry, there is a substantial change in water chemistry between TFC2 and TFC3. DOC inputs in this region should receive the most attention in future research on Tenderfoot Creek.

Brown Creek flows out of Kickapoo Lake and meets with another stream flowing out of Brown Lake. An interesting area for further research would be to look at the water chemistry of these separate streams and compare them to the water chemistry of Brown Creek south of the junction. There is one interesting trend in the sites at Brown Creek: (1) BCAS has a lower DOC concentration than BC. The most plausible explanation for this is that there is more soil water draining into Brown Creek in the region between BCAS and BC. BCCS, a small stream draining into Brown Creek, is one source of soil water between these two sites. It has a higher concentration of DOC than BCAS. BCCS is probably one of many sources of soil water that makes the DOC concentration at BC greater than the DOC concentration at BCAS. This area would be interesting for further research along Brown Creek.

CONCLUSION

The dynamics that affect DOC concentration in streams are important in understanding the aquatic ecosystems of streams. Many studies have looked at the importance of DOC to stream ecosystems and many studies have looked at ways in which DOC enters streams. However, there has never been a study that combines the two by looking at the inputs of DOC into a specific stream and the subsequent effect on stream chemistry. This study did not even begin to address this complicated problem, but it did provide a preliminary step in the process.

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INTRODUCTION

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As a consequence, wetland hydrology is vital in understanding the inputs of soil water with respect to DOC concentration in the streams of northern Wisconsin. Most wetlands associated with the streams at UNDERC are peatlands, which arise because the decomposition rate of organic matter is lower than productivity in this area. As a consequence, organic matter builds up over the years and forms deep deposits of peat. The hydrology of peatlands is interesting because there are greater groundwater flow rates through the uppermost part of the peat column (Schiff et al., 1998). The greater groundwater flow and subsequent leaching of DOC in the uppermost 0.5m of the peat column explains the lower concentration of DOC in that layer (Schiff et al., 1998). This phenomenon is illustrated in Figure 1.

The hydrology in the uppermost portion of the peat column is especially important for stream chemistry. In areas where wetlands are in close proximity to a stream, the top 0.5m of peat provides most of the soil water to the stream. Figure 2 clearly illustrates how this is important to DOC concentrations in streams. The wet conditions of a nearby wetland expand the surface of the seepage face, which provides the stream with DOC from nearby soils. At UNDERC, the nearby soils of the seepage face consist of the upper layer of peat.

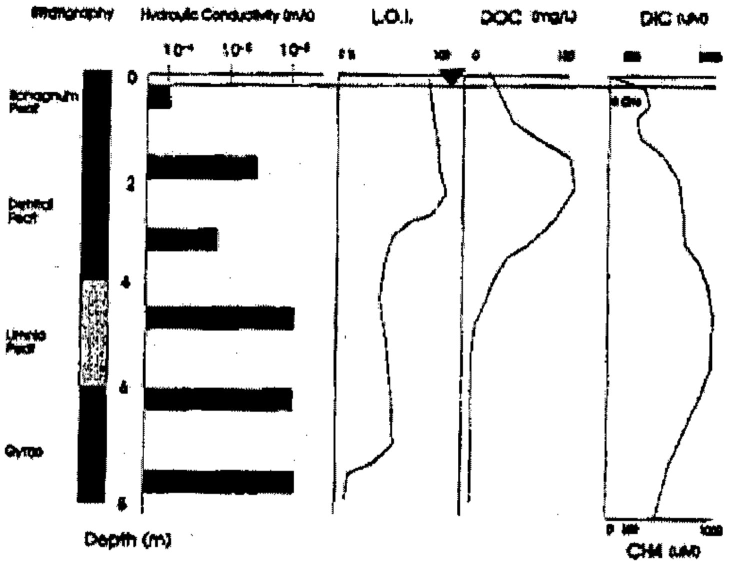


Figure 1. Shows that in the upper 0.5m of peat the higher conductivity is related to lower DOC concentrations. This situation is created by higher water flow in the upper layer of peat, which results in substantial leaching of DOC. (Figure 2 is from Schiff et al., 1998.)

This study contains preliminary research on DOC levels in two streams at the University of Notre Dame Environmental Research Center: (1) Tenderfoot Creek and (2) Brown Creek. It provides limited information on the following characteristics that relate to the interaction between groundwater inputs of DOC and soil water inputs of DOC:

(1) water temperature, which can indicate the amount of groundwater entering a stream even though there are other factors affecting temperature;
(2) conductivity, which has a positive correlation with groundwater inputs;
(3) pH, which should be negatively correlated with DOC concentrations;
(4) the DOC concentration of the water at each site in ppm,
(5) absorbance at 330 nm, which should correlate closely with DOC concentrations;
(6) and absorbance at 280 nm, which reflects the aromaticity of organic compounds.

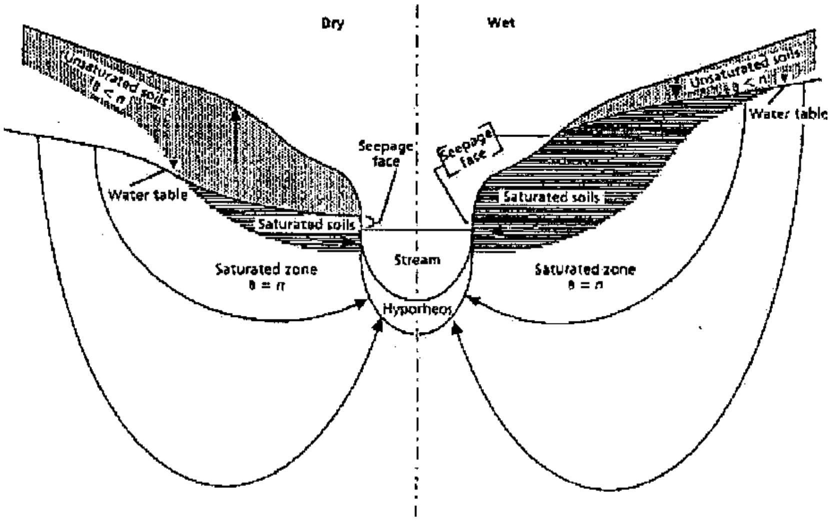


Figure 2. Shows expansion of DOC inputs in wet conditions through the saturated soils of the seepage face. The streams that were studied at UNDERC, Tenderfoot Creek and Brown Creek are associated with wetlands that represent the wet conditions in this figure. (Figure is from Kaplan and Newbold, 1993.)

MATERIALS AND METHODS

Description of the Sites

Sampling was conducted at seven sites chosen for easy access along two streams that flow through the University of Notre Dame's Environmental Research Center (UNDERC). The streams were chosen to show distinct differences in DOC content, pH and conductivity. Tenderfoot Creek is a relatively clear stream flowing north from its source, Tenderfoot Lake. It should reflect the water chemistry of Tenderfoot Lake at its source, but its water chemistry should change as it becomes associated with fens further downstream. Four sites were sampled along Tenderfoot Creek: (1) on Tenderfoot Lake near the wet lab (TFL), (2) at a bridge approximately a quarter-mile downstream from the source of the stream (TFC1), (3) at a bridge approximately three miles further downstream (TFC2), and (4) at another point 10 miles downstream after interactions with wetlands (TFC3).

Brown Creek has a substantial tan color and flows from Kickapoo Lake to the southwest until it reaches Palmer Lake. Kickapoo Lake is a eutrophic lake that has tan water because of moderate DOC concentrations. It would have been interesting to study Brown Creek near its source, but the difficulty of traveling along the stream limited sampling to the last half mile. Despite these limitations, sites were chosen in areas where wetlands could have altered water chemistry. The three sites sampled along Brown Creek were (1) where it flows into Palmer Lake (BC), (2) a small stream emptying into Brown Creek from a Cedar Swamp one quarter mile upstream (BCCS), (3) and at an Alder Swamp further upstream from there (BCAS).

Water Sampling

Each of the seven sites was sampled once in the morning for five consecutive days. Extracting water from the streams was done in a way that limited outside influences on water chemistry and DOC levels. Samples were taken six inches below the surface with a one liter bottle at the end of a five foot pole to prevent contamination and avoid photodegradation of DOC. All samples were transported to filtering equipment in the shade with a six-liter plastic container, which was rinsed with one liter of water from the site and then filled with two liters of sample for filtering. Temperature, pH, and conductivity were measured on-site before filtering. Temperature and conductivity were measured with an Orion conductivity meter (model 122). Temperature was measured in degrees Celsius and conductivity was measured at 199.99 μS/cm. pH was measured with a Orion portable pH meter (model 290 A). When temperature, pH and conductivity were effectively measured, the stream water was filtered through acid-washed GF/F filters into a 125 mL bottle, which was acid-washed and baked before use. Bottles from each site were placed on ice in a sealed cooler to prevent microbial action and photodegradation during transport to a refrigerator in the lab.

DOC Measurements

The samples were kept in the refrigerators at the Jerry Hank laboratory at UNDERC until they could be taken to the University of Notre Dame to measure absorbance at 280 nm, absorbance at 330 nm, and DOC concentrations in ppm.

Absorbance was measured with a Fischer UV-VIS machine and DOC was measured by a Hewlett-Packard TOC Analyzer in ppm.

Data Analysis

All data was analyzed through SYSTAT to create matrixes of pairwise comparison probabilities for each measured characteristic of water chemistry (temperature, conductivity, pH, absorbance at 330 nm, absorbance at 280 nm, and DOC concentration) between the seven sites. SYSTAT was also used to examine the correlation between the six water characteristics through a Pearson correlation matrix.

RESULTS

Water Temperature

Although there were no distinct differences in water temperature between the sites on Tenderfoot Creek and the sites on Brown Creek, there are differences in water temperature between the sites on Brown Creek (Figure 3). The temperature of water at BCCS was significantly lower (19.3 ± 1.87 °C) than the temperature at BC and BCAS (22.08 ± 0.92 °C, $p = 0.01$; 22.17 ± 1.48 °C, $p = 0.008$; respectively). There are also differences in water temperature between the sites on Tenderfoot Creek. The temperature at TFC3 was significantly lower (20.55 ± 0.49 °C) than the temperature at TFC2 (23.6 ± 2.03 °C, $p = 0.038$). If there had been more replicates, the temperature at TFC3 would most likely have been significantly lower than the temperature at TFC1 and TFL (23.3 ± 2.03 °C, $p = 0.056$; 23.1 ± 1.91, $p = 0.083$).

Conductivity

Overall, the sites on Tenderfoot Creek, except for TFC2, are significantly lower in conductivity than the sites on Brown Creek (Figure 4). BC (114.1 ± 6.50 μS/cm) has a conductivity that is significantly lower than the conductivity at TFC1, TFC3, and TFL

(104.5 ± 1.40 μS/cm, p = 0.003; 100.8 ± 2.05 μS/cm, p = 0.003; 104.0 ± 2.33 μS/cm). BCAS (115.8 ± 6.33 μS/cm) has a conductivity that is significantly lower than the conductivity at TFC1, TFC2, TFC3, and TFL (104.5 ± 1.40 μS/cm, p = 0.001; 109.4 ± 2.85 μS/cm, p = 0.040; 100.8 ± 2.05 μS/cm, p = 0.001; 104.0 ± 2.33 μS/cm, p = 0.000). BCCS has a conductivity that is significantly lower than the conductivity at TFC1, TFC3, and TFL (104.5 ± 1.40 μS/cm, p = 0.003; 100.8 ± 2.05 μS/cm, p = 0.003; 104.0 ± 2.33 μS/cm, p = 0.002).

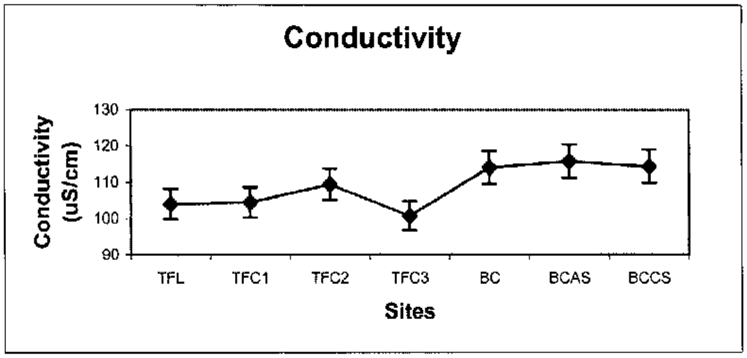


Figure 4. Shows the conductivity for 7 sites along Tenderfoot Creek and Brown Creek.

pH

The sites on Tenderfoot Creek have a significantly higher pH than the sites at Brown Creek (Figure 5). TFC1 (7.6 ± 0.17) has a significantly higher pH than BC, BCAS, and BCCS on Brown Creek (7.2 ± 0.070, p = 0.000; 7.1 ± 0.052, p = 0.000; 7.1 ± 0.16, p = 0.000). TFC2 (7.5 ± 0.15) has a significantly higher pH than BC, BCAS, and BCCS (7.2 ± 0.070, p = 0.000; 7.1 ± 0.052, p = 0.000; 7.1 ± 0.16, p = 0.000). TFC3 (7.6 ± 0.13) has a significantly higher pH than BC, BCAS, and BCCS (7.2 ± 0.070, p = 0.001; 7.1 ± 0.052, p = 0.000; 7.1 ± 0.16, p = 0.000). TFL (8.2 ± 0.19) has a significantly higher pH than BC, BCAS, and BCCS (7.2 ± 0.070, p = 0.000; 7.1 ± 0.052, p = 0.000; 7.1 ± 0.16, p = 0.000). It is interesting that TFL, the Tenderfoot Lake site, has a pH that is significantly higher than the pH at TFC1, TFC2, and TFC3 (7.6 ± 0.17, p = 0.000; 7.5 ± 0.15, p = 0.000; 7.6 ± 0.13, p = 0.000).

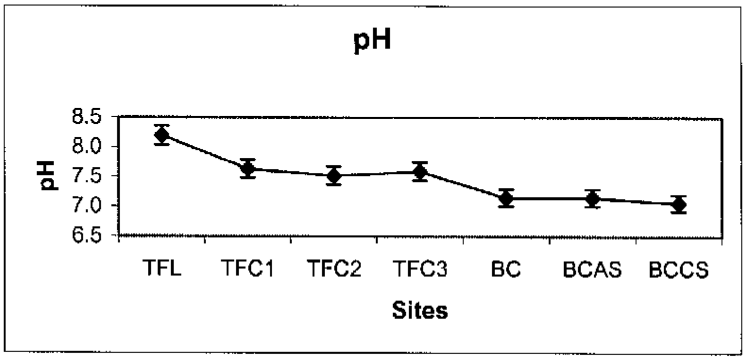


Figure 5. Shows the pH at 7 sites along Tenderfoot Creek and Brown Creek.

Absorbance at 330 nm

The absorbance at 330 nm shows two interesting trends in the data (Figure 6). One is that the sites further downstream on Tenderfoot Creek have a higher absorbance. Although this trend was not shown to be significant in all cases, it was most likely a result of a small number of replicates: TFL (0.080 ± 0.025), TFC1 (0.083 ± 0.017), TFC2 (0.113 ± 0.020), and TFC3 (0.203 ± 0.028). The other trend is that Brown Creek sites have a higher absorbance at 330 nm than Tenderfoot Creek sites. This does not include TFC3, which has the highest absorbance of all sites with 0.203 ± 0.025. BC (0.136 ± 0.19) has a significantly higher absorbance than TFL and TFC1 (0.080 ± 0.025, p = 0.008; 0.083 ± 0.017, p = 0.011). BCAS (0.128 ± 0.030) has a significantly higher absorbance than TFL and TFC1 (0.080 ± 0.025, p = 0.024; 0.083 ± 0.017, p = 0.017). BCCS has a significantly higher absorbance than TFL, TFC1, and TFC2 (0.080 ± 0.025, p = 0.000; 0.083 ± 0.017, p = 0.000; 0.113 ± 0.020, p = 0.007).

It is important to note that there are significant differences in the absorbance at 330 nm between sites along the same stream. The absorbance at 330 nm of BCAS (0.13 ± 0.030) is significantly lower than the absorbance at 330 nm of BCCS (0.17 ± 0.061, p = 0.040). Along Tenderfoot Creek, TFC3 is significantly distinct from TFC1, TFC2, and TFL (0.083 ± 0.017, p = 0.000; 0.11 ± 0.020, p = 0.002; 0.80 ± 0.025, p = 0.000) with an absorbance of 0.20 ± 0.028 at 330 nm.

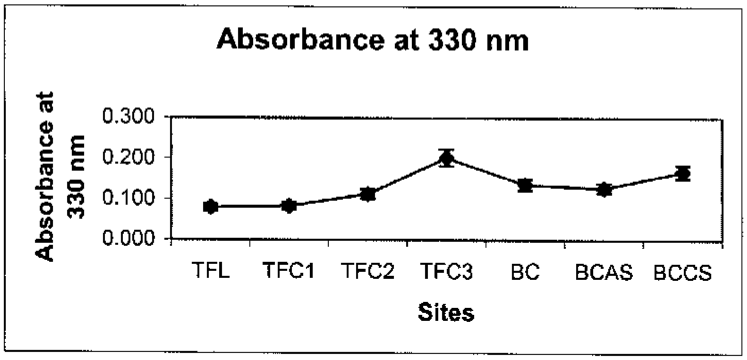


Figure 6. Shows the absorbance at 330 nm for the 7 sites along Tenderfoot Creek and Brown Creek

Absorbance at 280 nm

The data for absorbance at 280 nm is more problematic than the data for absorbance at 330 nm (Figure 7). Despite a low number of replicates, there seems to be a trend of increasing absorbance on Tenderfoot Creek as sites get further downstream: TFC1 (0.194 ± 0.042), TFC2 (0.245 ± 0.050), and TFC3 (0.417 ± 0.031). TFL (0.205 ± 0.040) has a higher absorbance than TFC1, but this difference is not significant. The data for absorbance at 280 nm provides less evidence that Brown Creek has a higher absorbance overall than Tenderfoot Creek.

Although it is difficult to show distinct trends with this data, there are significant differences between sites along the same stream. Along Brown Creek, BCCS has an absorbance at 280 nm (0.39 ± 0.11), which is significantly greater than the absorbance at BC and BCAS (0.25 ± 0.029, $p = 0.000$; 0.29 ± 0.039, $p = 0.008$). Along Tenderfoot Creek, TFC3 has an absorbance at 280 nm (0.42 ± 0.050) that is significantly greater than the absorbance at TFC1, TFC2, and TFL (0.19 ± 0.040, $p = 0.000$; 0.24 ± 0.042, $p = 0.001$; 0.21 ± 0.030, $p = 0.000$).

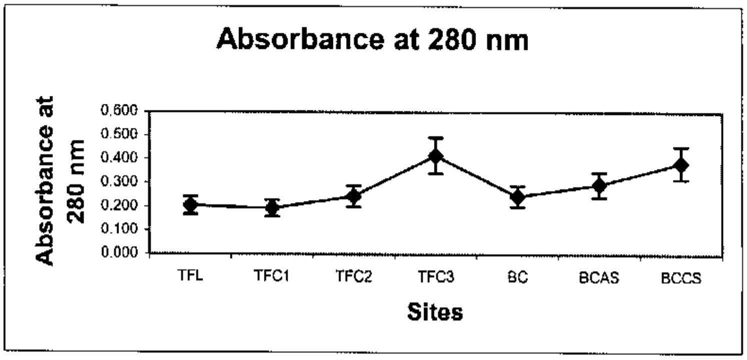


Figure 7. Shows the absorbance at 280 nm for 7 sites along Tenderfoot Creek and Brown Creek.

DOC

The data for DOC shows an increasing concentration of DOC further downstream on Tenderfoot Creek: TFL (11.01 ± 1.74 ppm), TFC1 (13.05 ± 3.43 ppm), TFC2 (13.65 ± 2.61 ppm), and TFC3 (18.30 ± 1.62 ppm). However, this trend was not significant between sites because of a lack of replicates. The lack of replicates created a large problem in determining significant differences between sites along the same creek. There is no significant difference in TOC among the sites at Brown Creek (Figure 8). However, there would most likely be a significant difference between the dissolved organic carbon at BCAS and BCCS if there were more replicates (13.7 ± 1.00; 17.2 ± 4.31, $p = 0.073$). Along Tenderfoot Creek, TFC3 (18.3 ± 2.61) was significantly different from TFC1 and TFL in terms of TOC (13.0 ± 1.74, $p = 0.048$; 11.0 ± 1.62, $p = 0.008$). TFC3 would probably have a significantly greater concentration of TOC than TFC2 if there were more replicates (13.7 ± 3.43, $p = 0.081$).

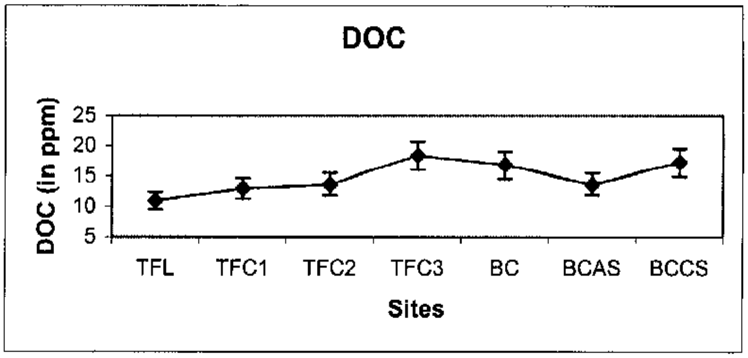


Figure 8. Shows the DOC concentrations for 7 sites along Tenderfoot Creek and Brown Creek.

The Correlation between Water Characteristics

Pearson Correlation Matrix

	Temperature	Conductivity	pH	UV-Vis 330	UV-Vis 280	DOC
Temperature	1.000					
Conductivity	-0.323	1.000				
pH	0.352	-0.565	1.000			
UV-Vis 330	-0.621	0.288	-0.502	1.000		
UV-Vis 280	-0.681	0.234	-0.470	0.887	1.000	
DOC	-0.357	0.194	-0.431	0.722	0.647	1.000

Table 1. This table contains a correlation matrix examining the interactions between 6 different characteristics the two study streams at UNDERC (Brown Creek and Tenderfoot Creek).

Temperature had a strong negative correlation with absorbance at 330 nm and absorbance at 280 nm (R = -0.621, R = -0.681), but only had a weak negative correlation with DOC (R = -0.357) (Table 1). Conductivity had a moderately strong negative correlation with pH (R = -0.565). pH had moderate negative correlation's with absorbance at 330 nm, absorbance at 280 nm, and DOC (R = -0.502, R = -0.470, R = -0.431). Absorbance at 330 nm had a very strong positive correlation with absorbance at 280 nm (R = 0.887). DOC had a strong positive correlation with both absorbance at 330 nm and absorbance at 280 nm (R = 0.722, R = 0.647).

Linear Regressions

The strength of the relationship between temperature and the measurements of DOC was unexpected. DOC and absorbance at 330 nm have a linear regression with an R^2 of 0.3863. DOC and absorbance at 280 nm have a linear regression with an R^2 of 0.4642. The following linear regression illustrates the nature of the negative relationship between temperature and a direct measure of DOC concentration in ppm (Figures 9). This regression only partly explains the variation in the data (R^2 = 0.1274).

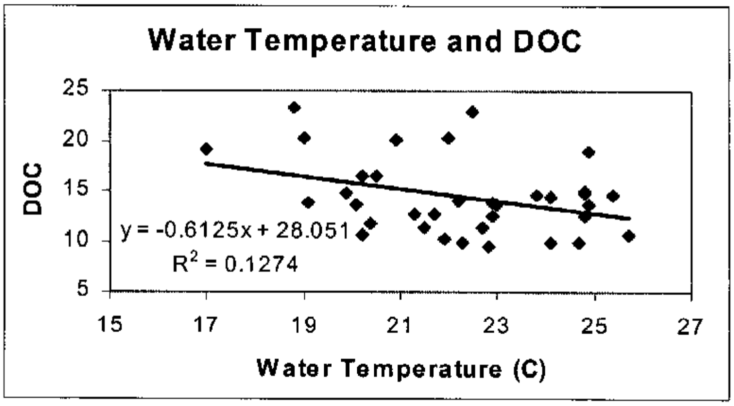


Figure 9. Shows the linear relationship between temperature and DOC concentration (R^2 = 0.1274). Interestingly enough, the linear regressions expressing the relationship between temperature and absorbance at 330 nm and between temperature and absorbance at 280 nm showed that temperature was more closely related to these measures than to DOC directly (R^2 = 0.3863, R^2 = 0.4642).

Conductivity and pH share a unique relationship. Conductivity is positively correlated with groundwater inputs into bodies of water, which are generally low in pH and DOC concentration. The linear regression of conductivity and pH show that it has a negative correlation at the 7 sites along Tenderfoot Creek and Brown Creek (Figure 10).

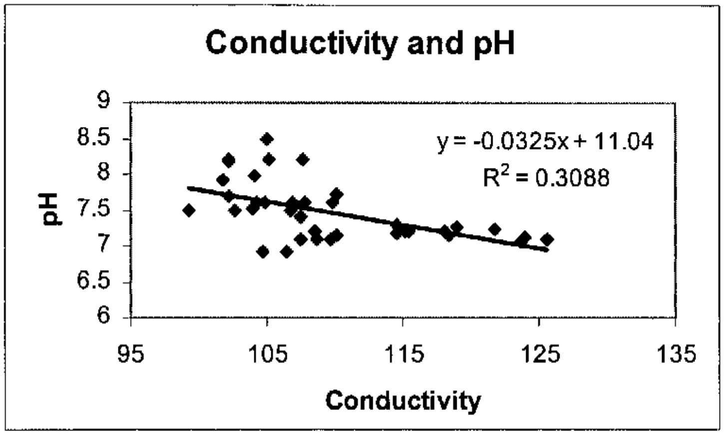


Figure 10. Shows the linear regression, y = -0.0325x + 11.04, and the extent at which the line represents the variation in the data (R^2 = 0.3088).

pH shows an interesting correlation with DOC concentrations. The regression, y = -4.1077x + 45.194, has an R^2 of 0.2065 (Figure 13). The relationship between DOC and absorbance at 330 nm and the relationship between DOC and absorbance at 280 nm are very close (Figures 14 and 15). This was expected because each is a measure of forms of DOC concentrations in solution. The linear regression between DOC and absorbance at 330 explains a majority of the variation in the data ($R^2 = 0.5185$). The linear regression between DOC and absorbance at 280 nm is not much worse than that ($R^2 = 0.4196$)

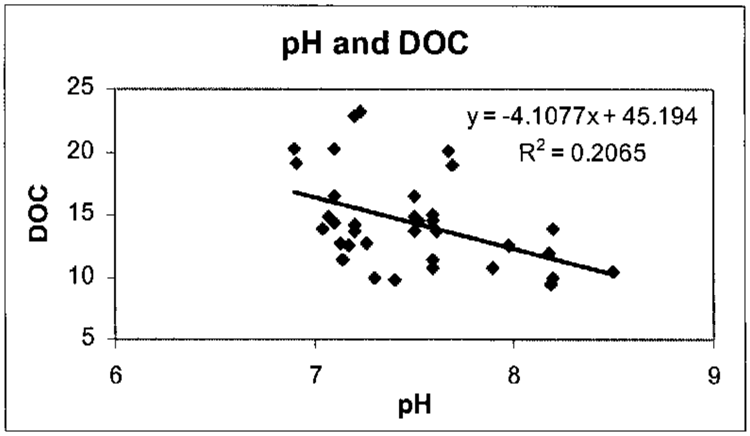
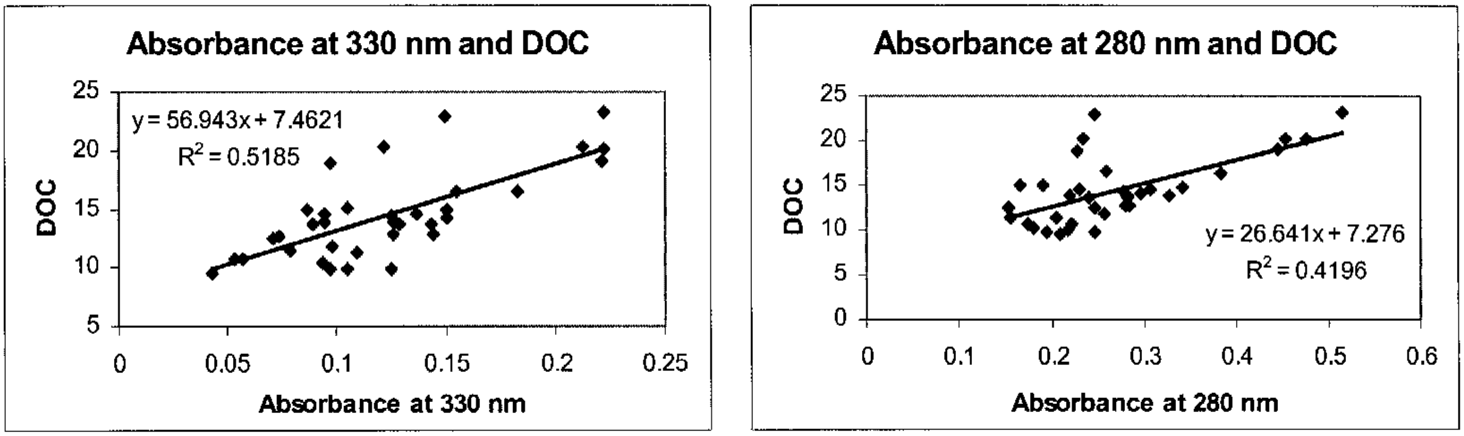


Figure 13. Shows the linear relationship between pH and DOC ($R^2 = 0.2065$).



Figures 14 and 15. Show the linear regression between DOC and absorbance at 330 nm ($R^2 = 0.5185$) and the linear relationship between DOC and absorbance at 280 nm ($R^2 = 0.4196$).

DISCUSSION

Water Characteristics and their Impacts on DOC Concentration

The most unexpected trend in the data was the correlation between water temperature and the various measurements of DOC (absorbance at 330 nm, absorbance at 280 nm, and DOC in ppm). Groundwater could be related to this trend because groundwater generally has a lower temperature than surface water and is correlated with a high conductivity. Conductivity between the two sites is related to pH through a negative correlation and has a weak positive correlation with DOC concentrations (Table 1). So, one would expect a site with a lower temperature to have a higher conductivity, a lower pH, and a higher DOC concentration. This prediction is supported by the data provided by Brown Creek and Tenderfoot Creek. Brown Creek sites have lower temperatures, higher conductivities, lower pHs, and higher DOC concentrations than Tenderfoot Creek sites, except for TFC3.

Despite its support at the site, this prediction is potentially controversial because groundwater is normally low in DOC concentrations (Kaplan and Newbold, 1993). A site with a high amount of groundwater flow should also experience lower DOC concentrations and this is normally true. However, the streams also received water flow from soil water inputs, which have very high concentrations of DOC. If Brown Creek were associated with extensive lengths of wetlands (and it is), soil water inputs could raise DOC concentrations without a significant change in temperature or conductivity.

Description of the Sites and Areas of Interest for Further Studies

Since the purpose of this study was to collect preliminary data for a larger project, a description of the streams will be most beneficial here. Tenderfoot Creek flows out of Tenderfoot Lake, a mesotrophic lake with a pH of 8.2, but has a different water chemistry only a quarter of a mile downstream. There are a few general trends in water chemistry along Tenderfoot Creek: (1) water temperature increased from TFL to TFC2, but decreased at TFC3; (2) conductivity increased from TFL to TFC2, but decreased at

TFC3; (3) pH decreased from TFL to TFC1, but remained relatively constant through TFC3; and (4) DOC concentrations increased through the studied length of Tenderfoot Creek. Although TFC1 and TFC2 are similar in water chemistry, there is a substantial change in water chemistry between TFC2 and TFC3. DOC inputs in this region should receive the most attention in future research on Tenderfoot Creek.

Brown Creek flows out of Kickapoo Lake and meets with another stream flowing out of Brown Lake. An interesting area for further research would be to look at the water chemistry of these separate streams and compare them to the water chemistry of Brown Creek south of the junction. There is one interesting trend in the sites at Brown Creek: (1) BCAS has a lower DOC concentration than BC. The most plausible explanation for this is that there is more soil water draining into Brown Creek in the region between BCAS and BC. BCCS, a small stream draining into Brown Creek, is one source of soil water between these two sites. It has a higher concentration of DOC than BCAS. BCCS is probably one of many sources of soil water that makes the DOC concentration at BC greater than the DOC concentration at BCAS. This area would be interesting for further research along Brown Creek.

CONCLUSION

The dynamics that affect DOC concentration in streams are important in understanding the aquatic ecosystems of streams. Many studies have looked at the importance of DOC to stream ecosystems and many studies have looked at ways in which DOC enters streams. However, there has never been a study that combines the two by looking at the inputs of DOC into a specific stream and the subsequent effect on stream chemistry. This study did not even begin to address this complicated problem, but it did provide a preliminary step in the process.

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Schiff, Sherry et al. 1998. "Precambrian Shield Wetlands: Hydrologic Control of the Sources and Export of Dissolved Organic Matter," *Climatic Change* 40: 167-188.