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PARTICULATE ORGANIC CARBON FATE AND TRANSPORT IN A LOWLAND, TEMPERATE WATERSHED

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ABSTRACT OF THESIS

PARTICULATE ORGANIC CARBON FATE AND TRANSPORT IN A LOWLAND, TEMPERATE WATERSHED

Small lowland agricultural systems promote conditions where benthic biological communities can thrive. These biogeochemical processes have significant impacts on terrestrial ecosystem processes including POC flux and fate, nutrient balances, water quality budges, and aquatic biological functioning. Limited information is available on coupled biological and hydrologic processes in fluvial systems. This study investigates the mixture of biological and hydrologic processes in the benthic layer in order to understand POC cycling in the South Elkhorn system. Further, comprehensive modeling of POC flux in lowland systems has not been performed previously and the behavior of potentially controlling variables, such as hydrologic forcing and seasonal temperature regimes, is not well understood. Conceptual hydraulic and sediment transport models were simulated for the South Elkhorn. Based on data and model results it was concluded that during a hydrologic event, upland and bank sources produce high variability of POC sources. Likewise, over time, the density of hydrologic events influenced accrual of benthic algal biomass in the POC pool. Environmental variables such as temperature and light availability drove seasonal variations of POC in the streambed. Based on model estimates, around 0.29 metric $tCkm^{-2}yr^{-1}$ of POC is flushed from the system annually with 13 % coming from autochthonous algae.

KEYWORDS: sediment transport modeling, surface fine grained lamina, erosion, HSPF, watershed

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PARTICULATE ORGANIC CARBON FATE AND TRANSPORT IN A LOWLAND, TEMPERATE WATERSHED

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THESIS

William Isaac Ford III

The Graduate School

University of Kentucky

2011

PARTICULATE ORGANIC CARBON FATE AND TRANSPORT IN A LOWLAND, TEMPERATE WATERSHED

THESIS

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science in Civil Engineering
in the College of Engineering at the University of Kentucky

By

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2011

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Chapter 1 Introduction

1.1) Introduction to Particulate Organic Carbon

The importance of fluvial organic carbon to the global carbon budget has been well documented in the literature with estimates of nearly 0.4 Gt C y^{-1} being transported to marine environments by the world's rivers (Meybeck, 1982). Within rivers, total organic carbon (TOC) is divided into two components, Particulate Organic Carbon (POC) and Dissolved Organic Carbon (DOC). Recently revised estimates have shown that approximately 0.18 Gt C y^{-1} of terrestrial POC is exported to the world's oceans while DOC exports are around 0.25 Gt C y^{-1}(Battin et al., 2008; Cauwet, 2002). Depending on the system, either form can dominate the organic pool, however DOC has been found, on average, to have a slightly higher ratio of DOC/TOC, thus it has received most of the focus in studies of fluvial organic carbon. The fate of POC in small lowland systems, where pronounced bed storage creates a substrate for biological activity, is relatively unknown.

The focus of this thesis is on the fate and transport of POC, in which POC specifies carbon associated with fine sediments. Fine sediments are defined herein as organic and inorganic materials less than 53 micrometers (μm) in diameter. All analysis and modeling efforts focus on the organic component of these sediments. Likewise, this sedimentary material is often referred to as Fine Particulate Organic Matter (FPOM) in studies focusing on organic matter in-stream. Bulk particulate material that is decomposed is referred to as Coarse Particulate Organic Matter (CPOM). If sediment originates from soil in the uplands of a watershed, it is referred to as Soil Organic Matter (SOM).

The substantial contribution of this study lies in the assessment of physical and biological processes in the streambed of a watershed, and how they alter the POC load. Here, biological processes include autochthonous production--the growth of algae in the streambed--and the influence of heterotrophic bacteria on decomposition rates, including decomposition of allocthonous leaf litter, CPOM, algae and fine SOM. Physical processes refer to the hydrologic/hydraulic forcing of sediments *via* erosion and transport.

1.2) Particulate Organic Carbon Modeling in a Lowland Watershed

In this thesis, a watershed modeling approach is applied to assess hydrologic, sediment transport, and biological impacts on POC. The modeling procedures are used to assess the carbon flux from a lowland system, and to budget the source of POC based on derived fractions. Ultimately, the goal is to quantify autochthonous and allochthonous inputs to the POC load, in order to assess the importance of lowland system with regard to fluvial carbon transport.

In past research, an existing conceptual hydrologic model was coupled with a newly developed conceptual hydraulic and sediment transport model for the study watershed (Russo, 2009). Herein, similar physical modeling is performed and is input to a newly developed conceptual POC model. The POC model takes a mass balance approach and implements an algal sub-model that accounts for epilithic algal growth on the stream bed (Rutherford et al., 2000) and microbial decomposition of autochthonous and allochthonous pools within the streambed.

1.3) Research Need

Lowland, agricultural stream systems promote conditions in which benthic biological communities can thrive. Little is understood about the role of the benthic biological community with regard to carbon fate and transport. The form and function of these benthic biological communities and their ensuing transport as particulate organic carbon has environmental significance for carbon and nutrient balances in terrestrial systems including POC flux and fate associated with the benthic community and its importance for regional and local C balances (Hedges et al., 1997), nutrient balances (Frost et al., 2002), water quality budgets (Hily, 1991), and aquatic biological functioning (Tank et al., 2010).

Fluvial transport of POC and its associated fate in streams and rivers has proven to be a significant component of local and global carbon budgets (Cole et al., 2007). Recently revised estimates have shown that approximately 0.18 Pg C y^{-1} of terrestrial POC is exported to the world's oceans (Battin et al., 2008; Cauwet, 2002). In individual systems, POC has been found to constitute anywhere from 10-80% of the total organic load (Abril et al., 2000; Carey et al., 2005; Gomez et al., 2003; Howarth et al., 1991; Lyons et al., 2002; Sharma and Rai 2004; Worall et al., 2003; Zhang et al., 2009).

Most studies of POC flux from different physiographic regions have looked at steep gradient systems where POC fluxes are high, even though they have small drainage areas (Lyons et al, 2002; Carey et al 2005; Gomez et al, 2003; Sharma and Rai 2004; Zhang et al. 2009). Lowland systems on the other hand have received relatively little study due to their low POC fluxes (Abril et al., 2000; Hope et al., 1994; Howarth et al., 1991). Although they have received little study, lowland systems typically have a substantial portion of mobilized sediment that is temporarily stored within the catchment (Walling et al., 2006) allowing for in-stream carbon transformations (i.e. accrual or decomposition).

Cole et al. (2007) has identified the pronounced storage typical in lowland systems as an unknown source of carbon to regional and global carbon budgets. Few studies have identified and discussed seasonal transformations of POC (Zhang et al., 2009). Likewise, few studies, if any, have taken a coupled modeling approach to estimate POC flux (Howarth et al., 1991). Therefore, this thesis focuses on a coupled modeling approach to account for the physical forcing of POC transport, and to account for the fate of POC in streambeds of lowland systems by modeling hydrologic, hydraulic, sediment transport, and biological processes.

1.4) Objectives

The overarching objective of this study is to develop and implement a comprehensive coupled modeling approach to estimate the fate and transport of POC in a lowland temperate watershed--the South Elkhorn watershed located in the Bluegrass Region of Central Kentucky. To meet this broad goal, the specific objectives of this thesis were to:

1. Review the literature to identify methodological approaches to estimating POC fluxes, and to understand how POC flux varies with topography.
2. Study biological processes that utilize organic carbon associated with the fine sediment pool placing a heavy focus on the active benthic layer.

3. Develop a conceptual modeling framework outlining physical and biological processes that impact POC in streams and rivers.
4. Implement current field and laboratory methods to measure water flowrate, sediment transport and organic carbon content of FPOM at the outlet of the study site.
5. Utilize a conceptually based hydrologic model, and develop a conceptually based hydraulic and sediment transport model to estimate how physical processes impact the POC load in streams and rivers.
6. Develop a conceptual POC model that incorporates physical processes and adds biologic components including autochthonous growth and decomposition by heterotrophic bacteria.
7. Test the sensitivity of the carbon model and calibrate the model using collected data at the outlet of the watershed.
8. Create a POC budget for the South Elkhorn watershed, highlighting the contribution of the newly derived autochthonous carbon, in addition to the fraction of POC originating from SOM in the bank and upland soils.
9. Provide some preliminary estimates of POC flux for lowland temperate watersheds on a regional scale using results from the POC model.

1.5) Thesis Contents

Chapter 1 provides an introduction to the environmental issues associated with fine sediments, the reason for studying POC in lowland systems characterized by temporary storage, and the objectives of the study.

Chapter 2 reviews literature that quantifies POC fluxes and discusses their methodological approach. Thereafter, a conceptual framework was developed to display the interplay between hydrologic, sediment transport and biological processes with regard to POC fate and transport.

Chapter 3 provides an overview of the study site, including GIS images of land-use and slope maps for the watershed.

Chapter 4 provides the methodology for field and laboratory sampling. This includes *in situ* sediment trap samples, collection of USGS gage data, and automated sampling using a Teledyne ISCO.

Chapter 5 provides the methodology for the coupled model setup. The feed forward model setup starts with a hydrologic model, which informs a conceptually based hydraulic and sediment transport model. Thereafter, results of the sediment transport model are used in the POC model to account for SOM and erosion/deposition dynamics in the streambed.

Chapter 6 provides results of the data collected for this study, including sedigraphs, hydrographs and percent organic carbon estimates from 2006-2009.

Chapter 7 provides the results of the hydrologic, sediment transport and POC model. Calibration and validation is conducted for each model. Sensitivity analysis of the POC model was conducted to understand what parameters have the greatest impacts on the POC load. Visual and statistical calibrations are provided for each model.

Chapter 8 provides POC budgets to predict the contribution of allocthonous and autochthonous carbon sources. Thereafter, temporal and hydrologic variability is quantified and the results of the model and of the POC budget are discussed.

Chapter 9 provides the conclusions of this thesis.

Chapter 2 Literature Review of POC Flux

2.1) Overview

Lowland, agricultural stream systems promote conditions in which benthic biological communities can thrive. Little is understood about the role of the benthic biological community with regard to carbon fate and transport. The form and function of these benthic biological communities and their ensuing transport as particulate organic carbon has environmental significance for carbon and nutrient balances in terrestrial systems including POC flux and fate associated with the benthic community and its importance for regional and local C balances (Hedges et al., 1997), nutrient balances (Frost et al., 2002), water quality budgets (Hily, 1991), and aquatic biological functioning (Tank et al., 2010)

It is recognized that the benthic behavior and its associated POC flux in lowland agricultural streams will be impacted by a number of watershed parameters including hydrologic regime at the event scale, for multiple events and seasonally as well as seasonal temperature regimes. However, in depth analysis of the benthic behavior and its associated POC flux has not been performed previously. Here new data and comprehensive modeling is performed to assess the contribution of upland, bed and bank sources to the POC load. The methodological approach provides a comprehensive analysis of POC fate and transport at the watershed scale. Alverez-Cobelas et al. (2010) calls for new methods to measure and estimate POC in order to better understand the biogeochemical fate of organic carbon in rivers. The modeling framework developed here incorporates inputs and decomposition of organic carbon in the streambed, transport of carbon from streambed, bank and upland sources, and an annual budget of POC exported from the system.

Further, it is recognized that the POC flux associated with the benthic community has potential importance for regional C balances. Increased emphasis has been placed in the literature upon gaining a better understanding of the global carbon cycle and how quantifying sediment and carbon transport by rivers to the sea is an increasing concern (Oeurng et al., 2011). Recent research has worked to quantify the importance of different watershed systems expected to produce high C loads (Aldrian et al., 2008; Bird et al., 2008; Oeurng et al., 2011; Waterloo et al., 2006) and specifically high gradient systems (Coynel et al., 2005; Gomez et al., 2003), peat/wetland systems (Worall et al., 2003), and the importance of the hydrologic regime (Dalzell et al., 2005; Sharma and Rai, 2004; Waterloo et al., 2006) and different sediment and carbon sources in stream systems (Gomez et al 2003; Guo and Macdonald) have received attention. POC flux associated with the benthic community is studied here because it has potential importance for regional C balances and has not been considered in the literature previously.

Fluvial transport of carbon is an important component of global and local carbon budgets and has been emphasized in recent aquatic carbon studies. Carbon can be transported through stream systems in three primary forms, dissolved and particulate organic matter (POM and DOM) and dissolved carbonates (Hope et al, 1994). Recently revised estimates have shown that approximately 0.18 Pg C y^{-1} of terrestrial POC is exported to the world's oceans while Dissolved Organic Carbon (DOC) exports around 0.25 Pg C y^{-1}(Battin et al, 2008 and Cauwet, 2002). In individual catchments, POC has been seen to constitute anywhere from 10-80% of the total organic load (Abril et al., 2000; Carey et al., 2005; Gomez et al., 2003; Howarth et al., 1991; Lyons et al., 2002; Sharma and Rai 2004; Worall et al., 2003; Zhang et al., 2009). A recent review by Alvarez et al (2010) compiled POC, TOC and DOC estimates for 550 catchments around the world. The review showed that all three had a wide range of export rates. TOC ranged from 0.0021-92.5 $tCkm^{-2}yr^{-1}$; POC ranged from 0.0004-74 $tCkm^{-2}yr^{-1}$; and DOC ranged from 0.0012-57 $tCkm^{-2}yr^{-1}$. Values from the Alvarez study may be lower than reported values in this review because the Alvarez study uses average fluxes for each study whereas this review reports all fluxes from each study.

Still, further work is needed with regard to biological transformations and processes impacting the POC load. A recent study suggests that inland waters oxidize much of the organic loads in streams (Cole et al., 2007). Likewise, biological growth (i.e. heterotrophic bacteria and algae) can result in enrichment of carbon content in FPOM.

In-stream transformations and enrichment are of particular importance in lowland systems defined by mild gradient streams and watersheds. The study of lowland systems has been less emphasized in the literature presumably because POC fluxes tend to be significantly lower compared to steep gradient systems (e.g. Gomez et al., 2003). While lowland systems typically have low sediment delivery ratios in the short term, the systems cover very large areas (e.g., Midwestern USA) and contain active temporarily stored sediments (Walling et al., 2006). Temporarily stored sediment is subjected to microbial communities including algal and bacterial biomass growth and decomposition of organic material. Therefore, the focus of this study has been placed on estimates of POC flux for lowland mixed land use systems.

It has been documented that a fraction of transported POC in river systems is available for consumption and is important with regards to net ecosystem metabolism (Battin et al., 2008). However, there has been a lack of comprehensive conceptual frameworks and models, primarily those incorporating microbial activity in bed sediments, analyzing the source fate and transport of POC. New methodology and modeling techniques are needed to bring standardization to POC estimates. This study analyzes such processes on a third order reach nested within a 61.8 km^2 watershed.

The following literature review will provide results of previous case studies in which POC flux was estimated (Section 2.2), a conceptual framework outlining the processes governing POC source, fate and transport (Section 2.3), and methods used to estimate POC flux (Section 2.4).

2.2) POC Flux Results from Watershed Systems

POC flux in fluvial systems has been measured and estimated in a wide variety of climates, physiographic regions and land uses. Case studies have been conducted in systems varying from relatively small catchments (Lyons et al., 2002; Waterloo et al., 2006; Worall et al., 2003) to large river basins (Aldrian et al., 2008; Bird et al., 2008; Gross et al., 1972; Guo and Macdonald 2006; Howarth et al., 1991; Malcolm and Durum, 1976). High variability of transported POC has been discussed in review papers that synthesize results from case studies (Alvarez et al., 2010; Hope et al., 1994). This section of the literature review takes a look at the relative importance of POC transport including the amount of organic carbon that is exported in the particulate vs. dissolved phase, variability of POC fluxes with respect to watershed characteristics, and discusses studies that have looked at variability of POC fluxes influenced by in-stream processes.

Organic carbon (OC) is estimated to provide approximately 40% of the total carbon flux carried by the world's rivers at 0.4 Gt y^{-1} (Meybeck, 1982). Organic carbon transport is composed of the dissolved and particulate phase, defined by a diameter less or greater than 0.45 microns, respectively. On average, the DOC fraction dominates OC export, composing around 73 % of the TOC, however the respective ranges of POC and DOC are 0.0004-74 $tCkm^{-2}yr^{-}1$ and 0.0012-57 $tCkm^{-2}yr^{-1}$ (Alvarez et al., 2010). Other studies have estimated that the DOC/TOC ratio is closer to 0.6 (Meybeck, 1982). In individual catchments, the dominant fraction varies based on variables such as the "quality" of the POC and watershed characteristics. Some studies showed POC flux dominated the export of organic carbon, (Abril et al., 2000; Carey et al., 2005; Howarth et al., 1991; Worall et al., 2003) while DOC flux controlled in other systems (Aldrian et al., 2008; Sharma and Rai, 2004; Zhang et al., 2009).

The current dataset of POC export is biased towards cold temperate climates (Alvarez et al., 2010). Furthermore, a focus of many POC studies has been on steep gradient systems (i.e. mountainous areas) because of their ability to transport high levels of POC during landslides. The Pacific Rim has been of particular interest, in that small systems in the area have been shown to have high specific POC fluxes ($tCkm^{-2}yr^{-1}$) (Hilton et al., 2008; Gomez et al., 2003; Lyons et al., 2002). Lyons' paper estimates that between 17-35 % of POC marine deposits originate from the high standing islands which make up only 3% of Earth's landmass. Likewise, of the aforementioned studies, Lyons et al. (2002) observed the highest specific POC flux with 245 $tCkm^{-2}yr^{-1}$ exported to marine waters. With regard to lowland, mild gradient areas, most of the studies have been conducted in large river basins (see Meybeck, 1982). Lowland systems are important because they promote pronounced storage of fine sediments, providing the microbial community with an organic substrate to grow on. Cole et al. (2007) calls for further study of these systems to understand the POC processes conducted in headwater drainage basins.

In-stream processes impacting POC flux have received little attention in fluvial carbon transport studies. Likewise, limited focus has been placed on small lowland systems, in which benthic processes can heavily impact carbon content of bed sediments. However, there are a few studies that have quantifiable evidence of temporal or spatial variability of POC flux. A study by Zhang et al. (2009) observed seasonal and spatial variability of POC and DOC. The study attributes hydrologic forcing of POC to explain some of the variability; however other environmental factors likely contributed. Likewise, a study by Dalzell et al. (2005) found DOC and TOC were exported primarily during flooding conditions. Furthermore, a study by Bungartz et al. (2006) analyzed the impacts of fluvial suspended sediment aggregation on transport of POC. Modeling and data results found that in stream aggregation resulted in an increase of POC deposition fluxes (i.e. decreasing the POC load and increasing POC in the bed). Aldrian et al. (2008) also looked at the spatial and temporal variability of carbon fluxes in fluvial systems. Although DOC and DIC saw seasonal patterns, POC and PIC had no definitive seasonality.

Alvarez et al. (2010) calls for better methods to estimate POC transport in order to enhance our understanding of the biogeochemical fate and role of organic carbon export from riverine systems. Therefore, this study will be useful in that it develops an advanced methodological approach to estimate POC flux, and it adds a component that is lacking from previous POC studies.

Table 2-1 reviews POC fluxes over the past 40 plus years. Many of these studies were obtained from the Hope et al. (1994) review. Of the review table published in the Hope paper, studies were only used for select streams and rivers. Furthermore, the table in this study is not fully comprehensive. Many studies look at TOC and DOC measurements, however little has been done to measure POC. For the Alvarez et al. (2010) review, much of the POC data was derived by subtracting DOC from TOC. Not all 550 catchments observed in the Alvarez study will be looked at here, but a substantial number have been obtained from a wide variety of climates, countries and topographic areas to have a thorough understanding of how POC varies throughout different parts of the world.

2.3) POC Fate and Transport Processes in a Watershed and Stream

To quantify POC flux, a thorough understanding of the POC fate and transport processes in a watershed and stream is necessary for accurate assessment. POC flux is influenced heavily by upland land use conditions, topography of the watershed, water quality, and hydrologic variables. In addition, underlying geologic parent material plays a significant role in the transport of carbon in a fluvial system. Figure 2-1 shows a conceptual representation outlining the processes influencing POC source fate and transport in a fluvial system at the watershed scale. Figure 2-2 depicts the processes impacting the POC load on the streambed and during transport at a reach scale. The following section will outline each of the processes impacting POC flux, thereafter tying each to the conceptual understanding of physical and biological processes.

2.3.1) Soil Detachment on Hillslopes

Although the focus of this study is on POC transported in stream systems, a general understanding of carbon processes at a watershed scale are important for deriving allocthonous inputs to the POC load. Sediment transported in river systems can originate from upland soils (rill and interill erosion), streambeds, streambanks, and gullies. Eroded organic materials contain varying levels of carbon depending on the depth of the eroded material. Uptake of carbon from the atmosphere occurs with vegetation growth. Higher carbon contents are typically seen in surface sediments where plant assimilation and carbon fixation is greatest. However, SOC (Soil Organic Carbon) can also be exposed and diminished through oxidation and mineralization (Lal, 2002).

Wind and water erosion are the dominant erosion processes in surface soils. However, wind erosion is negligible with regards to its contribution to the POC load in a fluvial system. Hence, this study focuses on the fluvial erosion of fine sediments and transport *via* rills and interrills (as discussed above). Fluvial detachment of surface soils is driven by shear stresses generated by raindrop impact and surface runoff over the land surface (Toy et al., 2002). Furthermore, surface runoff is a function of hydrologic variables including precipitation, infiltration rates, canopy storage, depression storage and evapotranspiration rates, and can be estimated using a hydrologic model. Erosion processes can be estimated using commonly accepted models such as the Revised Universal Soil Loss Equation (RUSLE) and the Water Erosion Prediction Project (WEPP). In addition, field studies can be conducted to quantify sediment detachment from hillslopes.

2.3.2) POC Transport to Stream Network

POC is transported to the stream system through rills. During transport to the stream network, changes can occur to the POC load. Preferential transport of fine material may result depending on the concavity of the hillslope and whether disaggregation occurs. There are various ways to account for sediment and carbon changes as it is transported to the stream from its place of origin. For sediment, a SDR (sediment delivery ratio) or hillslope routing (WEPP model) can be used to quantify delivery to a stream. The SDR is defined as the percentage relationship between sediment yields at a specific point in the watershed relative to the gross erosion in the watershed upstream of that point (Roehl, 1962). The method is broadly used; however it relies heavily on data collection and can provide crude estimates of sediment load. Alternatively, the WEPP model (Flanagan et al., 1995) uses a steady state sediment continuity equation to describe movement of sediment in a rill.

Likewise, variability of carbon during transport from source to the fluvial system can be accounted for using a Carbon Enrichment Ratio (CER). CER is defined as the ratio of SOC content in sediments to that in the topsoil.

2.3.3) Dissolved Inorganic Carbon

Dissolved Inorganic Carbon (DIC) can occur in ionic form (HCO_3^-, CO_3^2, H_2CO_3) or dissolved free CO_2 (Hope et al., 1994). These carbonate and bicarbonate ions heavily influence the pH of stream water. Carbonate and bicarbonate ions in surface water are generated from weathering of the underlying geologic material, and are delivered to channel *via* groundwater flow. Furthermore, inputs from groundwater can be enriched with carbon dioxide due to microbial processing of organic matter as it passes through soil because CO_2 is also respired by microbial organisms that use organic matter as an energy source (Allan, 1995). With regards to POC, it is important that these elements are present in order for autochthonous growth to occur (serves as energy source). For this study, this component is not expressly taken into account in the model; however it is important to understand conceptually, and can aid in developing POC models in the future.

2.3.4) In-stream Processes and Alterations to POC Content

In-stream processes have significant bearing on POC loads in streams and rivers. This section covers two main facets of in-stream processes impacting POC loads, namely in-stream erosion and biological processes. In-stream erosion refers to detachment of sediments from surfaces in a channel. This includes gully, bed and bank erosion. With regards to POC, erosion sources are of particular importance, because OC content is highly variable from one source to the next. Furthermore, the ability of heterotrophic biota to utilize organic matter and autotrophic algae to fix inorganic carbon in the water column significantly impacts the POC content of fine sediments in the streambed.

2.3.4.1) In-stream Erosion

Incision of gullies removes weathered bedrock and delivers it directly to the stream channel. Gomez et al. (2003) performed a study in which they found gully erosion was the dominant process responsible for delivering sediment to the stream channel. During low flows it was observed that POC values had high variability, and that it was likely a result of contributions from sources other than gully erosion such as C_3 plants and humus. POC content at high discharges was substantially lower than that at low flows because sediment discharged from gullies has a lower organic carbon load than plants and humus delivered from riparian areas. From these results, the author infers that the bulk of riverine POC exported from many high gradient watersheds may consist of ancient organic matter derived from sedimentary rock.

Bank sediment erosion is a significant source of transported sediment in many watersheds. A study in Minnesota found streambank slumping contributed anywhere from 31% to 44% of the total suspended sediment load (Sekely et al., 2002). Bank erosion has been found to be significantly pronounced in urbanizing areas as a result of decreased surface runoff (impervious surfaces), and higher flow volumes (Nelson, 2002; Trimble, 1997). Bank erosion is a function of shear stresses imparted on the bank by the fluid. Organic carbon content of bank sediments is highly dependent upon SOC distributions in soil profiles. Vertical placement of carbon in the soil is impacted by root distributions; hence profiles vary with vegetation cover (Jobbagy and Jackson, 2000). In general, bank sediments typically have a lower OC content than surface soils.

Bed erosion is the final source, with regard to transported sediment. Bed erosion, similar to bank erosion, is a function of the shear stress that the fluid imparts on the surface. POC content of fine streambed sediments varies due to biological assimilation of organic material in the bed, breakdown of CPOM to FPOM, and autochthonous growth and fixation of carbon dioxide. The following section goes into detail on each of the biological processes impacting the POC load in the bed.

2.3.4.2) Biological Transformations to POC

Organic matter and carbon can be incorporated into stream ecosystems either through autotrophic or heterotrophic pathways. Autotrophy is the production of new plant material through photosynthesis, and heterotrophy is the assimilation of organic matter by consumers (Naiman and Bilby, 1998). The following discussion provides a synthesis of how these two pathways impact the POC load. Furthermore, a brief discussion of spatial variability of biological processes will conclude this section. To summarize these processes, Figure 2-2 depicts in-stream processes impacting the POC load.

Autochthonous—defined as matter that is formed or originated in the place where found--organic matter is generated by autotrophic organisms. Autochthonous OM is a significant source of POC because such organic matter is generated from inorganic materials in the water column, i.e. dissolved inorganic carbon from chemical weathering (Naiman and Bilby, 1998). The primary autotrophs found in headwaters and upper reach sections include periphyton and occasionally bryophytes. Periphyton (green and red algae) is typically found in intimate association with heterotrophic microbes and an extracellular matrix (Allan, 1995). Benthic autotrophs can occur on nearly any surface in a river including stones (epilithon), soft sediments (epipelon) and other plants (epiphyton) (Allan, 1995). Nitrogen and Phosphorous are often limiting nutrients for benthic algal biomass in rivers because they are often in short supply relative to cellular growth requirements (Dodds et al., 2002). When algal material becomes senescent and dies it can become part of the detrital pool, or carried downstream (Naiman and Bilby, 1998); hence becoming a significant addition to POC in the bed, or POC suspended in the water column during transport. Accounting for algal biomass in streams requires a thorough understanding of the processes impacting algal growth. Much work has been conducted with regard to seasonal variability of benthic algal biomass accounting for variables such as flow, nutrient supply, light and temperature (Biggs, 1996 ;Cox, 1990; Francoeur et al., 1999). Studies on the Loire River in France have shown seasonality of algal POC with concentrations of 0.8 mgC/L in winter and 5 mgC/L in summer (Meybeck, 2006). Further discussion of empirical models used to estimate algal biomass growth in a given stream reach will be discussed in the Methods section of this thesis.

Heterotrophic material also plays a significant role in influencing POC content in bed sediments. Bacteria are the main heterotrophic microorganisms in freshwater systems. A study in a European stream showed that bacteria constituted 36% of heterotrophic biomass and 71% of heterotrophic production (Marxsen, 2006). Within a freshwater environment, bacteria are ecologically important because they recycle algal secretory products, are able to out compete algae for nitrates and phosphates in nutrient-limiting conditions, and are able to form key associations with other biota (Sigee, 2005). With regards to POC, bacteria break down organic matter and get energy from either allocthonous or autochthonous organic carbon sources; however they are also recognized as important producers of POC. Such processes occur through the consumption and assimilation of DOC (Bell et al., 1983; Ducklow and Kirchman, 1983; White et al., 1991). The ability of heterotrophic bacteria to degrade POC is influenced by several factors including the need to synthesize extracellular enzymes specific for available substrates, proximity to the substrate which impacts efficiency of applying enzymes, and nutritional quality of the available substrate (Fischer et al., 2002). Benthic bacterial respiration constitutes a significant portion of microbial respiration in streams and rivers. A study on the Ogeechee River (Fischer and Pusch, 2001; Edwards et al., 1990) showed that benthic bacterial respiration constituted >97% of the bacterial respiration, and bacterial respiration constituted nearly 100% of the total system respiration. Hence, the importance of benthic bacteria in stream systems is evident and must be considered in any study analyzing biogeochemical processes.

Fungal biomass is the other major component of heterotrophic material. Fungal biomass has less of an impact on POC flux associated with fine sediments because fungi in streams have been found to be restricted to coarse particulate organic matter (Gessner, 1997). Fungi in streams are predominantly composed of aquatic hyphomycetes (Ingold, 1942). Gessner (1997) states that erogosterol concentrations, an indicator of fungal biomass, increase with increasing particle size and appear to have their main habitat in CPOM. Therefore for this study, fungal impacts on carbon cycling in fine sediments will be assumed negligible.

Biological processes are significantly different from headwater reaches to higher order reaches. Autotrophic production is often regulated by light and flow conditions; hence the scale of the reach is significant. Periphyton dominates primary production in headwater, fast moving reaches (Naiman and Bilby, 1998), and phytoplankton (planktonic autotrophs) maintains populations in slower-flowing rivers downstream (Allan, 1995). Bacterial production can also vary as a function of reach order. In downstream reaches bacterial carbon production has been found to increase due to higher algal biomass supply (Battin et al., 2001).

Likewise, variability occurs with vertical gradients in the streambed. With regard to bacterial productivity, shifting sediments (a more permeable sediment structure) have flatter gradients then stratified sediments (Fischer et al., 2002). This means that higher bacterial productivity can occur in deep sediments if there is a permeable structure in which high quality POM can reside. For sediments that are stratified or have an impermeable structure, bacterial productivity decreases significantly with depth due to low quality POM and anaerobic conditions.

2.3.5) Transport of POC in a Fluvial System

POC flux is a function of carbon content of suspended sediments and mass of suspended sediment leaving the system. As discussed above, POC content of temporarily stored bed sediments is difficult to quantify and requires significant analysis of erosion and biological processes. However, quantifying suspended sediment loads is a process that has been well developed. Chapter 5 of this thesis will go into more detail on how transport of POC can be modeled.

2.4) Review of Methods to Estimate POC Flux

Currently, there is a lack of uniformity in the methodological approach to estimate POC flux at the watershed scale. The purpose of this section is to review the methodology that has been implemented up to this point. Alvarez et al. (2010) states that many studies simply use the difference between TOC and DOC to estimate POC and new methodology is needed to fully understand the role of POC in organic carbon transport processes. Generally, studies have estimated POC flux as the product of sediment flux and carbon content of transported sediments (Abril et al., 2000; Aldrian et al., 2008; Bird et al., 2008; Lyons et al., 2002; Sharma and Rai, 2004; Worall et al., 2003; Zhang et al., 2009). The methods used to generate sediment flux and carbon content of suspended sediment account for most of the variability.

Sediment collection and analysis methods vary in the case studies seen in Table 2-1. Few studies coupled sediment transport and POC models, with the exception of

Howarth et al. (1991). With regard to sediment, most studies relied on previous estimates of sediment flux, (Lyons et al., 2002) utilized previously developed models, such as a sediment rating curve (Carey et al., 2005; Gomez et al., 2003; Sharma and Rai, 2004), or estimated sediment transport through sample collection and analysis (Zhang et al., 2009).

For carbon analysis, many studies used water samples collected from the stream or river and performed sample analysis of C content. Some studies utilized elemental analyzers such as the Shimadzu TOC 5000 Analyzer (Abril et al., 2000; Aldrian et al., 2008), the Perkin-Elmer 2400 series II CHNS/O Elemental Analyzer (Zhang et al., 2009), or the Costech Elemental Analyzer (Bird et al., 2008). Other studies used a coarser method where carbon was estimated as a percent of organic matter (Carey et al., 2005; Lyons et al., 2002; Worall et al., 2003). Howarth et al. (1991) modeled POC flux in the Hudson River using sub-models for different land uses and aggregating POC and DOC into one estimate. For POC estimates, the product of total sediment transported, % C in bulk soil and enrichment ratio was used.

There are several water quality models that can perform modeling of the biological, physical, and hydrologic processes such as the WASP and the AQUATOX models. However, organic matter generated by biological models is not internally coupled with sediment transport or toxic chemical models. Models such as WASP and AQUATOX do a good job modeling the fate component, and the carbon exchange with the bed; however they lack the erosion deposition dynamics of a sediment transport model. Likewise these models use the underlying assumption that spatial and temporal variability, with regard to biological processes, can be described by repeatable annual patterns (Imhoff et al., 2003). Although these models are very useful tools, one important aspect of this study is to assess the annual variability of POC; therefore these models are not applicable.

Other approaches have been taken to assess source, fate and transport of POC. The use of tracer technology to model the source and fate of POC has been a recurring trend in recent studies. Most studies are utilizing the stable carbon isotope $\delta^{13}C$ and the carbon to nitrogen ratio (C:N ratio). Bird et al. (2008) utilizes $\delta^{13}C$ and the C:N ratio of DOC and POC to geochemically characterize the POC and DOC fluxes of two large rivers in Myanmar. Gomez et al. (2003) utilized $\delta^{13}C$ and C:N ratios to determine that gully erosion was the primary source of POC in their system. Galy et al. (2008) used $\delta^{13}C_{org}$ to assess the fate of organic carbon in a Himalayan system. Leithold et al. (2006) used $\Delta^{14}C$ to assess the role of erosion in governing the character of transported POC and found that POC is contributed directly from deep gully erosion. Finally, a study assessing the impact of climate change on POC was conducted by Gordeev et al. (2009). The study aimed to provide initial predictions of POC flux from Russian Arctic Rivers through the year 2100. Further method advancement and understanding of POC fate and transport will allow for stronger predictive estimates of POC flux in the future *via* coupling of new tracer-based methods with comprehensive models such as the one presented here.

Table 2-1) POC Flux results for global case studies (*Specified non-fossil POC Flux)

Authors	Watershed Location	Watershed Description	Watershed Area (km^2)	Sediment Flux ($tkm^{-2}yr^{-1}$)	POC Flux ($tCkm^{-2}yr^{-1}$)
POC studies reviewed					
Howarth et al. 1991	Lower Hudson River Basin	Mixed land use (forested, ag,pasture, urban)	13,670	20.8	1.64
	Upper Hudson River Basin	Mixed land use (forested, ag,pasture, urban)	10,110	8.3	0.65
	Mohawk River Basin	Mixed land use (forested, ag,pasture, urban)	6,770	20.35	1.7
Worall et al 2003	Moor House National Nature Reserve, North Pennine,Brittain	Cover by glacial till. Blanket Peat covers 90% of the catchment	11.4	0.044	19.9
Carey et al 2005	Southwestern Region of New Zealands North Island(Waitara)	Dominated by agriculture and non-native vegetation	1122	N/A	2.9
	Southwestern Region of New Zealands North Island(Waitotara)	Dominated by agriculture and non-native vegetation	1098	N/A	2.3
	Southwestern Region of New Zealands North Island(Whanganai)	Dominated by agriculture and non-native vegetation	6785	N/A	3.8
	Southwestern Region of New Zealands North Island(Whangachu)	Dominated by agriculture and non-native vegetation	1944	N/A	2.6
	Southwestern Region of New Zealands North Island(Rangitikei)	Dominated by agriculture and non-native vegetation	3541	N/A	1.3
	Southwestern Region of New Zealands North Island(Waiau)	Dominated by agriculture and non-native vegetation	1626	N/A	17.4
	New Zealand Rivers(Hokitika)	Forested/steep gradient)	352	$17*10^3$	47.4

Table 2-1 (Continued)

Authors	Watershed Location	Watershed Description	Watershed Area (km^2)	Sediment Flux ($tkm^{-2}yr^{-1}$)	POC Flux ($tCkm^{-2}yr^{-1}$)
Lyons et al. 2002	New Zealand Rivers(Cropp)	Forested (high reaching island/very steep gradient)	29	$30*10^3$	57.3
	New Zealand Rivers(Haast)	Forested (high reaching island/very steep gradient)	1020	$12.7*10^3$	185.2
	New Zealand Rivers(Hikuwai)	Forested (high reaching island/very steep gradient)	307	$13.9*10^3$	244.71
Zhang et al 2009	Waipaoa River Basin, New Zealand	Mountainous Tributary / Human disturbed	3,164	84.9	1.06
Abril et al 2000	Rivers in Schledt Estuary(Schledt)	Agriculture, industrial population density (115)	10,505	N/A	2.2
	Rivers in Schledt Estuary(Dender)	Agriculture, industrial , population density (319)	1,381	N/A	6.2
	Rivers in Schledt Estuary(Zenne)	Agriculture, industrial, population density (1177)	1,150	N/A	17.44
	Rivers in Schledt Estuary(Dijile)	Agriculture, industrial, population density (259)	3,420	N/A	2.2
	Rivers in Schledt Estuary(Nete)	Agriculture, industrial, population density (243)	1,605	N/A	2.68
Gomez et al 2003	North Island of New Zealand	Steep Gradient, forested, pasture, scrub	1,580	6750	55
Sharma and Rai 2004	Eastern Himalayan Biogeographic zone, India	Forest, wasteland and agriculture	30.14	668	27.64

Table 2-1 (Continued)

Authors	Watershed Location	Watershed Description	Watershed Area (km^2)	Sediment Flux ($tkm^{-2}yr^{-1}$)	POC Flux ($tCkm^{-2}yr^{-1}$)
Aldrian et al 2008	Brantas Catchment in East Java	Tropical Monsoon Climate/ Urban, Ag and Industrial land use	110,050	272	4.29
Bird et al 2008	Ayerwady River primarily in Myanmar	Forested, with a Monsoonal Climate/ Steep Slopes	413,710	677	7.9
	Thanlwin River in China Thailand and Myanmar	Forested, with a Monsoonal Climate/ Steep Slopes	271,914	724	10.7
Coynel et al 2005	Nivelle River draining to the Bay of Biscay	Pyrenean Mountainous River	160	N/A	5.3
Oeurng et al 2011	Save catchment in the Gascogne area of south-west France	Agricultural, lowland area (Peak Elevation of 663 meters)	1110	48	1.2
Hilton et al 2008	LiWu catchment in the west Pacific Rim	Prone to tropical cyclones, steep gradient systems	423	$41*10^3$	109*
Guo and Macdonald 2006	Upper Yukon River in Northwestern Canada and Alaska	Vast alpine and arctic regions	855,000	70.2	0.32
Waterloo et al. 2006	Blackwater Igarape Asu Catchment	Tropical Rainforest with moderately steep slopes	6.8	3.2	0.89
From Hope et al 1994 Review					
Wetzel and Manny 1977	Augusta Creek, Michigan	Temperate Forest	68	N/A	0.68
Fisher 1977	Fort River, Massachusetts	Temperate Forest	107	N/A	0.77
Naiman and Sedell 1979	MacKenzie River, Oregon	Temperate Forest	1287	N/A	0.64
Weber and Moore 1967	Little Miami River, Ohio	Temperate Forest	1024	N/A	0.81
Malcolm and Durum 1976	Neuse River, N.C.	Temperate Forest	6694	N/A	0.68

Table 2-1 (Continued)

Authors	Watershed Location	Watershed Description	Watershed Area (km^2)	Sediment Flux ($tkm^{-2}yr^{-1}$)	POC Flux ($tCkm^{-2}yr^{-1}$)
Flemer and Biggs 1971	Susquehanna River	Temperate Forest	72,492	N/A	1.16
Gross et al. 1972	Columbia River	Temperate Forest	670,000	N/A	0.24
Dance et al 1979	Canagagugue Creek, Ontario	Temperate Forest	25	N/A	.05
Naiman 1982	First Choice Creek, Quebec	Boreal Forest	0.25	N/A	0.54
	Beaver Creek, Quebec	Boreal Forest	0.83	N/A	3.37
	Muskrat Creek, Quebec	Boreal Forest	207	N/A	0.96
	Matamek Creek, Quebec	Boreal Forest	673	N/A	0.67
	Moisie Creek, Quebec	Boreal Forest	19,871	N/A	0.48
Malcolm and Durum 1976	Brazos River	Temperate Grasslands	113,968	N/A	0.21
	Missouri River	Temperate Grasslands	1,084,545	N/A	0.51
	Mississippi River	Temperate Grasslands	3,220,716	N/A	0.56
	Sopchoppy River in Florida	Wetland	750	N/A	4.29
Naiman and Sibert 1978	Nanaimo River and Estuary	Wetland	894	N/A	0.4
Karlstrom and Backlund 1977	River Ricklean	Boreal Forest	1673	N/A	0.45

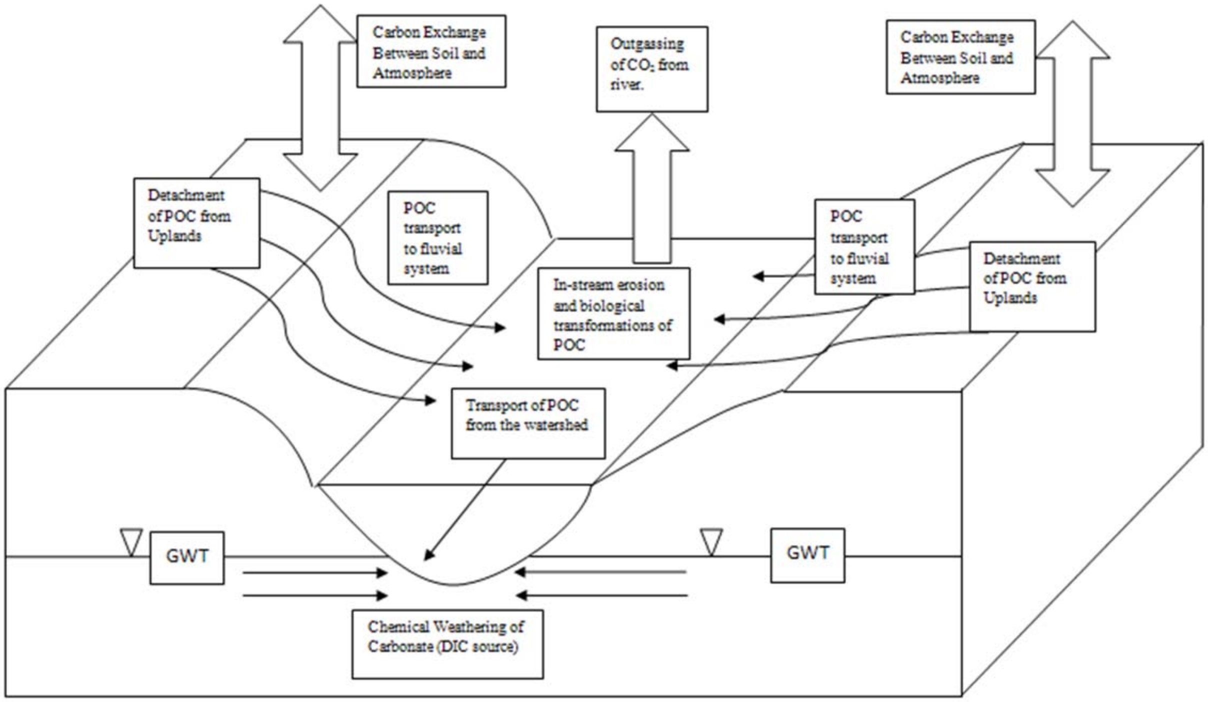


Figure 2-1) Conceptual framework of POC Flux (GWT denotes ground water table)

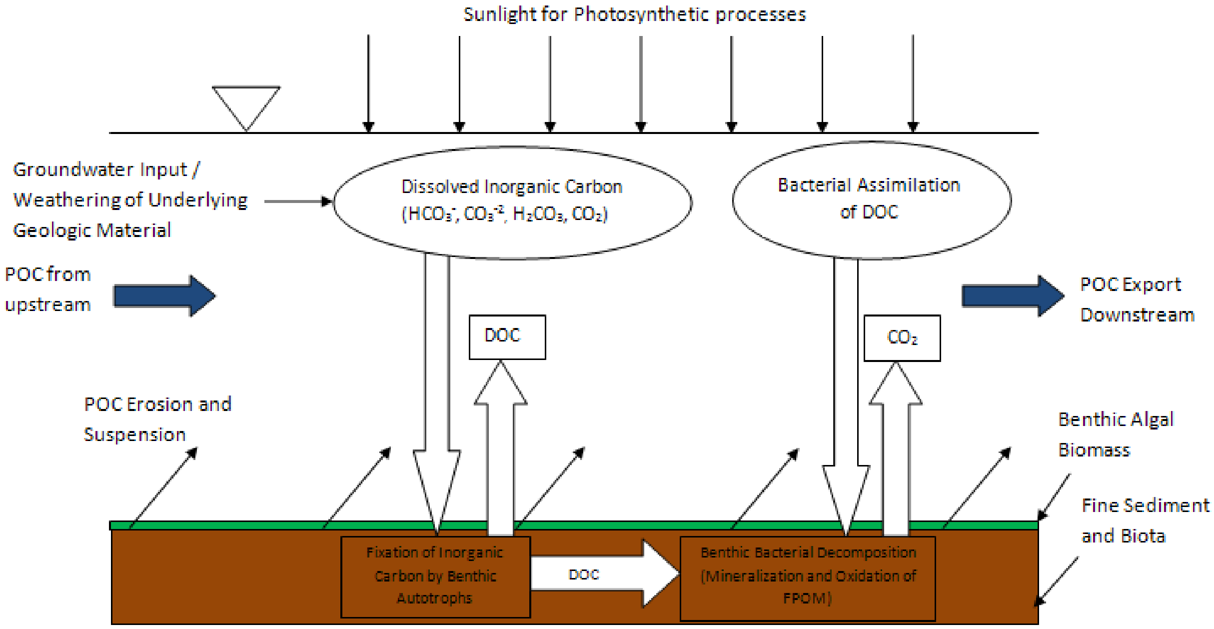


Figure 2-2) In-stream alterations to POC Load (Emphasis on Microbial Processes)

Chapter 3 Study Site: South Elkhorn Watershed

The South Elkhorn (SE) watershed (61.8 km^2) is a lowland, temperate, mixed land-use system located in the Inner Bluegrass Physiographic Region of Central Kentucky. The South Elkhorn was chosen as the test bed for this study for four primary reasons (i)the lowland system allows persistence of in-stream processes; (ii) the mixed land use system promotes investigation and data collection for an urbanizing agricultural watershed; (iii) the work of previous research studies including aggregate analysis (Sliter, 2007), sediment fingerprinting (Davis, 2008), hydrologic and sediment transport modeling (Russo, 2009), and nitrogen modeling (Fox et al., 2010); (iv) proximity of the site to the University of Kentucky.

The stream is characterized as a lowland system due to its relatively mild gradients (Figure 3-2). The lowland system provides a condition in which pronounced temporary storage of fine sediments occurs. Carbon stored in these temporary storage zones has been relatively understudied and represents an unknown source of carbon to regional and global carbon budgets (Cole et al., 2007). Likewise, lowland systems provide a testbed for coupled physical and biological model development.

In addition to being a lowland temperate system, the South Elkhorn is unique in that it is an urbanizing watershed with agriculture being the predominant land use. Unlike many agricultural systems, the South Elkhorn is predominantly composed of horse farms and grazing pasture land. Protective measures have been conducted to ensure that erosion is minimized in these upland hillslopes. Figure 3-3 depicts the different land uses found in the South Elkhorn Basin. Estimates predict that approximately 55% of the watershed is agriculture and 45 % is urban area. Previous studies (such as Russo, 2009) have investigated the impact of urbanization on sediment transport processes in the watershed. A similar analysis for POC would be advantageous; however it is out of the scope of this study and will be conducted at a later time. This watershed is representative of other watersheds throughout the region. Hence, there is an opportunity to upscale results from this system to the entire region in order to make regional estimates and future predictions with regards to carbon cycling and sediment transport processes.

The South Elkhorn watershed is located in the Inner Bluegrass Region, minutes away from the University of Kentucky. This has allowed researchers to perform high temporal and spatial resolution sampling with regard to sedimentary and hydrologic processes for the past 5 years (2006-2010). Likewise, a USGS gauging station has provided continuous five minute flow and precipitation data. A NOAA weather station at the Bluegrass Airport, located at the center of the study basin, is used to collect meteorological data. Figure 3-1 shows the location of the test site relative to the state. Additionally, geospatial data is readily available for the watershed, including 30 meter DEMs, land use maps, a region map, and a soils map.

Although a dense data set of hydrologic, sediment transport, sediment fingerprinting, and aggregate data has been collected, ongoing studies in the watershed drive the need for further data collection. To accurately assess the impacts of processes such as urbanization, many more years of data will be necessary. Likewise, modeling biological processes can occur on a relatively slow timescale. Therefore, long term datasets are needed to develop trends and fully understand the processes. For example, as is seen later in this thesis, carbon content can vary seasonally, but it can also vary from year to year, thus the five years used in this study would be a minimum of what is desired for a model with a biological component.

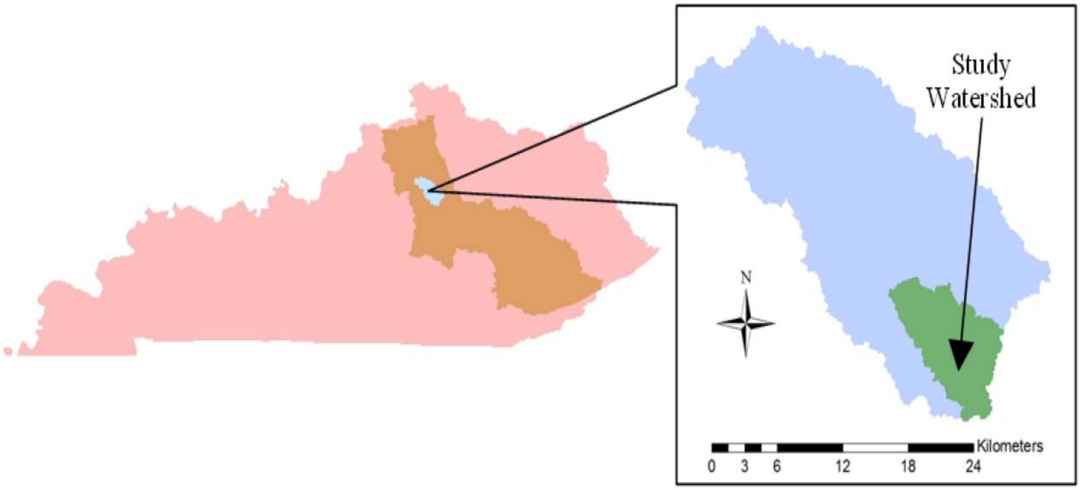


Figure 3-1) Study site location (Russo 2009)

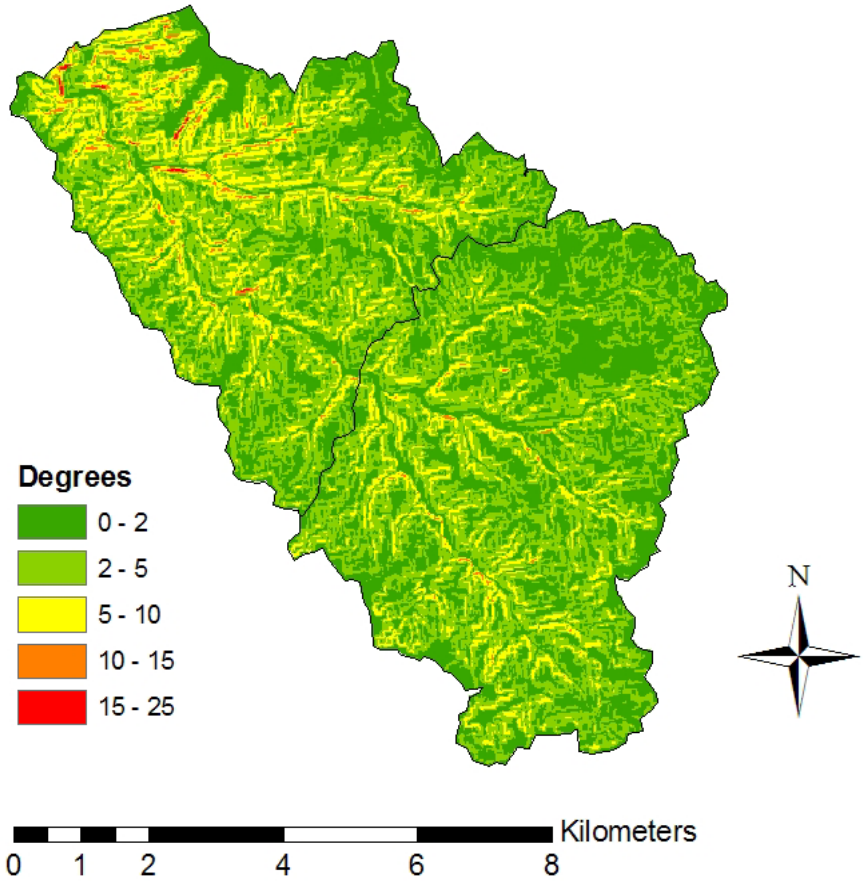


Figure 3-2) Slope map of the South Elkhorn watershed

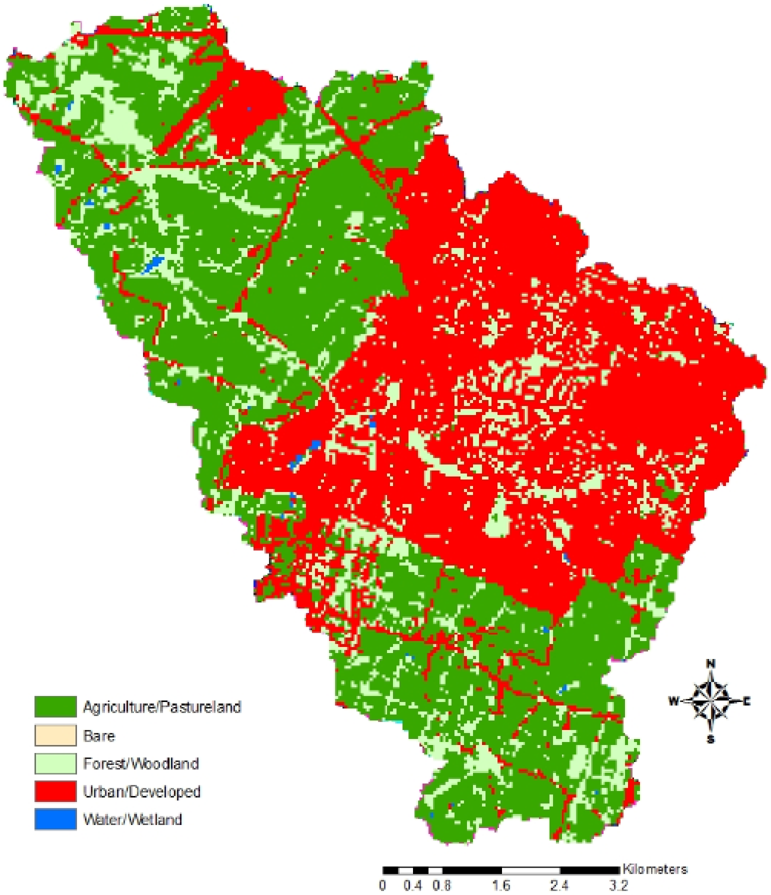


Figure 3-3) Land-use map for the South Elkhorn watershed

Chapter 4 Data Collection Methods

4.1) Hydrologic Data

For models impacted by physical processes, such as sediment and carbon transport in a river system, flowrates are necessary to drive the models. For this study, flowrates were obtained on a five minute basis from a USGS gauging station at the watershed outlet. The identifier for the gauging station is "USGS 03289000 SOUTH ELKHORN CREEK AT FORT SPRING, KY". Stage and precipitation data was also collected from the gauging station at five minute intervals. Precipitation, wind speed, percent sun, and daily and hourly temperature was collected from a NOAA weather station located at the Blue Grass Regional Airport in the center of the watershed.

4.2) Sediment Transport Data

Sediment concentration can be measured through direct measurements using an automated pump sampler. A Teledyne ISCO automated pump sampler was installed at the outlet of the study watershed in order to obtain sediment concentrations during storm events of various magnitudes. Samples were analyzed in the lab using Whatman filters, which retain sediments greater than 0.45 microns. Since the sampling and laboratory analysis doesn't account for fine sediment alone, a fine sediment fraction was applied to each sample based on an average fines fraction measured from the *in situ* sediment traps.

Concentration measurements and velocity profiles were used to estimate suspended sediment flux (Q_{ss}) *via* the following equation (Chang, 1988)

$$Qss = B\int_a^H u(z)C(z)dz\,, \tag{1}$$

where, *u(z)* represents the velocity profile as it changes with flow depth, *B* is the average width of the channel cross section, *C(z)* is the concentration profile equation, *a* is the depth at which fine sediment suspension begins and *H* is the flow depth.

4.2.1) Sediment Concentration Profile

Because sediment concentrations were obtained at a fixed point in the stream, the Rouse equation was used to generate the concentration profile. The following represents the general form of the equation,

$$\frac{C}{C_a} = \left(\frac{D-z}{z} - \frac{a}{D-a}\right)^{z_*}, \tag{2}$$

$$Z_* = \frac{\omega_s}{\kappa U_*}, \tag{3}$$

where, C is the concentration at a point z in the stream, C_a denotes the concentration of sediment with fall velocity (ω_s) at the level $z = a$, D is the depth of the water, z_* is the exponent for the Rouse equation, defined by settling velocity, the von Karman constant and U_* which is the friction, or shear, velocity defined as

$$U_* = \sqrt{\mathrm{gRS}}, \tag{4}$$

where, g is the acceleration due to gravity, R is the hydraulic radius and S is the slope of the water surface.

Flow depth was calculated by developing a relationship between the stage height at the gauging station and at the ISCO nozzle sampler. Height measurements were collected over five years from 2006-2010. Although there was some scatter in the data, the stage relationship showed a strong correlation as seen in Figure 4-1.

4.2.2) Velocity Profiles

Velocity profiles are also needed to derive sediment flux estimates. These profiles can be generated in the field using propellometers, acoustic Doppler sensors, or vertical-axis meters. Likewise, models can be used to simulate profiles for given flow depth conditions. For this study, the log law was used to model the profiles based on a given flow depth. The following is the equation used to model the profiles over a hydraulically-rough channel bed

$$\frac{u}{U_*} = 8.5 + 2.5 \ln \frac{z}{k_s}, \quad (5)$$

where, k_s is the mean diameter of sand grains, and z is the depth of water.

4.3) POC Data

In this study, OC content of suspended sediments was obtained at the outlet of the South Elkhorn Watershed. The data, as described below, is used to calibrate the POC model. Currently, carbon data is available from 2006-2009. This extensive dataset allows the temporal seasonal component to be assessed.

4.3.1) Field Method

Transported POC was measured using samples collected over a four year period (2006-2009). This data is used to calibrate the POC flux model for the subwatershed. Samples were collected using *in situ* sediment trap samplers (Phillips et al., 2000) at the outlet of the watershed. The test section is composed of PVC pipe and is cleaned thoroughly, rinsing with DI/DO water after each use. The sampler works by accelerating suspended slurry of sediment and water into the test section through a small opening. As the cross sectional area increases, the velocity decreases and the sediment particles settle out. The water then exits the test section through a small outlet.

According to Phillips et al. (2000) the *in-situ* trap has a trapping efficiency ranging from 31-71% depending upon the size class. However, the sediment fraction in the sampler is coarser then inflowing sediment. Although the trapping efficiency is not ideal for fine sediments, the sediment collected by the sampler provides a representative weighted estimate of total carbon over the sampling period. Figure 4-2 displays the setup of the PVC test section. Likewise, Figure 4-3 displays the sampler implemented in the field.

4.3.2) Lab Method

Approximately 100 samples were collected in the field from March of 2006 through the end of 2009. The samples were used to generate estimates of TOC content of sediments. Sediment samples were brought back to lab and processed for elemental analysis through centrifugation, freezing, freeze drying, consolidating and weighing, wet sieving and elemental analysis processes.

Sediment trap samples were collected in 5 gallon buckets, placed in a refrigerator and settled for 48 hours. Water on top of the sample was then siphoned off and the sediment slurry was dispensed into 750 mL bottles. Samples were centrifuged using a SH-3000 rotor, rotating at a velocity of 4250 rpm for 4-7 minutes. Water was decanted and the bottles were consolidated. After separating a significant portion of the water from the sample, the samples were then placed in a freezer overnight. Once in a solid state, the samples were placed in a freeze drier until the sediment sample was completely dry. Freeze-dried samples were consolidated into one container and the mass of bulk sediment was weighed.

A subsample was taken based on the weight of sediment in the bulk sample. The subsample was then wet-sieved to separate the fine material (<53 µm) for further analysis. Samples were sieved until clear water passed through the sieve and the bulk sample. After sieving, samples were poured into 250 mL bottles. Because water was reintroduced during the wet sieving process; further centrifugation was needed on the samples. Samples were centrifuged in a similar fashion as before. If samples were still murky after centrifugation, 10mL Magnesium Chloride Hexahydrate was added to the sample to help sediments settle. Samples were frozen and freeze dried in the same manner as before. Freeze-dried samples were consolidated into one container and the mass of the fine sediment sample was weighed in order to obtain a fines fraction.

Samples were then ground in order for them to be easily combustible during elemental analysis. Powdered samples were weighed into silver capsules that were subsequently acidified repeatedly with 6% sulfurous acid in order to remove carbonate phases. Samples were analyzed using a Costech 4010 elemental analyzer. Average standard deviations for the samples of the elemental standard (acetanilide) were 0.82% and 0.11% for %C and %N, respectively.

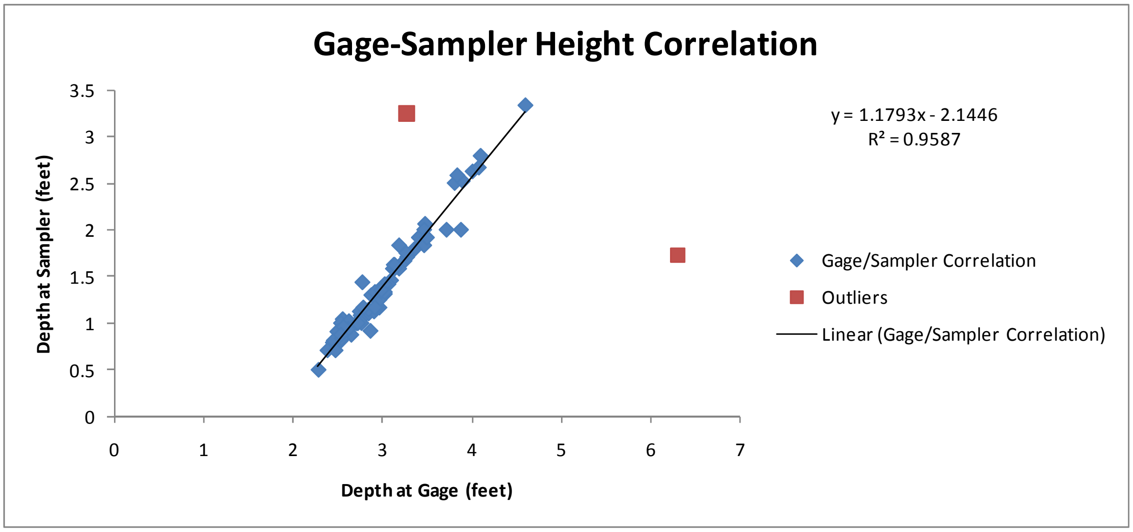


Figure 4-1) Height correlation between sampling site and USGS gauging station

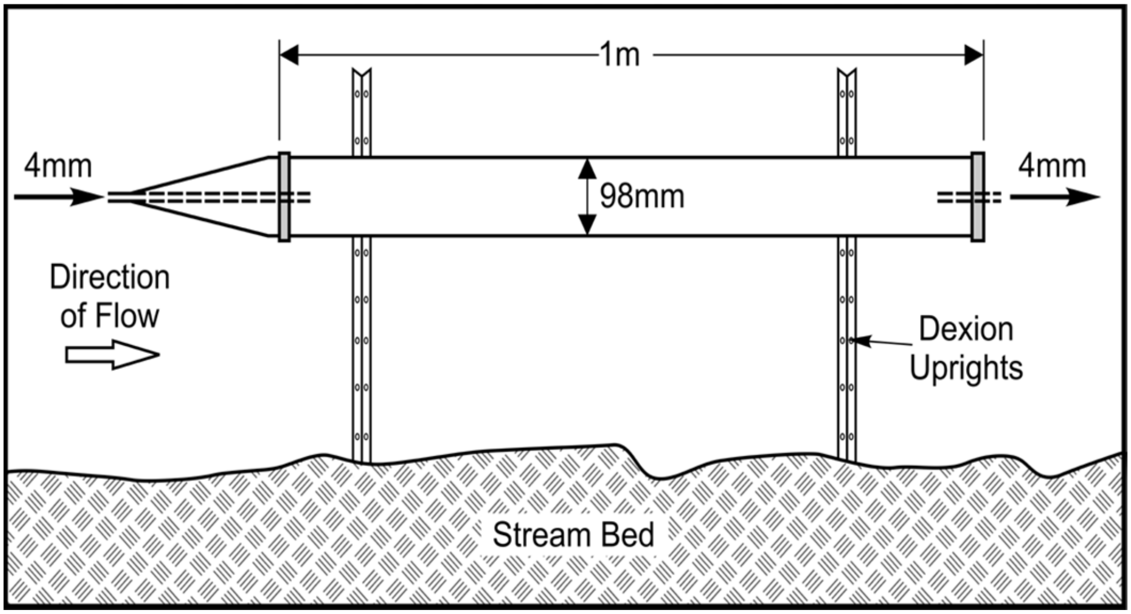
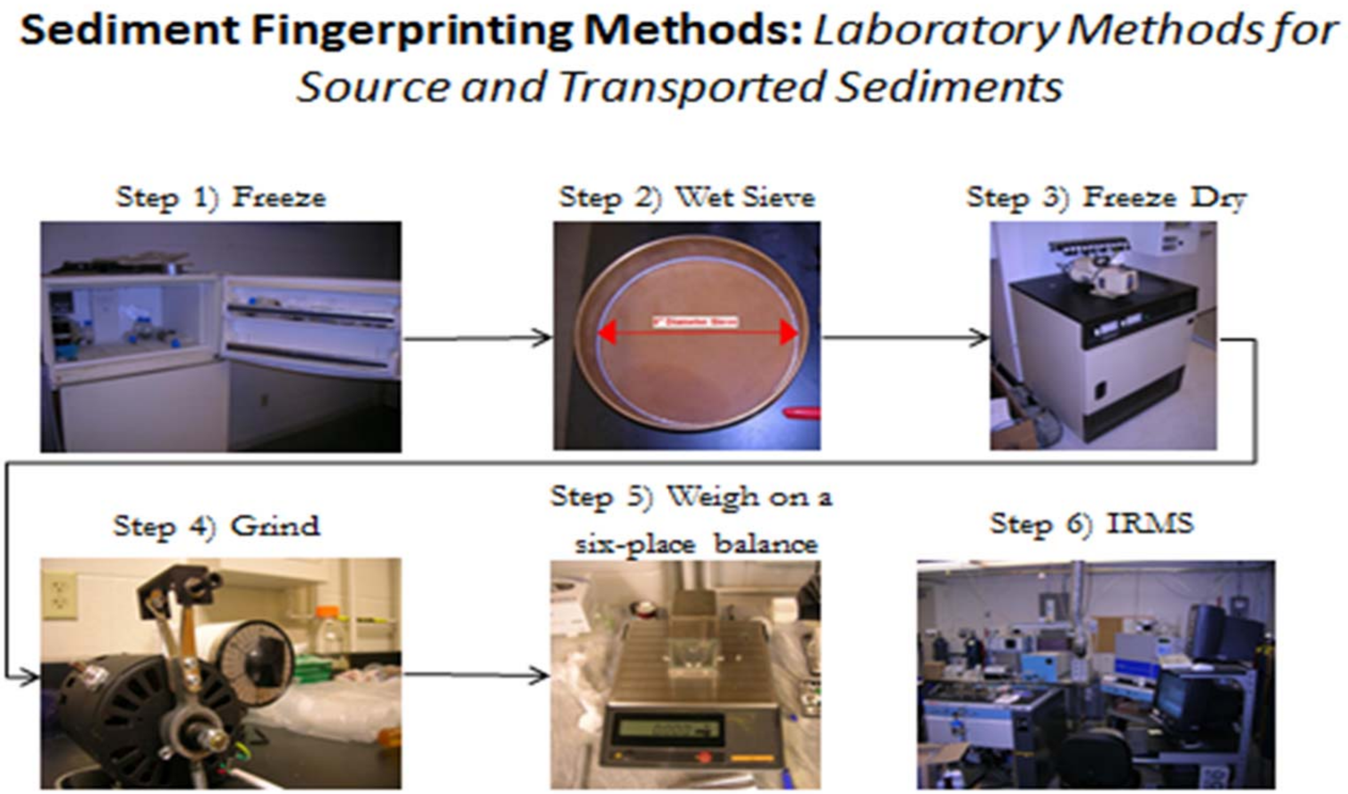


Figure 4-2) ***In-situ*** **sediment trap (Phillips et al. 2000)**

Figure 4-3) ***In-situ*** **sediment trap implemented in the field**



Sediment Fingerprinting Methods: *Laboratory Methods for Source and Transported Sediments*

Step 1) Freeze

Step 2) Wet Sieve

Step 3) Freeze Dry

Step 4) Grind

Step 5) Weigh on a six-place balance

Step 6) IRMS

Figure 4-4) Laboratory procedures used to prepare samples for elemental analysis

Chapter 5 POC Modeling Methodology and Development

5.1) Overview and Framework Development

The purpose of this study is to generate new estimates of POC flux, and to provide a comprehensive methodological approach developed from the conceptual framework. In fluvial systems, POC flux is a function of fluvial transport and carbon content of suspended sediments. Field and lab analysis was performed for the South Elkhorn watershed (third order reach), and a POC budget was generated for the South Elkhorn stream reach. The following section will outline the processes involved in modeling POC flux using a coupled, feed-forward modeling approach.

Modeling of POC flux at the watershed scale was conducted using a coupled model framework including hydrologic, sediment transport, and POC models. The drainage-area ratio method was utilized to estimate flowrates at each of the watershed outlet nodes delineated in GIS. From the hydrologic model, flowrates are used to drive the sediment transport model. Sediment transport modeling is used to quantify the loads leaving the reach and to perform a mass balance of bed sediments. The sediment transport model is used as an input for the POC model. POC modeling accounts for growth and decomposition rates of carbon in bed sediments including autochthonous growth, mineralization of organic carbon, and transformation of DIN to POC *via* autotrophs. These processes can impart significant changes to the POC load, especially in lowland systems such as the Upper South Elkhorn. Figure 5-1 displays a flowchart of the processes whereas Figure 5-2 depicts a pictorial representation of the processes occurring in the watershed. Although the framework addresses the upland processes that impact POC in the stream, it is important to point out that the focus of this project is on the in-stream transformations. Future work may look more into processes in the uplands that impact the POC load; however for the time being this modeling effort focuses on in-stream transformations to the POC load.

5.2) Hydrologic Model

Although flowrates are available at the outlet of the watershed, estimated flows are needed along the stream reach in order to model sediment transport processes at a higher temporal resolution.

The POC and sediment transport models are driven by the hydrology of the watershed. Currently, flowrates are generated using the drainage-area method which is highly data driven. In order to simulate future climate and land use scenarios a hydrologic model will be needed. Hydrologic models can simulate single events, continuously, or a combination of both. Event hydrologic models aid in understanding underlying hydrologic processes and identifying relevant parameters, whereas continuous models synthesize processes and phenomena over a longer period of time including wet and dry conditions (Chu and Steinman, 2009). When selecting a model it's important to identify if the model was developed for continuous or event based modeling. For example, a study by Borah and Bera (2003) analyzed eleven watershed-scale hydrologic models and found their mathematical strengths and applicability to various types of watersheds. Continuous simulation models include AnnAGNPS, ANSWERS-Continuous, HSPF, and SWAT. Event based models in the study were AGNPS, ANSWERS, DWSM, and KINEROS. Models with both continuous and event based simulation functionality included CASC2D, MIKE SHE, and PRMS. This study is useful for choosing a hydrologic model that best fits a certain watershed.

In the present study, the common modeling tool known as the Hydrologic Engineering Center's Hydrologic Modeling System (HEC-HMS) was explored for potential application in future climate and land use scenarios. HEC-HMS is mostly used for event based simulations. However, Chu and Steinman (2009) utilized HEC-HMS as an event based and continuous modeling system by using the SCS curve number method as the event based simulation model and a soil moisture accounting (SMA) model for continuous simulations. The analysis was performed in order to strengthen the overall modeling capacity. They found that using calibrated parameters from the event based model strengthened the results of the continuous model.

A data driven drainage-area ratio method is used as the model to drive the sediment transport and POC models in this thesis. The Drainage-Area Ratio method is commonly used in hydrologic analysis. Emerson, Vecchia, and Dahl (2005) performed a study on streams in which this method was applied. The equation was modified slightly to account for transport time as

$$Y_{i-1} = \left(\frac{A_y}{A_x}\right) X_i, \tag{6}$$

where, Y is the flowrate at the outlet of the modeled watershed at time i-1, X is the the flowrate of the reference basin at time i, A_y is the area of the modeled watershed, and A_x is the area of the reference watershed. Further development of a predictive hydrologic model is needed to assess climate change and various land management scenarios.

5.3) Sediment Transport Model

5.3.1) Flow Depth and Volume Inputs

Sediment flux estimates were generated by coupling a conceptual and empirical modeling approach. The flowrate was determined using flow depth data from the aforementioned hydrologic model, which was calibrated using data from a USGS gauging station. To determine flow depth a power function was fit to Manning's equation. Manning's equation solves for the flowrate (Q) using the following equation

$$Q = \frac{1}{n} A R^{2/3} S^{1/2}, \tag{7}$$

where, A is the cross sectional area (m^2), S is the slope of the water surface (m/m) and n is the manning's roughness coefficient (0.03 for rivers). Fitting a power function to Manning's equation, the following equation was used to generate average flow depth estimates for each time step,

$$H = C_1 (Q)^{C_2}, \tag{8}$$

where, C_1 is the flow coefficient and C_2 is the exponential coefficient.

Since the model uses a Eulerian approach, the outputs are generated for a specific cross section. First the water volume, V, is obtained as

$$V_i = V_{i-1} + [Q_i - Q_{i-1}]\Delta t, \tag{9}$$

where, Δt is the time step in seconds. Initial Volume is determined based off the following equation

$$V_{initial} = (B + zH) H_{initial} L, \tag{10}$$

where, B is the width of the channel (meters), and z is the ratio of the horizontal to the vertical component of the side slope, and $H_{initial}$ is based off $Q_{initial}$.

5.3.2) Driving Equation for Sediment Transport

A mass balance is conducted to estimate the mass of suspended sediment flux in a stream reach. The mass of sediment in suspension during a given time step is defined as

$$SS_i = SS_{i-1} + E_{i_{bank}} + E_{i_{bed}} - D_i + Q_{ssin_i}\Delta t - Q_{ssout_i}\Delta t, \tag{11}$$

where, SS_{i-1} is the mass of sediment in suspension at the start of the time step (kg), E_{ibank} is the mass of sediment eroded from the bank (kg), E_{ibed} is the mass of sediment eroded from the bed (kg), D_i is the mass of deposited sediments (kg), Q_{ssin_i} is the sediment flow rate into the stream reach (kg/s) and Q_{ssout_i} is the sediment flow rate out of the stream reach (kg/s).

Information regarding sediment inflow to the model reach is limited in the South Elkhorn watershed. Therefore, sediment inflow was estimated using an empirical equation as follows

$$Q_{ssin_i} = C_3\, Q^2\ , \tag{12}$$

where, C_3 is the coefficient used to adjust sediment inflow into the reach. Likewise, sediment outflow during a given time step is calculated as

$$Q_{ssout_i} = \frac{SS_i}{V_i} * Q_i. \tag{13}$$

Thus, substituting equation (28) into equation (26) and rearranging the equation for SS_i we find,

$$SS_i = SS_{i-1} + E_{i_{bank}} + E_{i_{bed}} - D_i + Q_{ssin_i}\Delta t - \frac{SS_i}{V_i} * Q_i\Delta t \tag{14}$$

and then isolated SS_i as

$$SS_i = \frac{SS_{i-1} + E_{i_{bank}} + E_{i_{bed}} - D_i + Q_{ssin_i} \Delta t}{1 + (\frac{Q_i \Delta t}{V_i})} \quad . \tag{15}$$

5.3.2.1) Bank Erosion

The initiation of bank erosion is dependent upon the energy of the flow and the erodibility of the bank. Bank erosion (${E_i}^{bank}$) is initiated where transport and shear are in excess as

If $[T_{c_i} > SS_{i-1} \, , {E_i}^{bank} \, , 0]$

and

$${E_i}^{bank} = \min[\frac{k\left(\tau_i - \tau_{cr}^{Bank}\right)^m \rho_s^{Bank} SA^{Bank} \Delta t}{1000}, T_{c_i} - SS_{i-1}, S_{i-1}^{Bank}] \, , \tag{16}$$

where, k is the erodibility coefficient (Hanson and Simon (2001)), τ_i is the shear stress of the fluid at the centroid of the erosion source (Pa), τ_{cr}^{Bank} is the critical shear stress of the bank (Pa), ρ_s^{Bank} is the bulk density of the bank material (g/cm^3), SA^{Bank} is the surface area of the eroded bank (m^2), T_{c_i} is the transport carrying capacity (kg) and S_{i-1}^{Bank} is the sediment supply from the banks (kg).

The erodibility coefficient (k) is defined as

$$k = 0.1{\tau_{cr}}^{-0.5}; \tag{17}$$

The fluid shear stress (τ_i) is defined as

$$\tau_i = \rho g H_i s \; ; \tag{18}$$

and the surface area of the streambank is defined as

$$SA^{Bank} = (z^2 + 1)^{.5} H_{Bankfull} * 2 * L \; . \tag{19}$$

The transport carrying capacity is modeled using the Bagnold equation (Chien and Wan 1999) and assuming the friction velocity is proportional to the square root of the turbulent shear stress of the fluid as follows

$$T_{c_i} = C_{T_c}(\frac{{\tau_i}^2}{\omega_s})L\Delta t, \tag{20}$$

where, C_{T_c} is the calibration coefficient ($m^{.5}s^2/kg^{.5}$), and ω_s is the settling velocity of the sediment particles.

5.3.2.2) Bed Erosion

Bed erosion is modeled in a similar fashion to bed erosion, except that supply of bed sediments is not infinite, and the critical shear stress of bed sediments is substantially lower. The erosion of bed sediments is defined as

If $[T_{c_i} > SS_{i-1}, {E_i}^{bed}, 0]$,

and

$${E_i}^{bed} = \min[\frac{k(\tau_i - \tau_{cr}^{Bed})^m \rho_s^{Bed} SA^{Bed} \Delta t}{1000}, T_{c_i} - SS_{i-1}, S_{i-1}^{Bed}], \tag{21}$$

where, τ_{cr}^{Bed} is the critical shear stress of the bed (Pa), ρ_s^{Bed} is the bulk density of the bed material (g/cm^3), SA^{Bed} is the surface area of the eroded bed (m^2), and S_{i-1}^{Bed} is the sediment supply from the bed (kg). The surface area of the bed is defined as

$$SA^{Bed} = \%cover * B * L \tag{22}$$

where, *% cover* is the percentage of the bed covered with fine sediment deposition.

5.3.2.3) Bed Depth Monitoring

When transport capacity is limited, deposition (D_i) occurs as

If $[T_{c_i} < SS_{i-1}, D_i, 0]$,

and

$$D_i = \frac{\omega_s \Delta t}{k_p * H_i} * [SS_{i-1} - T_{c_i}], \quad (23)$$

where, k_p is the concentration profile coefficient. A mass balance of the streambed is performed in the model as

$$S_i = S_{i-1} + D_i - E_i^{bed}, \quad (24)$$

where, S_{i-1} is the bed sediment supply at the beginning of the time step (kg). The sediment supply is initialized as

$$S_{initial} = d_{sed} B L \rho_s^{Bed} * 1000, \quad (25)$$

where, d_{sed} is the sediment depth. Stream depth monitoring of the bed (d_i) was conducted as follows,

$$d_i = \frac{S_i}{B L \rho_s^{Bed} * 1000}. \quad (26)$$

The model must account for speed of propagation of the numerical scheme. Hence, the modeled reach was broken up into 5 sub-reaches. A similar mass balance approach was taken on each sub-reach in order to estimate the POC flux at the outlet.

5.4) Instream Carbon Model

5.4.1) POC Bed Sub-model

Carbon content of sediment is modeled during temporary storage of sediment in which the microbial pool can impart changes to the POC load. POC in the bed (POC_{Bed}) and each sub component was budgeted continuously in the model as follows

$$POC_{Bed_i} = POC_{Algae_i} + POC_{SOC_i} + POC_{LD_i} \tag{27}$$

where, $POC_{Algae_i}$is the mass of algal carbon in the active layer during the time step (kgC), POC_{SOC_i} is the mass of carbon from SOM during the time step (kgC), and POC_{LD_i} is the carbon from leaf detritus in the active layer (kgC).

5.4.1.1) Algal Carbon in the active layer ($\boldsymbol{POC_{Algae_i}}$)

Autochthonous carbon is considered to contribute a significant amount of carbon to the POC load especially for lowland systems such as the South Elkhorn watershed. For this study, epilithic algal growth (autochthonous growth on rock surfaces in stream) is modeled to account for this term. Rutherford et al (2000) provides a modeling framework to estimate the rate of biomass accrual of epilithic algae. A generalization of the model was used to account for periphyton growth in streams for the WASP model (Martin et al., 2006). Likewise, this study uses a generalization of the model to account for the quantity of biomass that goes into the fine sediment pool.

Herein, a mass balance approach is taken to determine to the amount of algal biomass present in the active layer as follows

$$POC_{Algae_i} = POC_{Algae_{i-1}} + A_{algal_i} - Res_{FineAlgae_i} - POC_{adjust_{algae_i}}, \tag{28}$$

where, A_{algal_i} is the accrual of algal biomass in the active layer during the given time step (kgC), $Res_{FineAlgae_i}$ is the algal biomass in the active layer that is decomposed and respired as CO_2 (kgC), and POC_{adjust} is used as a term to adjust losses of benthic algal biomass in the active layer due to erosion and deposition processes (kgC).

5.4.1.1.1) Accrual of fine benthic algae in the active layer (A_{algal_i})

Accrual of algal biomass in the active layer is defined as

$$A_{algal_i} = \left(Dec_{CoarseAlgae_i}(F_i + P_{i-1} + P_{col_i} - R_i - S_i)\right) * SA_{Bed} * \Delta t \,, \tag{29}$$

where, $Dec_{CoarseAlgae_i}$ is the decomposition rate of the coarse epilithic algal mat (day^{-1}), F_i is the carbon fixation rate (kgC/day), P_i is the biomass accrual rate in the epilithic algal mat (kgC/day), P_{col_i} is the algal colonization rate (kgC/day), R_i is the respiration rate of the algal mat (kgC/day), and S_i is the scour rate of the algal mat (kgC/day).

Since heterotrophic bacteria are the primary decomposers of organic material in the benthic layer, decomposition rates are assumed to vary proportionally with heterotrophic bacterial growth rates. White et al (1991) modeled heterotrophic bacterial growth rate ($log(SGR_{Bac})_i$) as

$$log(SGR_{Bac})_i = -1.04 + .031 \pm .015 * T_i \tag{30}$$

where, T_i is the water temperature in degrees Celsius. Using a generalized form of this model, decomposition of coarse algae ($Dec_{CoarseAlgae_i}$) is modeled as

$$Dec_{CoarseAlgae_i} = -1.04 + C_4 T_i \tag{31}$$

where, C_4 is the decomposition coefficient. Generally, decomposition rates are modeled in the same fashion as equation (46).

Algal fixation rate determines how quickly the algal mat grows. It is a function of temperature, light intensity, algal population and a maximum fixation rate. The fixation rate of epilithic algae is defined as

$$F_i = p_{max} f(I)_i f(T)_i f(P)_i \tag{32}$$

where, p_{max} is the maximum fixation rate ($gCm^{-2}d^{-1}$), I is the photosynthetically available radiation incident on the surface of the algal mat, and T is the temperature. The light limiting term can be generated using an average $f(I)$ for a 24 hour period as

$$f(I)_{average} = \left(\frac{Day_i}{12\pi}\right)\left[\left(\frac{I_{max}}{I_k}\right) - \sqrt{\left(\frac{I_{max}}{I_k}\right)^2 - 1} + \left(\frac{\pi}{2}\right) - sin^{-1}\left(\frac{I_k}{I_{max}}\right)\right] if \quad I_{max} > I_k \tag{33}$$

and

$$f(I)_{average} = \left(\frac{Day_i}{12\pi}\right)\left(\frac{I_{max}}{I_k}\right) \qquad if \quad I_{max} < I_k \tag{34}$$

where, I_k is the saturation radiation, I_{max} is the maximum daily radiation, and Day is the day length. To estimate the day length, a model developed by Brock (1981) was incorporated. It is out of the scope of this project to discuss the theory behind the model; hence readers should refer to Brock (1981) for detailed information with regards to the model theory. Day length is estimated as

$$Day = 2 * \left(\frac{W}{15}\right), \tag{35}$$

where, W is the hour angle. The hour angle is defined as

$$W = cos^{-1}(-[\tan(lat)\tan(DL)]) \;, \tag{36}$$

where, *lat* is the latitude of the watershed, and *DL* is the declination. The declination is defined as

$$DL = 23.45 * \sin(\frac{360(284+N)}{365}) \;\;, \tag{37}$$

where, *N* is the number of days after January 1^{rst}.

Benthic algal growth is limited by water temperature. The impact of temperature is model as

$$f(T) = e^{-(\frac{T-T_{opt}}{\Delta T_{lower}})^2} \qquad if \quad T_{min} < T < T_{opt} \tag{38}$$

and

$$f(T) = e^{-(\frac{T-T_{opt}}{\Delta T_{upper}})^2} \qquad if \quad T_{opt} < T < T_{max} \;, \tag{39}$$

where, T_{min} is the minimum temperature at which fixation occurs, T_{opt} is the optimum temperature at which the maximum fixation rate for epilithic algae occurs, ΔT_{lower} is the low temperature range, T_{max} is the maximum temperature at which fixation occurs, and ΔT_{upper} is the upper temperature range. The lower and upper temperature ranges are defined as

$$\Delta T_{lower} = (T_{opt} - T_{min})/\sqrt{(ln20)} \quad \text{and} \quad \Delta T_{upper} = (T_{max} - T_{opt})/\sqrt{(ln20)}, \tag{40}$$

As the algal mat becomes thicker, basal cells are shaded and are unable to photosynthesize. Therefore the population level consequence is represented by

$$f(P) = \left(\frac{P}{P_{sat} + P}\right), \qquad (41)$$

where, P_{sat} is the density dependence coefficient (gCm^{-2}) which is defined as the algal biomass at which fixation is half the maximum rate.

The epilithic biomass term (P) is calculated at each time step using the same mass balance approach as equation (44). The colonization term is difficult to model due to complexities in quantifying dislodged material during flooding events. Therefore, for this study (similar to the Rutherford study) the colonization term is a set value.

Respiration is modeled as a first order process, and is a function of temperature. Respiration rate of the algal mat is defined as

$$R = P_{res} f_2(T) P, \qquad (42)$$

where, P_{res} is the respiration rate measured at the reference temperature, and $f_2(T)$ is temperature limitation function for the respiration term. To represent this limitation, the equation is defined as

$$f_2(T) = Pk_{res}^{T-Tref}, \qquad (43)$$

where, Pk_{res} is the temperature coefficient for algal respiration.

Scour was modeled using sediment erosion methods discussed earlier in this section. Critical shear of the algae was used as a coefficient to calibrate the model because it is difficult to pinpoint the type of algae and conditions in which the algae developed. Algal scour occurs at low flows. Erosion and scouring of algal mats is primarily a function of the shear and supply term. For periods of high flows (floods), a large loss of algal growth is sustained. Therefore, algal mat loss is modeled as

$$S_i = \%OC_{algae}\min[\frac{k\left(\tau_i - \tau_{cr}^{algae}\right)^m \rho_s^{algae} SA^{algae} \Delta t}{1000},\ S_{i-1}^{algae}], \tag{44}$$

where, τ_{cr}^{algae} is the critical shear stress of the algae, ρ_s^{algae} is the density of algal material, SA^{algae} is the surface area of the bed covered by the algal mat, and S_{i-1}^{algae} is the algal supply. Similar to bed and bank erosion, the erodibility coefficient (*k*) is defined as

$$k = 0.1{\tau_{cr}}^{algae^{-0.5}} . \tag{45}$$

5.4.1.1.2) Respiration of fine algae ($Res_{FineAlgae_i}$)

For this thesis, it is operationally defined that the second stage of algal decomposition is the respiration stage. At this point, algal carbon in the bed is lost as CO_2. The respiration rate of fine algae is defined as

$$Res_{FineAlgae_i} = Dec_{FineAlgae_i} * POC_{algal_{i-1}} * \Delta t , \tag{46}$$

where, $Dec_{FineAlgae_i}$ is the decomposition rate of fine algae (day^{-1}) and is defined in the same manner as equation (46).

5.4.1.1.3) Adjustment of the active benthic layer ($POC_{adjust_{algae_i}}$)

Erosion and deposition dynamics heavily impact the active layer. Because the active layer is defined as the first 5 mm of the benthic layer, erosion slowly cuts away at the active layer. Algae in the fine pool are assumed to be well mixed throughout the active layer. Therefore, to adjust the algal pool for erosion, the remaining algae in the fine pool are scaled by the depth of the active layer remaining. The adjustment to the algal pool if erosion is greater than zero is defined by

$$POC_{adjust_{algae_i}} = \frac{d_{eroded_i}}{5} POC_{algal_{i-1}} \qquad if \;\; E_{bed_i} > 0 \;, \tag{47}$$

where, d_{eroded} is the depth of sediment eroded during the timestep (mm).

Deposition also reduces algae in the active layer because SOM is the predominant sediment source during deposition. If an event deposits more than 5 mm of sediment, the active layer would be reset to the mass of carbon in SOM. The adjustment of algae in the fine pool due to deposition in a given time step is defined by

$$POC_{adjust_{algae_i}} = \left(\frac{d_{deposited_i}}{5}\right) POC_{algal_{i-1}} \qquad if \;\; D_{sed_i} > 0 \;, \tag{48}$$

where, $d_{deposited_i}$ is the depth of sediment deposited on top of the active layer (mm).

5.4.1.2) Carbon associated with SOM (POC_{SOC_i})

The SOM pool is herein defined as fine sediment particles eroded from upland soils, or coarse SOM that is decomposed to FPOM. When the benthic layer adjusts laterally, this thesis uses the assumption that the material is SOM. Similar to algae, a mass balance approach is needed to assess the SOC pool in the active layer. Initially, the model uses the assumption that the entire active layer is composed of SOM. The mass balance approach to budget benthic SOC is

$$POC_{SOC_i} = POC_{SOC_{i-1}} + POC_{Dep_{SOC_i}} - POC_{Erosion_{SOC_i}} - POC_{adjust_{SOC_i}} - Res_{SOC_i} + \\ POC_{CoarseSOC_i}, \tag{49}$$

where, $POC_{Dep_{SOC_i}}$ is the mass of SOC deposited to the streambed in a given timestep (kgC), $POC_{Erosion_{SOC_i}}$ is mass of SOC eroded from the active layer during a given timestep (kgC), $POC_{adjust_{SOC_i}}$ is the term used to adjust the SOC pool to account for the shifting of the benthic layer (kgC), and $POC_{CoarseSOC}$is the coarse SOC that is decomposed and enters the fine pool during a given timestep (kgC).

5.4.1.2.1) Erosion and Deposition ($POC_{Dep_{SOC_i}}$ & $POC_{Erosion_{SOC_i}}$)

The mass of POC deposited to the streambed is defined as

$$POC_{Dep_{SOC_i}} = \frac{(\%\,OC_{SOM})}{100} * D_{sed_i}\ , \tag{50}$$

where, $\%OC_{SOM}$ represents the carbon content of suspended SOM. Erosion of fine SOC from the bed was modeled in a similar fashion, using erosion estimates from the sediment transport model as

$$POC_{Erosion_{SOC_i}} = \frac{(\%\,OC_{SOM})}{100} * E_{bed_i}\ . \tag{51}$$

5.4.1.2.2) Adjustment of the Active Layer ($POC_{adjust_{SOC_i}}$)

Further exploration of the anoxic layer underneath the active layer is needed to improve this model. Currently, the assumption is that the anoxic layer is composed of SOM with the same %OC as the upland soils; hence the adjustment and erosion components cancel out. Similarly, as sediment is deposited onto the active layer, the upward adjustment of POC from SOM would cancel out the mass of SOM that is deposited to the streambed. For now, these assumptions are valid, however further exploration of deposited sediments and the anoxic layer will allow for a more in depth model. Furthermore, adjustments for erosion will be negative and deposition will be positive based on the sign convention in the mass balance equation. The adjustment term is defined as

$$POC_{adjust_{SOC_i}} = -\, d_{eroded_i} * \%OC_{anoxic} * \rho_s^{anoxic} * SA_{bed} \qquad if\ E_{bed_i} > 0 \tag{52}$$

and

$$POC_{adjust_{SOC_i}} = d_{deposited_i} * \%OC_{SOM} * \rho_s^{SOM} * SA_{bed} \qquad if\ D_{sed_i} > 0, \tag{53}$$

where, $\%OC_{anoxic}$ is the organic carbon content of the anoxic layer, ρ_s^{anoxic} is the density of the anoxic layer (kg/m^3), and ρ_s^{SOM} is the bulk density of the SOM (kg/m^3).

5.4.1.2.3) Respiration of fine SOM (Res_{SOC_i})

Respiration of fine SOM to the water column as CO_2 is estimated in a similar manner as the fine algal pool. The respiration of fine SOM is determined by

$$Res_{SOC_i} = Dec_{SOC_i} * POC_{SOC_{i-1}} * \Delta t, \tag{54}$$

where, Dec_{SOC_i} is the decomposition of fine SOC (day^{-1}) and is modeled in the same manner as before.

5.4.1.2.4) Addition of Coarse SOM to the Fine SOM Pool ($POC_{CoarseSOC_i}$)

Based on the size class modeled, Coarse SOM undergoes one stage of decomposition before it goes into the fine SOM pool. The mass of Coarse SOM that goes into the fine pool is determined by

$$POC_{CoarseSOC_i} = CSOM * \%OC_{CoarseSOC} * Dec_{CoarseSOC_i} * \Delta t\ , \tag{55}$$

where, $CSOM$ is the mass of coarse SOM present in the bed (kg), $\%OC_{CoarseSOC}$ is the percent of organic carbon present in the Coarse SOM, and $Dec_{CoarseSOC_i}$ is the decomposition rate of coarse SOM (day^{-1}). The mass of coarse SOM is assumed constant throughout the modeling period and is estimated using the initial mass of fines and a fine/coarse sediment fraction. The decomposition term was modeled the same manner as equation (46).

5.4.1.3) Allochthonous Leaf Litter (POC_{LD_i})

Though the South Elkhorn is a watershed dominated by agricultural and urban land uses, a significant quantity of allochthonous leaf detritus is available for consumption by the microbial pool. As the allochthonous leaf litter is broken down it goes through different size pools. To get to the fine pool, the leaf litter is operationally defined to go through two stages of decomposition. After the first stage of decomposition, the “medium” size leaf litter (LD_{medium}) is defined as

$$LD_{medium_i} = (\%OC_{LD} * Dec_{CLD_i} * M_{LD} * \Delta t) - POC_{LD_i} - Adjust_{MLD_i} \quad , \qquad (56)$$

where, $\%OC_{LD}$ is the percent organic carbon of leaf detritus, Dec_{CLD} is the decomposition rate of coarse leaf detritus (day^{-1}), M_{LD} is the mass of benthically available leaf detritus on the streambed surface(kg), and $Adjust_{MLD}$ accounts for deposition erosion dynamics of the impacting the fine pool (kgC). The decomposition rate was modeled in the same manner as before, and the adjustment to the medium leaf detritus pool was conducted in the same manner as before. POC that goes from the medium pool into the fine pool is defined as

$$POC_{LD_i} = Dec_{MLD_i} * LD_{medium_{i-1}} * \Delta t - Res_{FLD_i} - Adjust_{FLD_i}, \qquad (57)$$

where, Dec_{MLD_i} is the decomposition rate of the medium leaf detritus (day^{-1}), Res_{FLD_i} is the respired mass of fine leaf detritus (kgC), and $Adjust_{FLD_i}$ is the adjustment for erosion, deposition dynamics (kgC). Decomposition was performed in the same manner as before, respiration was performed in the same manner as before and physical adjustments were performed in the same manner as before.

5.4.2) POC Transport Sub-model

For this study it was assumed that bed, bank and upland material were the primary sources of POC to the system. Since erosion of bedrock is negligible in the South Elkhorn watershed, fossil POC was ignored. Using results from the sediment transport model, fractions for eroded bed ($f_{E^{bed}}$), bank ($f_{E^{bank}}$) and upland ($f_{Q_{ssin}}$) material were identified for each timestep in each reach. A mass balance approach was taken in which the suspended sediment was assumed to be well mixed.

POC flux estimates were then generated for the reach using a mass balance approach as follows

$$POC_{flux_i} = \frac{(f_{E^{Bed}_i} * \%OC_{bed_i} * Q_{ssout_i}) + (f_{E^{Bank}_i} * \%OC_{bank_i} * Q_{ssout_i}) + (f_{Q_{ssin_i}} * \%OC_{Q_{ssin_i}} * Q_{ssout_i})}{\Delta T * A_w} \qquad (58)$$

where, $\%OC_{bed_i}$ is the organic carbon content of the bed at a given timestep, $\%OC_{bank_i}$ is the organic carbon content of bank sediments, and A_w is the area of the watershed. Percent OC of the bed is estimated as the POC in the active layer divided by the total mass of sediments in the active layer.

Likewise the %OC transported in the stream can be tracked for each time step using a weighted average of the fractions as

$$\%OC_{Transported_i} = (f_{E^{Bed}_i} * \%OC_{bed_i}) + (f_{E^{Bank}_i} * \%OC_{bank_i}) + (f_{Q_{ssin_i}} * \%OC_{Q_{ssin_i}}) \qquad (59)$$

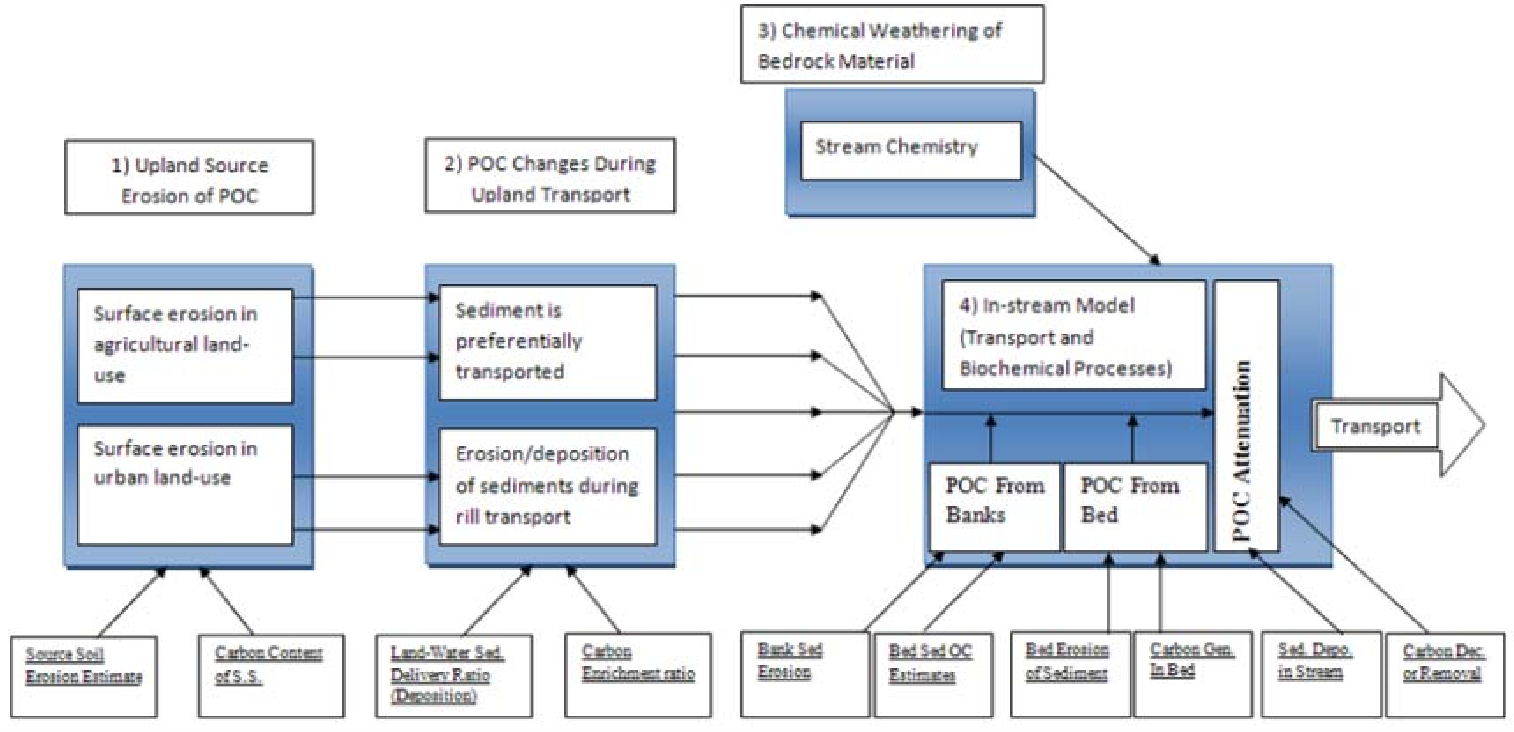


Figure 5-1) Modeling framework flowchart

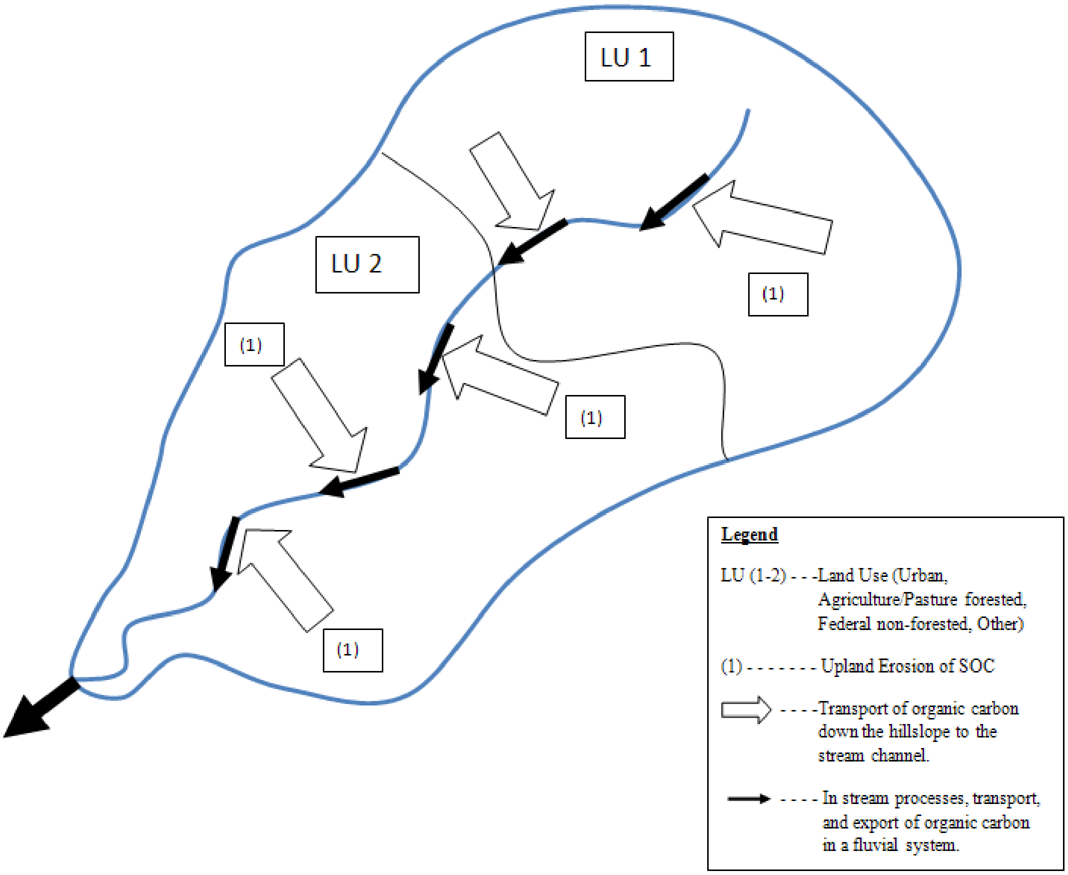


Figure 5-2) Picture of the watershed processes impacting POC

Chapter 6 Data Results

6.1) Hydrologic Flowrates

Flowrates from the South Elkhorn are obtained from the USGS gauging station at Fort Springs (USGS 03289000). Hydrologic variables such as stage, discharge, temperature, turbidity and precipitation are recorded at the gage. The station has been active for 60 years, with annual peak flows available. The peak flow during this time period was 145 cms on September 23rd 2006. Real time data for the past 120 days and historic data sets are available at waterdata.usgs.gov. Five minute flowrate data from 2006-2010 was obtained and used for the present study. Figure 6-1 displays the time series dataset obtained from the South Elkhorn. The peak flowrate for this time period was the same as the peak flowrate for the entire 60 year data collection period. The average for the five year period was 1.19 cms. Baseflow was estimated at 0.3-0.4 cms.

6.2) Sediment Transport

Hydrology drives the transport of fine sediments in watersheds. Hence the flowrates obtained above were utilized to analyze sediment fluxes at the outlet of the watershed. As discussed in the data methods section, sediment concentration samples were obtained at the outlet of the watershed. Furthermore, sediment flux estimates were calculated using the Rouse equation and log law. Eleven events were sampled using the Teledyne ISCOs. The log law and Rouse equation depend on water depth. It is believed that these equations may be sensitive to the step size (i.e. the depth increment) used to calculate the sedigraphs. In order to test the sensitivity, sediment fluxes were calculated for an event which had variation in sediment concentration, velocity and water depth. Figure 6-2 shows the results of the sensitivity analysis.

The values in the Figure 6-2 reflect percent differences between the sediment flux for a given interval vs. the sediment flux for 20 intervals. Twenty intervals were chosen as the reference through an iterative process in which analysis was performed for a given amount of intervals and the percent difference was computed until the solution converged. The sensitivity analysis showed that breaking the water column up into 10 even steps would yield strong results but not overburden the analysis. Although further finite step sizes could be used, small differences in sediment flux results. Hence for each of the eleven sedigraphs used to calibrate the model, sediment fluxes were calculated. Table 6-1 provides a summary of the event date, peak flowrate and peak sediment flow rate. Likewise, Figure 6-3 shows the calculated sedigraphs that are used for the calibration of the sediment transport model.

6.3) POC

For this study, elemental analysis was performed on sediment trap samples (discussed in methods) from 2006-2009. Figure 6-4 shows the resulting dataset. The red line shows the approximate mean through time and is superimposed on the dataset. Visually, it is evident that there is some seasonality to the data which is believed to be a result of the benthic processes in the streambed. Variability in the dataset can be caused by several things. First, origins of transported sediments during an event and from one event to the next can be highly variable. This is believed to be the main cause for the variability in the data. In addition, errors in the collection and analysis (methodological approach) can propagate through and cause some variability and bias in the results.

6.3.1) Discussion of POC Data Results

The seasonality shown in this data set is an important finding that has not had a strong emphasis placed on it up to this point. Although many studies discuss the importance of hydrologic/hydraulic forcing of carbon (such as Gomez et al. 2003, Dalzell et al. 2005) studies typically do not discuss the seasonality of exported POC (with the exception of Zhang et al. 2009). The following section seeks to describe the POC data set, highlighting possible explanations to the seasonality based on the POC fate and transport understanding.

Seasonal variability can result from a multitude of processes. Because seasonal patterns are typically related to temperature and light availability, biological alterations to the POC load are expected to be the driving force behind the seasonal variation. Autochthonous production is one way in which POC can experience seasonal variability. Rutherford et al. (2000) developed a model to estimate epilithic algal biomass throughout the year, using temperature and light intensity as the primary variables. Furthermore, a study in Turkey (Kara and Sahin 2001), discussed seasonal variations in epipelic algae. The study showed that the highest algal density was found in August, while the lowest was found in December. Many other studies have been conducted to assess the seasonality of algae with regards to light, nutrient, temperature and flow parameters (Fracoeur et al. 1999, Cox 1990, Meybeck 2006 and Biggs 1996).

Allochthonous inputs can also impart seasonal variability to the transported POC load. Leaf fall in the autumn results in available benthic leaf litter detritus for heterotrophic bacteria. As the material breaks down, it goes into the fine pool as POC. In heavily forested environments, (Richardson 1992) benthic detritus can constitute a significant portion of the POC pool. However, in urban /agriculture systems, benthic detritus may not contribute a significant portion to the POC load because it takes a long time for the detritus to be decomposed to the POC size class.

Based on this discussion, it is believed that algal inputs during warm months are the primary cause for seasonality of the transported POC data. Variability of the results is likely heavily influenced by erosive floods that can “reset” the algal biomass (Rutherford et al. 2000) and erode carbon from a variety of sources. Although it is outside the scope of this thesis, testing algal biomass in-stream could be conducted similar to the methodology of Ziegler and Lyons (2010). The study looked at how nutrient availability, stoichiometry, and active biofilm composition regulate carbon cycling in epilithic biofilms. Chapter 7 and 8 of this thesis go more in depth with regards to seasonal and annual variation of POC.

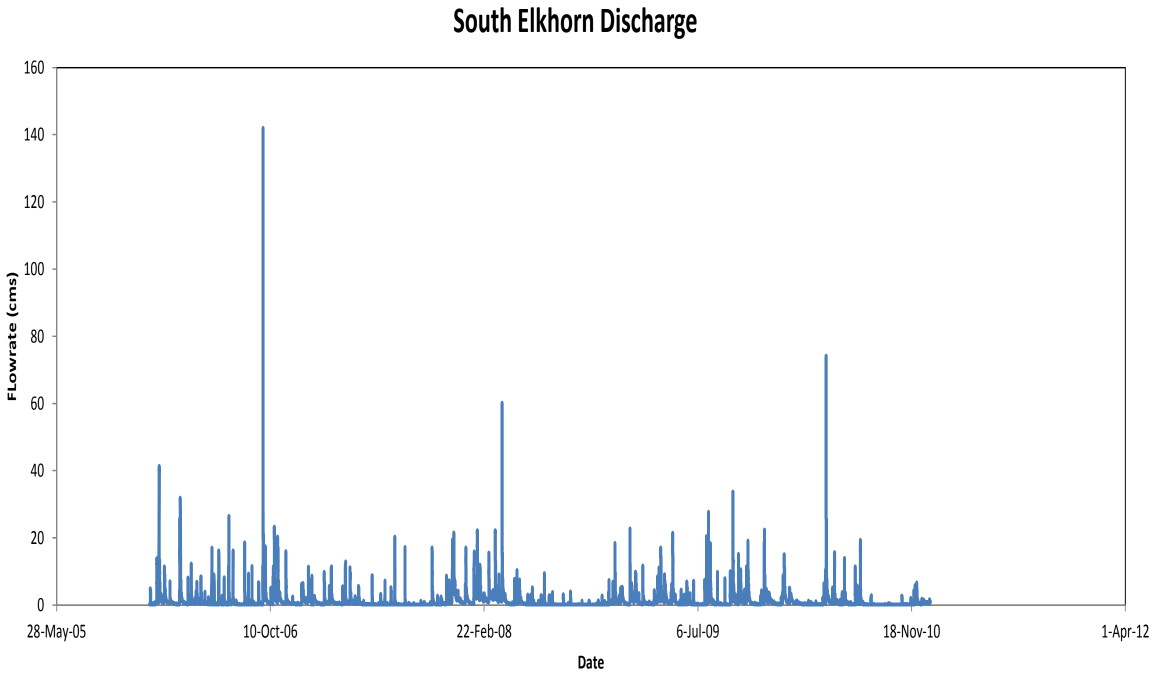


Figure 6-1) Discharge measurements from USGS 03289000 from January 2006-December 2010.

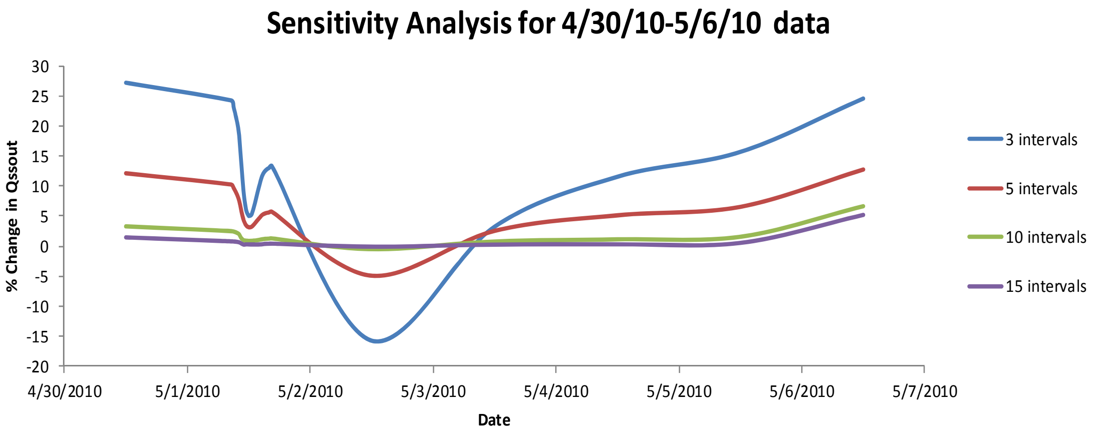


Figure 6-2) Sensitivity of the Rouse equation to a variety of depth intervals.

Table 6-1) Summary of events used to generate sediment loads at the outlet of the watershed (cms is cubic meters per second and kg/s is kilograms per second).

Event Date	*Peak Flow (cms)*	*Peak Sediment Flow (kg/s)*
12/2/07-12/5/07	7.32	0.26
2/21/08-2/23/08	3.46	0.021
4/10/08-4/11/08	3.24	0.019
5/14/08-5/16/08	7.53	0.18
7/30/08-7/31/08	3.61	0.12
10/7/08-10/8/08	1.25	0.014
2/26/09-2/28/09	11.69	0.61
4/13/09-4/14/09	3.84	0.05
5/8/2009	21.44	1.62
4/15/10-4/24/10	2.35	0.056
4/30/10-5/6/10	57.77	4.83
10/22/10-10/28/10	2.72	0.12

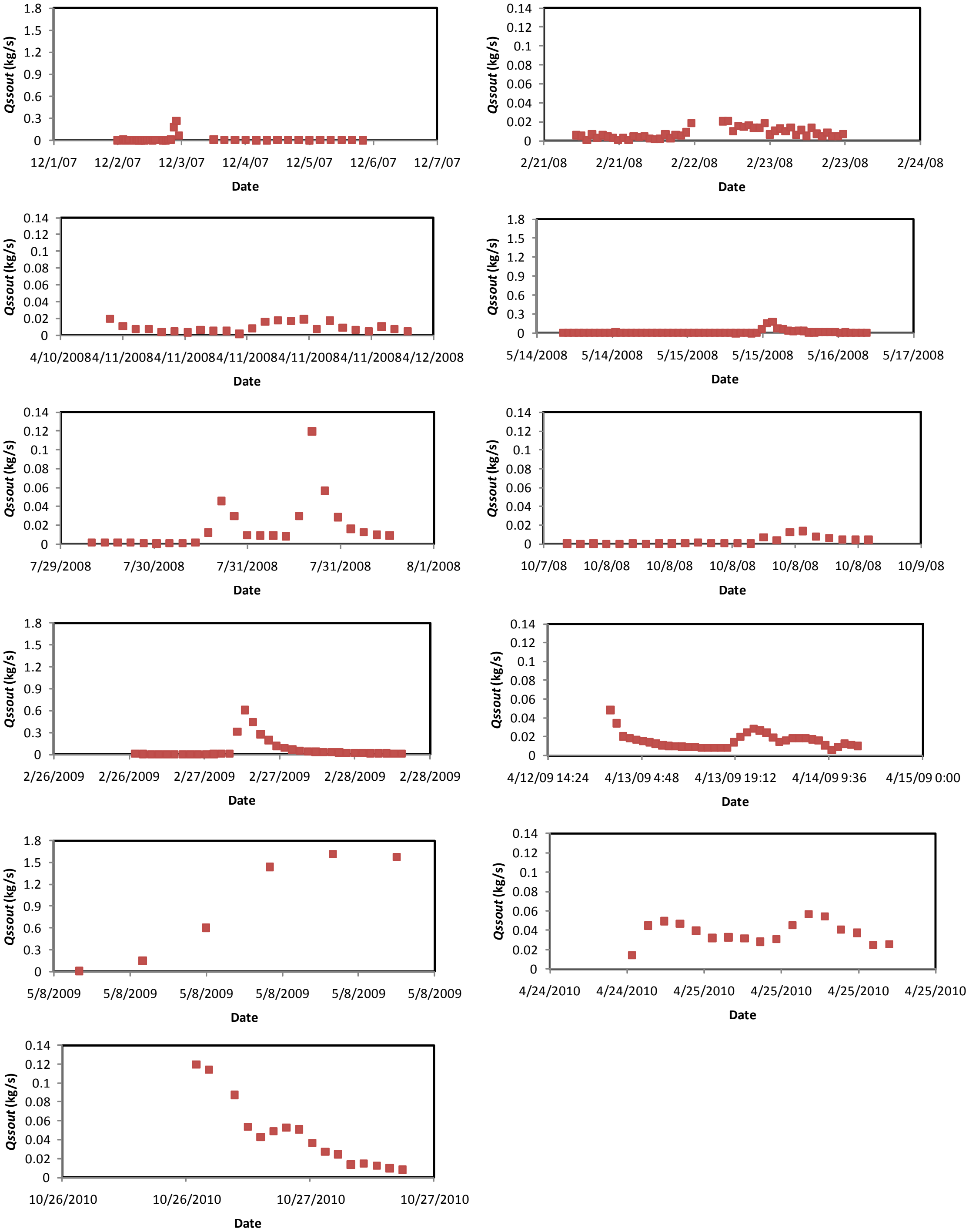
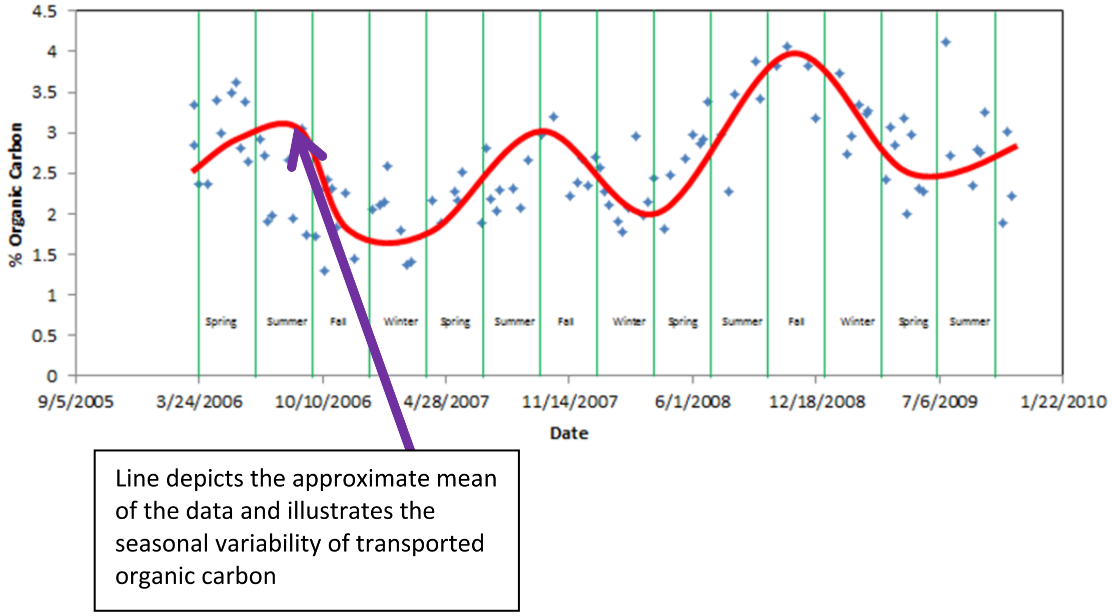


Figure 6-3) Sedigraphs Measured at the Outlet of the South Elkhorn Watershed



Line depicts the approximate mean of the data and illustrates the seasonal variability of transported organic carbon

Figure 6-4) POC data collected at the outlet of the watershed

Chapter 7 Model Application, Results and Sensitivity

7.1) Hydrologic Inputs (Drainage-Area Method)

7.1.1) Drainage-Area Method

Since this model is simply an area weighting method, the data isn't shown for all reaches here. The hydrograph is scaled to account for the contributing drainage area and lagged to account for travel time of the fluid. Figure 6-1 shows the data set that was scaled and lagged. This data was used as the input to the sediment transport model. The limitation of this method is that predictive models can't be developed because it doesn't account for basin characteristics other than drainage area. Figure 7-1 displays the main reach and delineated subcatchments for the South Elkhorn watershed

As discussed in Chapter 3, the South Elkhorn is a mixed landuse watershed. It is assumed that the landuse difference between the basins being scaled does not have a significant impact on the flowrate in each of the subbasins. It's believed that this assumption is fair because the majority of urbanization occurs in the upper part of the watershed, before the modeled reach begins. Hence the flowrate is being scaled for areas where a single landuse is dominant. It was also assumed that lagging the flowrates by the time step of the model was an appropriate action because the average travel time was estimated to be the length of the time step.

7.2) Sediment Transport Model

7.2.1) Inputs and Parameterization

Parameterization of the sediment transport model relies on measurements from the field, values obtained from previous studies and calibration parameters. Typically, parameters that are difficult to measure in the field will be used as calibration parameters.

For this thesis, the transport carrying capacity coefficient and the coefficient for lateral inflow were used as the primary calibration parameters.

Parameters relying on stream bathymetry were either estimated based on field measurements, or obtained from the sediment transport model developed in Russo (2009). An average stream width and estimated bankfull depth were used for all reaches in the model. Likewise, the side slope was estimated using a standard side slope for trapezoidal channels.

Physically based parameters such as critical shear stress of the bed or banks were estimated based on ranges in the literature. The settling velocity of the sediment particles were estimated using the settling velocity equation. An average particle size of 30 μm was used in the settling velocity equation. Table 7-1 displays the coefficients and input parameters used in the model for each reach.

7.2.2) Results of Calibration and Validation

In order to calibrate the sediment transport model, measured sediment fluxes are needed. For this study, sediment fluxes were measured at the outlet. A global calibration of the parameters was used to generate the desired sediment flux. Figure 7-2 and Figure 7-3 show the calibration and validation charts of $Q_{ss_{out}}$ vs. Time, in which modeled and measured results are compared. For the 5 year sampling period, 11 events were used (7 for calibration and 4 for validation). The most sensitive parameters in the model were the transport carrying capacity coefficient (Russo 2009), and the sediment inflow coefficient.

Furthermore, it is believed that the sediment bed is in equilibrium over long periods of time (Russo 2009 and Fox et al 2010). However, after initial calibrations the first reach of the model experienced over one cm of degradation (Figure 4) and the second reach aggraded around one cm (Figure 5), with all other reaches going to equilibrium in the long term. The likely cause of this degredation in the first reach is clear water scour, meaning the flow coming into the reach has low sediment concentrations due to urbanized areas upstream; however the transport carrying capacity is high, resulting in degradation of the channel bed and scour of the banks. Thereafter, the second reach aggrades as it transitions to an agricultural stretch in which sediment loading from the uplands are typically higher (i.e the sediment loads in stream are higher with the same transport carrying capacity, resulting in high deposition). In order to mitigate this issue, the C_{TC} and the coefficient for sediment inflow (lateral inflow) were adjusted for Reach 1 and 2. Only slight adjustments were needed to bring all the beds to equilibrium. An example of the equilibrium depth of the bed can be seen in Figure 7-6.

In addition to visual output, statistical confirmation of the calibration and validation is needed. For the sediment transport model a coefficient of determination (R^2) and % Diff was calculated as.

$$R^2 = \left[\frac{\sum_{i=1}^{n}(O_i - O_{avg})(S_i - S_{avg})}{\left(\sum_{i=1}^{n}(O_i - O_{avg})\right)^{\frac{1}{2}} * \left(\sum_{i=1}^{n}(S_i - S_{avg})\right)^{\frac{1}{2}}}\right]^2 , \tag{60}$$

$$\%Diff = \frac{O - S}{O} * 100 , \tag{61}$$

where, O_i is the observed value during time period *i*, O_{avg} is the average observed value during the sampling period, S_i is the simulated value during a given time period, and S_{avg} is the average simulated value over the modeling period.

A summary of the calibration and validation statistical information can be found in Table 7-2. The calibration considered two transport capacities because it was observed that all low flows over predicted, while all high flows under predicted with the same transport carrying capacity. Through analysis it was found that the cut off between a high and low flow event was 6 cms. The calibration and validation charts use two different scales, one for high flows and another for low flows; otherwise it is difficult to see the calibration chart for the low flows.

Results of the statistical analysis, are promising and show strong correlations between modeled and measured sediment yields. Based on guidelines from Donigian (2002), the percent difference falls in the very good category for the calibration and total periods, and falls in the good category for the validation period. The statistics for the sediment model in this thesis were similar to the statistics observed in Russo (2009).

An important component of the sediment transport model is to quantify the fraction of the sediment load that originates from each source. Three sources are considered for this study including sediment flow rate into the given stream reach, including lateral inflow, contribution from the streambed, and contribution from the stream banks. Figures 7-7 through 7-12 displays the fraction originating from each source over time. The fraction originating from the bed varies strongly with hydrologic forcing. With regards to small events bed contribution is small because the Qssin fulfills the majority of the transport carrying capacity at low flows. However, during high flows the bed erodes and provides a significant contribution to the sediment load. This timing of bed erosion allows for benthic processes to act on the organic substrate during periods in between hydrologic events. Likewise, streambanks follow a similar trend. The contribution of the streambanks is relatively low, but consistent throughout the sub-reaches. During high flow events, high shear stress on the banks results in quantifiable erosion that was observed to make up as much as 40 percent of the sediment flux at a given point. For this figure only one year of results was used because it is difficult to see the trends with all five years.

It is believed that the use of two sediment transport capacity coefficients is a reasonable assumption for the South Elkhorn system. Spatial heterogeneity (i.e. stream bathymetry) heavily impacts the transport capacity during low flows because sediment in pool sections will likely settle out faster than sediment in riffles or runs. Furthermore, during high flow events, the higher water level will dampen the impact of riffle-pool bathymetry thus a higher transport capacity would be needed. A similar assumption was made in Russo (2009).

Another possible explanation for different coefficients is that settling velocity will change from low to high flow events. During high flow events, the sediment slurry makes it difficult for fine sediments to settle back to bed thus decreasing the settling velocity. In turn, a lower settling velocity would entail a higher transport capacity. Thus, by using a different C_{TC} for high and low flows, the variability in settling velocity can be accounted for.

7.3) POC Model

POC in the bed as well as POC transported was budgeted continuously in the POC model. Bed monitoring was conducted in order to assess the hydrologic and biologic transformations to the carbon content of bed sediments. Likewise, POC transported accounts for POC from varying sources (i.e. scoured algae, eroded bed material, eroded bank material, and material from the uplands that is transported directly). High variability is present in POC transported, which makes assessing the sensitivity of the model difficult. As a result, the bed POC is used to address the sensitivity analysis, as well as seasonal and annual variability.

7.3.1) Inputs and Parameterization

Inputs for the POC model were primarily obtained from the literature, because algal and detritus sampling has not yet been conducted in the South Elkhorn watershed. Table 7-3 shows the calibrated parameter values for the POC model. For the algal submodel, ranges reported in Rutherford et al. (2000) were used for most of the parameters ($P_{col},\ \rho_{max},I_{k},\ T_{min},\ T_{opt},\ T_{max},\ P_{sat},\ P_{resp},\ Pk_{resp},$ *and* T_{ref}). To use the algal submodel many underlying assumption were needed. First, algae are modeled only in the main reach therefore the contribution of algal POC in the tributaries is assumed negligible. At this time the data is not available to determine the significance of the algal contribution in the tributaries, so the algal component is underestimated in this study. Furthermore, initial standing stock of algal biomass was assumed to be 0.3kgC/m^2. Since no data was available to give an exact initial biomass, the study of Rutherford et al. (2000) was used. Varying the initial biomass value in an appropriate range showed that it had little impact on the long term results of the POC model, thus this assumption is reasonable. It’s also assumed that low flow scour is negligible. At this time, the impact of low flow scour is unclear, however it is a process that will be further explored in future work.

The epilithic algae model operates under the assumption that nutrients, specifically nitrogen and phosphorous, sustain a high enough concentration to support algal growth throughout the year. Table 7-4 displays average nitrogen and phosphorous data obtained from the system. Average concentrations show that nitrogen and phosphorous is readily available for algal growth. Based on this data, minimum concentrations also provide sufficient nutrient availability for algal growth. Early results show that ammonia is undetectable in the water column. Phosphorous data is based off two sampling efforts in the summer, whereas nitrate samples were obtained at least once per season over a period of a year and a half. Based on information from Dodds et al. (2002) concentrations of nitrogen and phosphorus exceeding 0.04 mgN/L and 0.03mgP/L provide thresholds above which chlorophyll vales were substantially higher.

Furthermore, light intensity measurements were obtained on the water surface *via* (Dunlap et al. 2001). Table 7-5 shows monthly values of maximum solar radiation that could occur in Lexington, Kentucky. It is based off 30 years of collected data from 1961-1990. The study was conducted by the NREL (National Renewable Energy Labaratory), and published in "Solar Radiation Data Manual for Flat-Plate and Concentrating Collectors". Furthermore, to estimate water temperature, a correlation between air and water temperature was derived (Figure 7-13). Carbon content of algae was obtained from Gosselain, Hamilton, and Descy (2000). Decomposition rates for the two operationally defined algal pool sizes were estimated using Table 7-6. This table Critical shear stress of the algae was used as a calibration parameter since it is difficult to pinpoint the flow regimes in which the algae grow.

The algal contribution to the South Elkhorn watershed is significant in that it drives the seasonality of POC flux. Although, in general, the algal contribution is underrepresented in this model, algae contribute a large amount of carbon to the POC flux that had previously been unaccounted for.

Inputs for the SOM submodel included erosion and deposition estimates from the bed--obtained from the sediment transport model. Carbon content of fine SOM, coarse SOM and bank SOM was measured in the field. Decomposition rates of coarse SOM and fine SOM were obtained from the literature review Table 7-6. Fine SOM is mostly recalcitrant material; hence a very slow decomposition rate was applied.

For the leaf detritus submodel, inputs were expressly obtained from the literature. Benthic standing stock of leaf detritus was obtained for a forested catchment, providing an over estimate, from (Richardson et al. 1992). For the three pool sizes of leaf detritus decomposition rates were obtained from the literature review Table 7-6.

7.3.2) Results of Calibration and Validation

Preliminary tests were run on the model to assess which parameters would have the most significant impact on the POC load. It was determined that allochthonous leaf litter and coarse SOC had relatively little impact on the POC load, whereas the algal pool and decomposition rates controlled the seasonal variability. Knowing that algae and decomposition have the most significant impacts on POC loads; it was then possible to adjust those parameters in order to calibrate the model. Percent TOC measurements at the outlet of the watershed were used as the data to which the model was calibrated. Likewise Figure 7-14 shows the calibration/validation chart for the sampling period. The calibration period was determined to be 2006-mid 2008, and validation period was mid 2008-2009.

Furthermore, Table 7-7 shows the results of the statistical analysis for the calibration and validation period. Since TOC measurements in the field were integrated samples over a week, an average weekly %OC was used as opposed to an instantaneous value. Furthermore, for statistical analysis, POC yields over the week were utilized as opposed to % OC, to place an emphasis on the organic carbon content during transport events. Figure 7-15 shows the measured vs. modeled POC yields for weekly events. Although it's evident that the physical forcing is important in the carbon model, the propagation of errors from the hydrologic and sediment transport model does not have a significant impact on the carbon model (i.e. a strong calibration was obtained regardless of the accuracy of the models that powered the carbon model). Figure 7-16 shows that there is no evident bias in the model, in that the model periodically under predicts and periodically over predicts.

The parameter's behavior heavily influenced values used for model calibration. Difficulty arose in the calibration process as a result of lacking algal biomass, leaf detritus and SOC greater than 53μm data. From assessment of the maximum possible contribution of leaf detritus and large SOC to the POC pool, it was determined that they have a negligible impact on POC loads in the South Elkhorn watershed. Hence, parameters with respect to those two processes were not of significance in the POC model calibration. Likewise, decomposition and respiration of carbon originating from fine SOM has little impact on the POC model and does not need to be addressed. The algal component, however, proved to be a highly sensitive input to the POC model. The parameters that were varied in the model included decomposition rates of fine algae, algal critical shear stress, fixation rate of epilithic algae, and the respiration rate of the algal mat. Overall these parameters were varied within ranges, obtained from studies quantifying these rates, in order to fit the transported carbon dataset. The calibrated value for the decomposition of fine algae is assumed to be fairly representative because it had a significant impact on the lateral shift of peak carbon content. Since this parameter was the only variable to shift that peak, the calibrated value is assumed to be fairly strong. Critical shear stress of algae, maximum fixation rate, and respiration rate of the algal mat were all observed to impact the POC model in a similar fashion. Hence, the parameters were estimated using the midpoint of reported literature values and each were adjusted until the model results fit the observed data.

Although it's beyond the scope of this study, measuring parameters in the algal submodel would aid in the calibration process. It is by suggestion of the author that biomass fixation and respiration rate be measured or estimated for each system that the model is applied to due to the highly sensitive nature, and high variability in the literature. For more information regarding the sensitivity of these parameters and possible methods to estimate those parameters, see section 7.3.3.4.

7.3.3) Results of the Sensitivity Analysis

The behavior of sediment transport and hydrologic models is relatively well understood. Although some sensitivity was performed on both models, it is understood that infilitration rates and runoff volume are the most critical component of the hydrologic model, and transport carrying capacity is the most sensitive component of a sediment transport model. However, the POC model is a new, untested model. Hence, extensive testing and sensitivity analysis is needed to understand what components will have the greatest impact on POC in the bed and POC in transport. There are three main components that are used in the model that can be utilized for testing including epilithic algae, decomposition rates, and allocthonous POM. By holding all variables constant then varying one at a time we can see how the model reacts. For each test scenario, a graph showing the % OC in the bed was provided. Since the sediment bed is the catalyst for the hydrologic and biological processes, the % OC of the bed is used as opposed to transported OC to keep focus on the impacts of the biological transformations occurring in the active layer. Table 7-8 shows the standard (default) conditions of each component of the model and their associated ranges. The standard conditions represent calibrated values and if the calibrated value is a maximum, then it will represent the maximum condition in the sensitivity analysis. In addition, a summary table (Table 7-9) is used to recap the conducted model runs.

7.3.3.1) Algae

It is believed that benthic processes play a significant role in the organic carbon content of bed sediments. Algal contributions, resulting from decomposition of coarse particles in epilithic algal mats, can be a significant source of organic carbon to the bed. To test the variability of the algal component, coefficients and parameters of the algal model were varied For the first condition all the coefficients, with respect to algae, were set to a median value to understand how each component impacted fine algal accrual in the bed. Results of the algal sensitivity are shown in Figure 7-17.

Shifting the values of the different components of the algal submodel primarily influenced the magnitude of the OC content in the bed. Increases in the decomposition rate of coarse algae, fixation rate of epilithic algae, and critical shear stress of the algal mat resulted in an increased impact of the algal pool on the % OC in the bed. Likewise, increases in the respiration rate dampened the effect of the algal pool on the %OC in the bed.

7.3.3.2) Allocthonous POM

The allocthonous POM pool has been simplified to two groups. The first is leaf litter, which comes from trees and riparian vegetation zones. The second group is the large POM from soil organic matter. Detritus must undergo decomposition before it can reach the FPOM pool. For this study, it is assumed that detritus goes through two stages of decomposition before it reaches the fine pool including size partitioning during decomposition to produce pools greater then 1mm, and 0.53mm-1mm. Yet again, the decomposition rates of detritus are held constant throughout the testing.

Results of the sensitivity analysis for coarse SOM are shown in Figure 7-18. The figure depicts maximum and minimum situations, predicting that the coarse SOM pool has next to no impact on the %OC in the bed (notice the scale of %OC). Coarse SOM was varied primarily by decomposition rates (i.e. the higher the decomposition rate, the larger the contribution to the FPOM pool). Remnants of coarse SOM after one phase of decomposition constitutes a very small pool relative to the entire FPOM pool. Hence regardless of the decomposition rates used, the FPOM from coarse SOM does not have a significant impact on the overall POC in the bed.

Results of the sensitivity for leaf detritus are shown in Figure 7-19. Leaf litter detritus can be varied to assess its impact on the POC load. For this study, the default setup uses an average standing stock of benthic detritus for a forested system; hence overestimating the allochthonous input (Richardson 1992). The standing stock is applied for the entire year. Leaf litter decomposition proved to be a relatively insignificant input to the POC load. This can be attributed to the fact that the decomposition occurs at an extremely slow rate, and much of the allochthonous material is transported directly as opposed to being available for the benthic community. The two extreme cases were used to observe whether any significant impact was observed on the POC load (i.e. zero standing stock / maximum standing stock for a forested system with maximum decomposition rates). Even with the maximum condition, leaf detritus had little impact on the POC in the bed.

7.3.3.3) Decomposition

It is evident that decomposition rates have significant impacts on organic carbon content and POC loads in fluvial systems. Decomposition rates are assumed to be proportional to the growth of heterotrophic bacteria since they have been shown to vary with season (Jackson and Vollaire 2007). Decomposition is present in the algal, detrital and fine sediment pools, thus heavily influencing biological reactions in the sediment bed. Multiple scenarios were run for decomposition rates to understand how they impact the POC load. First, decomposition of fine algal material was investigated by fixing the growth rate and varying the decomposition rate through a high medium and low range (Figure 7-20).

Based on Figure 7-20, it is evident that varying the fine decomposition rate influences the seasonal variation as well as magnitude of % OC in the bed. In particular, the shifting of peaks is an interesting component because it can be used to adjust the model results from side to side. Therefore an assessment of what parameters impact both decomposition rates and algal growth was investigated. A series of first order functions are used to model algal growth based on temperature and photosynthetically active radiation. For algal growth, temperature dependent parameters include the respiration and dimensionless temperature limitation term. Furthermore, the photosynthetically active radiation term is a function of light intensity. For decomposition of fine algae, temperature is the only variable used. Graphs were generated to understand what caused the shift in % OC from one mean decomposition rate to another. The two algal growth parameters that were dependent upon temperature had very similar trends to that of the decomposition rates, so those graphs aren't shown here. However, Figure 7-21 shows that the peak irradiance occurs earlier in the summer than peak decomposition (depicts spring through winter results from the POC model). Hence, as decomposition increases from the min to max state, the seasonal peaks will shift back towards the peak of the light parameter. At high decomposition rates, maximum annual values are heavily influenced by light intensity instead of temperature.

As was discussed earlier, the allochthonous POM did not have a significant impact on the results of the POC model. Likewise, decomposition of that fine pool showed no significant changes to the total POC pool. Hence it was determined that the decomposition of fine allocthonous POM was not a sensitive component in the model.

Lastly, the impact of the slow decomposition of fine SOC particles in the streambed was investigated. This includes the small portion of FPOM that comes from large allochthonous SOM. Figure 7-22 depicts the sensitivity of the model to the decomposition rate of the fine SOC pool. This pool is mostly recalcitrant so a slow decomposition rate was used. From the figure, it is evident that even at the maximum decomposition rate; the model results do not change significantly from the default conditions where the fine SOC is assumed completely recalcitrant. Hence this parameter is not sensitive with regards to transported organic carbon.

7.3.3.4) Sensitivity Analysis Summary and Parameter Discussion

The sensitivity of each parameter is prioritized in Figures 7-23, 7-24 and 7-25. Each parameter was varied over an appropriate range and had a low medium and high condition. The results were referenced to a percent change of the POC yield in the medium condition. In most cases the medium condition is approximately halfway between the high and low condition. In total, seven parameters were tested for sensitivity. Figure 7-23 displays the sensitivity of the three variables tested in the algal submodel, figure 7-24 displays the sensitivity of the two allochthonous origin inputs, and figure 7-25 displays the sensitivity of the two decomposition rates resulting in POC losses from the system.

As was discussed during the calibration measurement of uncertain variables can be essential to models so that over prediction of certain processes occurs. For the POC model, the uncertain parameters used in the calibration included decomposition of fine algae, algal critical shear stress, fixation rate of epilithic algae, and the respiration rate of the algal mat. Methods are currently available to measure each of these parameters however, as previously discussed. It was outside the scope of this thesis to apply those methods, however they will be discussed. Measuring decomposition rates of organic matter in lotic systems is difficult due to non-uniformity of POM quality. Likewise, studies typically measure FPOM decomposition using a mesh-bag approach (see Tank et al. (2010) review); however Sinsabaugh et al. (1994) found that using this method for FPOM underestimates decomposition rates. As an alternative, decomposition rates could be measured using laboratory incubation experiments similar to that of Lehmann et al. (2002). In these experiments a sediment surface is place in 5 L bottles and water from the natural system is used as the medium in the incubation chamber.

A variety of methods are available to measure the critical shear stress of algae. An *in situ* jet-testing apparatus has been used to estimate critical shear stress of in stream sediments (Hanson and Simon, 2001). Further, if a source, such as a streambed or streambank, is isolated the sediment load can be measured upstream and downstream of the eroding source. Thereafter, the critical shear stress can be backed out. *In situ* flume measurements from a straight 3 meter long test section (e.g. Ravens, 2007) can also be utilized to measure critical shear stress in the field. The laboratory can also be utilized to estimate critical shear stress. A sedflume (Mcneil et al., 1996) is a straight laboratory flume in which a coring tube of sediment can be inserted into a rectangular cross section.

Based on the methodology of Ziegler and Lyons (2010), epilithic biomass can be assessed by using *in situ* enclosure experiments in-stream. Initial biomass was accounted for, then after a certain time interval the final biomass was measured. Estimates of epilithic algal respiration can be made by detecting dissolved oxygen (DO) differences in chamber tests (Arscott et al., 1998). Chamber tests are a popular method to investigate overall net primary production in the lab. From these tests, it possible to back out respiration rate, fixation rate and decomposition rates of epilithic algae. Furthermore, investigation of the applicability of using specific assays to measure respiration of epilithic algae in the lab is ongoing.

7.3.4) Discussion of Results

POC in the bed is influenced by both biological and physical processes. Figure 7-26 illustrates these processes. With regards to physical forcing, erosion and deposition processes result in a shift of the active layer to maintain the 5 mm depth. Likewise, the inactive sediments beneath the active layer is assumed to be SOM as well (hence the active layer returns to the organic carbon content of fine SOC during events that would deposit greater than 5 millimeters or during erosion of the active layer). This is seen to some extent during the September 2006 storm event (largest hydrologic event during the modeling period).

Biological processes also have a significant impact on the model results. 2007 and 2008 clearly show the seasonal variability of % OC in the bed. The rising limb occurs as a result of significant algal input into the active benthic layer. Likewise, the falling limb represents a change from algal accrual in the benthic layer to net decomposition in the benthic layer. As was shown above, the time at which the peak organic carbon content occurs can either be light limited or temperature limited, depending upon magnitude of the fine algal decomposition rate.

POC in the bed vs. POC transported will be different due to variations in erosion source for each time step. During hydrologic events, transported sediments can come from the banks, bed, or upstream reaches (this includes lateral inflow). The variability of the sources impacts the transported POC because %OC of the material from the sources is highly variable. Likewise, the transported POC is highly unpredictable as a result of the varying sources. Figure 7-27 depicts this by showing %OC transported and %OC in the bed on the same graph.

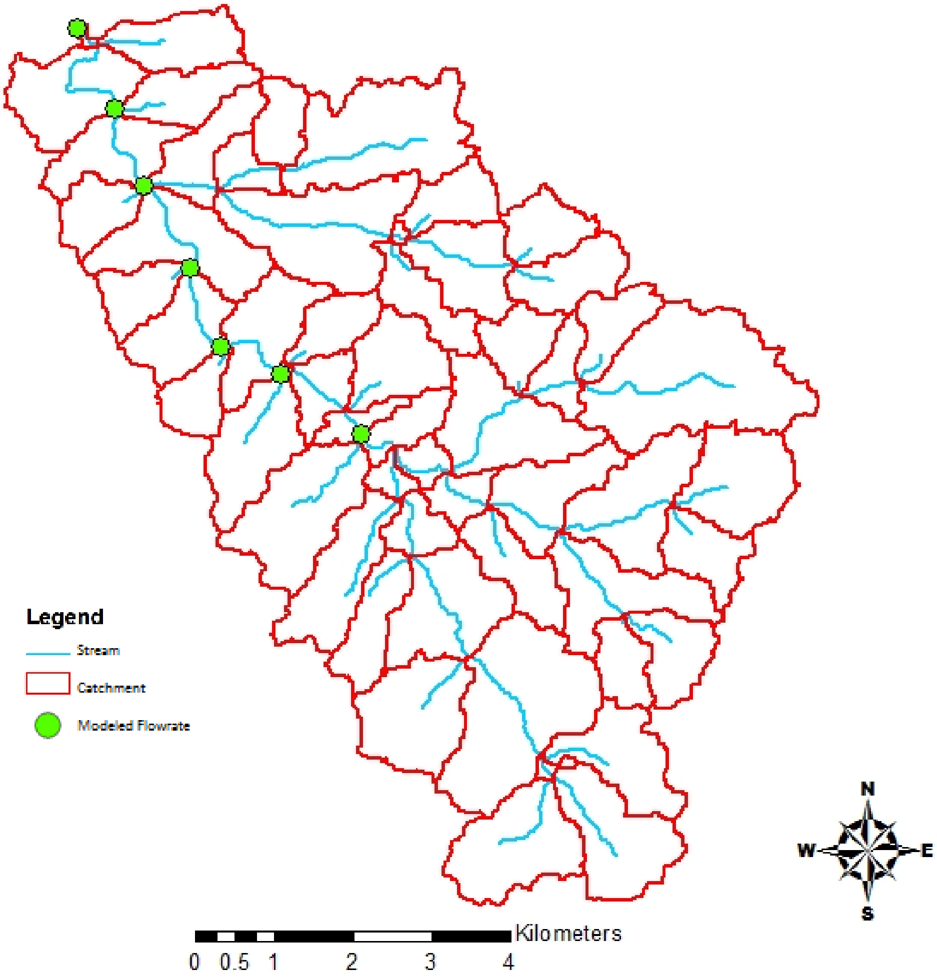
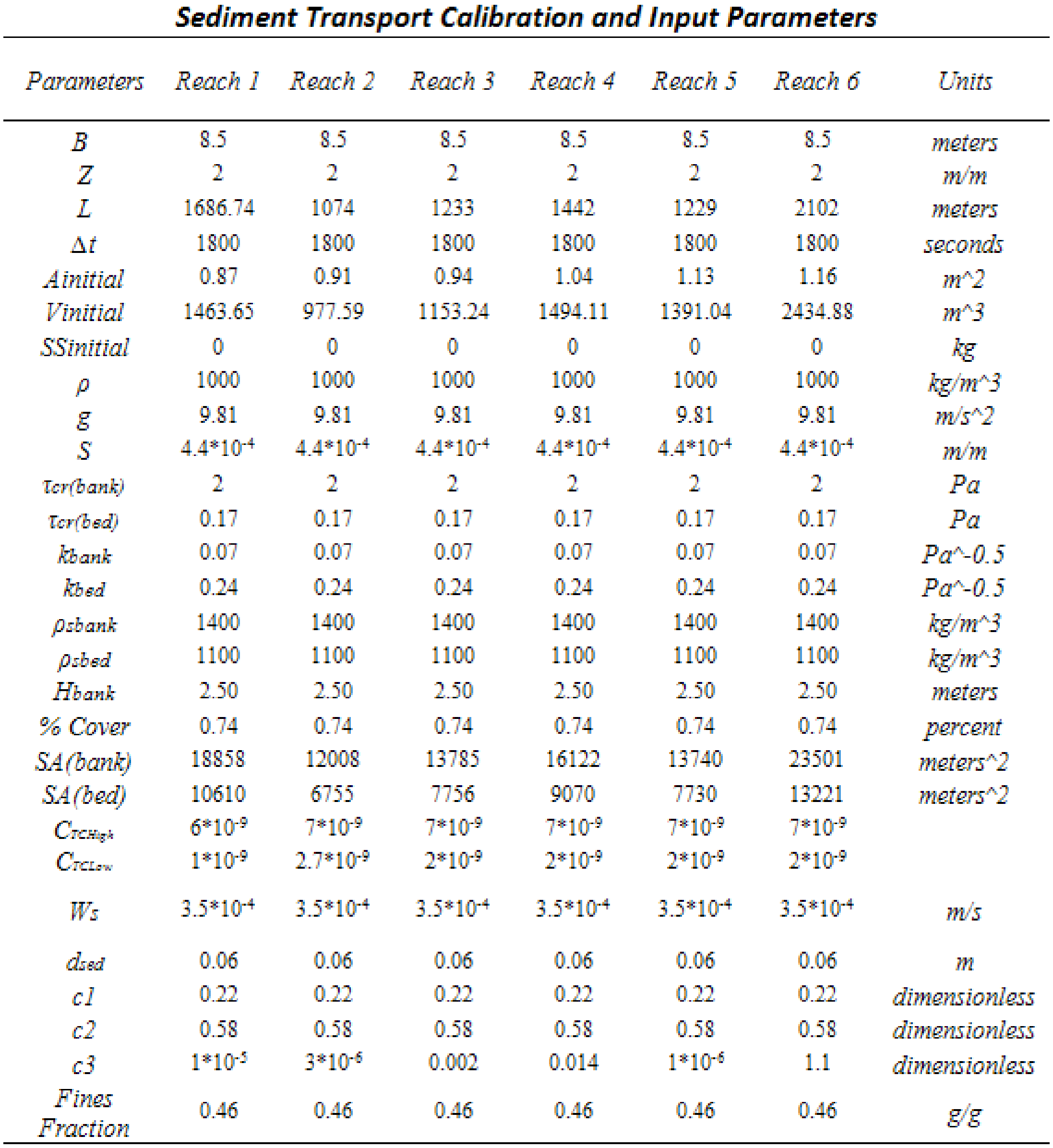


Figure 7-1) Delineation of the subcatchments in the Upper South Elkhorn watershed.

Table 7-1) Inputs and parameters for the sediment transport model



Sediment Transport Calibration and Input Parameters

Parameters	Reach 1	Reach 2	Reach 3	Reach 4	Reach 5	Reach 6	Units
B	8.5	8.5	8.5	8.5	8.5	8.5	meters
Z	2	2	2	2	2	2	m/m
L	1686.74	1074	1233	1442	1229	2102	meters
Δt	1800	1800	1800	1800	1800	1800	seconds
$A_{initial}$	0.87	0.91	0.94	1.04	1.13	1.16	m^2
$V_{initial}$	1463.65	977.59	1153.24	1494.11	1391.04	2434.88	m^3
$SS_{initial}$	0	0	0	0	0	0	kg
ρ	1000	1000	1000	1000	1000	1000	kg/m^3
g	9.81	9.81	9.81	9.81	9.81	9.81	m/s^2
S	$4.4*10^{-4}$	$4.4*10^{-4}$	$4.4*10^{-4}$	$4.4*10^{-4}$	$4.4*10^{-4}$	$4.4*10^{-4}$	m/m
$\tau_{cr(bank)}$	2	2	2	2	2	2	Pa
$\tau_{cr(bed)}$	0.17	0.17	0.17	0.17	0.17	0.17	Pa
k_{bank}	0.07	0.07	0.07	0.07	0.07	0.07	Pa^-0.5
k_{bed}	0.24	0.24	0.24	0.24	0.24	0.24	Pa^-0.5
ρ_{sbank}	1400	1400	1400	1400	1400	1400	kg/m^3
ρ_{sbed}	1100	1100	1100	1100	1100	1100	kg/m^3
H_{bank}	2.50	2.50	2.50	2.50	2.50	2.50	meters
% Cover	0.74	0.74	0.74	0.74	0.74	0.74	percent
SA(bank)	18858	12008	13785	16122	13740	23501	meters^2
SA(bed)	10610	6755	7756	9070	7730	13221	meters^2
C_{TCHigh}	$6*10^{-9}$	$7*10^{-9}$	$7*10^{-9}$	$7*10^{-9}$	$7*10^{-9}$	$7*10^{-9}$	
C_{TCLow}	$1*10^{-9}$	$2.7*10^{-9}$	$2*10^{-9}$	$2*10^{-9}$	$2*10^{-9}$	$2*10^{-9}$	
W_s	$3.5*10^{-4}$	$3.5*10^{-4}$	$3.5*10^{-4}$	$3.5*10^{-4}$	$3.5*10^{-4}$	$3.5*10^{-4}$	m/s
d_{sed}	0.06	0.06	0.06	0.06	0.06	0.06	m
$c1$	0.22	0.22	0.22	0.22	0.22	0.22	dimensionless
$c2$	0.58	0.58	0.58	0.58	0.58	0.58	dimensionless
$c3$	$1*10^{-5}$	$3*10^{-6}$	0.002	0.014	$1*10^{-6}$	1.1	dimensionless
Fines Fraction	0.46	0.46	0.46	0.46	0.46	0.46	g/g

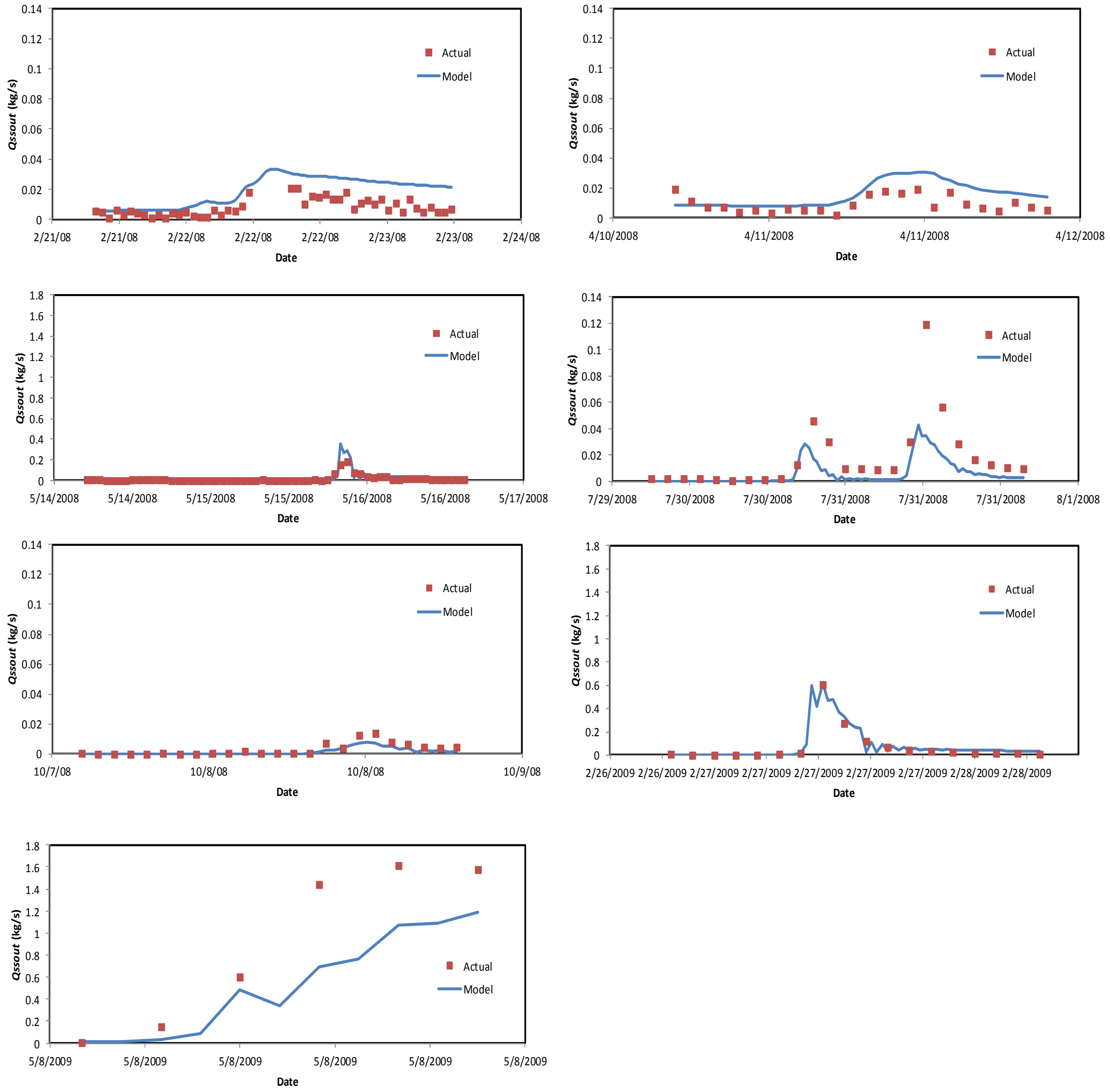


Figure 7-2) Calibration curves for the sediment transport model

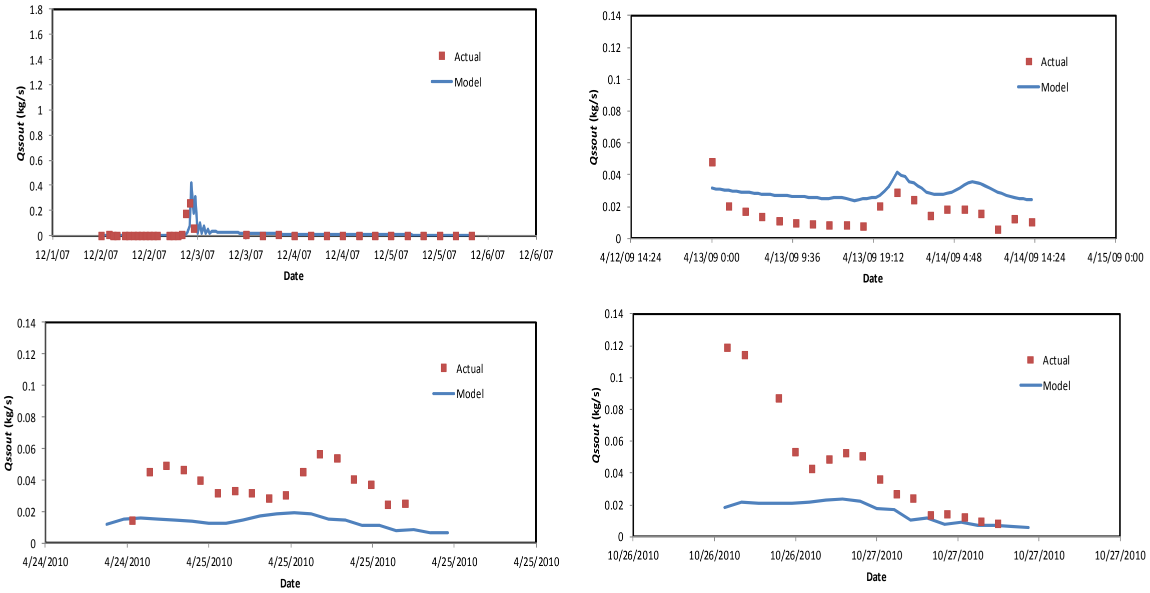


Figure 7-3) Validation curves for the sediment transport model

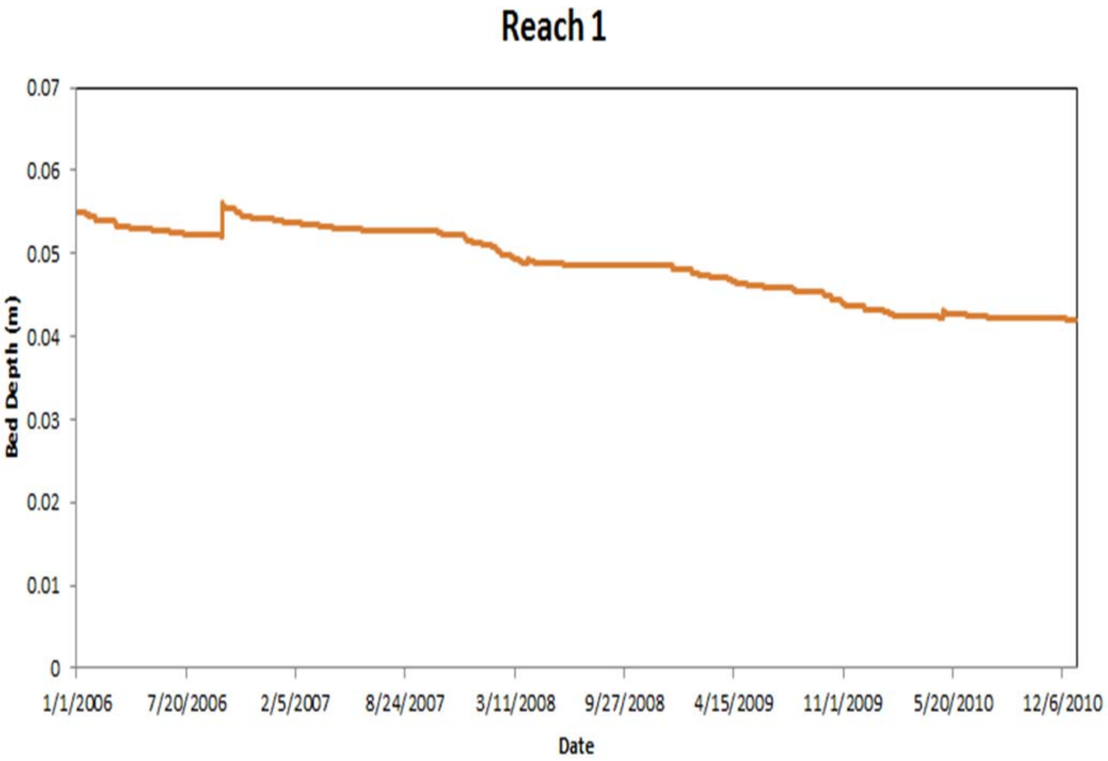


Figure 7-4) Reach 1 before calibration for long term equilibrium bed depth. (Predicts streambed degredation)

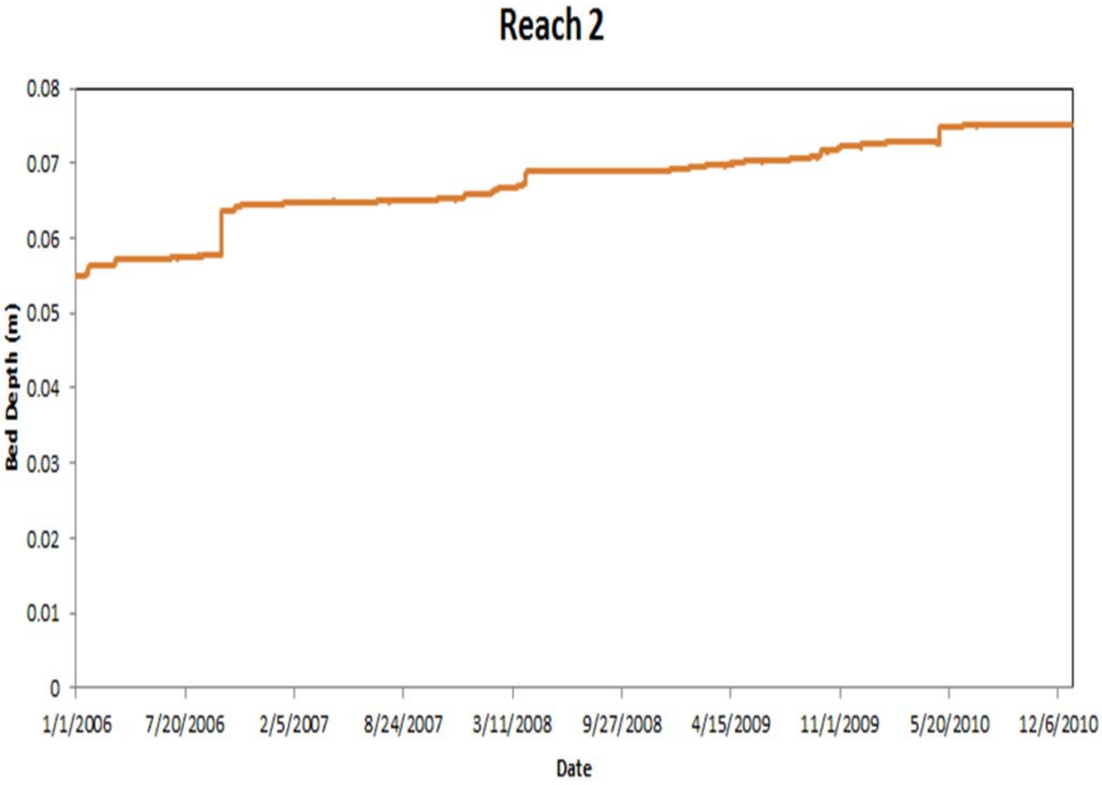


Figure 7-5) Reach 2 before calibration for long term equilibrium bed depth. (Predicts streambed aggradation)

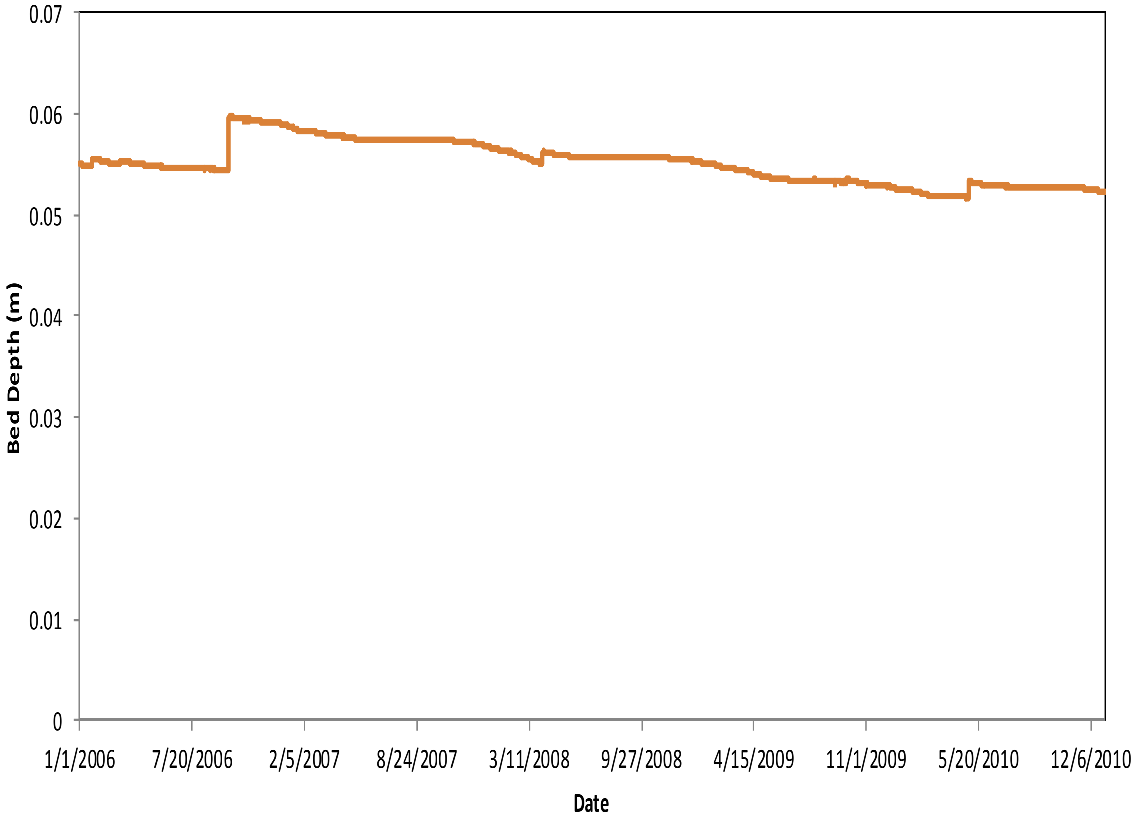


Figure 7-6) Bed depth monitoring of stream reach that is in equilibrium over an extended period of time.

Table 7-2) Statistical analysis of the sediment transport model

	% Diff	R^2
Calibration	2.52	0.73
Validation	-20.8	0.87
Total	-2.2	0.72

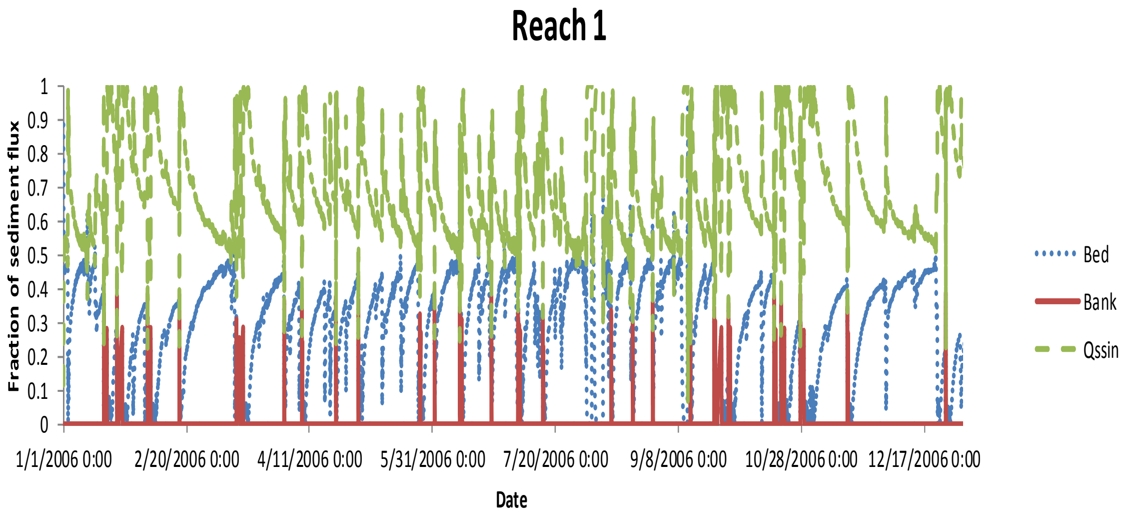


Figure 7-7) Fraction of Sediment Originating from each source (Reach 1)

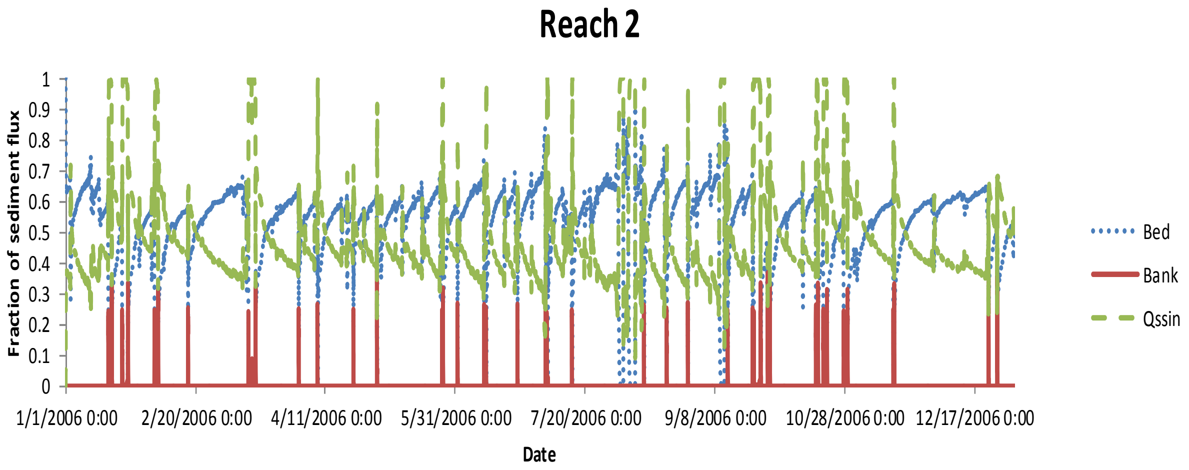


Figure 7-8) Fraction of Sediment Originating from each source (Reach 2)

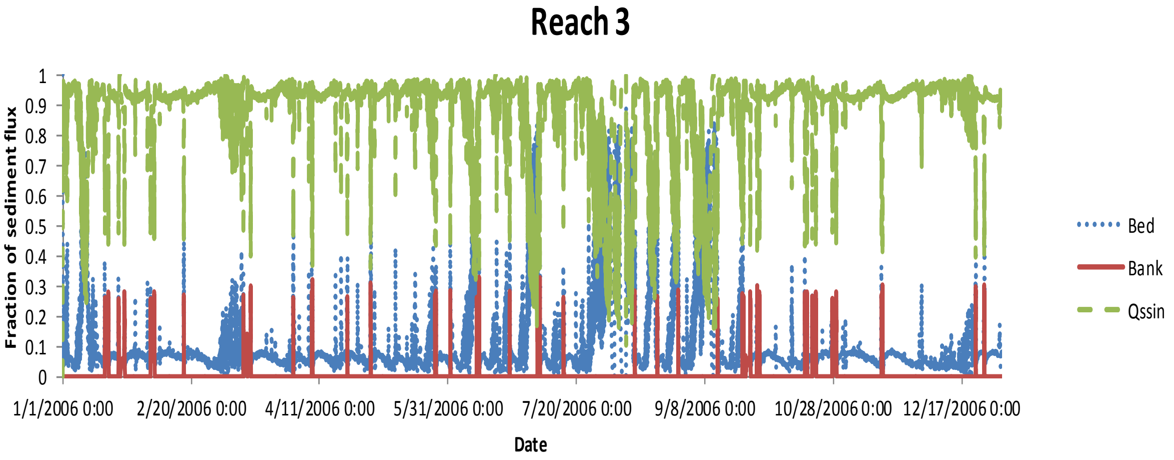


Figure 7-9) Fraction of Sediment Originating from each source (Reach 3)

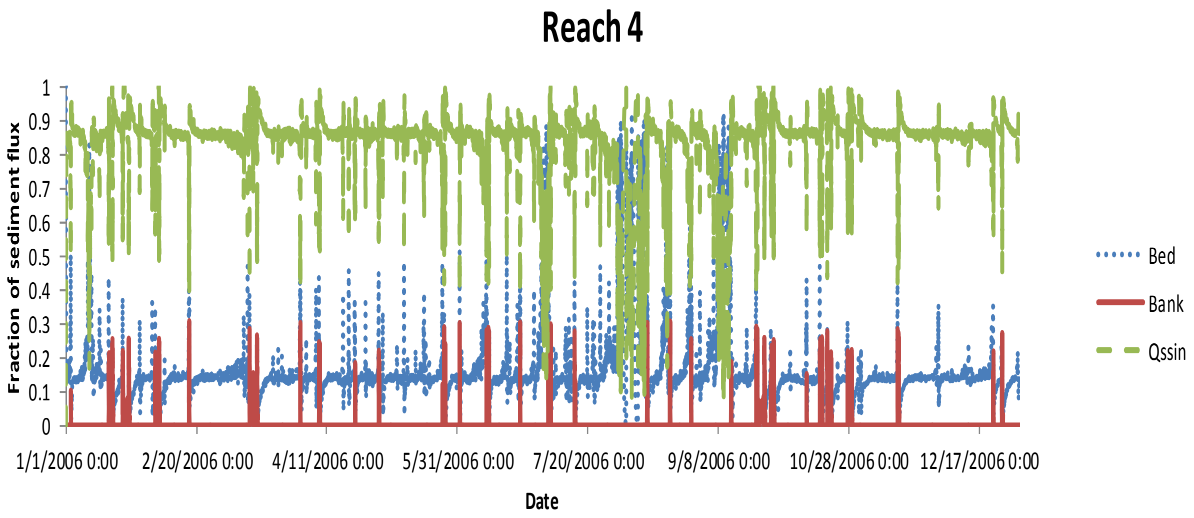


Figure 7-10) Fraction of Sediment Originating from each source (Reach 4)

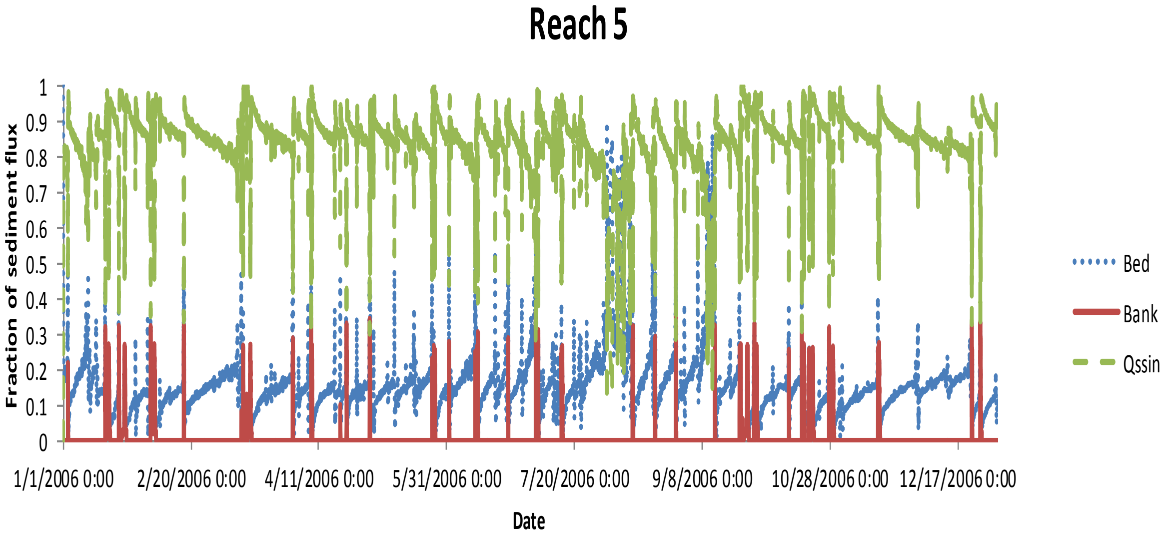


Figure 7-11) Fraction of Sediment Originating from each source (Reach 5)

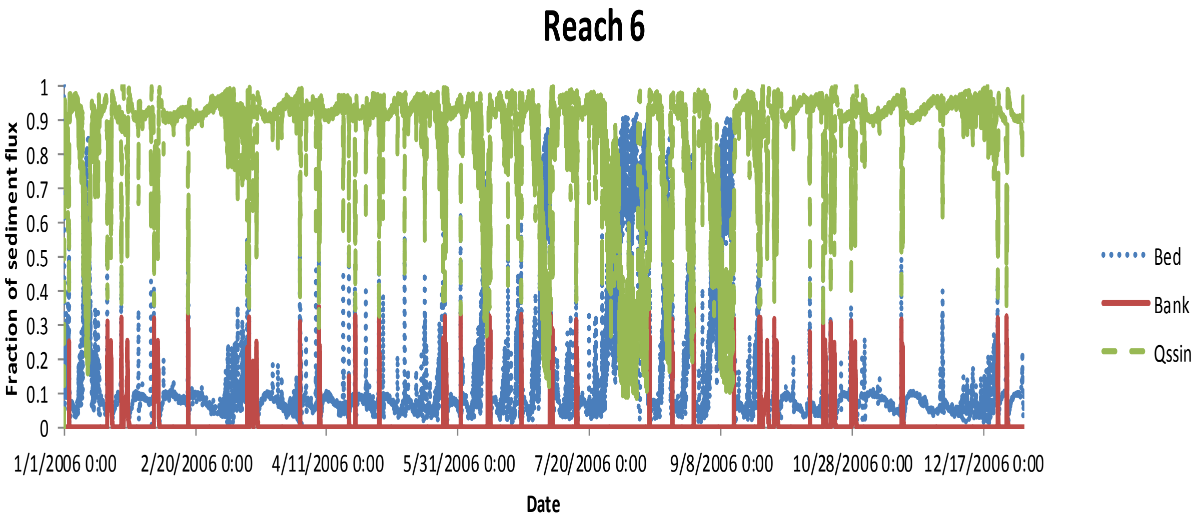


Figure 7-12) Fraction of Sediment Originating from each source (Reach 6)

Table 7-3) Calibrated input parameters for the POC Model.

Calibration Table For the POC Model

Parameters	*Values*	*Units*	*Source*
$\%OC_{Qss\ (initial)}$	0.018	gC/gOM	*Assumed*
$\%OC_{bank}$	0.016	gC/gOM	*Measured in Field*
$\%OC_{anoxic}$	0.018	gc/gOM	*Calibrated*
$\%OC_{soc}$	0.018	gC/gOM	*Measured in Field*
$\%OC_{dep\ (initial)}$	0.018	gC/gOM	*Assumed*
$\%OC_{algae}$	0.41	gC/gOM	*Gosselain, Hamilton & Descy, 2000*
$\%OC_{det(leaf)}$	0.31	gC/gOM	*Robertson et al. 1982*
$\%OC_{det(CSOM)}$	0.04	gC/gOM	*Measured in Field*
ρ_{sbed}	1100	kg/m^3	*Estimated*
ρ_{salgae}	1100	kg/m^3	*Estimated*
$M_{fines(initial)}$	72719	kg	*Calculated*
$POC_{fines(initial)}$	1527	kgC	*Sediment Model*
Pcol	0.0001	kgC/m^2*d	*Rutherford et al 2000*
pmax	0.0024	kgC/m^2*d	*Rutherford et al 2000*
Ik	230	µmol/m^2/s	*Rutherford et al 2000*
Tmin	5	celsius	*Rutherford et al 2000*
Topt	20	celsius	*Rutherford et al 2000*
Tmax	30	celsius	*Rutherford et al 2000*
Psat	0.0025	kgC/m^2	*Rutherford et al 2000*
Presp	0.13	day^-1	*Rutherford et al 2000*
Pkresp	1.05		*Rutherford et al 2000*
Tref	20	celsius	*Rutherford et al 2000*
ΔTlower	8.67	celsius	*Calculated*
ΔTupper	5.78	celsius	*Calculated*
Pinitial	0.3	kgC/m^2	*Rutherford et al 2000*
τcr(algae) (Pa)	0.35	Pa	*Calibration*
kalgae	0.17	Pa^-0.5	*Calculated*
Biofilm Depth	0.005	meters	*Assumed*
Standing Crop (Detritus)	0.016	kgC/m^2	*Richardson et al. 1992*
$DEC_{SOC\ (FPOM)}$	0.00003	day^-1	*Review Table*
$DEC_{algae/detritus\ (FPOM)}$	0.0013	day^-1	*Review Table*
$DEC_{OM>1mm}$	0.015	day^-1	*Review Table*
$DEC_{.053mm<OM<1mm}$	0.0026	day^-1	*Review Table*

Table 7-4) Nutrient data from the South Elkhorn Watershed.

Site	Average Nitrogen as NO3 (mg/L)	Average Total Phosphorous (mg/L)	Minimum Nitrogen as NO3 (mg/L)	Minimum Phosphorous (mg/L)
Tributary	2.06	0.19	1.20	0.19
Outlet	2.58	0.24	1.40	0.23
Watershed Midpoint	2.37	0.22	1.80	0.21

Table 7-5) Maximum daily radiation (μmol/m^2/s)

Month	*Imax*	Month	*Imax*	Month	*Imax*
January	346.76	May	528.81	September	520.14
February	407.44	June	580.82	October	520.14
March	459.46	July	511.47	November	372.77
April	546.15	August	537.48	December	312.08

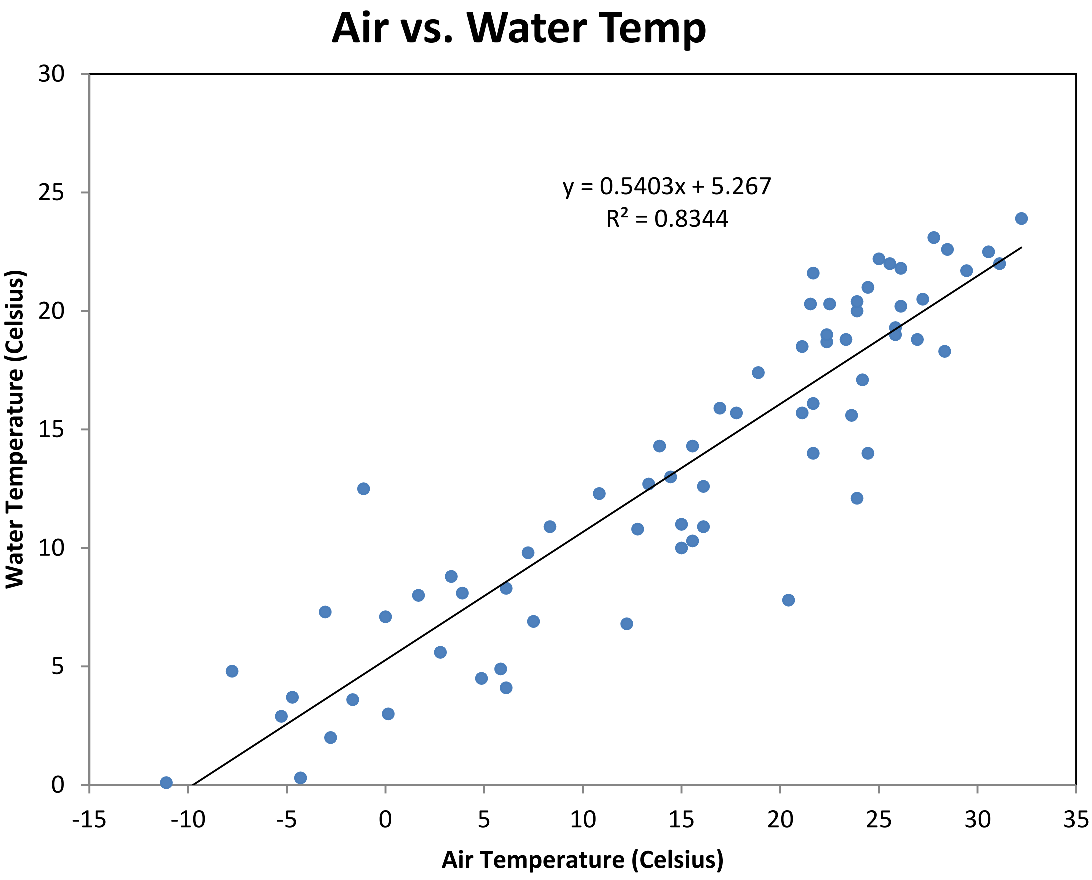


Figure 7-13) Correlation between air temperature at the NOAA station and water temperature at the outlet of the watershed.

Table 7-6) Decomposition rates of varying size classes of organic matter

Table Review of Decomposition Rates

Study	Water Body	Particle Size	Decomposition rates
Alvarez and Guerrero 2000	Ponds fed by ephemeral streams during floods	Fine POM (.063-0.5mm) and Coarse POM (>1mm)	Fine POM = 0.036% per day and 0.023% per day at two sites; Coarse POM = 0.667% per day and 0.261% per day at two sites
Jackson and Vollaire 2007	Lagoon	Very Fine POM (0.063-0.25mm) and Fine POM (0.25-1mm)	Very Fine POM = 0.4-0.8% per day in winter, 0.9-1.4% per day in spring/summer at two sites; Fine POM = 0.2-0.25% per day in winter, 0.3-0.4% per day in summer at two sites
Sinsabaugh et al. 1994	Eutrophic woodland stream	Fine POM (.063-0.5mm) Medium POM (0.5-4mm) and Coarse POM (>4mm)	Fine POM = 0.54% per day; Medium POM = 0.69% per day; Coarse POM = 0.78% per day
Short et al. 1980	3rd-order mountain stream	Coarse POM (alder willow, aspen and pine leaf litter)	Alder = 0.87% per day; Willow = 0.7% per day; Aspen = 0.43% per day; Pine = 0.28% per day
Rier et al. 2007	3rd-order river	Coarse POM (quaking aspen leaf litter)	High-light treatment = 0.85% per day; Low-light treatment = 0.49% per day
Minshall et al. 1983	Four streams ranging from 1rst to 7th order	Coarse POM (mockernut hickory leaf litter)	Values varied from 0.1%per day to 1.53% per day based on site
Webster et al. 1999	Forested stream network draining 2185-ha	Coarse POM (>1 mm) and Fine POM (0.00045-1 mm)	Fine POM = 0.104% per day for an average of 40 first and second order streams; Coarse POM = .98% per day for an average of 40 first and second order streams
Yoshimura et al. 2008	7th-order river	Coarse POM (>1mm) and Fine POM (0.1-0.5 mm)	Fine POM = 0.15% per day; Coarse POM = 0.607% per day

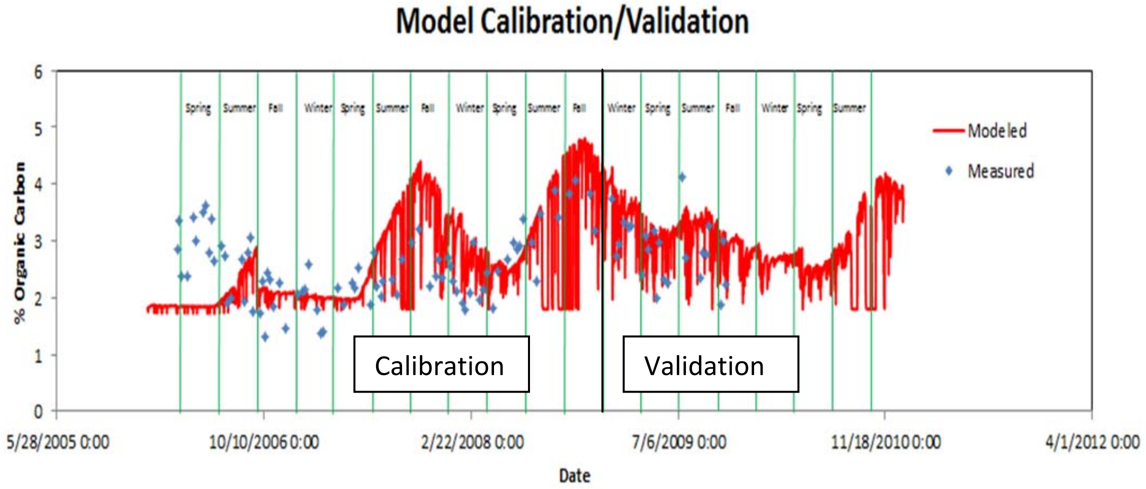


Figure 7-14) Calibration and validation of the POC model

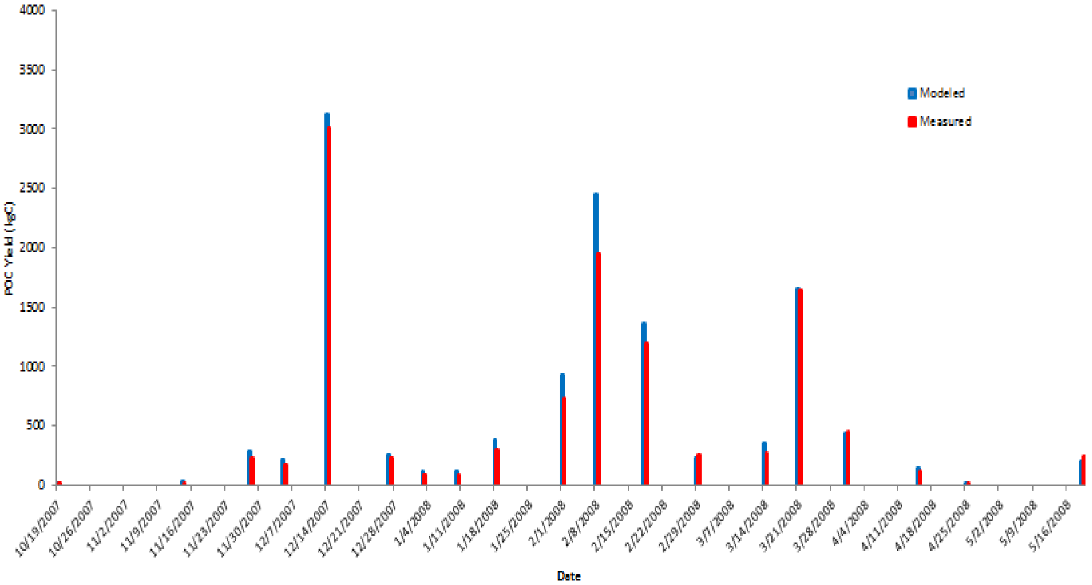


Figure 7-15) Measured and modeled POC yields

Table 7-7) Calibration and validation results for POC yield

	R^2	*% Diff*
Calibration	0.94	8.79
Validation	0.95	-1.61
Total	0.94	7.07

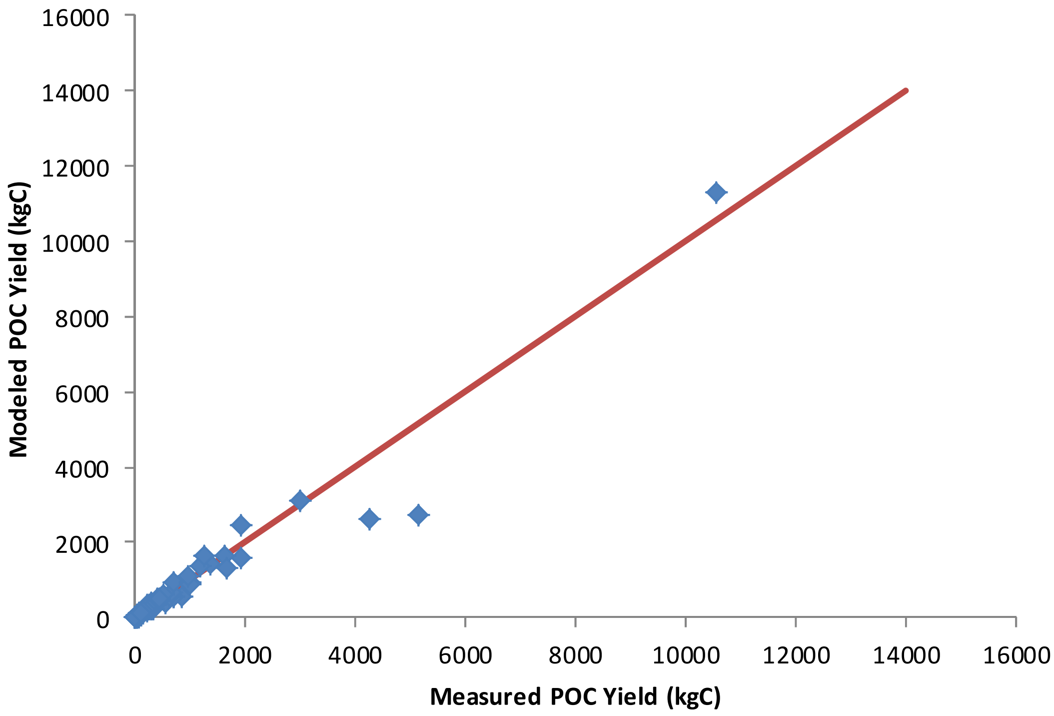


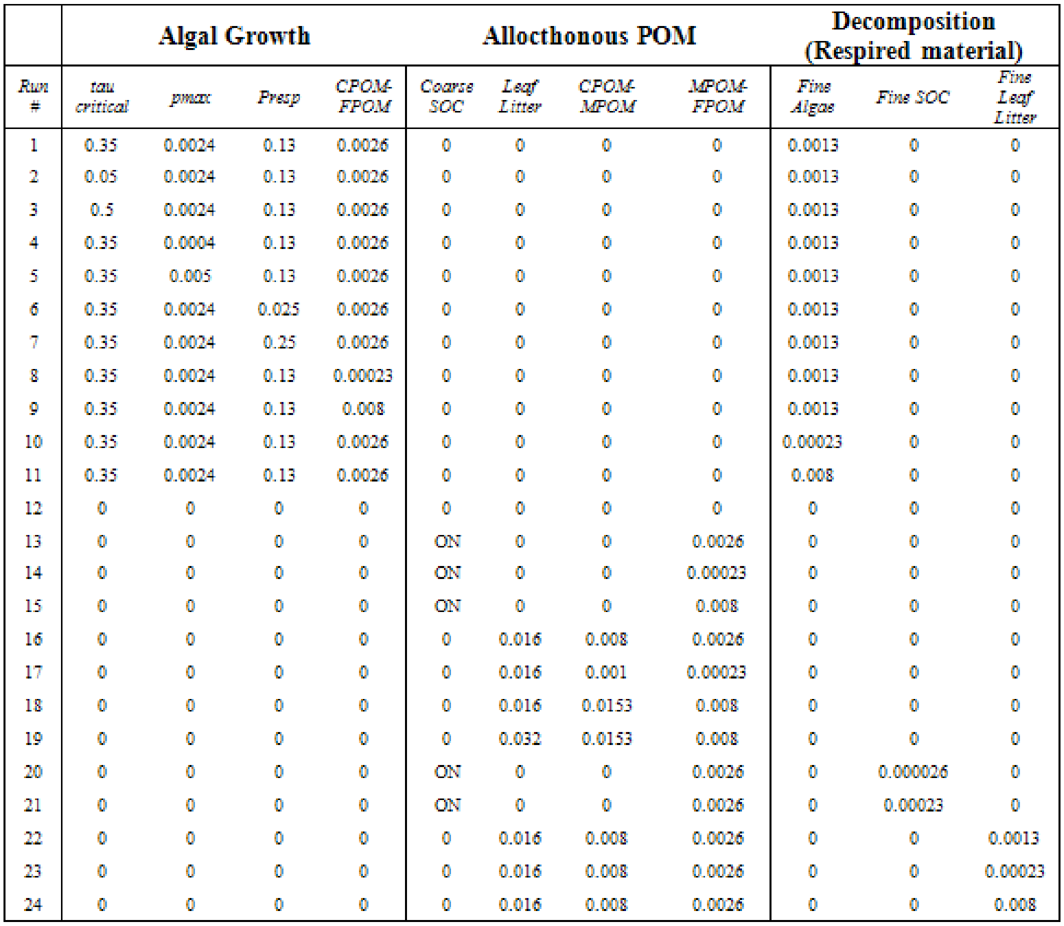
Figure 7-16) Measured vs. modeled values for the POC model

Table 7-8) Ranges utilized for the sensitivity analysis.

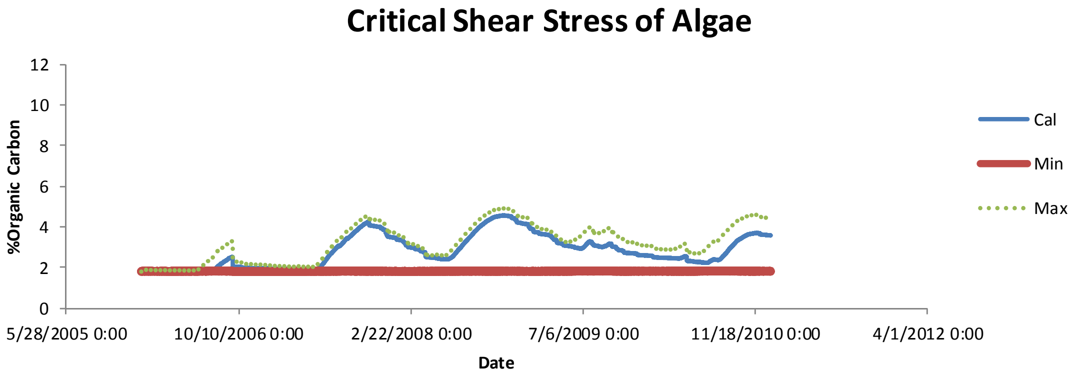
Sensitivity Ranges for POC Model Parameters

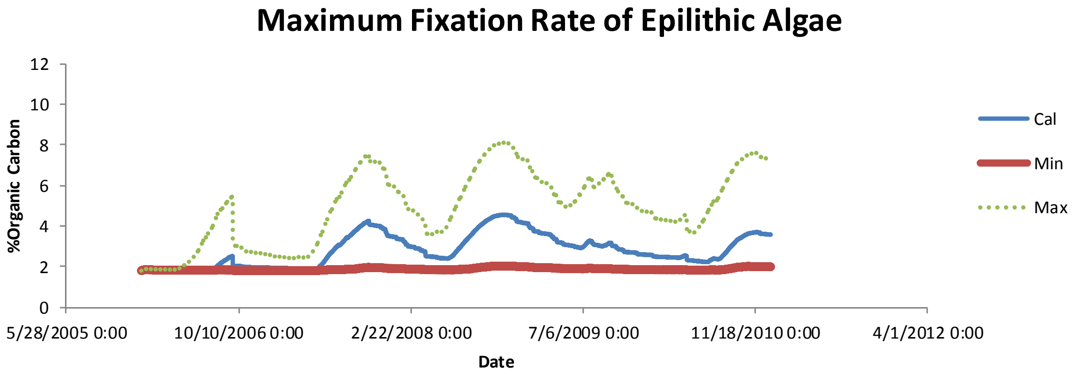
Parameters	*Default*	*Minimum*	*Maximum*	*Units*
Pmax	0.0024	0.0004	0.005	*kgC/m^2*d*
Presp	0.13	0.025	0.25	*day^-1*
$\tau_{cr(algae)}$	0.35	0.05	0.5	*Pa*
Standing Crop (Detritus)	0.016	0	0.032	*kgC/m^2*
$DEC_{SOC\ (FPOM)}$	0.000026	0	0.00023	*day^-1*
$DEC_{algae/detritus\ (FPOM)}$	0.0013	0.00023	0.008	*day^-1*
$DEC_{OM>1mm}$	0.0153	0.001	0.0153	*day^-1*
$DEC_{.053mm<OM<1mm}$	0.0026	0.00023	0.008	*day^-1*

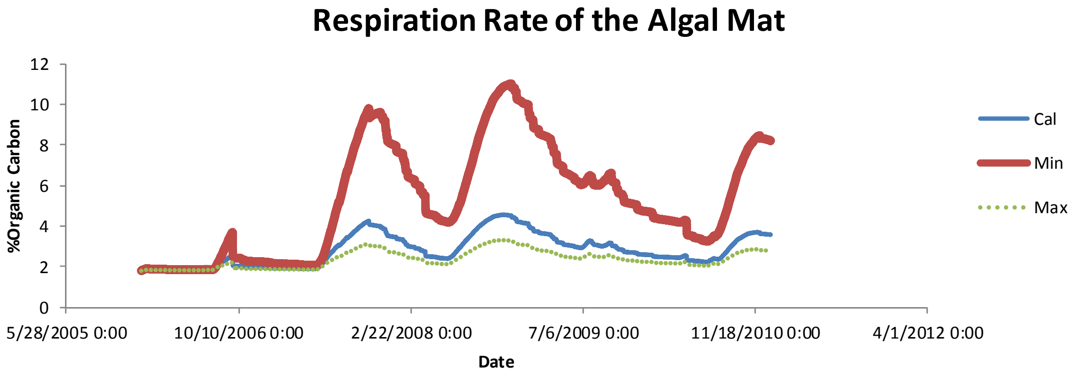
Table 7-9) Summary Table of the sensitivity analysis runs.



	Algal Growth				Allocthonous POM				Decomposition (Respired material)		
Run #	*tau critical*	*pmax*	*Presp*	*CPOM-FPOM*	*Coarse SOC*	*Leaf Litter*	*CPOM-MPOM*	*MPOM-FPOM*	*Fine Algae*	*Fine SOC*	*Fine Leaf Litter*
1	0.35	0.0024	0.13	0.0026	0	0	0	0	0.0013	0	0
2	0.05	0.0024	0.13	0.0026	0	0	0	0	0.0013	0	0
3	0.5	0.0024	0.13	0.0026	0	0	0	0	0.0013	0	0
4	0.35	0.0004	0.13	0.0026	0	0	0	0	0.0013	0	0
5	0.35	0.005	0.13	0.0026	0	0	0	0	0.0013	0	0
6	0.35	0.0024	0.025	0.0026	0	0	0	0	0.0013	0	0
7	0.35	0.0024	0.25	0.0026	0	0	0	0	0.0013	0	0
8	0.35	0.0024	0.13	0.00023	0	0	0	0	0.0013	0	0
9	0.35	0.0024	0.13	0.008	0	0	0	0	0.0013	0	0
10	0.35	0.0024	0.13	0.0026	0	0	0	0	0.00023	0	0
11	0.35	0.0024	0.13	0.0026	0	0	0	0	0.008	0	0
12	0	0	0	0	0	0	0	0	0	0	0
13	0	0	0	0	ON	0	0	0.0026	0	0	0
14	0	0	0	0	ON	0	0	0.00023	0	0	0
15	0	0	0	0	ON	0	0	0.008	0	0	0
16	0	0	0	0	0	0.016	0.008	0.0026	0	0	0
17	0	0	0	0	0	0.016	0.001	0.00023	0	0	0
18	0	0	0	0	0	0.016	0.0153	0.008	0	0	0
19	0	0	0	0	0	0.032	0.0153	0.008	0	0	0
20	0	0	0	0	ON	0	0	0.0026	0	0.000026	0
21	0	0	0	0	ON	0	0	0.0026	0	0.00023	0
22	0	0	0	0	0	0.016	0.008	0.0026	0	0	0.0013
23	0	0	0	0	0	0.016	0.008	0.0026	0	0	0.00023
24	0	0	0	0	0	0.016	0.008	0.0026	0	0	0.008







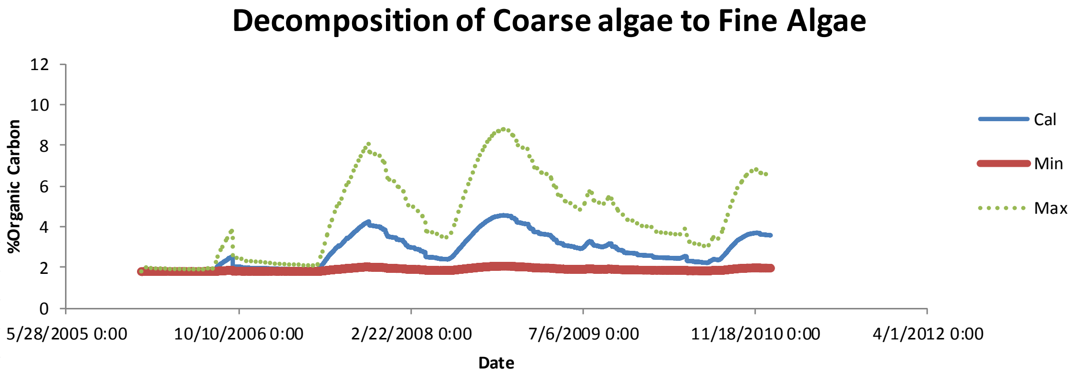


Figure 7-17) Sensitivity of the algal submodel.

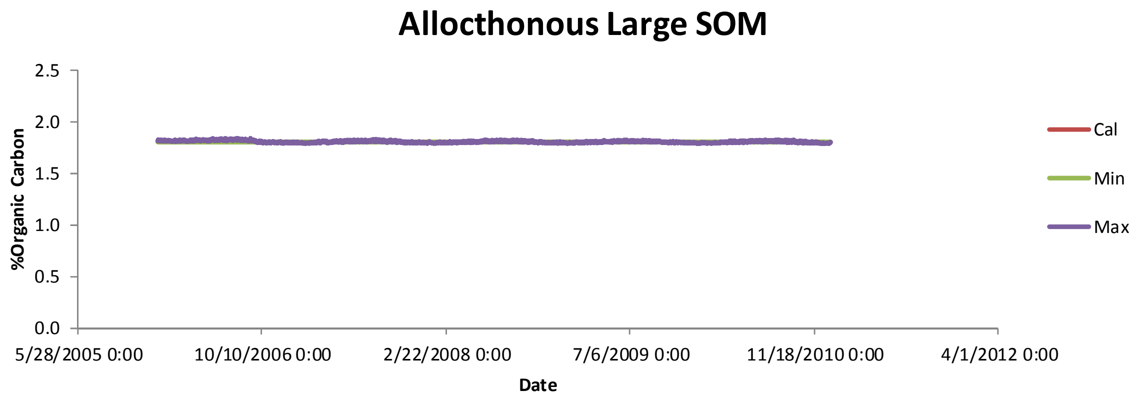


Figure 7-18) Sensitivity of the allochthonous coarse SOM

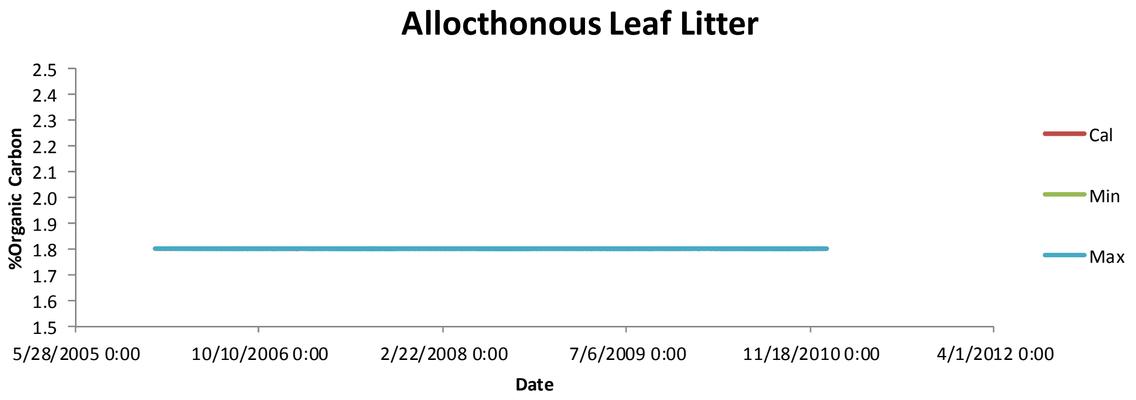


Figure 7-19) Sensitivity of the allochthonous leaf litter detritus.

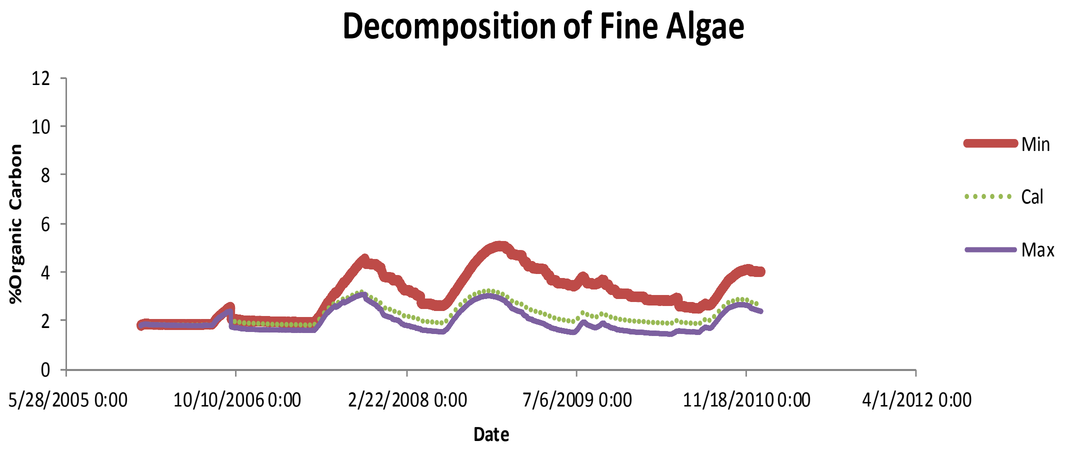


Figure 7-20) Sensitivity of the decomposition rate of fine algae.

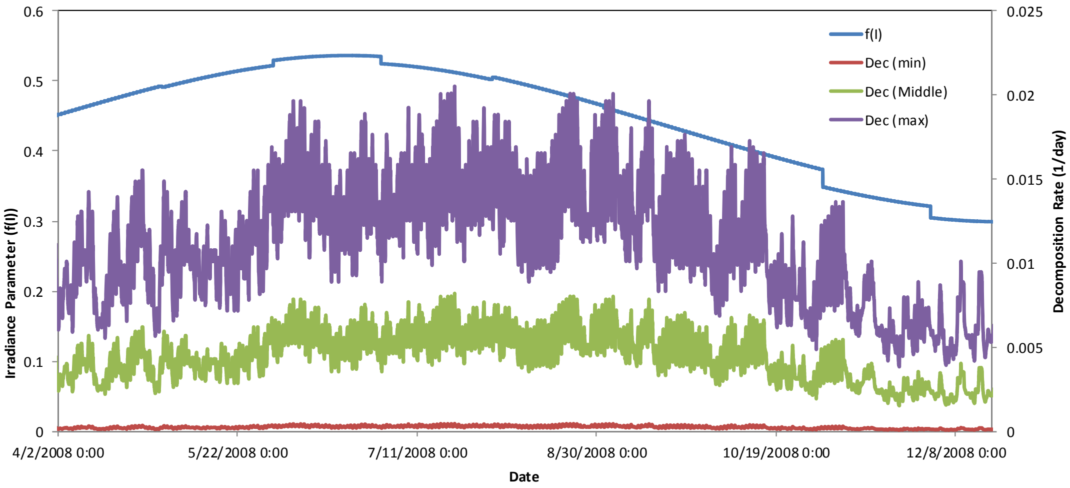


Figure 7-21) Sensitivity of the %OC peak with respect to decomposition and irradiance parameters.

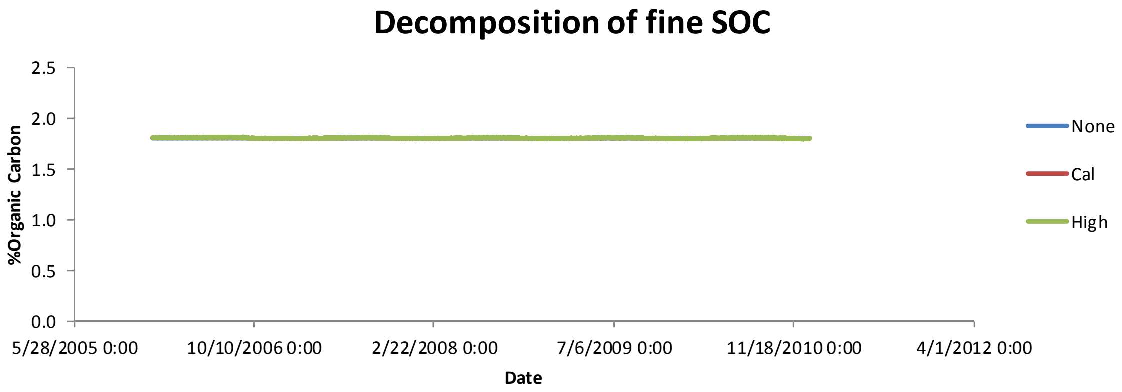


Figure 7-22) Sensitivity of decomposition of fine SOC.

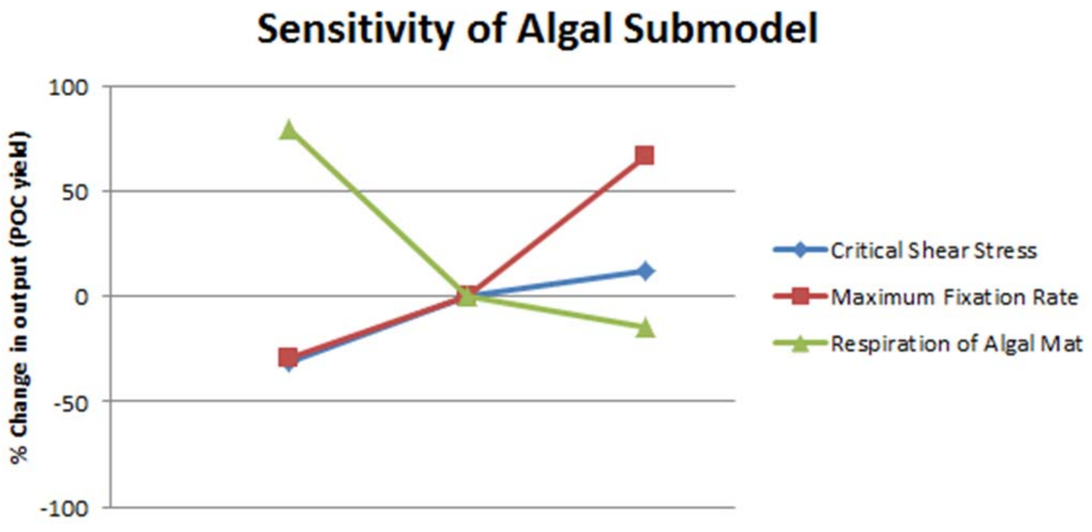


Figure 7-23) Response of the POC model based on variation of parameters in the algal submodel.

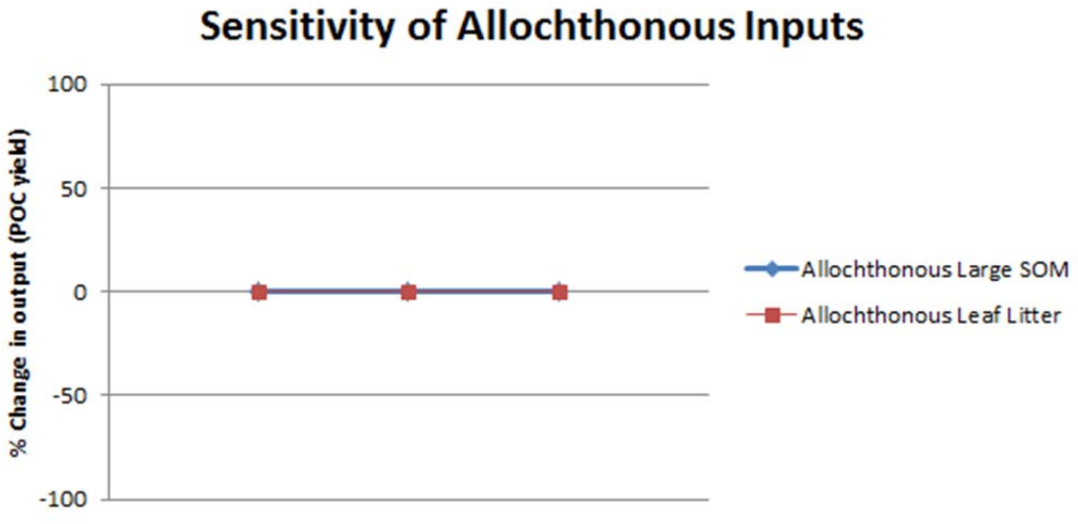


Figure 7-24) Response of the POC model based on variation of allocthonous inputs.

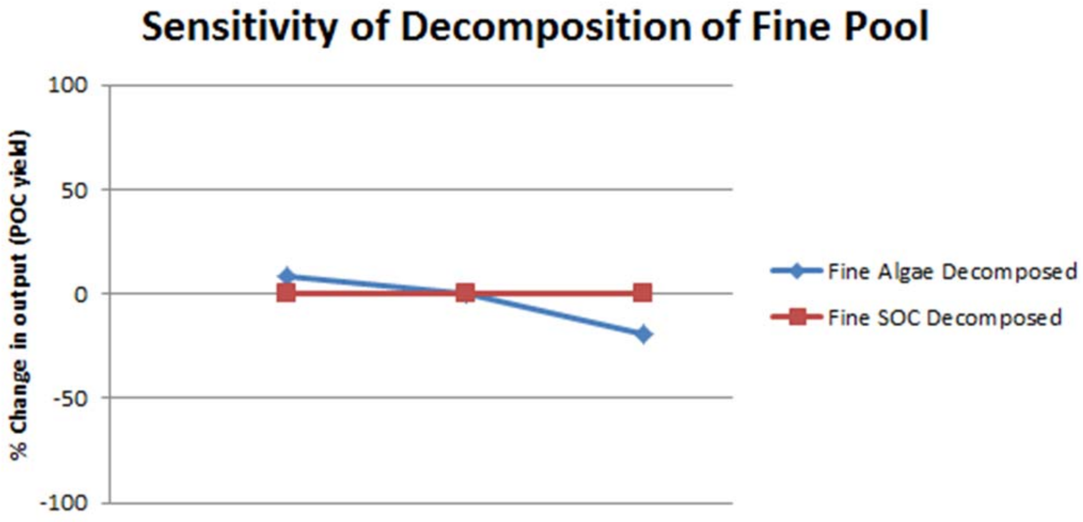


Figure 7-25) Response of the POC model based on losses due to decomposition of fine pool.

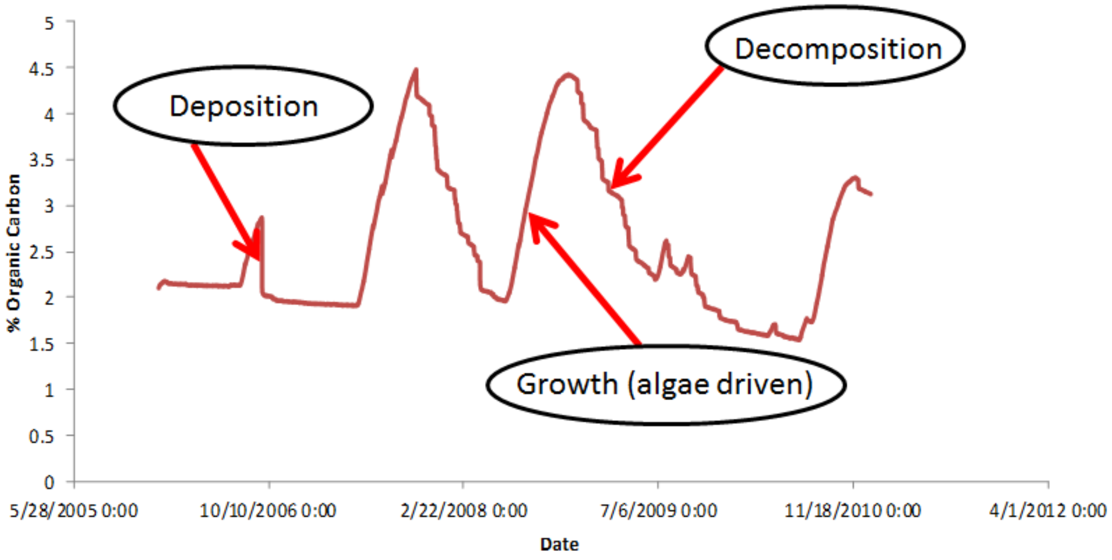


Figure 7-26) Influence of biological and physical processes on carbon in the bed.

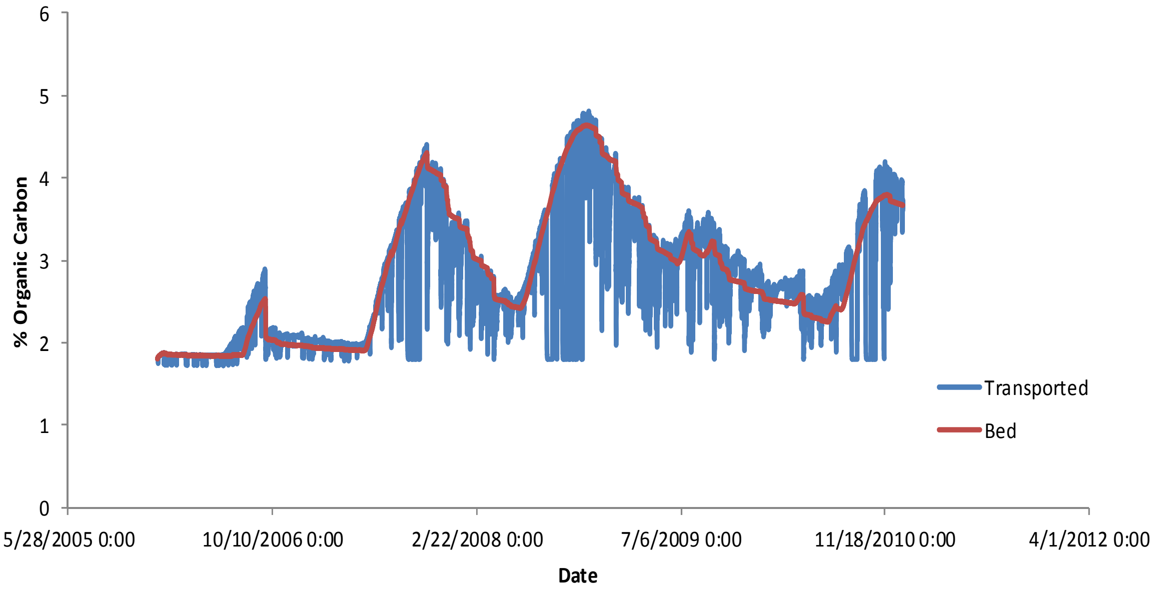


Figure 7-27) Transported vs. bed carbon.

Chapter 8 POC Budget Results

8.1) POC Budget

The focus of this study is to analyze the source and transport of carbon at the watershed scale. As stated before, most studies have focused on steep gradient systems where the carbon primarily comes from SOC and fossil material (i.e. weathered bedrock). However, low gradient systems are heavily influenced by benthic processes, meaning that the autochthonous growth can have a significant influence on the POC load. The primary sources contributing to the POC load were identified as SOC, allocthonous leaf detritus, fine bank sediments, and autochthonous produced algae. Budgets were conducted seasonally and annually to show the importance of the autochthonous contribution throughout the year.

8.1.1) Annual POC Budgets

Based on the model results, not only do POC loads vary seasonally, but they can also vary annually. The purpose of this section is to highlight how variable POC flux is on an annual scale. There are only 5 years to compare, however there are notable variations during this time frame that may highlight some processes causing variability in POC flux. For example, hydrologic variability (annual precipitation) will drive the transport and fluvial erosion of fine sediments and can limit the growth of autochthonous carbon. Likewise, climate variables such as temperature can heavily impact the autochthonous contribution to the POC load. Figure 8-1 reports the average annual POC budget over the five year modeling period.

Based on this budget, the autochthonous production constitutes nearly 13% of the annual POC load. As was discussed before, the allocthonous contribution from leaf litter, similar to the biomass of heterotrophic bacteria, was insignificant with regards to the overall POC flux. As expected, carbon from fine SOM made up 68 percent of the total POC flux on average. The importance of bank erosion was evident, in that around 19 percent of the POC flux came from fine sediments eroded from streambanks. The influence of annual variability of climate and hydrologic variables is significant to the POC budget. Therefore, the following set of Figures (8-2 through 8-6) depicts the POC budgets for each year during the five year modeling period.

The influence of the autochthonous carbon is significant for all years. Thus, it's evident that for studies such as these, where hydrologic, biologic, and climatologic variables can have significant influences on POC loads, long term data sets and models need to be generated to pinpoint causation of variability in POC flux. Likewise, using this model to predict POC loads with respect to climate change or urbanization would give some insight into how significant the autochthonous contribution can become.

8.1.2) Seasonal POC Budgets

Although it's important to analyze models on an annual basis, the focus of this study is on the model's ability to generate detailed predictions of the seasonal variability of POC. As was seen earlier, transported OC percentage can vary anywhere from 1.7-5% based on the calibrated model. Figures (8-7-8-10) show the seasonal variability of POC. Seasonal averages for POC flux were taken to attempt to mitigate the influence of individual hydrologic events that would sway the budget one way or another in a given season.

Based on the above budgets, it is evident that POC fluxes in the summer are far less significant than any other season. Likewise, fall has the largest POC flux. The autochthonous contribution increases throughout the seasons plateauing in the winter and bottoming out during the spring. The allochthonous contribution to the POC load is insignificant throughout the year; however it shows some seasonal variability due to the growth of heterotrophic bacteria which facilitate higher decomposition rates with increasing temperature.

8.2) Discussion of POC Model Results

8.2.1) Summary

Based on the budgets derived in section 8.1, it is evident that POC fluxes in small lowland systems are heavily influenced by benthic processes occurring in the temporarily stored bed sediments. Model results returned an average POC flux value of 0.29 tC km^{-2} y^{-1}, which fits in the range of POC fluxes from lowland systems found in the literature review (Table 2-1). Furthermore it fits well within the range of POC fluxes published by Alvarez et al (2010). Autochthonous production, from the modeled reach, accounted for around 13% of the annual POC flux. Seasonal variability of carbon flux was observed, with autochthonous production controlling the seasonality. Likewise, the physical forcing of POC in the watershed by rainfall events had significant impacts on the POC load. These results are supported by previous POC studies, for example in Zhang et al. (2009) POC was found to decrease with increasing TSS concentrations. Zhang states that there are several mechanisms that could cause this including limited light availability for photosynthetic processes, and dilution of POC by mineral matter originating from terrigenous soils (i.e. heavy upland soil erosion and transport during hydrologic events).

8.2.2) Annual Variability

The purpose of this section is to generate a qualitative and quantitative assessment of the impact of biology and physics on POC flux. Understanding when the majority of carbon is being transported is important for aquatic carbon budgets. Although large events constitute a much higher percentage of the sediment load, extended periods of baseflow provide a more static bed in which the biological processes can impart changes to the organic carbon content of bed sediments.

8.2.2.1) Hydrologic Variability

A delineation was made to determine how much POC was discharged during low to high flow regimes. A significant hydrologic event was considered to occur whenever the flowrate exceeded 2.5 cms which is operationally defined as the flowrate that differentiates high and low flows. Table 8-1 displays the hydrologic conditions as the fraction of time the average flowrate is exceeded and the mass of POC transported for the two conditions. Likewise Figures 8-11 and 8-12 predicts the mass of carbon transported over the five year period. Notice the scales are different in Figure 8-12 because low flow fluxes are periodically orders of magnitudes less than high flow fluxes. Based on these results, it is evident that POC flux is dominated by rainfall events in which high flows occur. Likewise, large events erode and dislodge algal material from the bed. Further investigation of the state of algae when its eroded or scoured away is ongoing.

Before and at the beginning of an event, the most easily eroded material (i.e. the bed material), dominates the transport load. The bed dominance is noticed in Figure 8-13 at the beginning of the hydrologic event the %OC increases. Later in the event when the uplands are more strongly connected with the main channel and the fluid shear stress increases, sediment supply from the uplands and the bank become more prominent components of the POC load and thus the % OC of the transported load decreases. Thereafter, as the flow returns to its previous state, the remaining sediments from the uplands are deposited to the streambed and the streambed material becomes the dominant source of suspended material again. Over time, the %OC gradually increases during low flow as the autochthonous biomass develops in the streambed.

Furthermore, it is believed that hydrologic variability on an annual basis can limit the carbon content of bed sediments. Algal production is limited due to erosion of the algal mat during an event. Likewise, erosion and deposition of the active layer limits the algal pool therefore lowering the carbon content. The focus here is on the extensive change from 2008 to 2009. Figure 8-14 shows the time series of flowrate, temperature, and algal decomposition to explain the annual variability of % OC in the bed. In 2009, when % OC in the bed experiences extensive dampening from other years, a higher density of hydrologic events is present. This limits the ability for the algal pool to develop in the benthic layer. Density of hydrologic events is also believed to explain some of the variability in 2006, however there are still uncertainties present with regards to model warm-up.

8.2.2.2) Biologic Variability

It is also believed that biologic variability explains the annual variability to some extent. Light intensity is fixed with regards to annual cycles, so it is evident that it will not impact the annual variability of POC. However, temperature does have some variation annually. A temperature component is present in the driving equation of the algal sub model, which can limit the production rate of epilithic algae. Likewise, decomposition rates vary expressly with temperature, so it's expected that annual temperature variations would likely impact the annual POC present in the streambed. Figure 8-14 shows the algal biomass present in the active layer for the five year modeling period. Three different scenarios were simulated to tease out the parameter that has the most significant impact on annual variability. The first looked at the calibrated condition of the model, the second removed erosion and deposition terms, and the third used an extremely high value for the critical shear stress of algae to remove the effects of flowrate on algal production. From this figure it is evident that although temperature does slightly impact the accrual of algal biomass in the active layer, the hydraulic forcing of the epilithic algal mat, along with the erosion and deposition dynamics has the largest impact on the annual variation in bed POC.

8.2.3) Seasonal Variability

Biological processes provide seasonality to the transported POC. Because algal production is driven by light availability, temperature and nutrients, algal blooms favor late spring to early fall. For the five year period modeled herein, the algal biomass causes an increase in the organic carbon in the bed during mid-spring to early fall. Thereafter, low temperatures and decreasing light availability result in little growth and decomposition of the algal material. From mid-fall to around mid-spring the decomposition of the algal material results in a decrease in organic carbon in the bed. Figure 8-16 shows the significant seasonal trends undergone by temperature and the light intensity parameter. The scenario in Figure 8-15 in which algal biomass is not impacted by hydrologic variables shows a seasonal pattern. It is evident that temperature and light intensity drive this seasonal variation. Depending on the decomposition rate of the fine algal biomass, either the light intensity or the temperature controls the peak of the algal biomass. Furthermore, results of the model predict that the POC loads are heavily weighted during summer, fall and winter due to a heavy presence of hydrologic activity.

8.2.3.1) Potential Impact of Sanitation Mandates on Seasonal Variability

Inputs from point sources can heavily impact water quality and nutrient loadings. Likewise, such sources can have a significant impact on in-stream carbon processes. The city of Lexington, Kentucky (location of the study site) was found to be in violation of the Clean Water Act by the EPA in 2006. As a result, the city is required to overhaul the sewer system to sufficiently withstand a minimum of a two to ten year flooding event. With cost estimates for the repair ranging from 500-800 million dollars, it's possible that the cheaper option will be utilized. Further, with respect to POC transport in the South Elkhorn, pronounced nutrient reduction could impact autochthonous supply in the streambed by limiting growth. Presently, nutrient supply is non-limiting and POC loads are dominated by hydrologic forcing of the streambed and erosion of upland sources in the watershed as well as seasonal variation (i.e. temperature) in the stream. A nutrient limited condition would require further analysis of POC loading.

8.3) Fate out of the Watershed

This study looked at quantifying the fate and transport of POC within the context of a small headwater drainage basin. The fate of POC as it leaves first through third order systems and travels to a higher order reach (i.e. 4th, 5th, 6th,etc.) is important to understand. Many older studies have looked at POC transport in large rivers of the world (Meybeck 1982, Ittekkot 1988, Howarth 1991) however further investigation and literature review is needed to assess the current state of fate studies in large lowland systems. Based on the literature and a conceptual understanding, periphyton dominates primary production in headwater, fast moving reaches (Naiman and Bilby 1998), and phytoplankton (Planktonic Autotrophs) maintains populations in slower-flowing rivers downstream (Allan 1995). This means that as stream order increases, autochthonous production shifts from benthic dominance to water column dominance (resulting from light availability). At the present time, no variability with stream order is being assessed. By further investigating the literature, we can understand how carbon processes vary from a first order headwater reach, to the 7th order river system. This is valuable, even for the model presented in this thesis because tributary autochthonous inputs are not expressly accounted for in the model (thus, the model underestimates the contribution from the autochthonous pool).

8.4) Extrapolation of Results

A need exists for extrapolation of results from small lowland watersheds to a regional, national and even global scale. Utilization of currently developed geospatial models as well as sediment transport models will be essential in the future. Wolock et al. (2004) conducted a GIS study in which areas in the United States were grouped based on Hydrologic characteristics. Coupling this work with a sediment transport and POC fate model would allow for general estimates of POC globally. Currently, studies such as Shih et al. (2010) have estimated transport of TOC using a national sediment transport model coupled with TOC point data. Although this study accounts for autochthonous production, the model uses a single calibration parameter to generate autochthonous growth. Likewise, seasonal variability is not expressly accounted for (i.e. the model works on an annual timestep). Studies such as this thesis can be utilized by large scale models to calibrate and inform seasonal and annual contributions of autochthonous carbon to the POC load.

Study of carbon dynamics in headwater draining watersheds, such as the South Elkhorn, and extrapolation of the results to a large scale can assist in regional and global carbon budgets called for in Cole et al. (2007). The results of this watershed can be extrapolated out to the Inner Bluegrass Region, which uses the underlying assumption that characteristics in the South Elkhorn are representative of the Inner Bluegrass Region. To estimate the area of the Inner Bluegrass Region, a Kentucky regional map was utilized in ArcGIS. It is estimated that the Inner Bluegrass region has an area of approximately 4700 km^2 which comprises about 5 percent of the land mass in Kentucky. Multiplying this by the POC flux estimated at the South Elkhorn watershed, it is estimated that around 1350 tC/yr is exported from the inner bluegrass region. Likewise, of the 1350 tC/yr around 180 of this is newly generated autochthonous carbon.

Currently, global estimates of POC flux neglect the contribution of autochthonous carbon to the POC load. Thus, it is critical to put the importance of the autochthonous contribution into perspective. The land mass of the world is estimated at around 148,940,000 km^2. It is also estimated that 24 % of the world's land mass is mountainous, thus 76 % can be considered lowland (113,194,400 km^2). Based on available resources and data it is estimated that around 4,301,387 tC yr^{-1} of newly generated autochthonous POC is transported *via* riverine systems. This represents a conservative estimate, because autochthonous production in mountainous areas is completely neglected. Using the most recent estimates of global POC flux from riverine systems, around 180,000,000 tC yr^{-1} is transported to the ocean. Thus, based on these estimates, approximately 2.5 % of the POC flux may be neglected in current estimates. This study therefore agrees with the literature, in that a better understanding of POC fate in small watersheds can provide significant information with regards to regional and global carbon budgets (Cole et al 2007).

With regards to POC transport from lowland systems versus steep gradient systems, the results of this study agreed with the literature. Steep gradient systems transport a large portion of POC *via* the stream network (Gomez et al. 2003, Lyons et al. 2002). Lyons et al. 2002 estimated that 17-35 % of POC flux was derived from the Pacific Rim, which constitutes approximately 3% of the world's surface area. Likewise, extrapolating the POC results from this study, around 18% of transported POC comes from lowland systems (0.03 Gt yr^{-1}). This estimate is conservative in that some of the larger lowland rivers of the world have been found to have POC fluxes closer to 1 tC km^{-2} y^{-1}. Using 1 tC km^{-2} y^{-1} as a high mark, lowland systems can transport as much as 76% of the world's POC.

8.5) Need for Uniformity in Methodology

A significant portion of this thesis is devoted to the development of a new modeling approach for POC estimates. To develop a thorough understanding of biogeochemical fate and POC transport in river systems, new methodological approaches to measure POC is needed (Alvarez et al. 2010). The coupled, feed forward modeling framework presented in this thesis is advantageous because it allows the modeler to plug in sub-models for any desired biogeochemical process. For example, further modeling efforts will look at aggregate analysis in the streambed, and nitrogen processes in the active and anoxic layer. With the current framework, the necessary carbon, sediment and hydrologic components are available; the sub model for nitrogen or aggregates can be added in with ease. This modeling framework differs heavily from previous POC flux studies with regards to spatial and temporal domain. Likewise, previous methodology used to collect data for sediment transport and organic carbon content of fine sediments varied widely.

Most studies reviewed in this paper, relied solely on collected data for their POC analysis. Sediment fluxes were measured in some studies (Zhang et al., 2009) and obtained from rating curves in others (Carey et al., 2005; Gomez et al., 2003). Likewise, carbon estimates were derived using a variety of sampling methods. Many cases utilized the carbon content of source soils. Howarth et al. (1991) used a model approach to estimate POC flux including different land-use sub models, however POC and DOC were combined for simplicity, thus eliminating the model's ability to simulate biological changes to the POC load. For this thesis, sediment loads were measured at the outlet of the watershed, and modeled throughout the stream reach. The modeling of sediment transport processes is advantageous, because it allows POC assessment at points throughout the watershed.

POC was measured from time integrated samples in the water. As previously discussed, most studies collected point samples of sediment using a grab sampler. This method is widely used for suspended sediment analysis; however the highly variable nature of the carbon content of POM makes it difficult to assess seasonality of POC with point samples. With regards to POC source, fractions of suspended sediment were assessed using the sediment transport model, however many studies use the isotopes, such as $\delta^{13}C$ and the carbon to nitrogen ratio, to build an unmixing model (Galy et al., 2008; Gomez et al., 2003; Leithold et al., 2006). Currently, isotopic source data is available and future work may utilize stable isotopes to better assess source contributions of POC.

More uniformity is needed with regards to data collection, modeling procedures and analysis of POC flux. Although the world's river systems differ greatly, POC flux can be broken down to source erosion, fate in stream and transport through the fluvial network. Coupling models that integrate all these processes will help to give a better understanding of global POC fluxes and give insight to how POC fate transport will be impacted by climate and land use changes in the future.

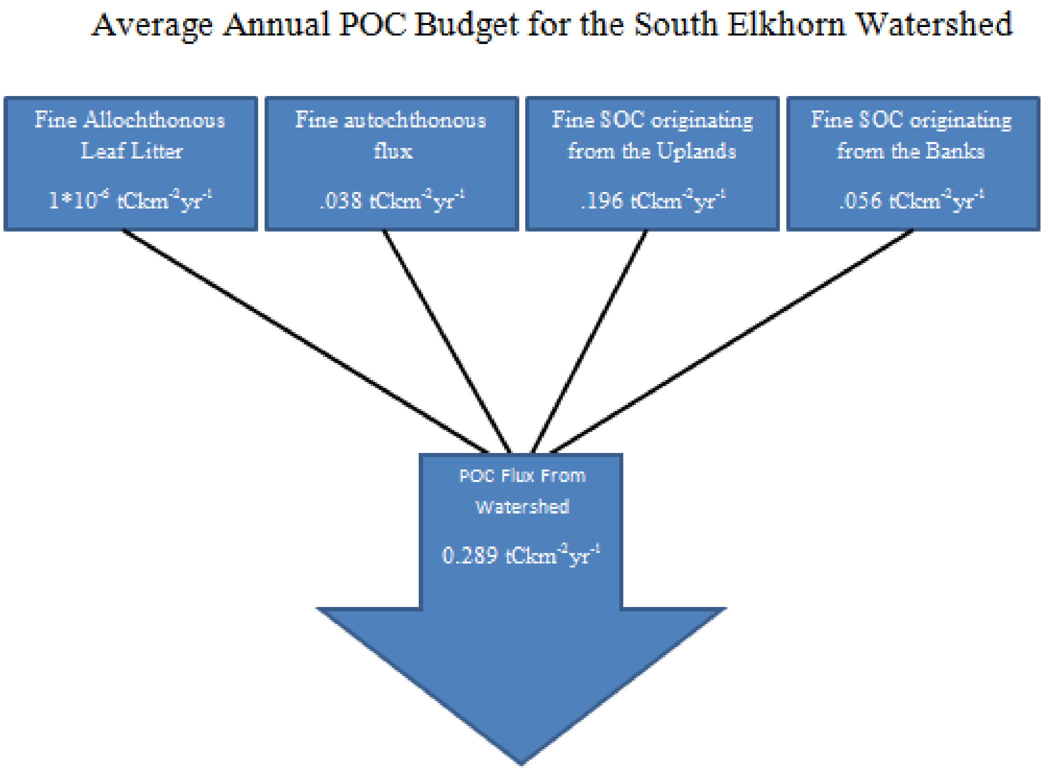


Figure 8-1) Average annual POC Budget from POC Model

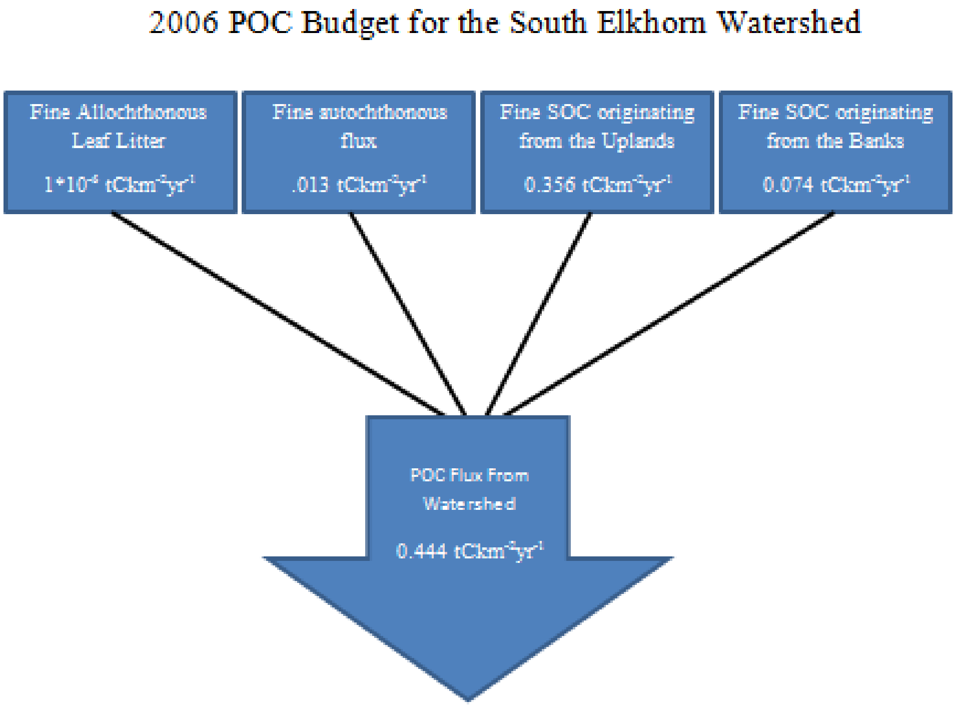


Figure 8-2) 2006 POC Budget from POC Model

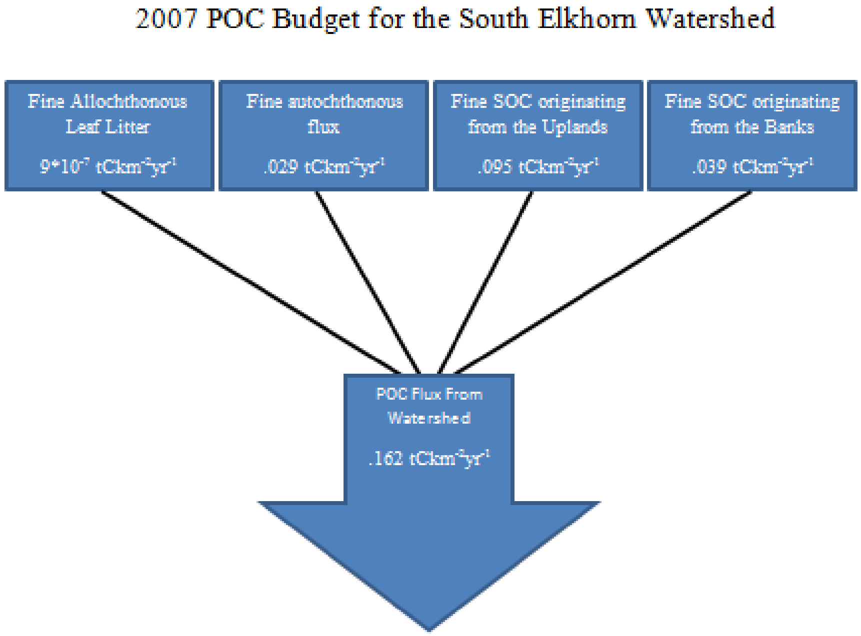


Figure 8-3) 2007 POC Budget from POC Model

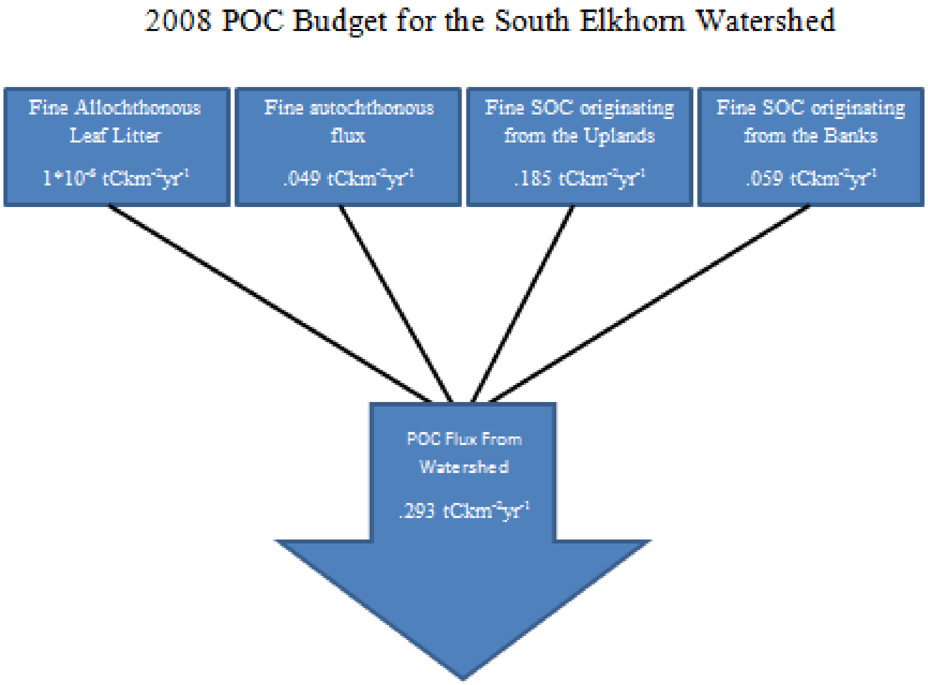


Figure 8-4) 2008 POC Budget from POC Model

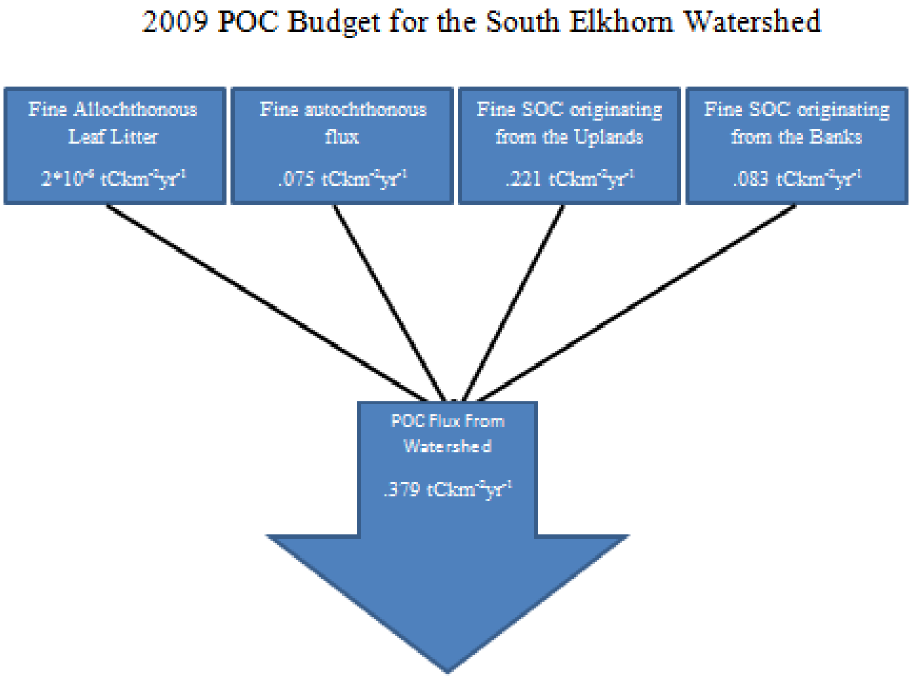


Figure 8-5) 2009 POC Budget from POC Model

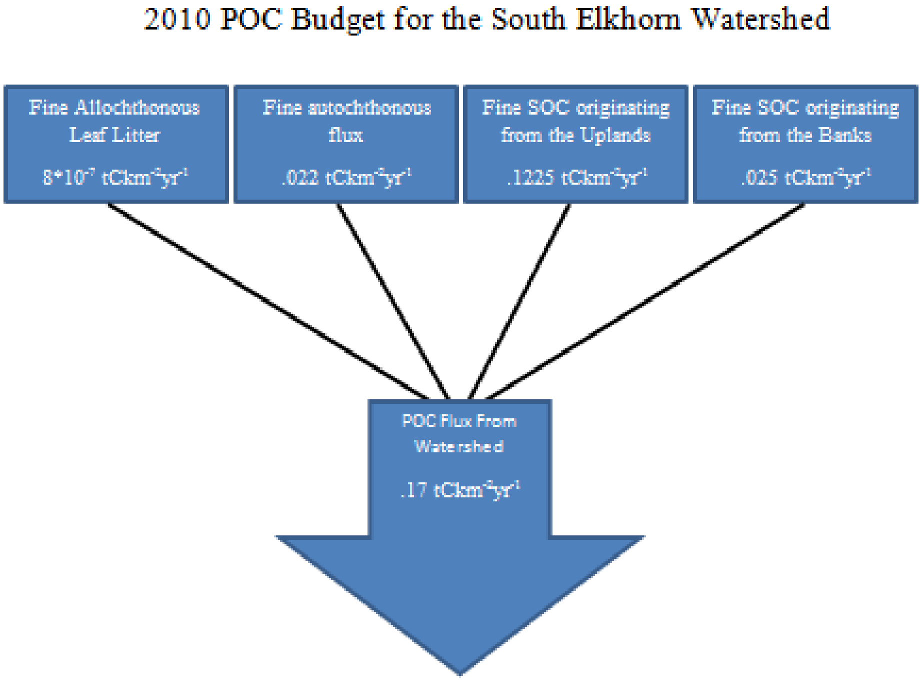


Figure 8-6) 2010 POC Budget from POC Model

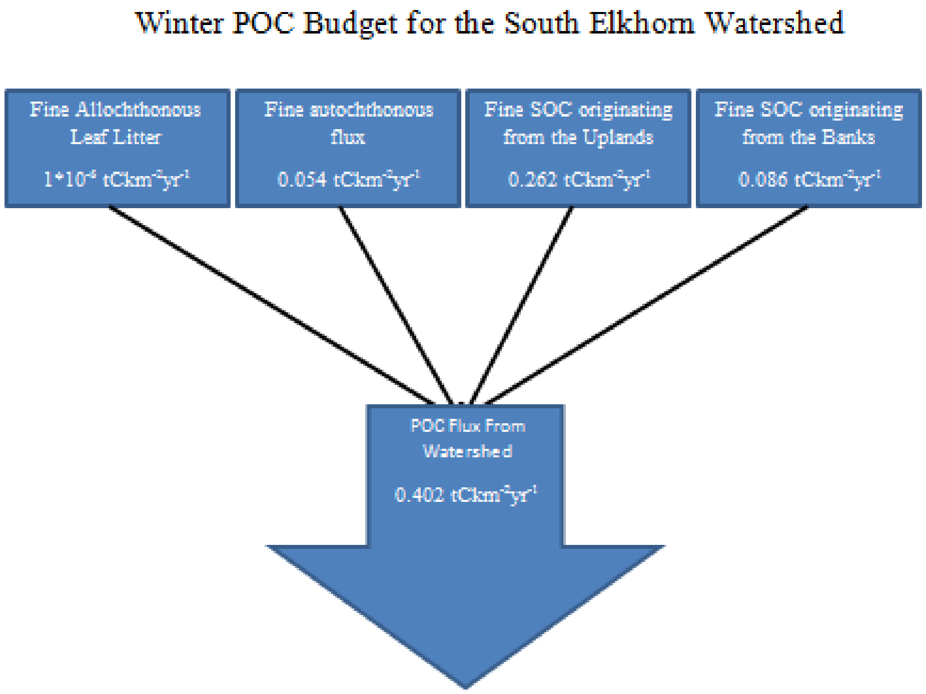


Figure 8-7) Average winter POC Budget for the South Elkhorn watershed from POC model

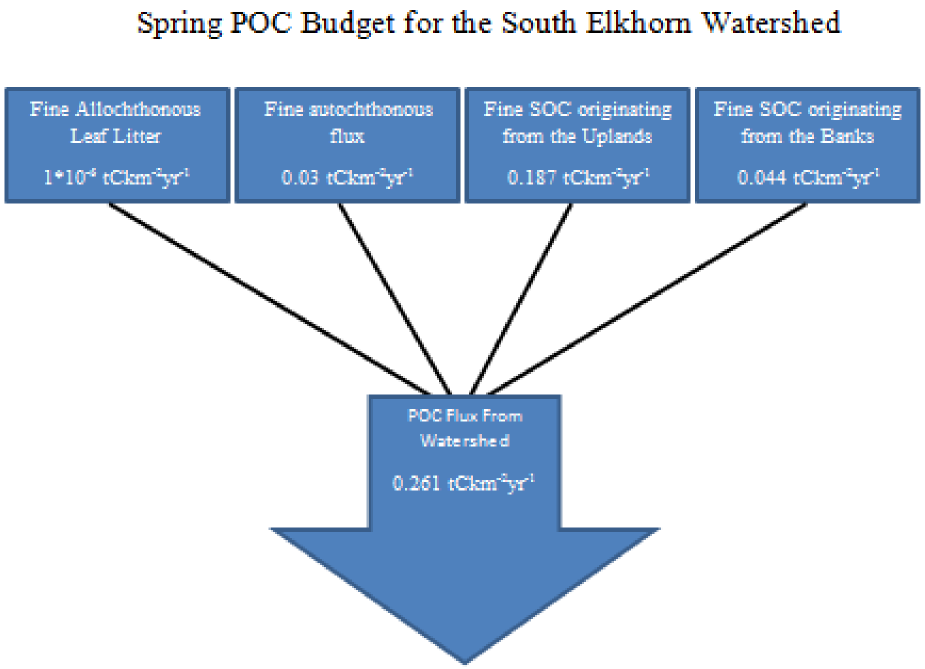


Figure 8-8) Average spring POC Budget for the South Elkhorn watershed from POC model

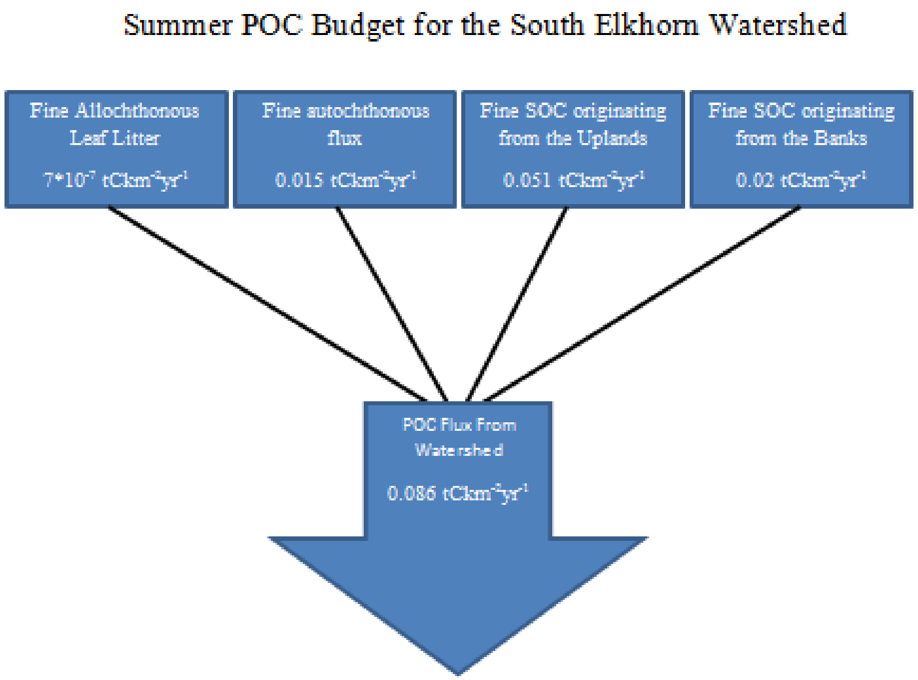


Figure 8-9) Average summer POC Budget for the South Elkhorn watershed from POC model

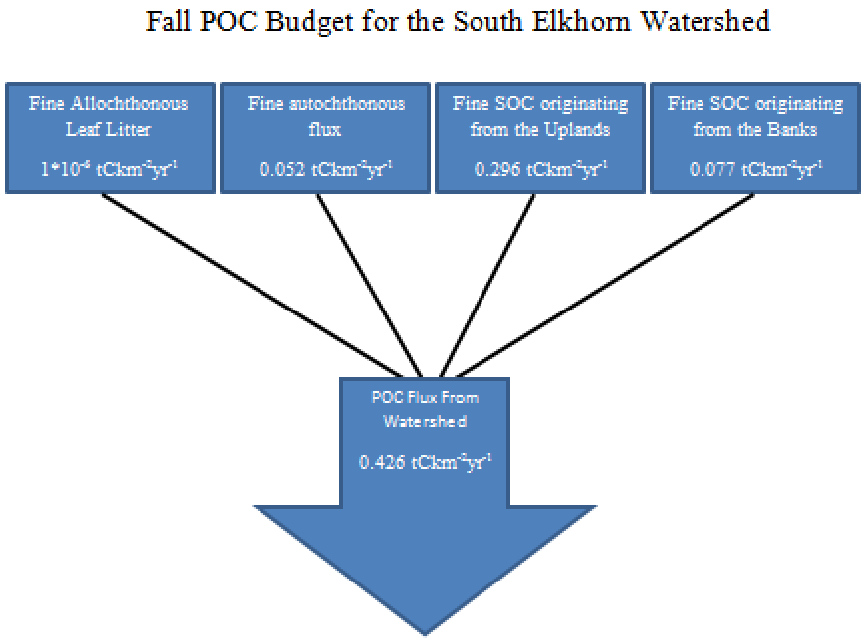


Figure 8-10) Average fall POC Budget for the South Elkhorn watershed from POC model

Table 8-1) Hydrologic forcing of POC through the fluvial network

	Percent occurrence	*POC Flux ($tCkm^{-2}yr^{-1}$)*	*%POC Flux*
Flow > 2.5 cms	10.76	0.25	87.49
Flow < 2.5 cms	89.24	0.04	12.51

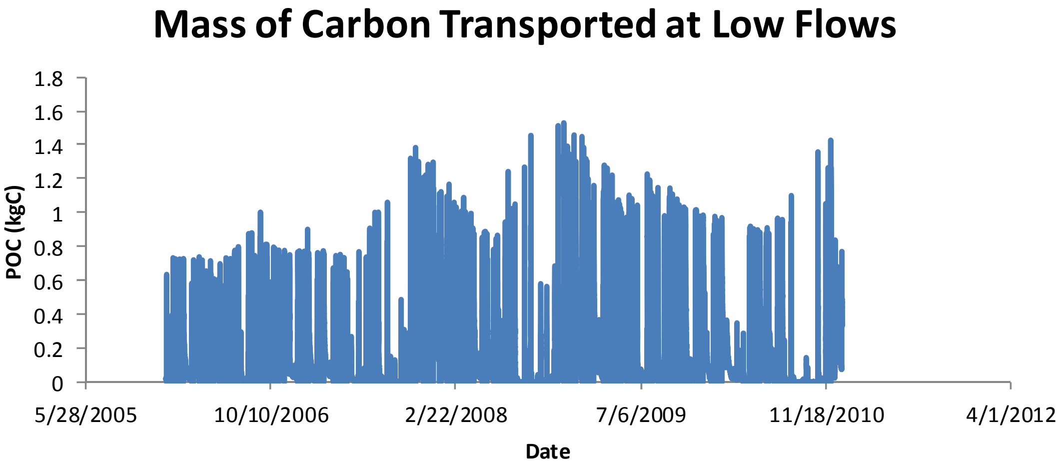


Figure 8-11) Low flow contribution to the POC load.

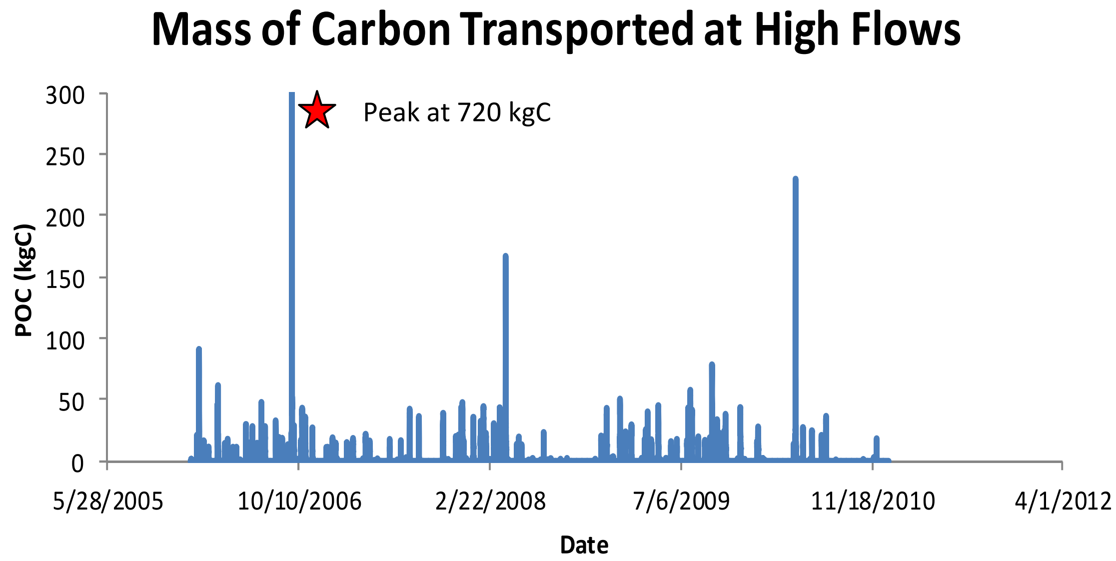


Figure 8-12) High flow contribution to the POC load.

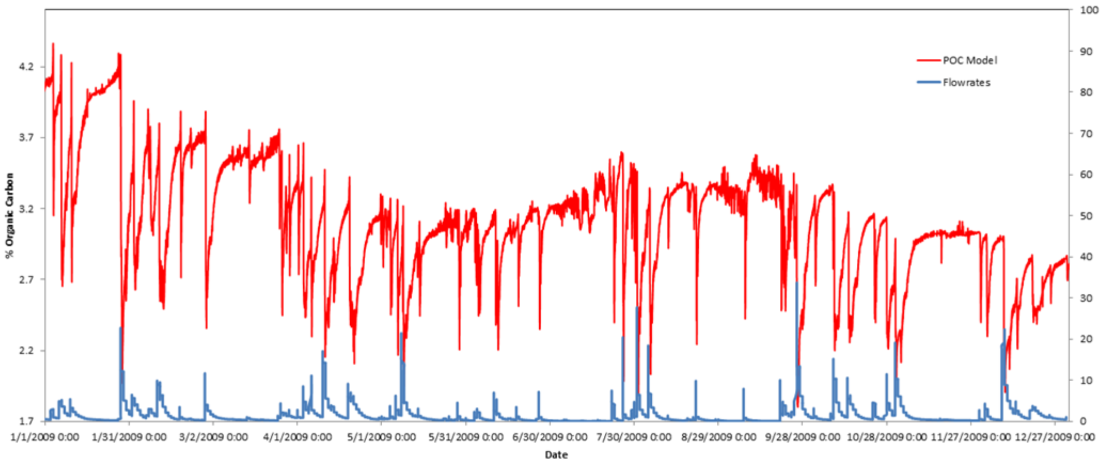


Figure 8-13) Fluctuations in % OC as a result of hydrologic variability

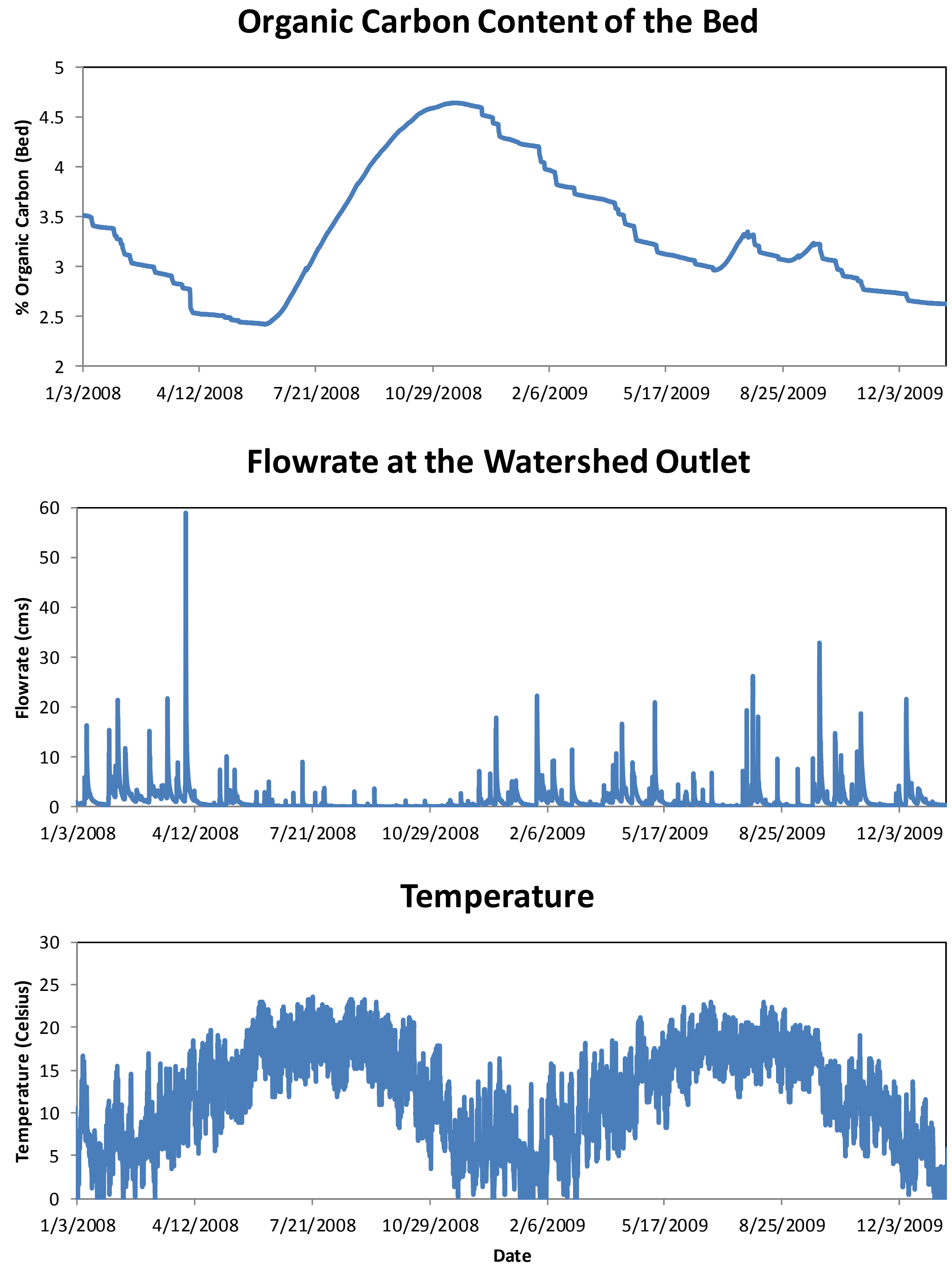
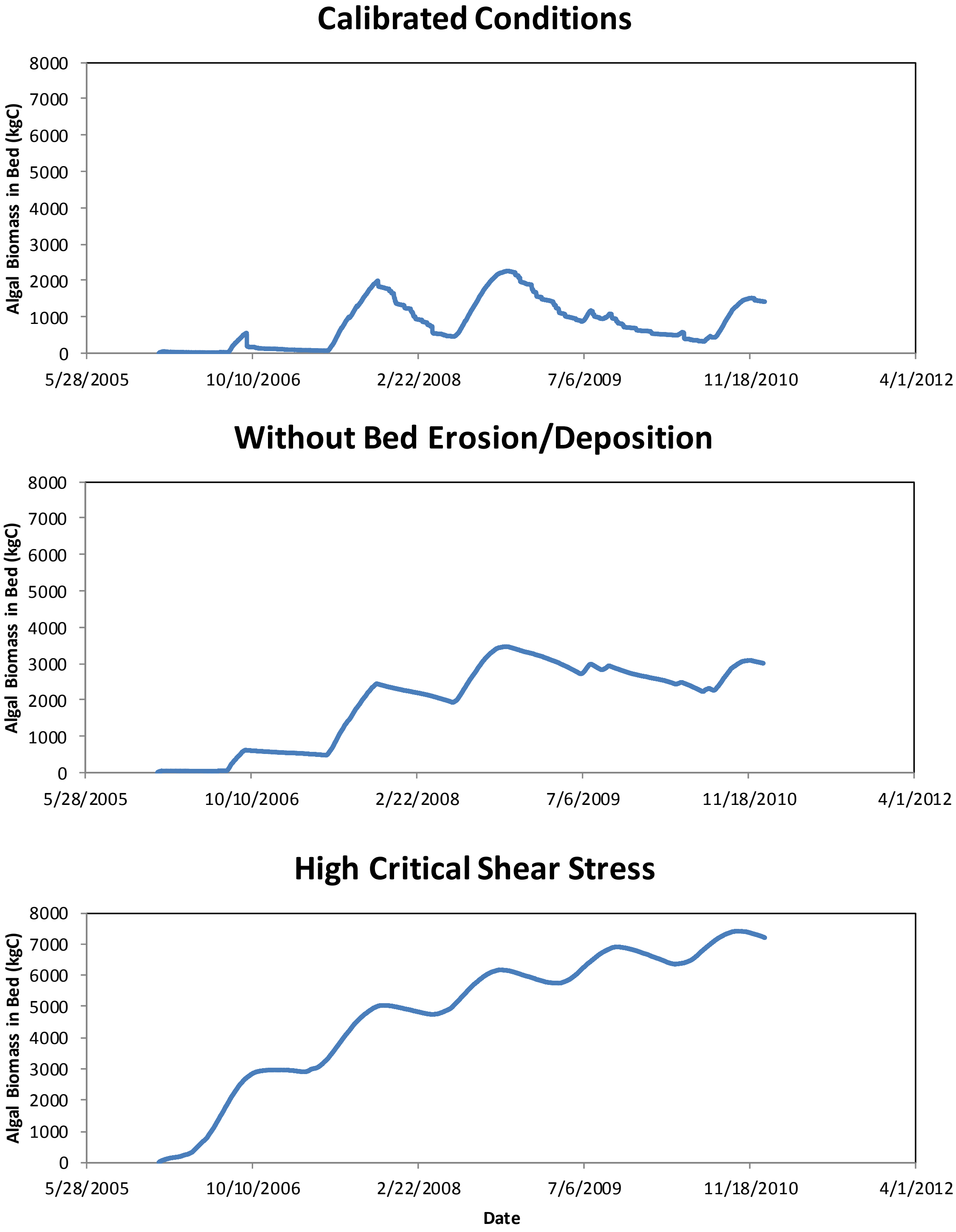


Figure 8-14) Annual and seasonal variability of POC flux from POC model


Calibrated Conditions

Without Bed Erosion/Deposition

High Critical Shear Stress

Figure 8-15) Biologic variability of algal biomass in the bed from POC model

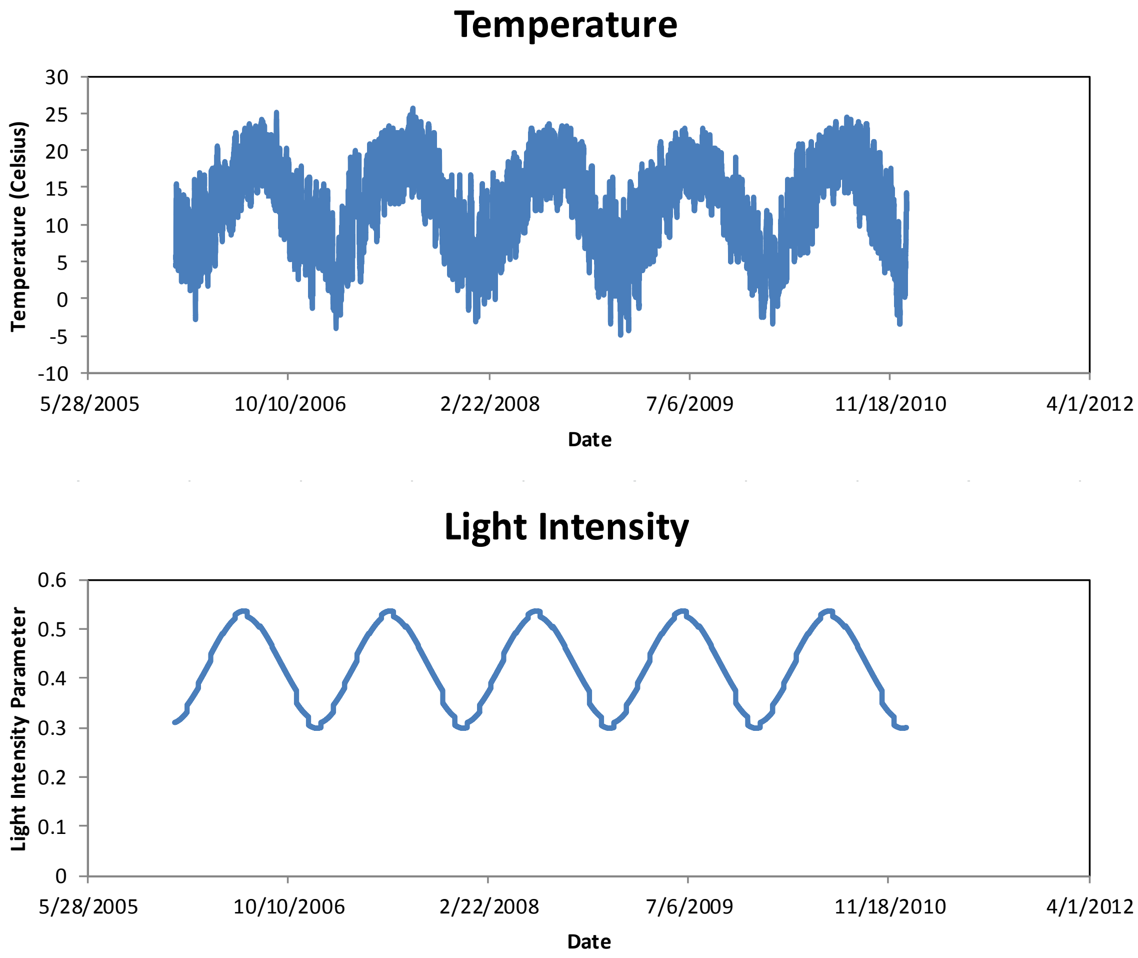


Figure 8-16) Seasonal variability of temperature and light intensity from POC model

Chapter 9 Conclusion

9.1) Conclusion from Results and Discussion

This study addresses the importance of carbon processes in small lowland temperate watersheds through the case study of a 62 km^2 watershed in the Inner Bluegrass region of Central Kentucky. Herein, a coupled physical and biological model framework was developed and implemented to estimate POC flux. Hydrologic modeling was utilized to drive a sediment transport and hydraulic model. A data driven hydrologic model was used for the models, and a conceptual based model was built for future predictions with regard to climate and land use change. Results from the sediment transport model predicts that high flow events transport a significant portion of sediment through the river channel, and that sediment inflow rate and transport carrying capacity are very sensitive parameters.

The newly developed POC model utilized a mass balance approach coupled with an algal sub model (Rutherford 2000). The model proved to be extremely sensitive to algal growth and decomposition parameters. Likewise, the algal model (specifically temperature and light intensity) was the primary factor impacting seasonal variability of POC flux. Furthermore, annual variability was observed, however it was more complex to describe than seasonal variability. Annual variability occurred as a result of annual temperature variations (i.e. in years where the average temperature was lower, the algal biomass in the fine pool was depleted). Furthermore, the density of hydrologic events during the algal growing period significantly impacted the amount of algal biomass production.

Results of the POC budget for the watershed showed that the South Elkhorn exports around 0.3 $tCkm^{-2}yr^{-1}$ with around 13% coming from autochthonous production, 19% from the streambanks and 68% from fine SOC in the uplands. The contribution of allochthonous FPOM (including CPOM and leaf litter) was insignificant and had little bearing on the model, which is expected for the watershed.

9.2) Improvement to the Method

Current knowledge of POC and sediment transport processes has allowed some weaknesses to be highlighted in the current research. The following list outlines the improvements for the model and data collection that will be considered in future work.

9.2.1) Data Collection Needs

- Need more water temperature data to reduce scatter in the air/water temperature relationship
- Need to collect data from the tributaries
  - Flowrate, suspended sediment, and carbon data
- Continued collection of integrated samples at the outlet to further investigate annual and seasonal trends.
- Further field investigation of the sediment bed to understand depth dynamics and carbon processes in the bed
- Use of an YSI turbidity probe as a surrogate for transported sediment.
- Collection of light intensity data as opposed to using the literature using a Photosynthetic Active Radiation sensor.

9.2.2) Modeling Needs

- Improvement of the hydrologic model for future simulations

- Integration of tributary data into the sediment transport model.
- Integration of tributary data into the POC model
    - Build a submodel to address the autochthonous contribution from the tributaries.
- Determining the significance of sloughing of the algal mat.
    - As material is sloughed does it go into the dissolved phase?
    - How much does that source contribute to the POC load?
- Inclusion of nutrient and aggregate models so that all impacting factors are assessed.
- Run the model a year early, so that it is “warmed up” by the time data collection has begun.

9.3) Future Work

To fully understand any of the processes occurring in the benthic and anoxic layers, one must have a firm grasp on all of the processes. Hence current work will be pushed forward, to build a fully integrated hydrologic, hydraulic, and biogeochemical model. The following list of future work is broad; however these goals need to be met before the overarching goal of a fully coupled hydrologic, sediment transport and biogeochemical can be met.

- Modeling the nitrogen cycle in the South Elkhorn to develop an aquatic nitrogen budget.
- Utilize a mass balance un-mixing model to better quantify the source contributions of POC.

- Model biological processes on a finer scale and upscale results to the watershed scale.
- Modeling aggregate formation and development in the sediment bed.
- Utilizing the current model to estimate the how much of the DIC is converted to DOC.
- Upscaling from the watershed scale to a regional/global scale

References

Abril, G., Etcheber, H., Borges, A. V. & Frankignoulle, M. (2000) Excess atmospheric carbon dioxide transported by rivers into the Scheldt Estuary. *Comptes Rendus l'Acade´mie des Sciences, Se´rie IIa* 330**,** 761–768.

Aldrian, E., C.-T. A. Chen, S. Adi, Prihartanto, N. Sudiana, and S. P. Nugroho (2008), Spatial and seasonal dynamics of riverine carbon fluxes of the Brantas catchment in East Java, *J. Geophys. Res.,* 113, G03029, doi:10.1029/2007JG000626.

Allan JD. 1995. *Stream Ecology: Structure and Function of Running Waters*. New York: Chapman & Hall

Alvarez-Cobelas M, Angeler D, Sa´nchez-Carrillo S, Almendros G (2010) A worldwide view of organic carbon export from catchments. *Biogeochemistry*. doi: 10.1007/s10533-010-9553-z

Alvarez, S., and Guerrero, M.C. (2000). Enzymatic activities associated with decomposition of particulate organic matter in two shallow ponds. *Soil Biology and Biochemistry*, 32, 1941-1951.

Arscott DB, Bowden WB, Finlay JC (1998) Comparison of epilithic algal and bryophyte metabolism in an arctic tundra stream, Alaska. J N Am Benthol Soc 17:210-227

Battin, T. J., A. Wille, B. Sattler, and R. Psenner. (2001). Phylogenetic and functional heterogeneity of sediment biofilms along environmental gradients in a glacial stream. *Appl. Environ. Microbiol.* 67:799–807.

Battin, T. J., L. A. Kaplan, S. Findlay, C. S. Hopkinson, E. Marti, A. I. Packman, J. D. Newbold, and F. Sabater (2008), Biophysical controls on organic carbon fluxes in fluvial networks, *Nat. Geosci.*, 1, 95 – 100, doi:10.1038/ngeo101.

Bell, R.T., Ahlgren, G.M., Ahlgren, I. (1983) Estimating bacterioplankton production by measuring [3H]thymidine incorporation in a eutrophic Swedish lake. *Appl Environ Microbiol* 45:1709-1721

Biggs, B.J, (1996). Patterns in Benthic Algae of Streams. In: Algal Ecology, R.J. Stevenson, M.L. Bothwell, and R.L. Lowe (Editors). Academic Press, New York, pp. 31-56.

Bird, M.I., Robinson, R.A.J., Oo, N.W., Aye, M.M., Lu, X.X., Higgitt, D.L., Swe, A., Tun, T., Win, S.L., Aye, K.S., Win, K.M.M., Hoey, T.B., (2008). A preliminary estimate of organic carbon transport by the Ayeyarwady (Irrawaddy) and Thanlwin (Salween) rivers of Myanmar. *Quaternary International* 186 (1), 113e122.

Borah, D.K., and M. Bera. 2003. Watershed-scale hydrologic and nonpoint-source pollution models: Review of mathematical bases. *Trans. ASAE* 46(6): 1553-1566.

Brock, T.D., 1981. Calculating solar radiation for ecological studies. *Ecol. Model.*, 14: 1-19.

Bungartz, H., A. Kruger, and C. Engelhardt (2006), Fluvial suspended sediment dynamics: Implications for particulate organic carbon transport modeling, *Water Resour. Res.*, 42, W10424, doi:10.1029/2005WR004486.

Carey, A. E., C. B. Gardner, S. T. Goldsmith, W. B. Lyons, and D. M. Hicks (2005). Organic carbon yields from small mountainous rivers, New Zealand, *Geophys. Res. Lett.*, 32, L15404, doi:10.1029/2005GL023159.

Cauwet, G. (2002). *Biogeochemistry of Marine Dissolved Organic Matter* (eds Hansell, D. A. & Carlson, C. A.) 579–602 (Academic Press, New York, 2002).

Chang, H. H. (1988). Fluvial Processes in River Engineering. *Krieger Publishing Company: Malabar, Florida.*

Chien, N., and Wan, Z. (1999). Mechanics of sediment transport, *ASCE, Reston, Virginia,* 446 pp.

Chu, X., and Steinman, A. (2009). Event and Continuous Hydrologic Modeling with HEC-HMS. Journal and Irrigation and Drainage Engineering. Vol. 135, No. 1, February 1, 2009.

Cole, J., Prairie, Y., Caraco, N., McDowell, W., Tranvik, L., Striegl, R., et al. (2007). Plumbing the global carbon cycle: Intergrating inland waters into the terrestrial carbon budget. *Ecosystems , 10*, 171-184.

Cooper, J. M. (1998). *Introduction to Partial Differential Equations with* MATLAB, Birkhauser, Boston, MA

Cox, E. J. (1990). Studies on the algae of a small softwater stream. I. Occurrence and distribution with particular reference to the diatoms. *Archiv frir Hydrobiologie Supplement* 83:525-552.

Coynel, A., et al (2005). Contribution of small mountainous rivers to particulate organic carbon input in the Bay of Biscay. *Biogeochemistry* 74:151–171

Dalzell, B. J., T. R. Filley, and J. M. Harbor (2005). Flood pulse influences on terrestrial organic matter export from an agricultural watershed, *J. Geophys. Res.*, 110, G02011, doi:10.1029/2005JG000043.

Dance, K.W., Hynes, H.B.N, & Kaushik, N.K. (1979). Seasonal drift of solid organic matter in two adjacent streams. *Arch. Hydrobiol.,* 87, 139-51

Davis, C. M. (2008). "Sediment fingerprinting using organic matter tracers to study streambank erosion and streambed sediment storage processes in the South Elkhorn Watershed." M.S. Dissertation, University of Kentucky, Lexington, Kentucky.

Dodds WK, Smith VH, Lohman K. (2002). Nitrogen and phosphorus relationships to benthic algal biomass in temperate streams. *Can J Fish Aquat Sci*;59, 865–74.

Ducklow, H.W., Kirchman, D.L. (1983). Bacterial dynamics and distribution during a spring diatom bloom in the Hudson River plume, USA. *J Plank Res* 5:333-355

Dunlap MA, Marion W, Wilcox S. (2001). Solar radiation data manual for flat-plate and concentrating collectors. Report no. NREL/ TP-463–5607. Golden (CO): National Renewable Energy Laboratory; 2001.

Edwards, R.T., Meyer, J.L. & Findlay, S.E.G. (1990). The relative contribution of benthic and suspended bacteria to system biomass, production, and metabolism in a low-gradient blackwater river. *Journal of the North American Benthological Society*, 9, 216±228.

Emerson, D. G., A. V. Vecchia, and A. L. Dahl. (2005). Evaluation of drainage-area ratio method used to estimate streamflow for the Red River of the North Basin, North Dakota and Minnesota. U.S. Geological Survey Scientific Investigations Report 2005–5017.

Fischer, H., & Pusch, M. (2001). Comparison of bacterial production in sediments, epiphyton, and the pelegiac zone of a lowland river. *Freshwater Biol*. 46:1335-1348.

Fischer, H., Wanner, S.C. and Pusch, M. (2002) Bacterial abundance and production in river sediments as related to the biochemical composition of particulate organic matter (POM). *Biogeochemistry* 61, 37-55.

Fisher, S.G. (1977). Organic matter processing by a stream segment ecosystem, Fort River, Massachusetts. *Int. Rev. Ges. Hydrobiol.*, 62, 701-27

Flanagan, D. C., J. C. Ascough II, A. D. Nicks, M. A. Nearing, and J. M. Laflen. (1995). Overview of the WEPP erosion prediction model. In *USDA-Water Erosion Prediction Project: Hillslope Profile and Watershed Model Documentation*, 1.1-1.12. NSERL Report No. 10. D. C. Flanagan and M. A. Nearing, eds. West Lafayette, Ind.: National Soil Erosion Research Laboratory.

Flemer, D.A., & Biggs, R.B. (1971). Particulate carbon: nitrogen relations in Northern Chesapeake Bay. *J. Fish. Res. Bd. Can.*, 28, 911-18

Fox, J., Davis, C. M., & Martin, D. K. (2010). Sediment source assessment in a lowland watershed using nitrogen stable isotopes. *Journal of American Water Resources Association , 46*, 1192-1204.

Francoeur, S. N., B. J. F. Biggs, R. A. Smith, and R.L. Lowe. (1999). Nutrient limitation of algal biomass accrual in streams: seasonal patterns and a comparison of methods. *Journal of the North American Benthological Society* 18:242–260.

Frost, P.C., Stelzer, R.S., Lamberti, G.A. & Elser, J.J. (2002). Ecological stoichiometry of trophic interactions in the benthos: understanding the role of C :N: P ratios on littoral and lotic habitats. J. N. Am. Benthol. Soc., 21, 515–528.

Galy, V., France-Lanord, C. & Lartiges, B. (2008). Loading and fate of particulate organic carbon from the Himalaya to the Ganga–Brahmaputra delta. *Geochimica et Cosmochimica Acta*, 72, 1767–1787.

Gessner, M.O. (1997) Fungal biomass, production and sporulation associated with particulate organic matter in streams. *Limnetica* **13**, 33–44. (In *Proceeding of the European Meeting on Litter Breakdown in Rivers and Streams*. Pozo, J. and Elosegi, A., Eds. *Limnetica* **13**, 1–102.)

Gosselain, V., Hamilton, P. B., & Descy, J. (2000). Estimating phytoplankton carbon from microscopic counts: an application for riverine systems. *Hydrobiologia* 438:75-90.

Gomez, B., Trustrum, N. A., Hicks, D. M., Rogers, K. M., Page, M. J., & Tate, K. (2003). Production, storage, and output of particulate organic carbon: Waipaoa River basin, New Zealand. *Water Resources Research , 39*.

Gordeev, V.V., & Kravchishina, M.D. (2009). River flux of dissolved organic carbon (DOC) and particulate organic carbon (POC) to the Arctic Ocean: what are the consequences of the global changes? *Influence of Climate Change on the Changing Arctic and Sub-Arctic Conditions*: 145-160.

Gross, M.G., Cary, A.G., Fowler, G.A., & Kulm, L.D. (1972). Distribution of organic carbon in surface sediment, Northeast Pacific Ocean. *In the Columbia River Estuary and Adjacent Ocean Waters*,ed. A.T. Pruter & D.L. Alverson. University of Washington Press, Seattle.

Guo, L., & Macdonald R. W. (2006). Source and transport of terrigenous organic matter in the upper Yukon River: Evidence from isotope (δ^{13}C, δ^{14}C, and δ^{15}N) composition of dissolved, colloidal, and particulate phases, *Global Biogeochem. Cycles,* 20, GB2011, doi:10.1029/ 2005GB002593.

Hanson GJ, Simon A. 2001. Erodibility of cohesive streambeds in the loess area of the midwestern USA. *Hydrological Processes* **15**(1): 23–38.

Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? Org. Geochem. 27, 195-212.

Hilton RG, Galy A, Hovius N (2008) Riverine particulate organic carbon from an active mountain belt: importance of landslides. *Global Biogeochem Cycles* 22. doi: 10.1029/2006GB002905

Hily C (1991). Is the activity of benthic suspension feeders a factor controlling water quality in the Bay of Brest? Mar Ecol Prog Ser 69: 179-188

Hope D, Billett MF, Cresser MS (1994) A review of the export of carbon in river water: fluxes and processes. *Environ Pollut* 84:301–324

Howarth, R.W.; Fruci, J.R.; Sherman, D. (1991). Inputs of sediment and carbon to an estuarine ecosystem: Influence of land use. *Ecological Applications.* 1(1): 27-39.

Imhoff, J.C., Stoddard, A., Buchak, E.M. (2003). Evaluation of contaminated sediment fate and transport models: Final report. Technical Report. Contract 68-C-01-037. U.S. Environmental Protection Agency Office, National Exposure Research Laboratory, Athens, GA, USA.

Ingold, C.T. (1942). Aquatic hyphomycetes on decaying alder leaves. *Transactions of the British Mycological Society* 25: 339–417.

Ittekot, V. (1988), Global trends in the nature of organic matter in river suspensions, *Nature*, 332, 436–438.

Jackson, C.R., and Vallaire, S.C. (2007). Microbial activity and decomposition of fine particulate organic matter in a Louisiana cypress swamp. *J. N. Am. Benthol. Soc.*, 26(4), 743-753.

Jobbagy EG, Jackson RB (2000) The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecological Applications*, 10, 423–436.

Karlstrom, U. & Backlund, S. (1977). Relationship between algal cell number, chlorophyll a and fine particulate organic matter in a river in Northern Sweden. *Archiv. Hydrobiol.*, 80, 192-9.

Kara, H. & Sahin, B. (2001). Epipelic and epilithic algae of Deg˘irmendere River (Trabzon, Turkey). *Turkish Journal of Botany* 25: 177–186.

Lal, R., (2002). Soil carbon dynamics in cropland and rangeland. *Environmental Pollution* 116, 353-362.

Lehmann M. F., Bernasconi S. M., Barbieri A., and McKenzie J. A. (2002) Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. *Geochim. Cosmochim. Acta* **66,** 3573–3584.

Leithold, E. L., N. E. Blair, and D. W. Perkey (2006), Geomorphologic controls on the age of particulate organic carbon from small mountainous and upland rivers, *Global Biogeochem. Cycles*, 20, GB3022, doi:10.1029/2005GB002677.

Lyons, W.B., Nezar, C.A., Carey, A.E., Hicks, D.M., 2002. Organic carbon fluxes to the ocean from high-standing islands. *Geology* 30, 334–446.

Malcolm, R.L., Durum, W.H. (1976). Organic carbon and nitrogen concentrations and annual organic carbon load of six selected rivers of the United States. USGS Water Supply Paper, 1817-F, 21pp.

Martin, J.L., Ambrose, R.A., Wool, T.A., (2006). WASP7 Benthic Algae—Model Theory and User's Guide. U.S. Environmental Protection Agency, Athens, GA.

Marxsen, J. (2006). Bacterial production in the carbon flow of a central European stream, the Breitenbach. *Freshwater Biol*. 51**:**1838-1861.

McNeil, J., Taylor, C., Lick, W., 1996. Measurements of erosion of undisturbed bottom sediments with depth. Journal of Hydraulic Engineering ASCE 122, 316–324.

Meybeck, M. (1982). Carbon, nitrogen and phosphorus transported by world rivers. American *Journal of Science* 282:401–50.

Meybeck, M. (2006). *Soil Erosion and Carbon Dynamics* (eds Roose, E.J., Lal, R., Feller, C., Barthes, B., & Stewart, B. A.) 209–238 (CRC Press, Boca Raton, Florida, 2006).

Minshall, G.W., Petersen, R.C., Cummins, K.W., Bott, T.L., Sedell, J.R., Cushing, C.E. and Vannote, R.L. (1983). Interbiome comparison of stream ecosystem dynamics. *Ecological Monographs*, 53(1), 2-25.

Naiman, R.J. (1982). Characteristics of sediment and organic carbon export from pristine boral forest watersheds. *Can. J. Fish. Aquat. Sci.*, 39, 1699-718

Naiman, R.J., & Sibert, J.R. (1978). Transport of nutrients and carbon from the Nanaimo River to its estuary. *Limnol. Oceanogr*., 23, 1183-93

Naiman, R.J., & Sedell, J.R. (1979). Characterization of particulate organic matter transported by some Cascade Mountain streams. *J. Fish. Res. Bd. Can*., 36,17-31

Naiman, R.J., Bilby, R.E. (1998) *River ecology and management: lessons from the Pacific coastal ecoregion* (ed. by R.J. Naiman and R.E. Bilby), Springer Verlag, New York.

Nelson, E.J., and Booth, D.B. (2002). Sediment sources in an urbanizing, mixed land-use watershed. *Journal of Hydrology*, Vol. 264, pp. 51-68.

Oeurng,C.,Sauvage,S., Sanchez-Perez,J.M. (2011). Assessment of hydrology, sediment and particulate organic carbon yield in a large agricultural catchment using the SWAT model, *Journal of Hydrology*, Volume 401, Issues 3-4, 3 May 2011, 145-153, DOI: 10.1016/j.jhydrol.2011.02.017.

Phillips, J. M., Russell, M. A., & Walling, D. E. (2000). Time-integrated sampling of fluvial suspended sediment: a simple methodology for small catchments. *Hydrological Processes , 14*, 2589-2602.

Ravens, T. M. (2007). "Comparison of Two Techniques to Measure Sediment Erodibility in the Fox River, Wisconsin." *Journal of Hydraulic Engineering*, ASCE, 133(1), 111-115.

Richardson JS (1992) Coarse particulate detritus dynamics in small montane streams of the southwestern British Columbia. *Canadian Journal of Fisheries and Aquatic Sciences*, 49, 337–346.

Rier, S.T., Kuehn, K.A., and Francoeur, S.N. (2007). Algal regulation of extracellular enzyme activity in stream microbial communities associated with inert substrata and detritus. *J. N. Am. Benthol. Soc.*, 26(3), 439–449.

Robertson, M.L., Mills, A.L., & Zieman, J.C. (1982). Microbial synthesis of detritus-like particulates from dissolved organic carbon released by tropical seagrasses. *Mat: Ecol. Prog. Set:* 7:279-85

Roehl JE. (1962). Sediment source areas, delivery ratios and influencing morphological factors. In *Colloque de Bari/Symposium of Bari* . IAHS Publication No. 59. IAHS Press: Wallingford; 202-213.

Russo, J. P. (2009). "Investigation of surface fine grained laminae, streambed, and streambank processes using a watershed scale hydrologic and sediment transport model." M.S. Dissertation, University of Kentucky, Lexington, Kentucky.

Rutherford JC, Scarsbrook MR, Broekhuizen N. (2000). Grazer control of stream algae: modeling temperature and flood effects. *Journal of Environmental Engineering* 126: 331–339.

Sekely, A.C., D.J. Mulla, and D.W. Bauer, (2002). Streambank slumping and its contribution to the phosphorus and suspended sediment loads of the Blue Earth River, Minnesota. *J. Soil and Water Conservation,* 57(5): 243-250.

Sharma, P., & Rai S. C. (2004), Streamflow, sediment and carbon transport from a Himalayan watershed, *J. Hydrol. Amsterdam*, 289, 190– 203.

Shih, J., Alexander, R.B., Smith, R.A., Boyer, E.W., Schwarz, G.E., & Chung, S. (2010). An Initial SPARROW Model of Land Use and In-Stream Controls on Total Organic Carbon in Streams of the Conterminous United States: U.S. Geological Survey Open-File Report 2010–1276, 22 p., available at *http://pubs.usgs.gov/of/2010/1276.*

Short, R.A., Canton, S.P., & Ward, J.V. (1980). Detrital processing and associated macroinvertebrates in a Colorado mountain stream. *Ecology*, 61(4), 728-732.

Sigee, D. C. (2005). Freshwater microbiology. John Wiley & Sons, Ltd., Chichester, England.

Sinsabaugh, R.L., Osgood, M.P., & Findlay, S. (1994). Enzymatic models for estimating decomposition rates of particulate detritus. *J. N. Am. Benthol. Soc.*, 13(2), 160-169.

Sliter, M. (2007). *Study of Sediment Aggregates at the Watershed Scale in the South Elkhorn Watershed*. MSCE Master's Report, University of Kentucky, Lexington, KY.

Tank, J. L., Rosi-Marshall, E. J., Griffiths, N.A., Entrekin, S. A., & Stephen, M. L. (2010). A review of allochthonous organic matter dynamics and metabolism in streams. *Journal of the North American Benthological Society* 29:118–146.

Toy, T.J., Foster, G.R., and Renard, K.G., (2002). Soil erosion: Processes, predictions, measurements, and control: New York, John Wiley & Sons.

Trimble, S.W. (1997). Contribution of stream channel erosion to sediment yield from an urbanizing watershed. *Science*, Vol. 278, pp. 1442-1444.

Walling, D. E., Collins, A. L., Jones, P. A., Leeks, G. J., & Old, G. (2006). Establishing fine-grained sediment budgets for the Pang and Lambourn LOCAR catchments, UK. *Journal of Hydrology , 330*, 126-141.

Waterloo MJ, Oliveira SM, Drucker DP et al. (2006) Export of organic carbon in run-off from an Amazonian rainforest blackwater catchment. *Hydrological Processes*, 20, 2581–2597.

Weber, C.I., & Moore, D.R. (1967). Phytoplankton, seston, and dissolved organic carbon in the Little Miami River at Cincinatti, Ohio. *Limnol. Oceanogr.*, 12, 311-18.

Webster, J. R., E. F Benfield, T. P. Ehrman, M. A. Schaeffer, J. L. Tank, J. J. Hutchens, and D. J. D'Angelo. (1999). What happens to allochthonous material that falls into streams? A synthesis of new and published information from Coweeta. *Freshwater Biology* 41:687-705.

Wetzel, R.G., & Manny, B.A. (1977). Seasonal changes in particulate and dissolved organic carbon and nitrogen in a hardwater stream. *Archiv. Hydrobiol.*, 80, 20-39

White, P.A., Kalff, J., Rasmussen, J.B., and Gasol, J.M. (1991). The effect of temperature and algal biomass on bacterial production and specific growth rate in freshwater and marine habitats. *Microbial Ecology*, 21, 99-118.

Wolock, D. M., Winter, T. C., & McMahon, G. (2004). Delineation and Evaluation of Hydrologic-Landscape regions in the United States and using geographic information system tools and multivariate statistcal analyses. *Environmental Management* 34(Suppl 1)

Worrall, F., Reed, M., Warburton, J., et al. (2003) Carbon budget for a British upland peat catchment. *The Science of the Total Environment*, 312, 133–146.

Yoshimura, C., Gessner, M. O., Tockner, K., & Furumai, H. (2008). Chemical properties, microbial respiration, and decomposition of coarse and fine particulate organic matter. *Journal of the North American Benthological Society* 27:664–673.

Zhang, S.R., Lu, X.X., Sun, H.G., Han, J.T., Higgitt, D.L. (2009). Geochemical characteristics and fluxes of organic carbon in a human-disturbed mountainous river (the Luodingjiang River) of the Zhujiang (Pearl River), China. *Sci Total Environ*;407:815–25.

Ziegler, S. E., D. R. Lyon, 2010. Factors regulating epilithic biofilm carbon cycling and release with nutrient enrichment in headwater streams. Hydrobiologia. doi:10.1007/s 10750-010-0296-6.

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