Modeling the evolution of in-stream dissolved organic carbon flux processing from Agricultural land use

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Abstract:

It has been recently reported that U.S. Rivers and Streams are saturated with carbon that cause substantial more release of carbon dioxide into the atmosphere than previously thought. A large proportion of riverine carbon is in the form of dissolved organic carbon (DOC) that has significant impacts on coastal ecology and carbon cycling processes. This paper presents a GIS-based spatial and temporal analysis of the terrestrial DOC source dynamic, and the fate and transport processes from landscape to stream network routing to rivers and lakes through hydrological connectivity. The study was based on a large data set collected monthly in multiple years and outlets of 64 sub-basins in watersheds of three rivers: Connecticut, Chippewa and Neponset rivers in U.S.A. DOC concentrations were generated spatially and temporally for the watersheds with the aid of the Soil & Watershed Analysis Tool (SWAT). Our results demonstrate that landscape ecology can be quantitatively linked to in-stream DOC concentrations through several variables: stream flow, land use type, vegetation density, annual surface temperature, and soil properties. Relatively, in-stream DOC concentrations drained from agricultural land use flux more DOC to stream flow. Even small proportions of wetland can generate much higher DOC to streams and rivers.

Introduction

Operationally, dissolved organic carbon (DOC) is defined as the organic compounds in water that pass through a 0.45 micrometers precombusted glass fiber filter (Knap et al., 1994). Generally, DOC forms from the decomposition of dead organic matter that enriches the soil when water, usually from rainfall events, contacts the highly organic soils, also referred to as Dissolved Organic Matter or DOM. “Being soluble, DOM is a significant means by which nutrients are transported across landscapes” (Wright et al., 2012) and resultantly, the DOM turns into DOC components, which become mobile and drain into rivers and lakes. Research indicates that “DOC in marine and freshwater systems is one of the greatest cycled reservoirs of organic matter on Earth” (Ogawa et al., 2003) and marine sources hold approximately as much carbon as is available in atmospheric carbon dioxide (Hedges, 1992). Ironically, “the origin, function, and fate of DOC in stream flow are not well-understood” (Tian et al., 2012). Furthermore, “the importance of small streams in relation to carbon budgets is not well understood because of a lack of globally-distributed data, especially from streams draining agricultural landscapes” (Griffiths et al., 2011). Discussed later, previous studies also failed to explore the seasonal variations of DOC related to agricultural runoff. Studies have established that while some DOC is beneficial to the environment, DOC can become too concentrated and allow detrimental effects to occur in the surrounding environment. DOC may also interact with agricultural pesticides; however, the effects of these interactions are not clear. Because high concentrations of DOC may be detrimental, this study tested in-stream DOC concentration and seasonality of agricultural stream DOC, especially because DOC is an indicator of environmental threats.

Two goals for this study were to: 1) quantitatively identify how land use type controls the spatial and seasonal variation of terrestrial DOC in the Chippewa River and to 2) build a watershed-based GIS model to access DOC contribution from the hydrological, biological, and physical units displaying predominately agricultural land use. More specifically, the study objectives were to determine 1) if the variables driving DOC concentration differ among agricultural, forested, and urban land uses; and 2) if the DOC concentration throughout the Chippewa River Watershed at approximately 10 to 15 sampling sites, distributed on a sub-basin level, have seasonal variation (e.g. before harvesting and after, before snow and after, during snow melting seasons, during leaf fall seasons, and during plow and seedling season, growing season) due to natural climatic factors or due to management practices.

It was hypothesized that the variables influencing the agricultural DOC load in the Chippewa River Watershed would be significantly different from the variables influencing DOC content in urban and forested watersheds and that the agricultural sites in the Chippewa river would show significantly different seasonal variation due to the anthropogenic influence of agricultural practices and land use management.

Using DOC measurements as an indicator of watershed health and a custom calibrated Soil & Water Analysis Tool (SWAT) model, this study attempted to identify the link between stream flow and in-stream DOC concentration within a predominately agricultural watershed, mainly the Chippewa River in Isabella County, Michigan to improve understanding of the terrestrial DOC processes originating from agricultural runoff. SWAT was selected because in-stream agricultural DOC can be observed rather economically by using the SWAT model, especially for instances over time where sampling would not be possible for various reasons. By combining watershed stream flow, land use, geometric characteristics and DOC concentration, a preliminary estimation of DOC flux in the Chippewa River Watershed was produced. The SWAT model, along with statistical analysis identified the environmental factors specific to the watershed that control the spatial and seasonal variation of agricultural DOC. The watershed model accessed DOC contribution from hydrological units under the selected controlling environmental factors, identified by previous studies then verified with statistical analysis.

While DOC studies from the past exist, much is still unknown about the subject, especially concerning the link between agriculture and DOC. Previous studies have laid the foundation for this study by identifying issues related to riverine DOC and give guidelines for future studies to expand upon. This study has introduced new knowledge on the relationship between agricultural land use and in-stream DOC flux, specifically related to the agricultural growing season, while also aiding in future analysis and model calibration to slow anthropogenic contributions that may be accelerating climate change and deteriorating water quality. This study on terrestrial DOC and stream flow, focusing on agricultural seasonality, is the first of its kind. Covered in the subsequent section, this paper fist reviewed previous research indicating that DOC is particularly of concern because high concentrations may halt or negatively alter normal ecosystem growth causing a shift in normal photosynthesis, algae growth, and prevent reproduction of native species.

Literature Review

“Dissolved organic carbon (DOC) is an abundant form of organic matter in streams and rivers, and represents a large flux of organic matter from watersheds (e.g., Mulholland, 1997, 2003). “DOC is a food supplement, which supports growth of microorganisms and plays an important role in the global carbon cycle through the microbial loop, DOC is an indicator of organic loadings in streams, and supports terrestrial processing (e.g., within soil, forests, and wetlands) of organic matter (Kirchman et al., 1991), and decomposition of DOM by microorganisms can serve to release metals and nutrients to the environment. The resultant tea-colored surface waters "tends to regulate sunlight penetration into the water column and thus influences nutrients, phytoplankton, and other organisms" (Wright et al., 2012) maintaining the dynamics of the natural system. However too much penetration reduces light for photosynthesis and "decomposition of DOM by microorganisms can serve to release metals and nutrients to the environment" and also interact with pesticides from agricultural practices. Depending on factors such as buffering capacity, or the ability of an aquatic system to stabilize its acidity/alkalinity, biomass composition and amount, and water depth, DOC necessary to support an ecosystem varies by area (Bruckner, 2012) meaning it is crucial to understand how DOC should vary within an identified normal range for an area to determine if water quality and the surrounding environment face degradation. Wright et al,. 2012 notes that "all soils have organic matter dissolved in soil solution or in floodwater, but DOC concentration is generally greater in wetland and aquatic ecosystems than agricultural soils," however the study does not quantify agricultural DOC flux, making the difference in DOC concentration for agricultural streams the focus of this study since it can be deducted that high concentrations of organic carbon could indicate negative alterations of natural systems. Also, an increased leaching of DOC from the soil is coupled with an increased leaching of metal ions and their transport into surface water (Monteith et al, 2007). This allows for the conclusion that this leaching could in turn halt ecosystem growth by preventing algae to grow, which decreases photosynthesis and in turn reduces vital nutrients for fish, preventing fish from returning to reproduce. High DOC concentrations are not only bad for the aquatic environment, but the resulting decrease in water quality and transparency increases the cost of water treatment and impacts our needs for clean water. In order to protect surface water quality, it is essential to clarify the processes that lead to the dissolution and transfer of dissolved organic matter (Sucker et al. 2010).

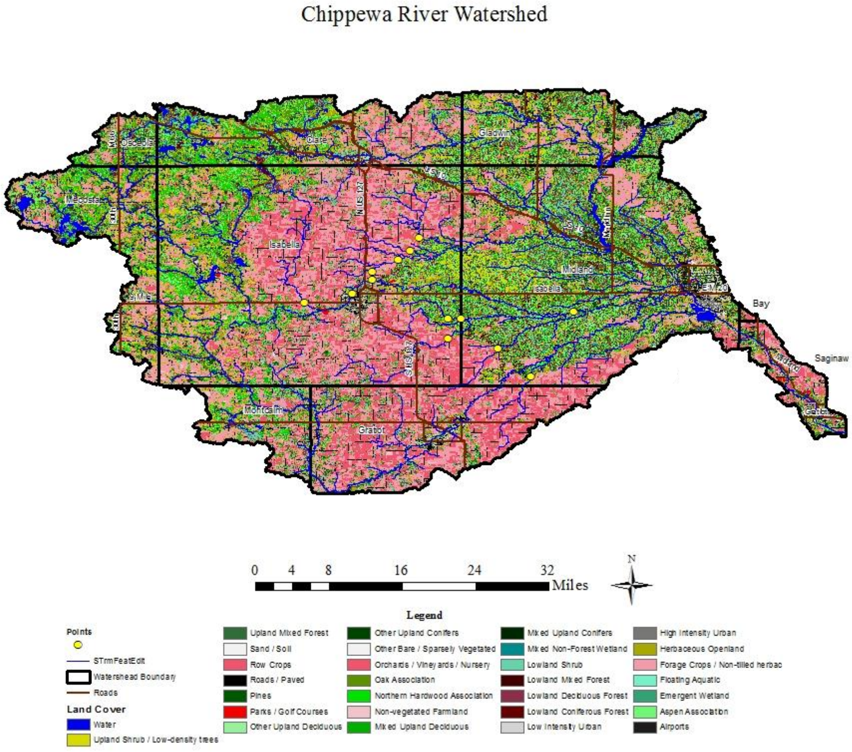
Many studies link agricultural land-use to degraded water quality including sediment, nutrient and organic loading (Jones et al., 2004; Jones and Knowlton, 2005; Monaghan et al., 2007; Valentin et al., in press). A study conducted by Griffiths et al., (2011) observed that in the agricultural Midwest, frequent dredging of streams to increase drainage efficiency has decreased channel complexity and removed in-stream structures that retain organic matter. This decrease in complexity allows DOC to move faster throughout the stream. Dai et al., (2012) notes an observed trend of river DOC increase in at least some terrestrial ecosystems, likely caused by rising temperature and atmospheric CO_2, which warrants further attention because according to Evans et al., (2005) long-term DOC increases may have wide-ranging impacts on freshwater biota, drinking water quality, coastal marine ecosystems and upland carbon balances. Brooks et al., (1999) also indicated that DOC from terrestrial sources forms the major component of the annual carbon budget in many headwater streams. Additionally, DOC may enhance the sorption and mobility of pesticides (Williams et al., 2000; Flores-Cespedes et al., 2002; Li et al., 2005) and heavy metals (Li and Shuman, 1997) and lead to drinking water quality problems (Pomes et al., 1999; Aitkenhead- Peterson et al., 2003). Given this information, this study improves the current knowledge base by studying seasonality of DOC in agricultural watersheds to determine how land use type affects DOC concentration.

Methods

Study Area

The study area was the Chippewa River, shown in figure 1 with the major land cover types, major roads, and sample sites. The watershed was predominately agricultural and both the Coldwater River and the Pine River feed the Chippewa River. The Chippewa River is located in the Lower Peninsula and cuts across Central Michigan, extending nearly 92 miles, beginning in Mecosta County and ending in Midland, flowing east into the Tittabawassee River. As a tributary of the Tittabawassee River, the Chippewa River is part of the Saginaw River drainage basin.

Figure 1: Chippewa River Watershed land cover, major roads, and sample sites

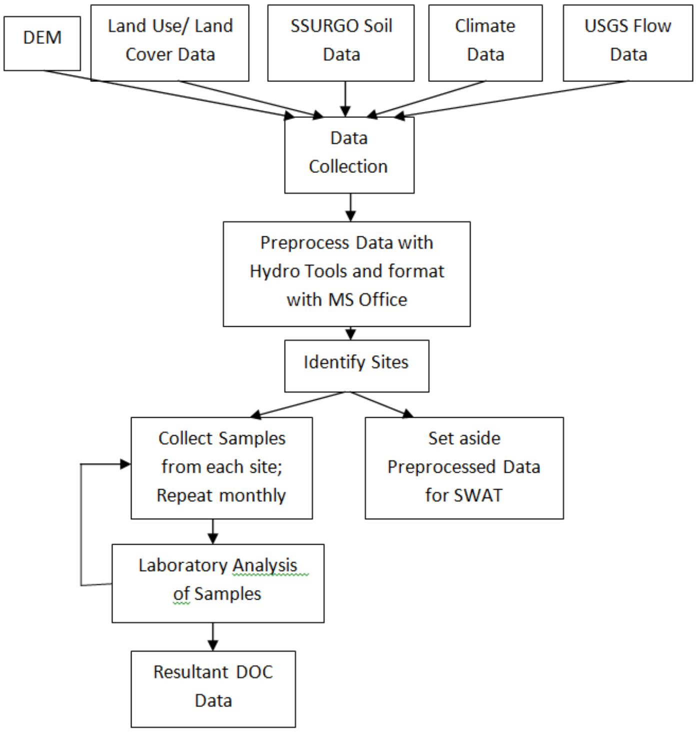


Model input data sources

The spatial data required to carry out this study included digital elevation models (DEMs), land use and land cover data, soil data, and climatic data for at least ten years. The DEMs were preprocessed in ArcGIS 10.1. Spatial soil data was obtained from the Soil Survey Geographic (SSURGO) database, which improves on previous studies use of STATSGO data. The land cover data was downloaded from the 2006 National Land Cover Data (NLCD) website. Data from the United States Geological Survey (USGS) hydrological gauge station, #04154000, within the Chippewa River, was used to obtain the sample site discharge and flow for calibrating and validating the SWAT model. The weather station data consisted of daily minimum and minimum air temperatures and daily precipitation for a period of at least ten years. Analysis of the land cover type was done on watershed sub-basins to ensure predominate agricultural cover. Sites did not have to be completely agricultural, but had to display at least 50% agricultural land use.

The area's DEM was needed to locate the area where the model would operate and aided in sample site selection by giving a DEM derived stream network. The DEM helped to delineate the watershed into sub basins. Because the Chippewa watershed had mixed land use types, "the use of sub basins in a simulation is particularly beneficial when different area of the watershed are dominated by land uses or soils dissimilar enough in properties to impact hydrology" (Neitsch et al., 2011). Furthermore, "by partitioning the watershed into sub basins, the user is able to reference different areas of the watershed to one another spatially" (Neitsch et al., 2011). Land use/land cover data also helps the user identify the predominate land use in each sub basin visually, to choose sampling sits associated with a particular land use especially when hydrological flow networks are added (to verify the derived stream networks) to help simulate

Figure 2: Data collection workflow



flow to the channel and the pathway of the channel. These inputs were necessary because "hydrologic response units are lumped land areas within the sub basin that are comprised of unique land cover, soil, and management combinations" (Neitsch et al., 2011). In addition to the above mentioned inputs, it was also important to have soil data for specific properties of each soil type as variables in the statistical analysis because soil properties impact how water flows to the stream channel. SSURGO soil data was preferred over STATSGO data because studies comparing STATSGO and SURGO models in SWAT have found that "results indicate that SWAT-SSURGO provided an overall better prediction of the discharges than SWAT-STATSGO (Wang et al., 2007). Furthermore, the weather data and drainage area were used in the hydrologic response units for climatic data to improve the accuracy of the model by simulating normal weather conditions. In particular, precipitation and stream flow were needed because "no matter what type of problem studied with SWAT, water balance is the driving force behind everything that happens in the watershed" (Neitsch et al., 2011). The need for these inputs and variables is solidified by the fact that "the climatic process modeled in SWAT consist of precipitation, air temperature, soil temperature and solar radiation" (Neitsch et al., 2011). The data collection process is illustrated in Figure 2.

Field Sampling protocols and laboratory analyses of DOC

The sample sites for this study were generated in ArcMap. Monthly field measurements were collected, taken at the outlet of sub-basins displaying predominately agriculture land use in 2012. The measurements collected were used in conjunction with the SWAT watershed model. The samples collected from the sites were then used to analyze the quantitative relationship between hydrological properties and DOC concentrations (statistical analysis or analytical modeling). Because the water samples came from base flow, samples were not taken immediately after a rainfall event, which would introduce surface flow. All samples were collected within a single 24 hour period from all sites. Cleaned 500 ml bottles were be used for collection and storage. Samples were immediately stored on ice in a cooler until arrival at the lab for immediate filtering and acidification. Water samples were filtered through precombusted glass fiber filters (nominal 0.7 µm pore size) and stored (acidified and refrigerated) until analysis for DOC content. The sample DOC concentration were measured using a Shimadzu TOC-V analyzer with high temperature combustion (Vlahos et al., 2002). Briefly, 50 µl injections of water samples were combusted at 800 °C. The DOC concentration was then calculated from the resultant CO_2 that was measured with a non-dispersive infrared detector. These field samples were used in the model as mean DOC concentration for the day on which they were collected. Monthly sampling began in October 2012 and continues through April 2013.

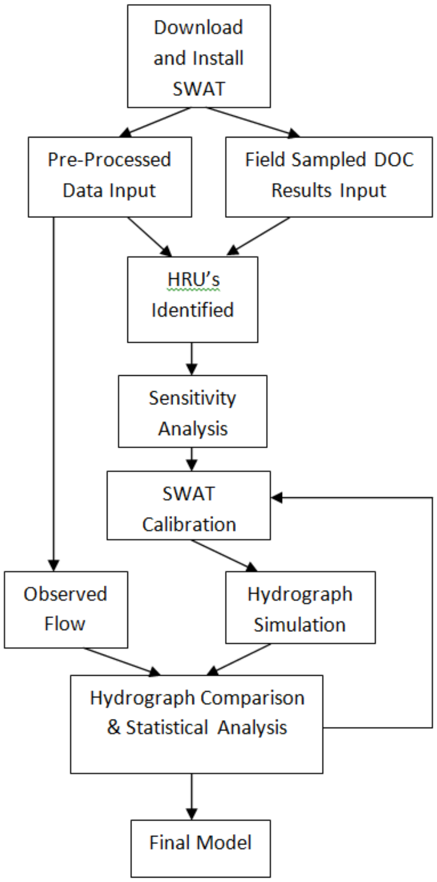
After model setup and calibration the end results of this study were compared to monthly data from the urban Neponset River watershed and from the forested Connecticut River watershed in Massachusetts (from a joint project with the University of Massachusetts-Amherst and Boston University) to understand how agricultural land use variables impact the quantity of

DOC export. The results from these watersheds have determined the controls on water quality resulting from natural and anthropogenic factors within these particular watersheds, therefore this study identifies the factors in the Chippewa river that are attributable to anthropogenic causes associated with agricultural land use.

SWAT hydrograph simulation

The SWAT methodology is shown in Figure 3. For the hydrograph simulation with SWAT, this study followed the method set forth by Tian et al., (2012) in *Using modeled runoff to study DOC dynamics in stream and river flow: A case study of an urban watershed southeast of Boston, Massachusetts* which used SWAT to simulate daily flow at each of the sub basin DOC sampling sites. The simulation of the watershed's hydrological cycle was divided into two categories: a land phase and a water or routing phase (Tian et al., 2012). The land phase described the movement of water, nutrients, pesticides, and sediments throughout the sub-watersheds (based on the hydrologic response unit—HRU) to their main channel (Sahu and Gu, 2009). At the scale of one HRU, watershed variables, such as soil properties, land use and management, climate, and topographic parameters were considered homogeneous (Arnold and Fohrer, 2005). In the water or routing phase, SWAT characterized how water moves through the water

Figure 3: Swat Methodology



channel system (Neitsch et al., 2005). The data used for the calibrating and running SWAT included SURGO 2006 soil properties, an improvement on the previous use of STATSGO 2001 data, hydrographs at gauge locations, the necessary Digital Elevation Models (DEMs), and the area's weather information. The key soil properties included runoff, infiltration, sediment and anion exchange. The key weather information included rainfall, minimum and maximum air temperature, solar radiation, wind speed and relative humidity. At least ten years of daily weather data, consisting of precipitation and minimum and maximum temperature, was needed. The study area was divided into sub-basins and hydrological response units (HRUs) by referring to the gauge stations and sample points. The sensitivity analysis ranked the top parameters. SWAT was then be manually calibrated for the parameters suggested by the Automated Sensitivity Analysis using the ArcSWAT system. The calibration was set to minimize errors between SWAT estimation and the observed runoff at the USGS gauge station for the ten years of data coverage. The runoff datasets were divided into a calibration period (the first seven years of data) and a verification period (the eighth year of data) and a sensitivity ranking was obtained. The simulated hydrographs will be evaluated against the observed daily flow from the USGS gauge station.

Tian et al. suggests that two criteria be used to assess the simulated results. First, both the simulated and the observed flow hydrographs should be plotted together with the precipitation so that the flow values' consistency with rainfall can be observed to allow a direct visual comparison. Second, the Nash-Sutcliffe efficiency index (E_{ns}), a normalized form of the sum of squares of residuals (SSR) should be used to evaluate the SWAT model performance for the Chippewa River Watershed. The Nash-Sutcliffe index (E_{ns}) describes the ability of the model to explain the variability in the data and is used as the quantitative criterion. Tian et al.

notes that a good model is one that has a good visual match to the observed data, with a value of E_{ns} close to one.

This study took the statistical analysis further by using a linear regression to test the suggested variables and additional variables found within the data sets. Variables supported by Tian et al., (2012) included soil properties such as runoff, infiltration, and sediment and anion exchange, land use and management, ten years of climate variables, such as rainfall, minimum air temperature, maximum air temperature, solar radiation, wind speed, and relative humidity. and topographic parameters. The 2009 Soil &Water Analysis Tool Theoretical Documentation lists numerous possible variables and this study will attempt to include more as suggested by the automated sensitivity analysis. Some of the variables expected for inclusion into the linear regressions are shown below in Table 1.

Table 1: Model variables for consideration and source for variable representing properties

Properties	Variables representing properties
Soil	Tian et al., (2012): Runoff, infiltration rate, sediment & anion exchange, land use and management, ground water flow, curve number for moisture condition II, soil available water capacity Evans et al., (2005): land use, nitrogen & CO_2 enrichment
Climate	Tian et al., (2012): Precipitation, minimum air temperature, maximum air temperature, solar radiation, wind speed, relative humidity, snow melt vs. surface ground runoff Evans et al., (2005): Temperature, rainfall, acid deposition
Topographic	Tian et al., (2012): Percent land cover type, high resolution vegetation density Wu et al., (2007): Plant water uptake compensation factor (EPCO)
Hydrologic	Tian et al., (2012): Stream flow, drainage area, base flow alpha factor, surface runoff lag time coefficient Wu et al., (2007): surface flow, ground water flow

	Neitsch et al., (2005): Channel water movement, channel length

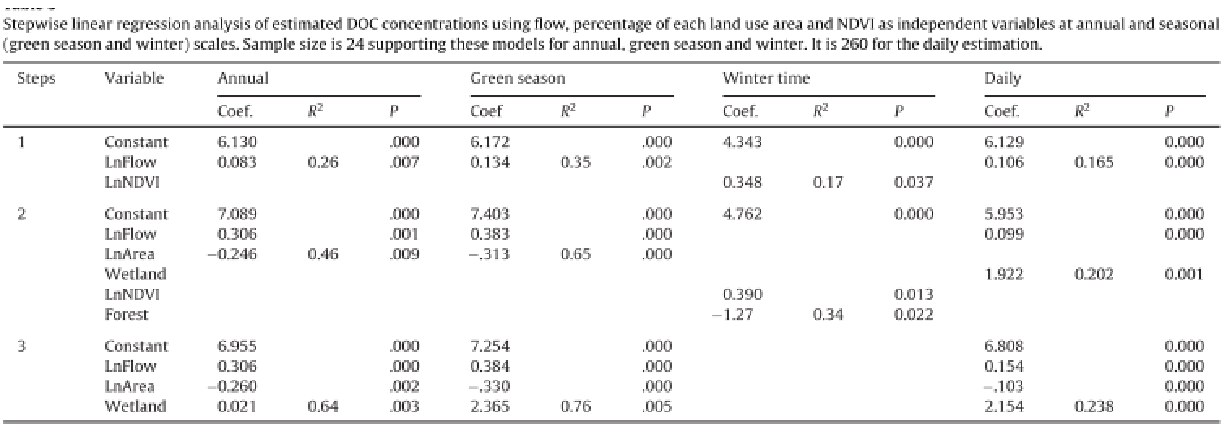
This statistical analysis expanded, with DOC concentrations as the response variable, to consider the following tentative independent variables in the multiple regressions:

> Flow velocity, in-stream water flow volumes, channel length, rate of snow melt, precipitation/ snowfall/unit area, tree cover, leaf shedding/accumulation, Manning's N (for overland flow), mean slope, sub basin size, a water quality measure, and point sources.

The variables were put into a linear regression equation in the form: $y_i = \beta_0 + \beta_{1x_{i1}} + \beta_2 x_{i2} + \ldots + \beta_k X_{ik} + \mathcal{E}_i$. Once the variables were put into the regression, these variables were checked for significance using p-values. Insignificant variables were removed from the model and the regression was refitted. Variables were also checked for collinearity using the correlation matrix and Variance Inflation Factor (VIF) $VIF_j = \frac{1}{1-R_j^2}$ where R_j^2 is the coefficient of determination from regressing x_j on the remaining explanatory variables. Highly correlated variables were eliminated to improve the model. To further assess the selection of independent variables, all possible regressions were performed using statistical software that runs best subset regression, backwards elimination, and stepwise regression, which all use a selection criteria that considers the sample error variance (S_e^2) where $s_\varepsilon^2 = \frac{SS(residual)}{n-(k+1)}$ and the adjusted coefficient of determination (R^2-adj.) where $R_{adj,k}^2 = 1 - \frac{n-1}{n-k-1}(1 - R_k^2)$. The model that had the lowest sample error variance and highest coefficient of determination was selected. The model diagnostics (residuals versus fits plot and normal probability plot) were checked to confirm the selected model's validity. If necessary, transformations were made by referring to the Box-Cox transformation technique. Splitting the original samples into two halves helped validate samples. One of the halves was used for fitting the regression model and the other half was used for model validation; all samples were used in establishing the final model.

Tian et al., (2012) findings are significant for this study because it set the guidelines for this study's method in the hydrograph simulation with SWAT. As a starting point, some of the key parameters included in the SWAT model included the same variables used in the Tian et al., (2012) study, as shown in Table 2 below that were suggested by the automated sensitivity analysis, such as the curve number for moisture condition II (CN2), the soil available water capacity in mm (Sol.AWC), the base flow alpha factor in days (Alpha.Bf), the surface runoff lag time coefficient (Surlag), the soil evaporation compensation factor (ESCO), and Manning's n for overland flow (OV.N). These parameters are model parameters calibrated for the Neponset River Watershed, and the guidelines shown are suggested ranges of parameter change based on default values. These parameters were changed within the given guideline range in the manual calibration. Further guidelines were identified at the time of calibration with the aid of the established guidelines in the SWAT 2009 Input/Output File Documentation manual at: http://swat.tamu.edu/media/19754/swat-io-2009.pdf in ("Soil and Water," 2011).

Table 2



Stepwise linear regression analysis of estimated DOC concentrations using flow, percentage of each land use area and NDVI as independent variables at annual and seasonal (green season and winter) scales. Sample size is 24 supporting these models for annual, green season and winter. It is 260 for the daily estimation.

Steps	Variable	Annual			Green season			Winter time			Daily		
		Coef.	R^2	P	Coef	R^2	P	Coef.	R^2	P	Coef.	R^2	P
1	Constant	6.130		.000	6.172		.000	4.343		0.000	6.129		0.000
	LnFlow	0.083	0.26	.007	0.134	0.35	.002				0.106	0.165	0.000
	LnNDVI							0.348	0.17	0.037			
2	Constant	7.089		.000	7.403		.000	4.762		0.000	5.953		0.000
	LnFlow	0.306		.001	0.383		.000				0.099		0.000
	LnArea	−0.246	0.46	.009	−.313	0.65	.000						
	Wetland										1.922	0.202	0.001
	LnNDVI							0.390		0.013			
	Forest							−1.27	0.34	0.022			
3	Constant	6.955		.000	7.254		.000				6.808		0.000
	LnFlow	0.306		.000	0.384		.000				0.154		0.000
	LnArea	−0.260		.002	−.330		.000				−.103		0.000
	Wetland	0.021	0.64	.003	2.365	0.76	.005				2.154	0.238	0.000

After beginning with the parameters suggested by Tian et al., (2012) this study expanded and made changes as necessary to suit the Chippewa River study area. Wu et al., (2007) results indicate that the EPCO variable appropriately reflects plant water uptake strategies under varying climatic conditions in forested watersheds. However, stream flow is not sensitive to modification of the ESCO variable (Wu & Johnston, 2007). All possible variables to make the most accurate model can be found on the SWAT website under theoretical documentation at http://twri.tamu.edu/reports/2011/tr406.pdf (Neitsch et al., 2011)

Possible Outcomes and Importance

This study takes place in three stages: (1) *in situ* sample measurement, (2) statistical analysis of the relationship between agriculture and water body DOC concentration, (3) modeling DOC flux at the sub-basin level.

The following possible methodologies were used for outcomes:

1) Present DOC seasonal variation at sample locations near sub-basin outlets in the Chippewa River watershed tributaries based on in situ data.
2) After statistically examining the relationships between in-stream DOC concentrations and agricultural land cover, a comparison between the Chippewa River and the forested Connecticut River was made and also between the Chippewa River and the urban Neponset River to understand how land use activities affect the variation of DOC. It was expected that the Chippewa River would have higher DOC variation.
3) Simulate DOC flux dynamics by using hydrological properties obtained from the SWAT GIS environment at daily or monthly intervals.

4) Conduct a scenario analysis based on the simulations from the previous step to predict DOC change in response to land use type.

Timeline

Table 3 lists the various tasks required for this study and their expected period for completion.

Table 3: Project Deadlines

Task	Deadline
Learn SWAT	May - August 2012
Data Collection	July – September 2012
Proposal Defense	October 2012
Chippewa River DOC sampling	October 2012 – April 2013
Sample Filtering	October 2012 – April 2013
SWAT Installation	December 2012
SWAT Spatial Data Input	December 2012 – January 2013
Field Data Formatted and Entered	April 2013
Analysis	April - June 2013
Creation of SWAT model for watershed	December 2012 – April 2012
DOC Model Validation	May - July 2013
Project finalized with results	August – September 2013
Thesis reviewed by committee	Late August – Early September 2013
Thesis Defense	September – October 2013

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