Effects of native perennial vegetation buffer strips on dissolved organic carbon in surface runoff from an agricultural landscape

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ABSTRACT

Dissolved organic carbon (DOC) constitutes a small yet important part of a watershed's carbon budget. While DOC generally comprises less than 1% of the overall carbon budget, it is important because it is the most mobile and biologically reactive form of carbon. The primary vegetation present within a watershed, rainfall intensity, and duration of storm events may impact the concentration of DOC in runoff water and the amount of DOC exported from watersheds. Agricultural practices which promote carbon sequestration may also influence DOC concentrations and load in surface runoff, consequently impacting stream ecosystem processes.

In a long-term experiment at the Neal Smith National Wildlife Refuge in Jasper County, Iowa, USA, selected native vegetation perennial cover treatments were randomly assigned to twelve small agricultural watersheds in a balanced incomplete block design. Treatments applied to the watersheds consist of native perennial vegetation (NPV) strips varying in location and percentage of the total area within each agricultural watershed. One of four treatments was randomly assigned to each watershed. Three watersheds were planted in 100% row-crops, three with 10% NPV only in the footslope position, three with 10% of their area in NPV divided into two strips; one on the hillslope and one in the footslope position, and three watersheds with 20% in NPV with strips on the hillslope and footslope positions. Two additional watersheds planted in 100% NPV located in the Neal Smith National Wildlife Refuge were also monitored but are not part of the balanced incomplete block design.

Samples from 2008-2010 were analyzed for DOC concentrations and correlated with flow data to determine flow weighted DOC concentrations and total flux per watershed. All three years of the study experienced higher than normal precipitation. From analysis over the full three year study, for flow weighted DOC concentrations, treatment was significant (p = 0.09) only between 10% NPV at the footslope and 20% NPV in contours watersheds. During an extreme storm event August 8-11, 2010, flow weighted DOC concentrations from the 100% agricultural watersheds was significantly higher than from all of the NPV treatment watersheds (p = 0.008).

Watersheds planted in 100% agriculture exported greater DOC loads than from the 10% NPV at footslope watersheds over the three year study (p = 0.04) and during the storm event August 8-11, 2010 (p = 0.07). Results from this study show that of the four treatments, the conversion of 10% of an agricultural watershed's area into NPV in the footslope position significantly increased DOC concentrations but decreased export when compared to 100% agricultural watersheds. Results indicate that the incorporation of NPV as buffer strips may be a valuable land management tool to reduce DOC loading to levels exported from tallgrass prairie watersheds.

CHAPTER ONE: LITERATURE REVIEW

1.0 Introduction

Dissolved organic carbon (DOC) makes up a small yet important part of a watershed's carbon budget. While it comprises less than 1% of the overall budget, it is the most mobile form of carbon. Sources of DOC are numerous and vary in chemical composition. The importance of DOC lies in how its reactivity affects aquatic ecosystem functions. Losses of DOC from a watershed can reduce soil quality and negatively impact surface water. The primary vegetation present within a watershed, rainfall intensity and duration of events, antecedent soil moisture, and soil type may impact concentration of DOC in runoff water and the amount of DOC exported from the watershed (Chantigny 2003, Royer & David 2005, Vidon et al. 2008, Sanderman & Amundson 2009, Delpla et al. 2011).

The benefits of native perennial vegetation (NPV) buffer strips are often associated primarily with increasing biological diversity rather than their influence on nutrient and carbon losses from within a watershed. However, as soil in buffer strips retains sediment, nutrients, and carbon, and is not subject to traditional agricultural cultivation practices, it can also accumulate more organic matter than surrounding row crop soil (Borin et al. 2010). Incorporation of management practices which promote carbon sequestration such as NPV into agricultural watersheds may influence the concentrations and total amount of DOC exported to surface water. Studies have shown that concentrations and total amount of DOC exported from perennial prairie grassland tends to be lower than that from agricultural or forested watersheds. Because NPV strips have been shown to reduce erosion from agricultural watersheds, these seem to be a viable management option to reduce carbon losses. While the impact of this practice on DOC export is not well studied, because of the reactivity of DOC in surface water and the importance of understanding the carbon balance in the Neal Smith National Wildlife Refuge (NSNWR) watersheds, it is necessary to assess whether the use of varying amounts of NPV in agricultural watersheds will impact DOC concentrations and total flux of carbon.

1.1 Dissolved organic carbon

Soil organic matter consists of any particles containing carbon ranging from fresh plant litter to dissolved molecules (Sanderman et al. 2008). Dissolved organic carbon (DOC) differs from soil organic carbon (SOC) by its smaller particle size. One common definition describes DOC as those particles which pass through a 0.45 um filter paper (Kalbitz et al. 2000). As soil organic carbon increases, soil fluxes of DOC increases as well (Kalbitz et al. 2000), since DOC is comprised of a variety of molecules representative of the total soil organic matter pool (Chantigny 2003). Sources of DOC are numerous and vary in chemical composition. Sources include terrestrial plant leachates, mechanical breakdown of plant material by invertebrates, or decomposition by microbial bacteria (Meyer et al. 1998). A weak in-stream relationship measured between terrestrial plant-derived DOC, composed of recalcitrant aromatic and humic compounds, and decomposition, indicated that stream water has numerous sources of DOC including algal production and in-stream decomposition of aquatic and terrestrial sources (Petrone et al. 2009).

The solubility of organic carbon is determined by its molecular structure. Organic carbon releases H^+ protons when in water, thus forming a negatively charged soluble molecule. Soil solution pH and ionic strength influences how readily this reaction occurs (Clark et al. 2010). Once organic carbon is dissolved in water, it can enter into aquatic ecosystems from terrestrial watersheds through overland surface runoff and subsurface flow

(Kaplan & Newbold 1993). While DOC is always present in soil water and surface runoff, it normally comprises less than 1% of the total soil organic carbon (Royer et al. 2007). It is important to measure, however, as it is the most mobile form of soil carbon and thus can represent a significant loss of carbon from a watershed.

DOC collected in surface runoff is measured as mg carbon L^{-1} runoff and is a commonly used parameter to measure organic matter. The concentration of DOC can be used to determine total export of carbon in the dissolved form as correlated to flow. DOC concentrations can be measured directly in agricultural soil solution but is most often measured as water-extractable organic carbon (Chantigny 2003).

The bio-reactivity of DOC molecules represents its importance in an ecosystem. If terrestrial dissolved organic matter is transported relatively quickly along surficial flow paths, contact time with soil is decreased and the chemical and biological properties of the DOC will not be greatly altered before entering a stream. If DOC is exported from a watershed in a form that is either more or less reactive than what is naturally available, however, downstream aquatic ecosystems processes can be altered (Hernes et al. 2008). It is therefore important to determine the carbon sources, and measure the reactive form and concentrations of DOC exported from an ecosystem. While the bio-degradability of water-extractable organic carbon is higher under corn crop soils than forest soils (Boyer & Groffman 1996), few studies have compared the bio-reactivity between DOC originating from trees and various agricultural crop residues (Chantigny 2003).

DOC exists in labile or recalcitrant forms depending on the carbon source. Labile (low molecular weight) forms include glucose, sucrose, and acetate which are more easily degradable (Johnson et al. 2009, Clark et al. 2010). Labile DOC can be released from plant roots and soil and aquatic microorganisms. Its release may promote increased biotic demand for carbon and consequently greater decomposition of higher molecular weight (recalcitrant) DOC from soil organic matter (Clark et al. 2010). Leaf leachate (a humic substance) is a more complex, recalcitrant carbon form (Johnson et al. 2009). Microorganisms prefer to consume non-humic substances like sugars as opposed to humic acids which are not as easily broken down (Clark et al. 2010). Hughes et al. (1990) reported that higher weight DOC molecules are found in forest soils, whereas more labile forms of DOC are found in agricultural soils (Delprat et al. 1997). As the amount of agricultural land in a watershed increases, the proportion of recalcitrant DOC in the outlet stream diminishes (Cronan et al. 1999).

Labile DOC is preferentially leached from surface soil horizons, and often earlier in the spring than other forms of carbon (Dalzell et al. 2007). The greater content of recalcitrant DOC in the forest canopy combined with the preferentiality of labile DOC leaching may explain why higher amounts of recalcitrant DOC are found in forest soils (Wickland et al. 2007). Poor drainage in forest soils may account for accumulation of more recalcitrant DOC after microbial processing reduces more labile forms. In comparison, agricultural crop residues leach higher amounts of labile DOC, so that even after export, this form comprises a larger proportion of the soil carbon solution (Chantigny 2003). Wickland et al. (2007) concluded that the differing chemical nature of DOC between different vegetation species influences whether the carbon is leached or retained in the soil solution to a greater extent than differing supply rates of decomposable carbon. Organic matter that is newly leached is less biologically degraded in surface soils. The DOC:DON (dissolved organic nitrogen) is higher, and the DOC chemistry will be similar to the leached source whether it is litter, soil organic matter, or biological exudates (Sebestyen et al. 2008). However, in forested watersheds with no riparian zone, van Verseveld et al. (2009) reported no trend between DOC:DON and soil depth. The middle soil layer had a greater DOC:DON ratio than either the organic soil horizon and deeper soil water.

Carbon originating from litter on the soil surface enters mineral soil horizons through leaching of DOC through the organic soil horizon or by biological and physical mixing. Sanderman & Amundson (2009) reported that the O soil horizon in a prairie site was the dominant source of DOC production. DOC concentrations were found to be highest in the O horizon, decreasing with depth at both a forested and prairie site despite differences in vegetation species; thus land use (forested or prairie) did not significantly influence DOC concentrations at varying soil depths (Sanderman et al. 2008). Similar results in a forested watershed were reported where DOC concentrations were high in surficial soil layers and lower in deeper groundwater (Sebestyen et al. 2008, van Verseveld et al. 2009).

In the same prairie site, DOC concentrations declined with depth by a factor of 20 or more, whereas water fluxes decreased by a factor of two. This trend was due to a large decrease in measured DOC concentrations and unrelated to declining water fluxes. Below one meter, the DOC concentrations were less than that of measured rainwater (Sanderman et al. 2008).

While DOC is leached through the soil, the most labile fraction is decomposed by microbes, which partially decreases DOC concentrations (Sanderman et al. 2008). Shorter soil residence times generally results in the transport of more labile DOC to downstream waters, whereas increased residence times generally provides longer opportunities for microbial breakdown of DOC prior to export (Wickland et al. 2007). However, because soil residence time of infiltrated water is generally not long enough for significant mineralization to occur, adsorption of DOC by mineral soils dominates its removal from the soil if not exported in return and runoff water (Sanderman & Amundson 2009). The ease with which DOC is adsorbed to mineral soil particles makes it the most readily stabilized carbon form (Wickland et al. 2007). Mean residence times of adsorbed DOC may vary from days to decades, which diminishes its bio-availability (Sanderman & Amundson 2009).

1.2 Importance of dissolved organic carbon (DOC)

DOC comprises a small yet highly mobile component of a watershed's carbon budget (Kothawala et al. 2009). Once exported from a watershed, DOC can become a large percentage of the organic matter found in streams and rivers (Royer & David 2005). According to Meyer et al. (1998), DOC can account for 3-98% (median 10%) of total organic matter inputs into stream ecosystems. Fisher & Likens (1973) reported a narrower range of 30-75%. DOC leached from leaf litter accounts for about 30% of daily DOC export from forested headwater streams (Meyer et al. 1998).

Dissolved organic carbon is a necessary component of any aquatic ecosystem to promote heterotrophic production, yet in high concentrations or altered states of bio-reactivity it may have negative effects (Hernes et al. 2008). Once DOC enters an aquatic ecosystem, it can be assimilated by microorganisms (van der Valk 2006). In streams, DOC becomes a large source of energy for food webs (Meyer et al. 1998) and promotes bacterial production (Royer & David 2005), which subsequently stimulates autotrophic productivity.

Royer & David (2005) suggest that allochthonous DOC accounts for most of in-stream DOC from late fall through early summer in agricultural watersheds, while the high availability of nutrients in the summer through early fall which promote algal blooms account for more autochthonous DOC production, and thus seasonal differences in DOC sources. Autochthonous DOC produced by algal and bacterial breakdown is less absorptive of ultraviolet radiation than allochthonous DOC leached from terrestrial sources (Frost et al. 2005). If a large value of ultraviolet radiation (UVR) absorbance per unit of carbon (C) (absorptivity of DOC) is measured in an aquatic ecosystem, light penetration that would otherwise damage aquatic organisms will be decreased (Xenopoulos & Schindler 2001, Frost et al. 2005). From a range of DOC concentrations between 2-35 mg C L^{-1}, rapid attenuation of ultraviolet B radiation (UVB) within 1% transmission depths in a stream water column suggested that its biological importance was most noted in top stream layers (Frost et al. 2005). Stream DOC absorptivity combined with forest canopy was effective at preventing UVB from reaching the benthic region.

The presence of stream DOC also influences nitrogen cycling. In stream samples from watersheds of mixed forest, agriculture, and urban use, Petrone et al. (2009) reported significant positive correlations between DOC and DON. Bernhardt & Likens (2002) reported a close relationship between labile DOC and nitrogen availability in heterotrophic headwater streams. While adding potassium acetate (a highly labile form of DOC) to a headwater stream in Hubbard Brook Experimental Forest, DOC concentrations increased from pre-treatment levels of 1.1 ± 0.01 mg C L^{-1} to 12.8 ± 4.0 mg C L^{-1}. This increase in DOC concentration promoted immediate and sustained microbial growth rates, particularly in *Sphaerotilus* species of benthic filamentous bacteria. Demand for both NO_3 and NH_4 increased significantly in the water column. Nitrification was reduced significantly, due to increased nitrogen (N) limitation as a result of greater C:N ratios and competition for remaining N between heterotrophs and nitrifying bacteria. Thus, the addition of a highly labile carbon form which increased DOC concentrations in the stream resulted in altered competitive relationships between microbes. Increased concentrations also promoted in-stream processes that may reduce or eliminate DON export from the stream (Bernhardt & Likens 2002).

Johnson et al. (2009) examined the relative uptake of labile DOC (acetate) and DON in comparison to the uptake of dissolved inorganic nitrogen (in the form of NH_4) in surface water downstream from agricultural, forested, and urban watersheds. Adding acetate stimulated biotic demand for NH_4, but not significantly. DOC demand within the water column was significantly higher than biotic demand for DON, implying that both DOC and NH_4 are limited in headwater streams.

The presence of DOC in surface runoff can also enhance the mobility of pesticides and heavy metals, which may have negative consequences for aquatic ecosystems. DOC can bind to metals and serve as transport carriers to surface waters, although this capability is related to molecular weight of the organic compound (Royer et al. 2007).

Finally, the presence of DOC in high concentrations can affect the quality of drinking water sources (Mailapalli et al. 2010). A range of 0.1 to 20 mg L^{-1} is typical for DOC concentrations in surface waters (Volk et al. 2002). DOC can react with chlorine during water treatment processes to produce potentially carcinogenic disinfection byproducts such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Volk et al. 2002, Yallop & Clutterbuck 2009). If in a drinking water source, the color produced by high DOC concentrations (as measured by water ‘color’ in Hazen units) also presents an aesthetic issue for consumers (Yallop & Clutterbuck 2009). Reduction of DOC concentrations during drinking water treatment processes reduces the need for excessive use of disinfectants thus diminishing formation of byproducts, improves taste and reduces odor, and decreases bacterial growth in the water distribution system. Water utility companies should monitor when peak DOC concentrations occur in source waters to minimize impact on disinfection processes (Volk et al. 2002).

1.3 Dissolved organic carbon and watershed land use

Terrestrial DOC sources and hydrological mobilization of the sources are the two main factors controlling export of DOC from a watershed and its concentration in streams (Agren et al. 2008). Large scale changes in land use and management affect the carbon cycle, yet are often poorly understood (Brye et al. 2002). Land use connected with the dominant form of vegetation in a watershed, and soil conservation and carbon sequestration practices such as organic material and fertilizer applications, conservation tillage, crop rotation, and irrigation influence soil organic matter (Stewart et al. 2007) and DOC production (Royer & David 2005, Warrner et al. 2009). These factors can subsequently influence hydrology and flow patterns, and consequently sediment, nutrient, and carbon transport to surface waters (Raymond & Saiers 2010), thus affecting the concentrations and total amount of DOC exported from a watershed. Loss of DOC from agricultural watersheds can decrease the quality of soil and downstream water by its association with SOC and transport of pesticides and heavy metals (Royer et al. 2007, Avalos et al. 2009, Veum et al. 2009), and can influence many ecological processes in aquatic ecosystems (Xenopoulos & Schindler 2001).

The top meter of soil globally stores ~1,500 Pg of carbon (Sanderman & Amundson 2009), but retention of both particulate and dissolved forms can be influenced by agricultural practices (Hernes et al. 2008). Retaining crop residues or adding manure or other organic amendments increase soil organic carbon (Brye et al. 2002, Stewart et al. 2007). Soil organic matter improves soil fertility, porosity, infiltration capacity, soil moisture, and resistance to water and wind erosion (Apezteguia et al. 2009). Increases in soil organic carbon could promote increased export of allochthonous DOC to streams in agricultural watersheds, however, and possibly increase microbial respiration and rates of in-stream biogeochemical cycles (Royer & David 2005).

Loss of soil organic matter can occur by erosion, leaching, and soil respiration (Lal 2004). DOC is carried to downstream surface waters through the dissolution of soil organic carbon in sediment during runoff producing events (Jacinthe et al. 2009). Higher concentrations of DOC in near surface soil than in lower soil horizons suggest that during rainfall events producing overland and near surface flow, the surface horizons are a significant source of DOC (Inamdar et al. 2004, Sanderman & Amundson 2009). McDowell & Likens (1998) also reported that when stored in mineral soils, transport of DOC increases during a storm event as water flow paths move upward from mineral to organic soil horizons, leading to increases in DOC export. Any agricultural tillage practice that minimizes disruption to the O soil horizon may decrease the amount of DOC exported through overland runoff (Avalos et al. 2009). Thus, it is important to study practices which retain the greatest amount of carbon within a watershed to maintain soil quality and diminish negative impacts on downstream surface waters. Changes in land management practices may influence total DOC export, although initial soil conditions and numerous environmental factors complicate the development of a management/DOC export relationship (Apezteguia et al. 2009).

Chantigny (2003) considered land use and consequently, vegetation, to have the greatest influence on DOC as plant litter comprises the primary organic matter input to a watershed's ecosystem. The dominant form of vegetation in a watershed influences hydrology and flow patterns, and therefore sediment, nutrient, and carbon transport to surface waters. (Raymond & Saiers 2010). Jacinthe et al. (2004) observed DOC export from agricultural and non-agricultural (pasture and forested) watersheds. DOC accounted for 11-28% and 67-76% of total carbon exported from agricultural and non-agricultural watersheds respectively. Carbon transported via sediment comprised the remaining fraction of total carbon. Others reported no significant relationship between land use and DOC concentrations (Johnson et al. 2009). It is important to determine how certain agricultural practices such as conservation tillage or land conversion through the installation of native perennial vegetation strips can influence DOC export from row crop watersheds.

Land conversion from unmanaged to highly managed can deplete the soil organic carbon by up to 60% in temperate regions (Lal 2004), and the conversion of land from forest to agriculture or grassland can decrease the total amount of DOC exported from a watershed (Post & Kwan 2000). In the short-term following a forest clearcut and subsequent tillage to prepare the soil for agriculture, several studies reported an initial increase in DOC concentrations from 10 to 150 mg L^{-1} due to mobilization of SOC in the form of DOC (Hughes et al. 1990, Qualls et al. 2000). Total DOC export from agricultural watersheds decreased over the long-term, however, because of lower organic matter input to the soil and stabilization of the remaining organic matter. Meyer et al. (1998) reported that land changes that reduce leaf litter input to headwater streams can alter biogeochemistry of a stream ecosystem as measured by decreased DOC concentrations and export.

Measurements of total organic carbon (TOC) from a previously forested watershed converted to agriculture demonstrated that after forty years of cultivation, a total of 38.4 Mg C ha^{-1} (or 44% of the original soil carbon) was lost (Apezteguia et al. 2009). Since prairie land in Midwestern states was converted to row crops, the amount of SOC has decreased by about 40% in agricultural watersheds (Warrner et al. 2009). Chantigny (2003) suggested that the conversion of grassland to agricultural soils promotes a depletion of soil organic matter and water-extractable organic carbon, and that a decline in total DOC flux correlates with the number of years the land is utilized in row crop production. Jacinthe et al. (2009) reported 1.6 times greater SOC concentrations in grassed buffer strips relative to the surrounding cultivated agricultural field. However, Royer & David (2005) reported lower total DOC export from agricultural watersheds in Illinois, USA than from forested watersheds, but the values were still higher than those reported for an undisturbed prairie stream in Kansas (Gray 1997) thus implying that perhaps management techniques such as tillage, which cause soil erosion, influence DOC fluxes regardless of SOC concentrations.

In an agricultural watershed, soil quality can be improved through the retention of crop residues to increase SOC or by planting other SOC favoring crops such as perennial vegetation with high levels of above and below ground biomass (Stewart et al. 2007). Generally, tillage practices increase crop residue decomposition, which may lead to lower quality soils by reducing organic matter content (Avalos et al. 2009). In one study, Jacinthe et al. (2009) reported an average contribution by corn residue to total SOC in the top 10 cm soil horizon of 69.8% (range: 54.6-78%) in a no-till watershed. Royer et al. (2007) reported that five days after corn residues were chopped and incorporated into the soil, increases of between 6 and 17 times pre-tillage DOC concentrations were observed. This was due to immediate leaching of DOC from the residue; the increased concentrations were temporary and returned to pre-tillage levels within days.

According to Armand et al. (2008), 30% soil coverage with residue is a marking point under conservation tillage practices which limits surface runoff. When a range of corn straw residues of 1-4 tons ha^{-1} was placed over bare soil in micro-plots, Avalos et al. (2009) reported that under four simulated rainfall events, organic carbon export in runoff samples decreased from the bare soil treatment through the 1-3 tons ha^{-1} treatment of corn straw coverage, but export increased under the 4 tons ha^{-1} treatment. The reduction in organic carbon losses was more than 80% between that exported from the bare soil to that lost under the highest coverage treatment. By leaving crop residues on the soil surface, however, more organic material can be subject to leaching which may lead to higher concentrations of DOC exported than from a conventionally tilled agricultural watershed (Mailapalli et al. 2010).

At the beginning of a study on carbon cycling in an agricultural and a prairie site nineteen years after restoration at the University of Wisconsin-Madison's Arlington Agricultural Research Station, total soil carbon in the top 30 cm was not significantly different (Brye et al. 2002). Contrary to reports from other studies in which SOC concentrations were greater in grassland than agricultural sites (Jacinthe et al. 2009), within the top 1.2 m at the Arlington site, soil carbon was significantly greater in the agricultural plot. During the five year study period, total soil carbon content decreased significantly in the agricultural plot, but not in the restored prairie. DOC concentrations were similar, but total export in leachate water was significantly greater from the agricultural versus prairie site due primarily to differences in drainage (Brye et al. 2002).

Land use also influences carbon inputs to soils, and thus what is available for eventual DOC export through surface runoff. Jackson et al. (1996) reported that biological mixing of carbon from direct root inputs in grasslands exceeds the amount of carbon introduced into soils from the organic soil horizon through DOC leaching, although comparison data is limited. In forest soils, however, the leaching of DOC exceeds that produced by coniferous tree roots, thus increasing the total amount of DOC available for export from forest soils. Sanderman & Amundson (2009) reported that in a comparison between a forest and grassland ecosystem, DOC inputs to the top 40 cm and to soil below 40 cm were 9% and 22% respectively in a forest. In grassland, however, only 2% of carbon inputs below 20 cm were due to DOC leaching. By multiplying net DOC retention measured at the sites by the estimated mean residence times, they calculated the fraction of the total soil carbon pool that was supplied by DOC transport. In the forest, 20% of the total organic carbon in the top meter of soil was controlled by DOC transport and retention, versus 8.6% in the grassland. This demonstrates that perhaps other forms of carbon are more significant in the carbon budget within grasslands than DOC production and mobility.

DOC concentrations may vary between differing watershed land uses. Concentrations of between 2 to 50 mg L^{-1} in agricultural watershed surface runoff were reported by Moore & Dalva (2001). Zsolnay (1996) reported DOC concentrations between 0 to 70 mg L^{-1} from agricultural watersheds versus 5 to 440 mg L^{-1} from forested watersheds. Another study reported higher DOC concentrations leached from agricultural landscapes versus prairie (Brye et al. 2001), and Wilson & Xenopoulos (2008) and Johnson et al. (2009) reported that agricultural land use was not an important predictor of DOC concentrations. Chantigny (2003) suggested that based on the available literature, the reasons responsible for conflicting trends in DOC concentrations exported from agricultural versus forested or grassed watersheds have not yet been clearly identified.

Dalzell et al. (2007) estimated total DOC loads from agricultural watersheds in the Midwest U.S. to be between 14.1 to 19.5 kg ha^{-1} $year^{-1}$. Royer & David (2005) estimated loss values between 3 to 23 kg ha^{-1} $year^{-1}$ from agricultural watersheds. These values are lower than estimates of DOC losses of 484 kg ha^{-1} $year^{-1}$ in boreal forest and wetland ecosystems, and between 3.4 to 417 kg ha^{-1} $year^{-1}$ from temperate forests. The loss of DOC from agricultural watersheds is generally greater than fluxes reported from grasslands of between 1.6 to 5.0 kg ha^{-1} $year^{-1}$ (Hope et al. 2004).

The conversion of perennial forestland or grassland into agricultural cropland decreases total organic carbon in a watershed (Apezteguia et al. 2009). However, Wilson & Xenopoulos (2008) found that the percentage of land in a watershed planted in monoculture (either agriculture or riparian vegetation) versus mixed agriculture versus total agriculture throughout the watershed did not significantly predict variations of DOC concentrations. Rather, they found that when incorporated into a modeling study, landscape characteristics such as slope, soil drainage capacity, and the presence of wetlands or other variables that affect overland flow paths were much better predictors of DOC concentrations in surface runoff. They concluded that these landscape characteristics correlate more strongly to DOC concentration than the more commonly used approach of relating land use to DOC losses. More importantly, they reported that resulting soil drainage improvements from land use changes contribute more to DOC losses than just the amount of land converted.

There are few studies in agricultural watersheds that relate the influence of land use on DOC concentrations and fluxes (Chantigny 2003). Fewer studies exist examining the export of DOC in surface runoff from agricultural watersheds containing tile drainage (Royer et al. 2007, Warrner et al. 2009). It is important to understand how varying land management practices can influence DOC export to streams, especially as Midwestern watersheds are responsible for the transport of nutrients and carbon to the Mississippi River and subsequently the Gulf of Mexico (Vidon et al. 2008).

Royer & David (2005) suggested that DOC concentrations downstream from agricultural watersheds are lower than concentrations exported from forested watersheds or those containing wetlands. However, in the Midwest, concentrations of stream water DOC are influenced by numerous factors such as soil type, disturbance, hydrologic flowpaths, wetland coverage, precipitation intensity and duration, tile drains, crop coverage, and antecedent soil moisture in addition to overall watershed land use (Hernes et al. 2008, Vidon et al. 2008, Petrone et al. 2009). Certain agricultural practices such as subsurface tile drainage and type of tilling, combined with soil types may impact the concentrations and flux of DOC exported from a watershed. Soils high in clay exhibit high DOC adsorption capacity (Kothawala et al. 2009). In higher clay content soils, DOC leaching may be reduced, while in sandier soils, DOC may be leached to greater depths, thus decreasing the amount available for export through return flow (Sanderman & Amundson 2009).

1.4 Subsurface drainage and dissolved organic carbon

While subsurface tile drains promote rapid transport of DOC into streams in agricultural landscapes (Royer & David 2005, Vidon et al. 2008), Royer et al. (2007) reported lower DOC concentrations in tile drain water (average of 6.5 mg C L^{-1}) than in surface runoff water (average of 12.7 mg C L^{-1}). Warrner et al. (2009) also measured lower DOC concentrations in tile drains than in stream water. They reported a range of undetectable to 27% bio-availability of DOC in tile drains versus consistently lower bio-availability in streams. Water reaching the tile drains passes through mineral soil layers which have a greater affinity for DOC adsorption (Kothawala et al. 2009), thus decreasing the DOC concentrations and altering bio-availability in tile drain water.

1.5 Crop rotation, nitrogen fertilization, and dissolved organic carbon

Chantigny (2003) suggested that land use and resulting vegetation type influences DOC export and concentrations. Crop rotations within agricultural watersheds have produced conflicting results regarding soil organic carbon levels and DOC concentrations.

There are few studies that relate corn-soybean cropping rotations to DOC export. Huggins et al. (1998) reported no significant difference in soil organic carbon levels when incorporating corn residues versus incorporating residues from a corn-soybean rotation over ten years. The inclusion of legumes in a cropping rotation increased the amount of organic carbon present in the soil by 2-44 kg ha^{-1} (Mazzarino et al. 1993) and increased the DOC concentrations under legumes versus gramineae species (Chantigny et al. 1997). Wilson & Xenopoulos (2009) reported that while continuous cropping versus rotational cropping was a significant factor when predicting the character of DOC, no agricultural land use was significantly related to DOC concentrations in streams. Veum et al. (2009) reported no significant differences between a corn and soybean rotation on DOC loads. They attributed this result to similar carbon content of corn and soybean residues and similar amounts of both remaining on the soil surface under conservation tillage practices. Finally, Apezteguia et al. (2009) reported greater differences in soil total organic carbon between tillage treatments in an experimental agricultural watershed than between cropping rotation (corn-soybean) treatments.

Correlating the application of inorganic N fertilizer with DOC has also produced conflicting results on its impact on DOC levels. Chantigny (2003) reported an immediate decrease in soil DOC following an application of 180 kg ha^{-1} N as ammonium nitrate to corn. The decrease was only temporary and DOC content soon returned to pre-fertilization levels. Studies have reported results ranging from no significant influence on soil organic carbon in agricultural soils following inorganic N fertilization (Zsolnay & Gorlitz 1994) to a positive influence on DOC production (Campbell et al. 1999). Chantigny (2003) concluded that inorganic N fertilization could both promote DOC production and consumption at the same time, and a net production value is difficult to measure at field levels.

1.6 Influence of precipitation and irrigation on dissolved organic carbon

Precipitation amount and storm intensity also have a direct correlation to total amount of DOC lost from agricultural watersheds (Royer & David 2005, Stedmon et al. 2006, Royer et al. 2007), which may be more important than land use and soil management when determining DOC losses (Jacinthe et al. 2004). Peaks in DOC concentration correlate with higher river discharge following storm events. High flow events occurring 20% of the year were responsible for 71% and 85% of annual DOC export in 2002 and 2003 respectively in a study by Dalzell et al. (2007). Raymond & Saiers (2010) reported that 86% of annual DOC flux occurred during storm events in a forested watershed. As flux correlates with discharge, less frequent events with greater discharge contribute disproportionately to annual DOC flux (Raymond & Saiers 2010). DOC sampling in runoff water and streams must occur during periods of high flow to properly report annual fluxes (Dalzell et al. 2007).

Royer & David (2005) and Vidon et al. (2008) found that storm precipitation characteristics had a greater effect on DOC concentrations and export than watershed land use. The highest measurements of DOC concentrations from agriculturally influenced streams occurred during both floods and periods of low discharge. In another study, peak

DOC concentrations in runoff from an agricultural watershed were recorded following storm events with close to or greater than 10 mm rainfall, which occurred after a period of one to two weeks with no precipitation (Royer et al. 2007). Jacinthe et al. (2004) reported no statistically significant effect of three rainfall intensities (low, medium, and high intensity) on DOC concentrations in runoff water from agricultural, pasture, and forested watersheds. Rainfall intensities significantly influenced sediment C concentrations, however, with export of lowest concentrations occurring during high intensity storms. Alternatively, Delpla et al. (2011) reported greater mobilization of sediment C related to increased rainfall intensity, and the most intensive storm events promoted the export of the largest DOC loads from agricultural sites, particularly in the fall (Delpla et al. 2011).

During summer storms in a forested watershed, Inamdar et al. (2004) reported gradually increasing DOC concentrations along the rising limb of the storm hydrograph, with peak concentrations measured slightly after peak discharge before decreasing through the hydrograph recession. The delayed peak was attributed to a disconnect between saturated surface areas which impacted surface runoff flow through which DOC is transported. Agren et al. (2008) reported similar results in the River Ore forested watershed in Sweden. Increases in storm runoff generally resulted in higher concentrations than under baseflow conditions.

Seasonally, higher flow in the summer and autumn correlated with 30-50% greater DOC concentrations even while maximum flow was only a third of that recorded during the spring (Agren et al. 2008). Dalzell et al. (2007) also reported lower DOC concentrations downstream of an agricultural watershed during spring months. Dilution of exported carbon caused by snowmelt and high stream flows is one possible explanation (Dalzell et al. 2007). As more carbon is available during summer months and its decomposition is temperature dependent, higher DOC concentrations can be expected in stream flow during summer and autumn (Agren et al. 2008). Greater allochthonous inputs from forested watersheds and autochthonous production in agricultural watersheds in late summer through fall also contribute to higher DOC concentrations (Royer & David 2005, Agren et al. 2008).

In streams connected to an agriculturally dominated and mixed use watershed (both including tile drainage), Vidon et al. (2008) reported that peaks in DOC concentration correlated with peak discharge on the storm hydrograph. DOC concentrations increased and decreased on the same time scale as discharge, regardless of land use between the two watersheds. Precipitation events and the resulting discharge dynamics controlled DOC concentrations more significantly than land use. The contribution of event water to the hydrograph in the form of direct precipitation and surface runoff correlates the increasing DOC concentrations with the amount of carbon flushed from the soil's surface horizons during storm events. The case that the rising hydrograph limb is correlated with greater DOC export from a watershed during a precipitation event implies that direct precipitation and surface runoff (which compose the discharge during that time period) impact DOC concentrations, regardless of land use (Inamdar et al. 2004, Vidon et al. 2008). Vidon et al. (2008) also reported that DOC originating from mineral soils was found in stream baseflow, whereas during a storm event the DOC originating from horizons closer to the soil surface was exported to the stream. Thus different sources of DOC were responsible for the increased concentrations in the stream instead of simply an increased mobilization of DOC during a storm event.

Irrigation practices in agricultural watersheds can alter DOC concentrations and amount exported in surface runoff (Hernes et al. 2008). Any agricultural practice such as irrigation which may promote sediment erosion will influence DOC concentrations and composition. In an irrigated agricultural watershed, DOC concentrations varied with hydrology as observed by Hernes et al. (2008). Stream water DOC concentrations increased from 2.0-3.0 mg L^{-1} during winter baseflow to 5.0-7.2 mg L^{-1} during summer irrigation and storm events. They reported lowest DOC concentrations under low flow winter baseflow, highest concentrations under slightly elevated irrigation flows, and DOC concentrations between highest and lowest measured concentrations during summer natural storm events.

Mailapalli et al. (2010) reported that a threefold increase in agricultural field length increased the amount of DOC retained in the field by between 55-70% under irrigated conditions. They attributed this retention to increased infiltration for irrigation water and consequently longer contact time with the soil. Measured runoff from the longer fields was less than that from the shorter field lengths, thus the reduced flow resulted in reduced total DOC export. Due to the longer residence time of the irrigation water and subsequent increased contact with crop residue, they reported increased DOC concentrations of 50% in runoff water during 2007, but data from 2008 revealed a 15% decrease in DOC concentrations. Irrigation rates increased from 2007 to 2008, and faster flowing water resulted in shorter residence time, and quicker export from the agricultural field and thus lower DOC concentrations. The rate of irrigation water application combined with field length significantly influenced total DOC export but not DOC concentrations.

1.7 Native perennial vegetation strips

Buffer strips are vegetated filter zones installed within a watershed or as a riparian zone between a watershed and its downstream surface water. The vegetation in buffer strips can consist of woody plants or native perennial grasses, depending on the landowners’ desires. Native perennial vegetation buffer strips are designed to slow surface runoff which helps to remove sediment, nutrients and carbon from surface runoff through increased water infiltration, absorption and adsorption of particles, sediment and organic matter deposition, water filtration, and organic matter decomposition to reduce loading into surface waters (Tim et al. 1995, EPA 2005). The effectiveness of buffer strips in removing sediment, nutrients, and carbon depends on runoff volume, slope and area of the landscape, and composition, age, and width of the strip (Chaubey et al. 1994, Borin et al. 2010).

Additional benefits of buffer strip installation include reduction in water treatment costs from downstream surface waters, promotion of wildlife diversity through improved habitat, increased ecological values of terrestrial and aquatic environments, and improved aesthetic and recreational values of streams and lakes (Tim et al. 1995). The benefits of buffer strips are often associated primarily with increasing biological diversity (Smukler et al. 2010) rather than their influence on carbon concentrations and loads from within a watershed. However, as soil in buffer strips retains sediment and nutrients and is not subject to traditional agricultural cultivation practices, it can also accumulate more organic matter than surrounding row crop soil (Borin et al. 2010). As buffer strips have been shown to effectively reduce nutrient losses, it is important to evaluate how their incorporation into agricultural management may influence other areas of concern for aquatic management such as DOC concentrations and export. Negative aspects of committing cropland to native perennial vegetation include loss of profit from row crops and interference with planting and harvesting techniques (Borin et al. 2010).

Tim et al. (1995) reported a 30% reduction in sediment yield at the outlet of an agricultural watershed containing a 30 m wide grassed buffer strip. The amount of sediment exported decreased with increased buffer strip width from 10-30 m. They concluded that installation of vegetated buffer strips into agricultural watersheds is an effective management technique to reduce sediment export and non-point source pollution. Buffer strip width, and watershed slope and soil determine the effectiveness of sediment and pollutant retention.

Following the installation of a 6 m wide buffer strip containing trees and shrubs into agricultural plots planted into maize (2000), soybean (2001), and sugar beet (2002), Borin et al. (2010) reported a significant reduction in surface runoff (78%) and total suspended solids (TSS) exported from 6.9 to 0.4 t ha^{-1} as compared to the non-treatment plot over the five year experiment. This reduction was particularly noted two years after buffer strip installation. Tree roots extending beyond the buffer strip increased plant nutrient uptake (total nitrogen, nitrate, ammonium, and soluble and total phosphorus), thus improving retention of TSS and nutrients to almost 100% within a buffer strip as narrow as 6 m. While between 0.08-0.17 g 100 g^{-1} of organic carbon also accumulated within the top 0.5 m of the buffer strip soil over the course of the experiment, DOC loads from these plots were not studied.

This poses an interesting dilemma for places such as Prince Edward Island, where recent legislation mandates the incorporation of 10 m and 20 m buffer strips for moderately sloped (<5%) and steep sloped (>5%) agricultural fields bordering streams (Dunn et al. 2011). In a study measuring nutrient and pesticide export from agricultural land containing buffers strips planted in grasses and forbs (white clover, meadow fescue, and timothy), Dunn et al. (2011) reported no significant correlation between slope type, buffer width, and retention of ammonia, phosphorus, total suspended solids, or nitrate-nitrogen, although generally, total loads exported were reduced as a result of the presence of the buffer strip. Less effective retention of dissolved nutrients in the buffer strips was due to relying on the infiltration capacity of the strip for removal, which during rainfall events, can become saturated and lead to increased surface runoff. The retention of lower molecular weight carbon in grassed buffer strips may be associated with a higher retention of clay and silt sized particles due to reduced flow velocity and subsequent increases in particle settling and infiltration (Jacinthe et al. 2009). Dunn et al. (2011) concluded that slope needs to be considered when determining buffer strip width, and that more importantly, techniques need to be used to minimize the formation of concentrated overland flow paths that reduce the effectiveness of buffer strips in nutrient and contaminant removal.

Numerous studies have been completed on DOC losses from forested watersheds, watersheds involving drainage into or out of wetland areas, or urbanized watersheds (Inamdar et al. 2004, Sebestyen et al. 2008, Johnson et al. 2009, van Verseveld et al. 2009). Less research has been done on agricultural watersheds in relation to DOC losses. Research in Midwestern agricultural watersheds often focus on nutrient and/or carbon losses from subsurface drainage (Bhattarai et al. 2009, Warrner et al. 2009), groundwater measured through lysimeters (Zhou et al. 2010), or the importance of different tillage practices on export in surface runoff (Apezteguia et al. 2009), rather than how the incorporation of different types of soil conservation practices such as buffer strips would affect carbon concentrations and export.

Finally, there have been few studies which evaluated the export of nutrients, carbon, and pollutants from watersheds containing both perennial vegetative buffer strips and subsurface drainage systems (Bhattarai et al. 2009). Tiling systems installed to improve drainage are a common agricultural management practice in the Midwestern United States. Subsurface drainage lowers the water table and improves soil aeration. The addition of subsurface drainage under NPV strips should improve the infiltration capacity of the soil, thus reducing nutrient and carbon losses in surface runoff (Bhattarai et al. 2009).

I am aware of only one other study which investigated how the establishment of buffer strips in agricultural watersheds influenced concentrations and export of DOC in surface runoff. Methodology in the study published by Veum et al. (2009) was similar to the design of the watersheds at the Neal Smith Wildlife Refuge, however, they incorporated agro-forestry buffer strips into one watershed in the paired watershed design and grassed buffer strips into the other. The paired-watershed method is a common approach to compare treatments at the watershed scale, however, steps should be taken to minimize differences in factors such as land use, management and hydrological properties. Factors such as precipitation, topography, and soil type should be considered when determining the location of paired watersheds (Feiner & Auerswald 2009).

While Veum et al. (2009) reported a reduction in runoff of 8.4% from the grassed buffer watershed following buffer installation, the surface runoff was still higher than the amount of runoff from the watershed with agro-forestry buffer strips. However, they reported lower total DOC export from the watershed with grassed buffer strips as compared to its paired watershed containing agro-forestry buffer strips. Typically DOC export correlates positively with runoff volume (Veum et al. 2009), thus they suspected that higher soil organic carbon in the agro-forestry strips relative to the grassed strips accounted for a greater total loss of DOC. Sanderman & Amundson (2009) reported a large input of DOC from forest canopy (13.2 g C m^{-2} yr^{-1}). DOC input from agro-forestry throughfall may have contributed to higher DOC export in the study by Veum et al. (2009). Finally, the influence of claypan soils on infiltration may have limited buffer treatment effects on DOC export.

Ultimately, Veum et al. (2009) concluded that neither grassed nor agro-forestry buffer strips significantly influence the amount of DOC lost from a watershed to downstream surface waters, but they do significantly reduce surface runoff. This conclusion may be important when trying to convince a farmer to commit some of their land into a conservation practice such as buffer strips. In contrast, Wilson & Xenopoulos (2008) demonstrated that land uses that control soil moisture or flow paths will strongly influence DOC mobility. Thus, the incorporation of NPV strips may decrease DOC export from agricultural watersheds by increasing water residence time within the buffer strips and by dissemination of overland flow paths.

A goal of the research project at the Neal Smith National Wildlife Refuge in Central Iowa is to demonstrate to area farmers how incorporation of NPV strips into row-crop agriculture can reduce export of sediment, nutrients, and carbon. In the future the challenge will be to promote the intrinsic benefits of incorporating NPV strips to farmers and to develop extrinsic reward systems (Smukler et al. 2010). This thesis details the data related to DOC concentrations and the total DOC load in surface runoff from twelve small watersheds at the Neal Smith National Wildlife Refuge.

1.8 Objectives

The objective of this study is to determine what effect, if any, the incorporation of varying amounts of NPV into small agricultural watersheds has on the concentrations and total amount of DOC exported in surface runoff. Any conclusions drawn from this research will be important when persuading farmers to convert portions of land from row-crop agriculture into NPV to preserve the quality of downstream surface water.

CHAPTER 2: MATERIALS AND METHODS

2.0 Site description and management

The study watersheds are located in the Neal Smith National Wildlife Refuge in Jasper County, Iowa, USA (NSNWR; 41°33'N; 93°16'W). Selected native vegetation perennial cover treatments were randomly assigned to twelve agricultural watersheds ranging in size from 0.47 ha to 3.19 ha in a balanced incomplete block design. There are two blocks containing six watersheds at the Basswood site, and one block each at Orbweaver and Interim with three watersheds at each location (Figure 2.1). Slope varies from 6.1 to 10.5% in the watersheds. Prior to 2007 all watersheds were planted in bromegrass (*Bromus* L) for at least ten years. The establishment of a no-till corn-soybean (*Zea mays* L. / *Glycine max* (L.) *Merr*.) two year rotation began in spring 2007 with the planting of soybeans. Crop rotation was identical in all watersheds. Conservation tillage practices utilized in the agricultural watersheds at the Neal Smith National Wildlife Refuge retain at least 30% of the crop residues on the soil surface after harvesting.

Treatments applied to the watersheds consist of native perennial vegetation (NPV) strips varying in location and percentage of the total area within each agricultural watershed. One of four treatments was randomly assigned to each watershed (Figure 2.2, Table 2.1). Three watersheds were planted in 100% row-crops, three with 10% of the total area planted in NPV only in the footslope position, three with 10% of their area in NPV divided into two strips; one on the hillslope and one in the footslope position, and three watersheds with 20% in NPV with strips on the hillslope and footslope positions. In July 2007, NPV strips were planted within treatment watersheds with a seed mixture of over 20 species, dominated by

Indian grass (*Sorghastrum nutans L*.), big bluestem (*Andropogon gerardii L*.), and little bluestem (*Schizachyrium scoparium L*.). Native prairie vegetation was planted in the buffer strips as it was the primary vegetation in Iowa prior to the 1880's; one of the overall goals of the refuge is to re-establish native prairie ecosystems.

The perennial vegetative strips vary in width from 37.6 to 78.2 m in the footslope position and 3.1 to 9.8 m on the hillslope. Additionally, two watersheds were planted in 2004 with 100% NPV as described by Tomer et al. (2010). Because these watersheds are not included in the replicated study design, only descriptive statistics are used to present the data and compare DOC concentrations and total export with the results from the twelve other watersheds.

The soil is similar between all watersheds with Ladoga silt loam (fine, smectitic, mesic Mollic Hapludalf) and Otley silty clay loam (fine, smectitic, mesic Oxyaquic Argiudolls) the two main soil types. According to sampling by Zhou et al. (2010), upper soil horizons consist of 7-10% sand, 63-68% silt, and 25-28% clay and have a bulk density of about 1.4 g cm^{-3}.

2.1 Sample collection and analysis

Automated ISCO 6712 Samplers (ISCO, Inc., Lincoln, NE) equipped with pressure transducers (720 Submerged Probe Module) installed at the outlet of each watershed collected 300 ml runoff samples for every 1.024 mm of runoff. The samplers recorded flow rate and collected runoff samples. They were removed prior to first snowfall to avoid freeze damage, and re-installed around April 1 of each year; thus, sampling occurred from April through October. Samples were retrieved within 24 hours of a rainfall event, filtered through 0.45 um HAWP filter paper to remove particulate carbon, acidified with 10% sulfuric acid to a pH of 2.0, and refrigerated at 4° C until analysis. A total of 2,121 runoff samples were analyzed for DOC.

Runoff samples from 2008 through 2010 were poured into 40 ml HCl acid-washed vials and analyzed for DOC concentration using the non-purgeable organic carbon (NPOC) method on a TOC-V_{CPH} Shimadzu Total Organic Carbon Analyzer (Shimadzu Corporation, Kyoto, Japan). Samples were acidified and purged with an inert gas to remove the inorganic carbon. Glucose standards and blanks were included as checks, and duplicate analyses were performed every ten samples to ensure quality control. Blanks measured less than 1.0 mg C L^{-1}. Ninety-one percent of duplicate results were within 10% of each other. One-hundred percent of the samples from 2008 and 2009 and 99.7% of the 2010 samples were analyzed. Due to continual mechanical problems with the ISCO sampler in the Basswood-5 watershed in 2009 and in the Orbweaver-1 watershed in 2010, data was not included in statistical analysis for those respective years.

Runoff was calculated as a flow-weighted volume per event. There were 21, 15, and 24 rainfall events in 2008, 2009, and 2010 respectively. Occasionally, smaller consecutive events were integrated into one event.

2.2 Precipitation

Precipitation data was obtained from a National Weather Service Mesonet weather station 1.3-3.6 km from the watersheds, and a U.S. Climate Reference Network (USCRN) weather station operated by the National Oceanic and Atmospheric Administration (NOAA) which is 1.1-3.3 km from the watersheds. Observations from the two stations were averaged to obtain mean monthly precipitation amounts.

2.3 Statistics

Daily DOC concentrations (mg L^{-1}) were multiplied by flow (L) to determine total export of DOC (kg). Daily totals were summed to get annual amounts, and normalized by watershed area to eliminate it as a variable and to allow comparisons of export between watersheds of different size. Total DOC annual export was divided by total flow to determine flow weighted annual DOC concentrations per watershed and per treatment. The same procedure was completed to calculate monthly total DOC concentrations and loads per watershed and treatment. The General Linear Model (GLM) procedure was used in SAS v. 9.2 (SAS Institute Inc., Cary, NC) to analyze the data. Statistical functions were performed on data over the full three year period (2008-2009), annually, seasonally (spring, summer, autumn), monthly, and for a large rainfall event that occurred August 8-11, 2010, to determine how flow weighted DOC concentrations and total loads compared between treatments and blocks from 2008 to 2010.

The null hypothesis is that the inclusion of NPV buffer strips into agricultural watersheds will have no effect on concentrations or fluxes of DOC. Statistically significant differences are reported at a p-level of 0.10.

The GLM procedure for Least Significant Difference (LSD) was performed on 2010 data from the twelve watersheds in the balanced incomplete block design. Use of the LSD values assumes that 100% NPV watersheds have the same properties as the watersheds within the randomized balanced incomplete block design. This approach does not allow rigorous statistical comparisons, but can be used to guide qualitative statements regarding what might be perceived as differences in concentrations and export of DOC from the two 100% NPV watersheds.

2.4 Hypotheses

Statistical analysis was performed on the data to determine whether treatment had an effect on DOC concentrations and amount exported in surface runoff from the NSNWR watersheds. My hypothesis is that the watersheds containing NPV will export lower concentrations of DOC than will 100% agricultural watersheds, but that there will be no significant differences between NPV treatments on DOC concentrations.

It is also hypothesized that the presence of native perennial vegetative (NPV) strips incorporated into agricultural watersheds will decrease the total load of dissolved organic carbon exported from a watershed through the reduction of surface runoff, but that the percentage of land converted into NPV strips will have no influence on the total amount of DOC exported. While the presence of crop residue within the agricultural watersheds provides carbon sources which may be similar to that from NPV, the reduction of runoff in buffer strips as observed by Helmers et al. (in review) may retain DOC thus reducing total load. The total amount of DOC exported from the NPV treatment watersheds would decrease mainly due to the retention of water in the NPV strips and the disruption to flow, thus decreasing surface runoff. Agricultural ecosystems may export more or less DOC than perennial grasslands, but the varying amounts of perennial vegetation disrupting concentrated surface runoff patterns would help retain carbon and thus lower the total amount exported.

Table 2.1 Watershed descriptions and experimental design

Watershed	Block	Size (ha)	Slope (%)	Treatment (Percentage and location of NPV strips)
Basswood-1	1	0.53	7.5	10% at footslope
Basswood-2	1	0.48	6.6	5% at footslope & 5% upslope
Basswood-3	1	0.47	6.4	10% at footslope & 10% upslope
Basswood-4	2	0.55	8.2	10% at footslope & 10% upslope
Basswood-5	2	1.24	8.9	5% at footslope & 5% upslope
Basswood-6	*2*	0.84	10.5	100% agriculture
Interim-1	3	3.00	7.7	3.3% at footslope, 3.3% at sideslope, & 3.3% upslope
Interim-2	3	3.19	6.1	10% at footslope
Interim-3	3	0.73	9.3	100% agriculture
Orbweaver-1	4	1.18	10.3	10% at footslope
Orbweaver-2	4	2.40	6.7	6.7% at footslope, 6.7% at sideslope, & 6.7% at upslope
Orbweaver-3	4	1.24	6.6	100% agriculture

Percentage of NPV strips = area of strips / area of watershed

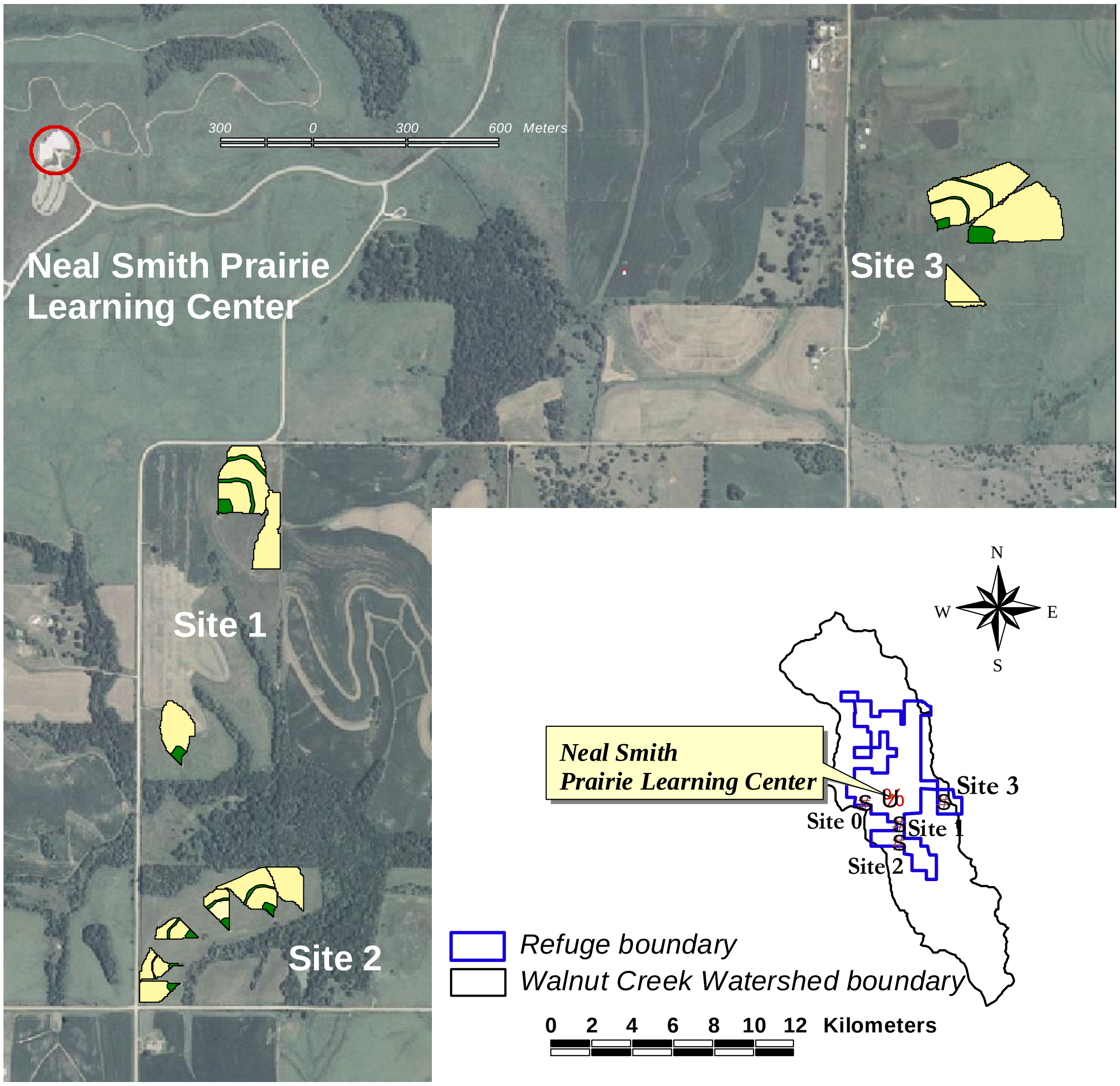

Figure 2.1 Location of experimental watersheds at the Neal Smith National Wildlife Refuge, Iowa. Site 1: Orbweaver, Site 2: Basswood, Site 3: Interim

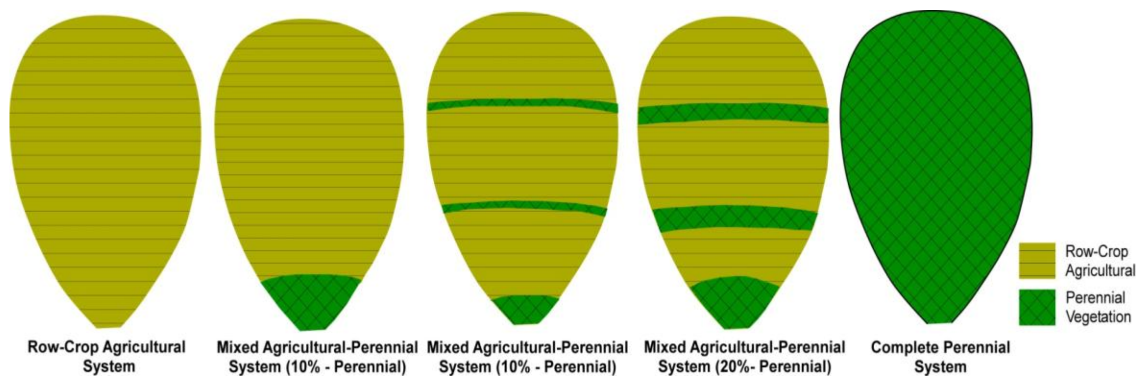

Figure 2.2: Experimental treatments: One of four treatments were randomly assigned to 12 watersheds. Two additional watersheds were planted in 100% NPV but are not a part of the balanced incomplete block design.

CHAPTER 3: RESULTS

3.0 Precipitation

Total rainfall exceeded the long term average rainfall of 713 mm during all three years of the study (2008-2010). Rainfall during the growing season (April through October) ranged from 811.1 mm in 2009 to 1220.9 mm in 2010 (Table 3.0.1). The driest month during the study period was October 2010 with only 12.4 mm of precipitation, followed by September 2009 and August 2008 with 56.4 mm rainfall in each month. An extreme event occurred from August 8-11, 2010, with 249.0 mm of rain falling during a four day period. August 10, 2010 was the wettest day recorded during the time period with 108.8 mm rainfall. Rainfall during August 2010 (372.7 mm) produced over half of the long term average annual rainfall for the area and was more than three times greater than normal August rainfall. With 336.9 mm of rain, June 2010 was the next wettest month during the monitored period, followed by June 2008 (265.8 mm).

Table 3.0.1 Monthly precipitation from April through October

Month	**2008**	**2009**	**2010**	**Normal**
	---------------------------------------	-mm-	---------------------------------------	
April	115.2	125.2	124.4	90.9
May	122.9	75.3	117.2	108.0
June	265.8	147.9	336.9	116.1
July	205.9	83.9	155.1	106.2
August	56.4	157.1	372.7	114.6
September	119.1	56.4	102.3	80.0
October	81.1	165.3	12.4	66.6
Total	**966.2**	**811.1**	**1220.9**	**682.2**

Adapted from Helmers et al. (in review)
Normal precipitation represents the 30 year average.

3.1 Flow weighted DOC concentrations

Mean annual flow weighted DOC concentrations ranged from 4.7 mg L^{-1} for 20% NPV in contour strips watersheds in 2010 to 10.8 mg L^{-1} for watersheds with 10% NPV in contour strips in 2009 (Table 3.1.1). Mean annual flow weighted DOC concentrations over the three year period (2008-2010) varied only slightly from a low value of 6.6 mg L^{-1} in watersheds with 20% NPV in contour strips to 8.5 mg L^{-1} in watersheds containing 10% NPV at the footslope position.

From analysis over the three year period of 2008 to 2010, treatment was significant only between 10% NPV at the footslope and 20% NPV in contours. Sites with 10% NPV at the footslope had significantly higher DOC concentrations than those with 20% NPV in contours. Annual data analyzed separately showed no significant differences between treatments for any year from 2008 to 2010 (Table 3.1.1).

Flow weighted DOC concentrations did not differ significantly between treatments for any individual month with the exception of August 2008 when precipitation and runoff were low (Table A.8). In August 2008, flow weighted DOC concentrations were significantly lower in the 100% agricultural watersheds than in the 10% and 20% in contour watersheds, however, only seven out of twelve watersheds recorded runoff and sample collection. Due to lack of other significant monthly treatment differences, data was not analyzed for seasonal treatment differences. However, during the extreme storm event of August 8-11, 2010, the lowest average concentration was in the 10% NPV in footslope watersheds (3.3 mg L^{-1}). Flow weighted DOC concentrations from the 100% agricultural watersheds (5.5 mg L^{-1}) was significantly higher than from all of the NPV treatment watersheds (Table 3.1.2).

Table 3.1.1 Mean flow weighted DOC concentrations in surface runoff

Year	100% agriculture	10% NPV footslope	10% NPV contours	20% NPV contours
	------------------------------mg L^{-1}-----------------------------------			
2008	7.8a	8.2a	9.6a	7.5a
2009	8.6a	10.1a	10.8a	7.6a
2010	6.3a	7.2a	4.9a	4.7a
Mean	**7.6ab**	**8.5b**	**8.4ab**	**6.6a**

Numbers followed by a common letter within a row indicates no significant differences existed between those treatments.

Table 3.1.2 Mean flow weighted DOC concentrations in surface runoff, August 8-11, 2010

100% Agriculture	10% NPV footslope	10% NPV contours	20% NPV contours
---mg L^{-1}--			
5.5a	3.3b	4.0b	3.6b

Numbers followed by a common letter within a row indicates no significant differences existed between those treatments.

3.2 Total DOC load exported

Mean annual DOC exported ranged from 2.9 kg ha^{-1} in watersheds with 10% NPV in the footslope position during 2009 to a high value of 28.6 kg ha^{-1} in the 100% agriculture watersheds in 2010 (Table 3.2.1). Mean annual DOC exported over the three year period per treatment ranged from 6.2 kg ha^{-1} from the 10% NPV in the footslope position watersheds to 17.3 kg ha^{-1} from the 100% agriculture watersheds.

From analysis over the three year period of 2008 to 2010 there were significant differences between treatments for total DOC load (kg ha^{-1}) exported from the watersheds (Table 3.2.1). Watersheds planted in 100% agriculture exported significantly greater DOC loads than did the 10% NPV at footslope and 20% NPV in contour watersheds. The presence of NPV strips thus influenced total DOC exported to varying degrees. Compared to the 100%

agriculture watersheds, during the study period (2008-2010), NPV strips reduced the amount of DOC exported by 64% and 48% from the 10% NPV at footslope and 20% NPV in contour strip watersheds, respectively. This correlates with a reduction in runoff in watersheds containing NPV strips as compared to 100% agriculture watersheds. Runoff was 59% and 27% less than that for the 100% row crop watershed for the 10% NPV at footslope and 20% NPV in contour strips, respectively, over the same period (Table 3.2.3). The 10% NPV in contours did not produce a significant reduction in DOC exported when compared to 100% agricultural watersheds (35%), which correlates with a 20% reduction in runoff.

Annual data analyzed separately showed no significant differences between treatments for any year from 2008 to 2010 (Table 3.2.1). Months were assigned to each season as determined by growth stage of crop vegetation. Spring season consisted of April and May, summer of June and July, and fall of August, September, and October. Seasonality did not affect differences between treatments for 2008 or 2009. In 2010 there was a difference between treatments in the fall (Table A.10). Total DOC load was significantly greater from 100% agricultural watersheds (12.9 kg ha^{-1}) than from 10% NPV at footslope watersheds (4.2 kg ha^{-1}).

When assessing monthly data, total DOC loads showed treatment effects to be significantly different only in May 2009 with significantly greater export from 100% agricultural watersheds (0.55 kg ha^{-1}) than from 10% and 20% NPV in contour watersheds (0.12 kg ha^{-1} and 0.06 kg ha^{-1} respectively), and in August 2010 (Table A.10). In August 2010, total DOC load was significantly greater from the 100% agricultural watersheds (12.4 kg ha^{-1}) than from the 10% NPV watersheds (3.4 kg ha^{-1} in 10% NPV in footslope and 7.6 kg ha^{-1} in 10% NPV in contours).

Table 3.2.1 Total DOC load exported in surface runoff

Year	100% Agriculture	10% NPV at footslope	10% NPV contours	20% NPV contours
	------------------------------kg ha^{-1}------------------------------			
2008	13.7a	5.9a	12.6a	7.8a
2009	9.6a	2.9a	6.8a	3.9a
2010	28.6a	9.8a	14.3a	15.4a
Mean	**17.3a**	**6.2b**	**11.2ab**	**9.0b**

Numbers followed by a common letter within a row indicates no significant differences existed between those treatments.

The analysis of the large storm event of August 8-11, 2010 showed significant differences with greater export from the 100% agricultural watersheds than from the 10% NPV at the footslope position watersheds (Table 3.2.2). Overall, watersheds containing NPV reduced runoff by 25% compared to runoff from 100% row crop watersheds (Helmers et al. in review). During this storm event, total DOC exported from watersheds containing 10% NPV at the footslope position was 76% less than that exported from 100% row crop watersheds.

Table 3.2.2 Total DOC load exported in surface runoff, August 8-11, 2010

100% Agriculture	10% NPV footslope	10% NPV contours	20% NPV contours
------------------------------kg ha^{-1}------------------------------			
11.6a	2.8b	7.1ab	7.4ab

Numbers followed by a common letter within a row indicates no significant differences existed between those treatments.

Table 3.2.3 Annual surface runoff

Year	100% Agriculture	10% NPV at footslope	10% NPV contour	20% NPV contour	Mean
	--------------------	--------------------	mm	--------------------	--------------------
2008	196.5a	62.0a	200.1a	158.3a	154.1
2009	128.8a	53.9a	112.7a	74.1a	92.4
2010	477.6a	209.8b	331.4ab	356.4ab	343.8
Average	**267.6a**	**108.6b**	**214.7ab**	**193.3ab**	

Letters indicate the significance test of mean difference among four treatments within each year at $p < 0.05$. Adapted from Helmers et al. (in review)

3.3 100% NPV watersheds

Flow and DOC measurements from the two watersheds containing 100% native perennial vegetation (NPV) (Cabbage-1 and Cabbage-2) are only available for 2010, and because they are located adjacently to one another and not randomly assigned to a treatment, they are not part of the balanced incomplete block design. The Proc GLM statistical function in SAS v. 9.2 was therefore not performed on the results from these two watersheds, however, it is worth considering the differences between the 100% NPV watersheds and the other treatments.

Results showed that flow weighted concentrations from Cabbage-1 and Cabbage-2 from 2010 were 3.9 mg L^{-1} and 4.1 mg L^{-1} respectively (mean 4.0 mg L^{-1}), as compared to 6.3 mg L^{-1} from the 100% agricultural watersheds, 7.2 mg L^{-1} from the 10% NPV at footslope treatment watersheds, 4.9 mg L^{-1} from the 10% NPV in footslope and upslope positions watersheds, and 4.7 mg L^{-1} from the 20% NPV in footslope and upslope positions watersheds (Table 3.3.1). The Proc GLM Least Significant Difference (LSD) for flow weighted concentration in 2010 in the twelve watersheds which were part of the statistical design was 1.8 mg L^{-1} at the 0.10 confidence level (Table 3.3.1). Understanding the limitations in using the assumptions made with using LSD analysis to compare between watersheds, flow weighted DOC concentrations in the 100% NPV watersheds would be considered significantly different from the 100% agricultural and 10% NPV at footslope watersheds, but not from the 10% and 20% NPV in contours watersheds.

Table 3.3.1 Mean annual flow weighted DOC concentrations and LSD values determined at the 0.10 confidence level for 2010 and August 8-11, 2010

Time period	100% Agriculture	10% NPV footslope	10% NPV contours	20% NPV contours	100% NPV	LSD
	--mg L^{-1}--					
2010	6.3	7.2	4.9	4.7	4.0	1.8
August 8-11, 2010	5.5	3.3	4.0	3.6	4.9	1.7

Flow weighted DOC concentrations during the storm event of August 8-11, 2010 were 4.6 mg L^{-1} (Cabbage-1) and 5.3 mg L^{-1} (Cabbage-2) with a mean value of 4.9 mg L^{-1}. In comparison, flow weighted DOC concentrations from the treatment watersheds (100% agricultural, 10% footslope, 10% contours, and 20% contours) were 5.5 mg L^{-1}, 3.3 mg L^{-1}, 4.0 mg L^{-1}, and 3.6 mg L^{-1}, respectively (Table 3.3.1). Based on the LSD value of 1.7 mg L^{-1} during this storm, flow weighted concentration from 100% NPV watersheds did not differ significantly from any of the watersheds (Table 3.3.1).

Total amount of carbon exported as DOC from Cabbage-1 and Cabbage-2 during 2010 was 5.8 kg ha^{-1} and 3.4 kg ha^{-1} respectively (mean 4.6 kg ha^{-1}), which is less than a fifth (16%) of that exported (28.6 kg ha^{-1}) from the 100% agricultural watersheds in 2010. Runoff in 2010 from 100% NPV watersheds was 152.5 mm, which is 68% less than runoff from 100% row crop (477.6 mm) and 49% less than runoff from watersheds with varying amounts of NPV (Helmers et al. in review). Thus, the reduction in DOC exported from 100% NPV watersheds (84%) correlates with reduced runoff from 100% NPV watersheds versus 100% agricultural (68%) and all other watersheds containing varying amounts of NPV (49%).

The LSD for total DOC load in 2010 from the twelve watersheds was 10.7 kg ha^{-1} at the 0.10 confidence level. Incorporation of assumptions made with the LSD analysis showed that the total load from the 100% NPV watersheds was not significantly different from any of the NPV watersheds (Table 3.3.2).

Table 3.3.2 Total DOC load and LSD values determined at the 0.10 confidence level for 2010 and August 8-11, 2010

Time period	**100% Agriculture**	**10% NPV footslope**	**10% NPV contours**	**20% NPV contours**	**100% NPV**	**LSD**
	--		-kg ha^{-1}-		--	
2010	28.6	9.8	14.3	15.4	4.6	10.7
August 8-11, 2010	11.6	2.8	7.1	7.4	2.6	4.7

Total amount of DOC exported during the major storm event of August 8-11, 2010 was 2.6 kg ha^{-1} from the 100% NPV watersheds. This was less than a quarter of total DOC exported from 100% agricultural watersheds (11.6 kg ha^{-1}), but similar to that exported from the watersheds containing only 10% NPV at the footslope (2.8 kg ha^{-1}). During this storm event, total DOC exported from watersheds containing 100% NPV was 78% less than that exported from 100% row crop watersheds. This was similar to a 76% reduction in DOC export from the 10% NPV at the footslope watersheds.

The LSD for total load during this storm was 4.7 kg ha^{-1} at the 0.10 confidence level, showing that total DOC export from 100% NPV watersheds during a major storm event was significantly different from 100% agricultural and 20% NPV in contour watersheds, but not from either of the 10% NPV watersheds (Table 3.3.2).

CHAPTER 4: DISCUSSION

4.1.0 Hypothesis 1: Watersheds containing NPV will export lower concentrations of DOC than will 100% agricultural watersheds, but that there will be no significant differences between NPV treatments on DOC concentrations.

4.1.1 Treatment effects on DOC concentrations for the study period (2008-2010)

DOC concentrations reported from this study fall within the range of concentrations in agricultural surface runoff reported by Zsolnay (1996), and Moore & Dalva (2001). From analysis over the three year period of 2008 to 2010 treatment was significantly different for flow weighted DOC concentrations only between 10% NPV at the footslope and 20% NPV in contours watersheds. Concentrations were generally lowest in the 20% NPV in contour watersheds, and highest in the 10% NPV in footslope watersheds.

Although 10% NPV watersheds had elevated DOC concentrations over the 100% agricultural watersheds, differences were not significant. However, the trend of increasing concentrations from 20% NPV to 100% agricultural to the highest values recorded in 10% NPV watersheds is not consistent with expectations based on the findings of Brye et al. (2001) as they reported higher concentrations from agricultural sites when compared to tallgrass prairie systems.

Over the study period, runoff was 59% and 27% less than that from the 100% agricultural watersheds for the 10% NPV at footslope and 20% NPV in contour strips watersheds, respectively. The closer similarity in runoff between 20% NPV and 100% agricultural watersheds when compared to the 10% NPV and 100% agricultural watersheds could explain both the lowest concentrations in 20% NPV watersheds and the higher concentrations in 10% NPV at footslope. As reported by Mailapalli et al. (2010), longer residence time for precipitation extends the water interaction with soil and vegetation. This promotes greater desorption and dissolution of DOC, which can lead to higher concentrations of DOC in surface runoff. As the lowest amounts of runoff over the three year period were reported from 10% NPV at footslope watersheds (Helmers et al. in review), precipitation retention was greatest in those watersheds. Thus, runoff water carried significantly greater concentrations of DOC than that which came from the 20% NPV watersheds. Secondly, runoff from 100% agricultural watersheds was only significantly greater than from 10% NPV at footslope watersheds (Helmers et al. in review). The lower water retention promoted the export of relatively lower DOC concentrations primarily due to shorter contact time between precipitation and soil. The correlation between significantly less runoff and therefore longer water residence times from the 10% NPV at footslope watersheds than 100% agricultural may explain the elevated concentrations.

4.1.2 Annual treatment effects on DOC concentrations

Even while receiving more annual precipitation than normal during the three year study period, small amounts of NPV (0%, 10%, and 20%) placed in footslope and contour strip positions within agricultural watersheds with slight to moderate slopes did not significantly influence DOC concentrations in surface runoff during any single year. Other studies have also noted no difference in DOC concentrations between runoff or leachate water exported from agricultural and prairie watersheds (Brye et al. 2002, Wilson & Xenopoulos 2008, Johnson et al. 2009).

Runoff differed significantly only between 100% agricultural and 10% NPV at footslope treatments in 2010, but not among treatments for 2008 or 2009 (Helmers et al. in review). Thus while not hypothesized, the lack of treatment differences for DOC concentrations in any single year is not surprising given similar runoff amounts.

Although I expected lower DOC concentrations in the NPV watersheds when compared to the 100% row crop watersheds, others have shown that greater infiltration capacity in riparian buffer strips could account for longer residence times in the NPV strips (Smukler et al. 2010), which could account for similar DOC concentrations between all four treatments. In a field study at NSNWR, no significant differences were reported between unsaturated hydraulic conductivities (and consequently infiltration capacities) in the NPV strips versus the surrounding field soil (Lockett unpublished data). However, Helmers et al. (in review) reported a delay in peak runoff time in NPV watersheds versus the 100% agricultural watersheds. A delay in peak runoff would indicate a longer residence time in NPV watersheds possibly leading to higher concentrations and more similar concentrations to the 100% agricultural watershed treatment. DOC concentrations in water associated with the upper organic soil horizons in agricultural systems may be relatively higher than from lower mineral soil horizons thus promoting export of higher concentrations of DOC in surface runoff (Brye et al. 2001). However, increased residence time in NPV strips and consequently greater dissolution from mineral soil horizons could also increase DOC concentrations.

In addition, prairie vegetation normally contributes a greater amount of organic matter to the soil than that produced in row crops (Borin et al. 2010); this may help explain the associated higher than expected DOC concentrations in the NPV watersheds. While other studies have reported greater DOC concentrations from agricultural systems (Brye et al. 2001), in this study it appears the NPV strips slowed surface runoff enough to increase water residence times, which combined with production of large amounts of carbon in prairie vegetation available for carbon-dissolution in surface runoff, led to DOC concentrations similar to or greater than those from 100% agricultural watersheds.

DOC concentrations were highest among all the treatments during 2009, which was the driest year during the study, and lowest in 2010 during which the NSNWR received the most precipitation. One explanation may be that during a relatively dry year such as 2009, soil moisture is still sufficient enough that soil and vegetative carbon is decomposed in the O soil horizon by macroinvertebrates and microorganisms (Wickland et al. 2007), which is consequently more easily dissolved during rainstorms. The buildup of leaf litter in the O soil horizon during the drier periods is flushed during periodic storms, resulting in runoff water containing higher levels of DOC than typically would exist during wetter periods (Sanderman et al. 2008). Furthermore, as previously mentioned, longer residence time for precipitation extends its interaction with soil and vegetation (Mailapalli et al. 2010), which promotes greater desorption from soil particles and dissolution of DOC in runoff water. This can lead to higher concentrations of DOC in surface runoff from watersheds retaining water for longer time periods. Longer water residence time during a drier year also increases the opportunity for microbial metabolism of DOC, whereas a shorter residence time can promote transport of more labile DOC to surface waters (Wickland et al. 2007).

4.1.3 Seasonal and monthly treatment effects on DOC concentrations

Although other studies have reported seasonal differences (Jacinthe et al. 2004, Dalzell et al. 2007, Agren et al. 2008, Wilson & Xenopoulos 2008), this study did not reveal any seasonal patterns of DOC. A likely time when seasonal patterns may occur is during snowmelt when concentrations are generally lower because of dilution (Dalzell et al. 2007). This pattern was not seen in this study; sampling started after snowmelt. Like this study, a lack of seasonal patterns in DOC concentrations has been reported in numerous studies (Eckhardt & Moore 1990, David et al. 1992, Brye et al. 2001, Inamdar & Mitchell 2006, Warrner et al. 2009), suggesting that patterns are not related to vegetation type or land use but rather to precipitation and occurrence of runoff events (Royer & David 2005, Vidon et al. 2008). Flow weighted DOC concentrations generally did not differ significantly between treatments for any individual month in this study, therefore, data was not analyzed for seasonal differences.

The one month (August 2008) where differences existed between the 100% agricultural and 10% and 20% NPV watersheds with contours was a drier than normal month. The result that DOC concentrations did not significantly differ between treatments on a monthly basis in this study suggests that there is little difference in the amounts of carbon leached from row crop and prairie plant residues (previous year's residues versus growing and senescing vegetation). The crop residues remaining on the soil surface due to conservation tillage practices provided a source of leachable DOC during the spring months of April and May (Warrner et al. 2009, Mailapalli et al. 2010), which was comparable to that leached from growing crops and prairie vegetation during summer months (June and July). In the fall season (August and September), while both crops and prairie vegetation ceased growing, their presence in the watersheds served as a comparable source of DOC.

As the upper soil horizons are significant sources of DOC (Inamdar et al. 2004, Sanderman & Amundson 2009), the lack of variation between treatments on seasonal and monthly DOC concentrations in this study suggests that the type of plant material supplying leachable carbon (leftover crop residue, growing or senescing vegetation) has minimal influence DOC concentrations in surface runoff.

Sanderman et al. (2008) found that the DOC source pool is finite in forest and grassland systems of California. Over a six month rainy period the DOC concentrations declined, thus indicating that amount of DOC available for transport in surface runoff decreased with time over the rainy season based on dilution from precipitation. In this study, concentrations did not vary substantially or decline over the growing (rainy) season. Thus, the pool of DOC in the watersheds at the NSNWR during this study period was not depleted.

4.1.4 Treatment effects during an extreme storm event August 8-11, 2010

During this high intensity, lengthy storm event (248 mm of rainfall over four days), the presence of NPV treatments in the watersheds significantly decreased DOC concentrations in runoff water. The lowest average concentration was in the 10% NPV in footslope watersheds (3.3 mg L^{-1}), and the highest was in the 100% agricultural watersheds (5.5 mg L^{-1}).

Soil saturation during this four day storm event promoted 25% greater runoff in the 100% agricultural watersheds when compared to the NPV watersheds (Helmers et al. in review). The water table in the footslope position of NPV watersheds was closer to the surface than in the footslope of 100% agricultural watersheds during this storm (Helmers et al. in review). The relationship between runoff and DOC concentrations could account for the significantly lower concentrations from the NPV watersheds. Dilution of concentrations due to the high water table may have also led to significantly lower DOC concentrations from the NPV watersheds. Under extremely high soil moisture conditions, soil flushing, runoff dilution, increased groundwater inputs with a rising water table (and subsequent dilution), and increased overland flow factor into lower DOC concentrations in surface runoff during large events (Wilson & Xenopoulos 2008). Soil residence time is minimal, especially towards the end of a rainfall event. Thus, while not statistically different, DOC concentrations were notably lower during this single storm than annual averages. The higher concentration from 100% agricultural watersheds is consistent with findings from Byre et al. (2001). The timing of the event during August when the corn crop was at its maximum production rate and comparably high evapotranspiration rates from both corn and the NPV (Mateos-Remigio et al. unpublished data) typically diminish runoff, coupled with the production of significantly larger runoff amounts during the event and greater dilution of concentrations from the NPV watersheds with higher water tables in the footslope positions led to significantly higher DOC concentrations in the 100% agricultural watersheds.

4.1.5 Comparison of DOC concentrations between 100% NPV and treatment watersheds in 2010

Using only assumptions based on LSD analysis to determine significance, the similarity between DOC concentrations in the 100% NPV watersheds in 2010 (4.0 mg L^{-1}) and 10% and 20% NPV in the contour strips watersheds (4.9 mg L^{-1} and 4.7 mg L^{-1} respectively) indicates that even a small area of multiple NPV buffer strips incorporated into an agricultural watershed, perhaps coupled with less concentrated flow paths (Dunn et al. 2011), can decrease DOC concentrations to levels found in 100% prairies. Perhaps the multiple buffer strips acted similarly to 100% NPV watersheds in disrupting concentrated flow paths to a level where DOC was retained in the buffers through increased water residence time, while more diluted water exited the buffers on the downward slope. Thus, significantly lower concentrations existed in runoff water exported from 100% NPV watersheds. These results are similar to those reported by Byre et al. (2001) in which DOC concentrations in a prairie site were lower than in a row-crop (corn) agro-ecosystem site.

DOC concentrations from 100% NPV watersheds were significantly lower (based on LSD analysis) from 100% agricultural and 10% NPV at footslope watersheds. The difference between 100% NPV and agricultural watersheds may be explained by 68% less runoff in 2010 from 100% NPV versus 100% agricultural watersheds. The significant difference in DOC concentration between 100% NPV and 10% NPV in footslope watersheds does not appear to be related to differences in runoff (68% and 57% less respectively from 100% NPV and 10% NPV footslope watersheds). I hypothesize that the higher concentrations in the 10% footslope is related to the small amount of prairie vegetation and possibly greater water residence time in the footslope buffer strip. Perhaps, however, the disruption to the establishment of concentrated flow paths by multiple buffer strips (Dunn et al. 2011) is the important component in lowering DOC concentrations to levels of 100% NPV watersheds.

4.1.6 Comparison of DOC concentrations between 100% NPV and treatment watersheds during August 8-11, 2010 storm event

Based on the LSD value for this storm event, concentrations from 100% NPV watersheds did not significantly differ from any of the treatment watersheds. These results are consistent with a lack of significant differences reported between DOC concentrations from land with varying land covers during large events (Brye et al. 2002, Wilson & Xenopoulos 2008). Under such extreme and lasting rainfall conditions when soil saturation was reached early in the event, the lack of differences are likely the result of the precipitation controlling DOC concentrations independent of land use (Inamdar et al. 2004, Royer &

David 2005, Vidon et al. 2008). Jacinthe et al. (2004) reported that rainfall characteristics more than any land management practices controlled soil C transport during storm events. While precipitation may be a source of DOC to a watershed (Eckhardt & Moore 1990), during large events there is a finite capacity for soil organic matter to continually supply DOC in runoff and towards the end of an event, a dilution effect may be observed on DOC concentrations (Delpla et al. 2011).

4.2.0 Hypothesis 2: The presence of NPV strips incorporated into agricultural watersheds will decrease the total load of dissolved organic carbon exported from a watershed through the reduction of surface runoff, but the percentage of land converted into NPV strips will have no influence on the total amount of DOC exported.

4.2.1 Treatment effects on DOC loads for the study period (2008-2010)

DOC loads reported in this study fall within a range of values reported by Royer & David (2005) and are less than the highest values reported by Dalzell et al. (2007) for agricultural watersheds. From analysis over the three year study period, treatment was significant, thus, the presence of NPV strips (10% in footslope and 20% in contours) significantly reduced the amount of DOC exported in surface runoff as compared to the 100% agricultural watersheds from 2008-2010. The DOC load from 10% NPV in contours was statistically similar to the load from both the 100% agricultural and the other NPV treatment watersheds.

The establishment of vegetative buffer strips in agricultural watersheds has been shown to effectively reduce surface runoff (Veum et al. 2009, Helmers et al. in review).

Runoff from the 10% NPV in contours watersheds was statistically similar to both 100% agricultural and the other NPV treatment watersheds, thus, the results correlate with DOC export. Jacinthe et al. (2004) also found that carbon losses were proportional to runoff. However, the overall reduction in export from the NPV treatment watersheds shows the effectiveness of incorporating buffer strips in agricultural watersheds, more convincingly than results from a similar experiment reported by Veum et al. (2009). Other factors such as the presence of a claypan soil horizon dominating the hydrology, low buffer strip area (8-10% of watershed area), and immaturity of agro-forestry trees in one of the paired watersheds may have increased variability between the buffer strip treatment watersheds in the Veum et al. (2009) study and reduced potential treatment effects on DOC loads. The presence of a wide buffer strip in the footslope position may also be an important factor to consider to reduce DOC loads from agricultural watersheds.

4.2.2 Annual treatment effects on DOC loads

While most annual loads were between the range of values reported by Royer & David (2005) of 3-23 kg ha^{-1}, the mean 2010 DOC load from 100% agricultural watersheds was greater, most likely due to the exceptional amount of precipitation received. There was no significant difference in total DOC exported between any of the watersheds in individual years, although export was consistently highest from the 100% agricultural watersheds, and lowest in the 10% NPV at footslope watersheds.

Concentrated flow in gullies or other naturally occurring drainage paths will influence the effectiveness of NPV strips to reduce nutrient and particle export (Dillaha et al. 1989). Coupled with decreased time to soil saturation during large storm events, this could also reduce the ability of NPV strips to retain DOC. Bhattarai et al. (2009) and Dunn et al. (2011)

recommended placement of NPV strips to spread concentrated flow so as to maximize the usefulness of the strips in reducing nutrient export. Helmers et al. (in review) concluded that the upslope strips which were established to minimize concentrated flow at the NSNWR did not significantly decrease sediment export. Similarly, the multiple strips did not reduce export of DOC.

DOC export from watersheds with 20% NPV in contours was not significantly different from the 100% agricultural watersheds in any single year, similar to runoff data (Helmers et al. in review). This was unexpected as it was hypothesized that while there may not be significant differences between NPV treatments on DOC export, it was thought that with increased area of land planted in NPV, there would be a greater chance for NPV strips to slow runoff and reduce DOC export. I present several possible explanations here.

First, it may be that as noted by Dunn et al. (2011), narrow buffer strips do not decrease export of highly-soluble dissolved materials over shorter widths as much as they reduce export of particulates, which have greater potential to be trapped even in a narrow strip. However, Dunn et al. (2011) noted that potentially, increasing buffer strip width to 30m could reduce export of dissolved materials. This may explain why total export was consistently lower in the 10% NPV at footslope watersheds with a single strip width between 38-78 m, whereas export from the 10% and 20% NPV in contours was elevated but the strips were narrower (between 37-52 m at the footslope and between 3-10 m on the contours). When the strips were divided (either 5% upslope and 5% footslope or 3% upslope, 3% sideslope, and 3% footslope) or (either 10% upslope, 10% footslope or 6.7%, upslope, 6.7% sideslope, 6.7% footslope) (Table 2.1), the reduction in DOC export as compared to the 100% agricultural watersheds was less. In the case of 20% NPV watersheds, the inclusion into the mean export values of Orbweaver-2 with the vegetation divided into three strips each containing 6.7% of the NPV did not reduce DOC transport in comparison with those watersheds with the 20% NPV divided into two wider strips each containing 10% of the NPV. In this study, as export was not significantly different between any of the NPV treatments, the additional narrower contour strips in the 10% and 20% NPV watersheds did not appear to decrease export of DOC.

In another study investigating the influence of 4.5 m buffer strips on DOC transport, five grassed buffer strips in one agricultural watershed and six agro-forestry buffer strips planted in its paired watershed did not significantly reduce DOC export when compared to the control 100% agricultural watershed (Veum et al. 2009). The strips were all planted on contours and not in the footslope position. While export in my study was not statistically less for NPV treatments in any single year, it was consistently lower from NPV treatment watersheds than from 100% agricultural watersheds, thus, the incorporation of a wide buffer strip in the footslope position may be the key to most effective DOC retention.

Secondly, removal of dissolved compounds by buffer strips relies on expected increased infiltration capacities within the strips (Tim et al. 1995). In a lab study, while saturated hydraulic conductivity (K_{sat}) was generally elevated in filter strip soil over row crop soil from the NSNWR, it did not significantly differ between land cover treatments (Lockett unpublished data). In a field study on the same soils, unsaturated hydraulic conductivity was determined to not be significantly different between treatments (Lockett unpublished data), thus indicating that infiltration capacities did not differ between agricultural soil and soil within buffer strips. As discussed earlier, perhaps the buffer strips slowed runoff enough to increase residence time in the soil, which upon production of runoff, consequently promoted the export of greater DOC loads similar to that exported from agricultural soils.

A final explanation involves a combination of several factors. The production of carbon in the NPV strips may be lesser, equal to, or greater than that in the row crops, but the buildup and retention of leachable plant material and soil organic matter in the strips increases the carbon pool from which DOC forms. This DOC production, combined with greater residence time promoting larger concentrations within buffer strips, could explain DOC export values similar to that from 100% agricultural watersheds. As reported by Royer & David (2005), total DOC export was greater from agricultural watersheds than prairie watersheds, which is consistent with my findings of greater export from agricultural versus watersheds containing prairie buffer strips over the three year study period. However, Borin et al. (2010) reported greater soil organic carbon accumulation in buffer strips than agricultural soil as it is not subject to tillage practices. Thus, the increased production of the carbon pool in the buffer strips may cancel out their retention capability, exporting carbon in the form of DOC at levels similar to that from 100% agricultural watersheds (Warrner et al. 2009).

Perhaps the key to examining this data is not in explaining a lack of significant differences in export between the treatment and 100% agricultural watersheds but rather to note that there appears to be an exhaustive supply of carbon to be exported from all the watersheds, thus diminishing significant differences in concentrations and total amounts exported between treatments.

4.2.3 Seasonal and monthly treatment effects on DOC loads

Seasonality did not influence DOC export between treatments except during fall 2010. A likely reason for lack of seasonal treatment effects on loads was that my sampling started after spring snowmelt which may influence the spring loads observed. In 2010 export was greatest in the fall in all the watershed treatments in conjunction with the extreme storm event in August. The result that seasons did not generally impact DOC export with the exception of fall 2010 indicates that the crop residues remaining on the soil surface due to conservation tillage practices provided a source of leachable DOC during the spring months (Lal et al. 1999), which was comparable to that leached from growing crops and prairie vegetation during summer months. In the fall season, while both crops and prairie vegetation ceased growing, the standing dead biomass in the watersheds served as a source of DOC.

Significant treatment effects on monthly DOC export were minimal, only observed during May 2009 and August 2010 (Table A.10), again signifying a lack of correlation between leachable carbon availability and monthly export. More notable, however, was how closely export patterns followed precipitation patterns. The greatest amount of precipitation was recorded in August 2010. Total DOC load was significantly greater from the 100% agricultural watersheds than from the 10% NPV watersheds. However, runoff produced during this month exported 43%, 38%, 53%, and 53% of the total annual DOC export for 2010 for 100% agricultural, 10% NPV footslope, 10% NPV contoured, and 20% NPV contoured watersheds respectively. This corresponds with average measurements of 231.7, 124.2, 187.0, and 200.9 mm of runoff in this month for 100% agriculture, 10% NPV footslope, 10% NPV contoured, and 20% NPV contoured watersheds.

While no significant differences were noted, June 2010 received the second highest amount of precipitation, and runoff exported 23%, 35%, 31%, and 29% of total DOC export for 2010 from 100% agricultural, 10% NPV footslope, 10% NPV contoured, and 20% NPV contoured watersheds. DOC exported corresponds with mean runoff of 150.0, 62.3, 97.2, and 99.2 mm from the respective watersheds during this month.

Sixty-three percent of DOC load exported in 2008 from 100% agricultural watersheds was during June, the month receiving the third highest amount of precipitation during the study period. Export from the 10% NPV at footslope, 10% and 20% in contours during June 2008 was 58%, 39%, and 38% of total annual export. Mean runoff during June 2008 from the 100% agricultural, 10% NPV at footslope, 10% NPV contour, and 20% NPV contour watersheds was 98.9, 43.7, 55.5, and 65.1 mm respectively.

Thus, during the three months receiving the highest precipitation, DOC export as a percentage of total annual export from the 10% and 20% NPV in contour strips watersheds were similar, while export from 100% agricultural and 10% NPV at the footslope watersheds was highly variable and did not always correlate with runoff produced. Months receiving the most precipitation producing the greatest amount of surface runoff contributed the greatest amount of DOC to the total annual load, consistent with results by Royer & David (2005) stating that precipitation strongly influenced the amount of DOC exported from agricultural watersheds, and Dalzell et al. (2007) who reported between 71-85% of total annual DOC load was exported in flow events occurring less than 20% of the time.

4.2.4 Treatment effects during an extreme storm event August 8-11, 2010

Export of DOC loads from the 100% agricultural watersheds during the extreme storm event experienced in August 2010 comprised 40% of the total load for 2010. From the

10% at footslope, 10% NPV in contours, and 20% NPV in contours watersheds, the loads exported during the storm were 29%, 50%, and 48%, respectively, of the total 2010 DOC loads. During this storm event, however, only the DOC exported from the 10% NPV at footslope watersheds differed significantly from that exported from 100% agricultural watersheds. During this storm event, total DOC exported from watersheds containing 10% NPV at the footslope position was 76% less than that exported from 100% row crop watersheds.

DOC export during this storm correlated with mean runoff. Runoff was greatest from 100% agricultural watersheds, followed by 20% NPV in contours, 10% NPV in contours, and 10% NPV at footslope. The similarity in DOC export from 10% and 20% NPV in contours watersheds and 100% agricultural watersheds can be explained by a close relationship between runoff and total export.

One explanation for a lack of significant difference between export from 100% agricultural watersheds and watersheds with NPV divided into strips is that the strips appeared to not minimize concentrated flow once soil reached saturation. Also, during this intense, lengthy storm, the soil in the strips essentially acted similar to the surrounding agricultural field soil, reaching saturation at similar stages and thus return flow carried similar amounts of DOC.

4.2.5 Comparison of DOC load between 100% NPV and treatment watersheds in 2010

According to the LSD value for 2010 and incorporating associated assumptions with the statistical procedure, DOC export from the 100% NPV watersheds was not significantly different from any of the NPV treatment watersheds in 2010. Total amount of carbon exported as DOC was 4.6 kg ha^{-1}, which falls within the range of values reported by Hope et al. (2004) for prairie watersheds. Total DOC export from the 100% NPV watersheds was 84% less than that from the 100% agricultural watersheds. This significantly lower export of DOC from prairie watersheds as compared to agricultural watersheds is similar to results reported by Byre et al. (2001) and Royer & David (2005). Brye et al. (2001) noted greater DOC losses in leachate from agro-ecosystems than from prairie sites. Royer & David (2005) reported DOC loads from their agricultural watersheds were greater than that reported for a prairie influenced stream (Gray 1997). Incorporating between 10-20% NPV treatments into agricultural watersheds may be sufficient to reduce total DOC load to a level achieved in 100% NPV watersheds.

In 2010, export from the 10% NPV at footslope watersheds was more similar to that from 100% NPV watersheds than to 100% agricultural watersheds. This demonstrates that a wide strip of NPV in the footslope position has the potential to reduce DOC export (Table 3.3.1, Table 3.4.3). While the inclusion of 100% NPV watersheds was not included in my hypothesis, results from this study serve to strengthen the argument that incorporation of only 10% NPV into the footslope position of a watershed may be as effective in reducing runoff (Helmers et al. in review) and DOC export during growing seasons receiving large amounts (above average) of precipitation as watersheds that are planted in prairie vegetation.

4.2.6 Comparison of DOC load between 100% NPV and treatment watersheds during August 8-11, 2010 storm event

Total amount of DOC exported during the major storm event of August 8-11, 2010 was 2.6 kg ha^{-1} from the 100% NPV watersheds. This was less than a quarter of total DOC exported from 100% agricultural watersheds (11.6 kg ha^{-1}). According to the LSD value, while export from 100% NPV watersheds was not significantly different from that of either of the 10% NPV watersheds, it was more similar to that exported from the watersheds containing only 10% NPV at the footslope (2.8 kg ha^{-1}). During this storm event, total DOC exported from watersheds containing 100% NPV was 78% less than that exported from 100% row crop watersheds. This was similar to a 76% reduction in DOC export from the 10% NPV at the footslope watersheds, thus demonstrating that during storms with heavy precipitation producing large amounts of runoff following soil saturation, a single strip of 10% NPV in the footslope position can be as effective in reducing DOC exported as from a watershed planted totally in NPV. The similarity in DOC loads between 10% NPV in footslope and 100% NPV watersheds also signifies the benefit of incorporating a wide buffer strip in the footslope position to decrease DOC export during intense storm events and annually.

4.3.0 Factors highlighting the need for future research

Other aspects of watershed management could complicate the relationship of DOC lost in surface runoff. Tile drains are a predominant feature in Iowa's agricultural landscape. During times of heavy precipitation, the tile effectively drains land to avoid flooding of crops. DOC is both highly mobile and soluble, as such, tiles are likely an important pathway that bypasses buffers and results in losses from the terrestrial ecosystem. Coupled with conservation tillage techniques employed at the NSNWR, as suggested by Armand et al. (2008), the increased amount of crop residues left on the surface may increase the potential for increased DOC leaching into groundwater or lost in runoff. Future research at the NSNWR should focus not only on DOC lost in surface runoff, but also in groundwater.

Future research efforts at the NSNWR might also concentrate on determining the bio-availability of DOC in surface runoff, and from where it originates in the watersheds.

Research on bio-reactivity would improve knowledge of terrestrial sources of DOC exported from NSNWR watersheds, and consequently what effects on downstream ecosystems the DOC might have.

Finally, as Borin et al. (2010) and Smukler et al. (2010) noted, the challenge with incorporating buffer strips is in determining whether the negative interference with crop productivity in planting NPV strips is economical, finding ways to encourage farmers to adopt innovative practices, and offering them rewards for doing so. Providing valuable data on DOC impacts on surface water from agricultural runoff will be helpful in informing land owners of some of the benefits of buffer strips.

CHAPTER 5: CONCLUSIONS

NPV buffer strips have been shown to reduce export of nutrients from agricultural watersheds. Results from this study at the NSNWR show that while incorporation of varying amounts of NPV into agricultural watersheds does not significantly decrease DOC concentrations, it may decrease the total amount of DOC exported.

Overall, the conversion of 10% of an agricultural watershed's area into native perennial vegetation in the footslope position most significantly increased DOC concentrations and decreased export when compared to 100% agricultural watersheds. Load from 10% NPV at footslope watersheds was significantly lower than from 100% agricultural watersheds over the three year study. Concentrations of DOC were higher, however, possibly due to increased water residence time in the footslope buffer strip, and subsequent desorption and dissolution of DOC in runoff water. In contrast to the reduction of sediment concentration decreasing sediment load from these NPV treatment watersheds (Helmers et al. in review), it appears the reduction in runoff was the reason for significantly less DOC export from 10% NPV at footslope watersheds than from the 100% agricultural watersheds.

With the growth and establishment of the buffer strips over 2008-2010, treatment effects in the 10% NPV at footslope and 20% NPV in contours became significantly different by decreasing loads in comparison to that exported from the 100% agricultural watersheds. This significant reduction in load over the three year period and during extreme storm events, which have strong erosive potential and cause excessive runoff, provides strong evidence of the value of incorporating NPV strips, particularly with greater area in the footslope position, as a viable management tool to reduce DOC loading to downstream surface water.

Finally, results that DOC concentrations and load from the NPV treatment watersheds did not as a whole significantly differ from 100% NPV watersheds located near the experimental watersheds, indicate that the incorporation of NPV as buffer strips into agricultural landscapes may be a valuable land management tool to reduce DOC loading to levels exported from tallgrass prairie watersheds.

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APPENDIX

Table A.1 Flow weighted DOC concentrations and load per watershed: Blocks 1 & 2 (Basswood) in 2008 and 2009

Month/Year	B-1	B-2	B-3	B-4	B-5	B-6
	---Concentrations (mg L^{-1})---					
April 2008	8.0	6.8	0	7.5	6.7	6.6
May 2008	.	8.2	8.9	8.4	7.7	3.5
June 2008	.	7.0	9.0	8.1	27.1	9.0
July 2008	.	6.2	13.3	6.8	9.3	5.0
August 2008	.	10.5	11.7	10.7	9.6	6.6
September 2008	8.4	5.8	10.9	7.0	33.1	4.4
October 2008	.	10.7	.	25.2	15.6	14.9
2008	8.1	7.0	8.8	7.7	11.3	7.1
	---Load (kg ha^{-1})---					
April 2008	0.2	0.8	0	1.4	2.0	2.5
May 2008	0	1.3	0.9	1.7	1.1	0.7
June 2008	0	7.6	1.6	4.7	3.6	12.3
July 2008	0	3.6	1.6	4.9	5.8	3.9
August 2008	0	0.2	0.1	0.2	0.1	0.1
September 2008	0.3	0.6	0.2	0.5	1.8	0.4
October 2008	0	0.6	0	0.4	0	0.1
2008	0.5	16.2	5.0	14.9	15.7	20.6
	---Concentrations (mg L^{-1})---					
April 2009	7.1	7.2	5.6	6.0	.	7.3
May 2009	13.2	10.9	7.2	7.4	.	9.9
June 2009	10.8	17.6	8.8	9.7	.	10.3
July 2009	17.4	.	9.8	9.9	.	6.2
August 2009	.	.	.	.	.	.
September 2009	.	.	.	.	.	.
October 2009	9.5	26.9	12.0	8.2	.	7.8
2009	10.2	11.5	7.3	8.1	.	8.3
	---Load (kg ha^{-1})---					
April 2009	0.6	3.2	0.5	2.2	0	5.1
May 2009	0.2	0.2	0.0	0.1	0	0.9
June 2009	0.3	4.6	0.2	3.2	0	4.7
July 2009	0.7	0	0.2	1.5	0	0.6
August 2009	0	0	0	0	0	0
Sept. 2009	0	0	0	0	0	0
October 2009	1.1	0.6	0.2	2.4	0	2.9
2009	2.8	8.7	1.0	9.4	0	14.2

Table A.2 Flow weighted DOC concentrations and load per watershed: Blocks 1 & 2 (Basswood) in 2010

Month/Year	B-1	B-2	B-3	B-4	B-5	B-6
	---------------------------Concentrations (mg L^{-1})------------------------------					
April 2010	12.7	8.2	.	9.0	8.4	26.8
May 2010	8.6	6.4	5.6	6.0	3.6	6.6
June 2010	6.7	5.6	5.6	5.9	6.0	5.5
July 2010	8.3	8.0	8.0	7.9	7.4	7.0
August 2010	3.9	4.3	4.7	3.6	3.7	5.7
September 2010	9.6	7.5	7.3	6.2	8.6	7.0
October 2010	.	.	.	.	.	.
2010	5.9	5.0	5.0	4.8	4.7	7.4
	---------------------------------Load (kg ha^{-1})-----------------------------------					
April 2010	1.3	0.7	0	1.5	0.9	12.1
May 2010	1.1	1.1	0.3	2.2	0.8	2.5
June 2010	3.9	5.8	3.6	8.1	5.5	10.9
July 2010	0.3	0.9	0.8	1.5	0.5	2.4
August 2010	3.6	11.4	8.7	9.5	6.0	15.2
September 2010	0.5	0.5	0.2	0.4	0.2	1.0
October 2010	0	0	0	0	0	0
2010	10.7	20.4	13.6	23.3	13.9	44.1

Table A.3. Flow weighted DOC concentrations and load per watershed: Block 3 in 2008 and 2009

Month/Year	Interim-1	Interim-2	Interim-3
	-------------------------	Concentrations (mg L^{-1})	-------------------------
April 2008	9.7	9.4	8.4
May 2008	9.3	8.8	8.8
June 2008	10.3	6.5	10.8
July 2008	11.7	6.3	5.8
August 2008	.	.	8.6
September 2008	10.0	17.0	5.9
October 2008	.	.	11.5
2008	10.5	7.2	9.0
	-------------------------	Load (kg ha^{-1})	-------------------------
April 2008	0.1	0.2	0.4
May 2008	0.5	0.6	1.6
June 2008	3.5	2.8	10.1
July 2008	1.6	1.4	3.2
August 2008	0	0	0.2
September 2008	0.1	0.3	0.2
October 2008	0	0	0.1
2008	5.9	5.6	16.5
	-------------------------	Concentrations (mg L^{-1})	-------------------------
April 2009	.	8.4	10.7
May 2009	11.3	8.9	6.9
June 2009	10.4	9.8	8.8
July 2009	10.2	10.8	7.7
August 2009	.	.	.
September 2009	.	.	.
October 2009	9.5	7.6	8.1
2009	10.0	8.8	9.7
	-------------------------	Load (kg ha^{-1})	-------------------------
April 2009	0	2.7	9.2
May 2009	0.1	0.3	0.5
June 2009	0.4	1.0	2.2
July 2009	0.5	0.6	0.9
August 2009	0	0	0
September 2009	0	0	0
October 2009	0.7	0.7	0.9
2009	4.9	5.3	13.7

Table A.4 Flow weighted DOC concentrations and load per watershed: Block 3 in 2010

Month/Year	Interim-1	Interim-2	Interim-3
	Concentrations (mg L^{-1})		
April 2010	13.0	13.1	.
May 2010	11.8	8.3	8.5
June 2010	5.8	6.0	6.6
July 2010	8.1	7.1	6.3
August 2010	4.3	8.2	6.2
September 2010	14.0	10.3	10.7
October 2010	.	.	.
2010	5.2	7.2	6.5
	Load (kg ha^{-1})		
April 2010	0.6	0.8	6.1
May 2010	0.8	0.8	2.1
June 2010	2.0	2.7	5.9
July 2010	0.0	0.1	0.4
August 2010	5.2	4.3	14.0
September 2010	0.0	0	0.5
October 2010	0	0	0
2010	8.7	8.8	29.1

Table A.5 Flow weighted DOC concentrations and load per watershed: Block 4 in 2008 and 2009

Month/Year	Orbweaver-1	Orbweaver-2	Orbweaver-3
	Concentrations (mg L^{-1})		
April 2008	7.8	6.9	6.3
May 2008	8.7	.	9.7
June 2008	9.5	5.6	7.3
July 2008	7.6	6.4	6.5
August 2008	.	7.3	.
September 2008	8.5	7.4	.
October 2008	.	.	.
2008	9.3	5.8	7.3
	Load (kg ha^{-1})		
April 2008	0.3	0.1	0.1
May 2008	0.1	0	0.1
June 2008	4.2	2.5	3.5
July 2008	1.1	0.8	0.1
August 2008	0	0.0	0
September 2008	0.0	0.1	0
October 2008	0	0	0
2008	6.4	3.5	3.8
	Concentrations (mg L^{-1})		
April 2009	5.9	5.8	.
May 2009	.	6.4	7.4
June 2009	12.6	8.7	8.6
July 2009	11.1	16.0	5.9
August 2009	.	.	.
September 2009	.	.	.
October 2009	12.2	.	9.8
2009	11.4	7.3	7.7
	Load (kg ha^{-1})		
April 2009	0.0	0.7	0.1
May 2009	0	0.0	0.3
June 2009	0.2	0.1	0.2
July 2009	0.1	0.3	0
August 2009	0	0	0
September 2009	0	0	0.2
October 2009	0.2	0	0
2009	0.5	1.2	0.9

Table A.6 Flow weighted DOC concentrations and load per watershed: Block 4 in 2010

Month/Year	Orbweaver-1	Orbweaver-2	Orbweaver-3
	Concentrations (mg L^{-1})		
April 2010	.	11.0	11.7
May 2010	.	6.5	6.4
June 2010	.	5.9	5.4
July 2010	.	9.3	13.8
August 2010	.	3.1	4.5
September 2010	.	12.8	11.3
October 2010	.	.	.
2010	.	4.1	5.0
	Load (kg ha^{-1})		
April 2010	0	0.2	0.8
May 2010	0	0.6	1.0
June 2010	0.3	2.1	2.8
July 2010	0	0.2	0.0
August 2010	2.4	6.2	7.9
September 2010	0.1	0.0	0.1
October 2010	0	0	0
2010	2.9	9.2	12.6

Table A.7 Summary of flow weighted DOC concentrations and load from experimental watersheds

	n	Mean	Median	Maximum	Minimum
Flow weighted concentrations (mg L^{-1})					
2008-2010	35	7.7	7.4	11.5	4.1
2008 Monthly	66	9.4	8.4	33.1	3.5
2009 Monthly	50	9.7	9.2	26.9	5.6
2010 Monthly	64	7.9	7.1	26.8	3.1
DOC load (kg ha^{-1})					
2008-2010	34	10.9	9.2	44.1	0.5
2008 Monthly	84	1.3	0.3	12.3	0
2009 Monthly	84	0.7	0.2	9.2	0
2010 Monthly	84	2.4	0.8	15.2	0

Table A.8 Summary table of analysis of treatment temporally on DOC concentration and load

Period	DOC concentration n	p	DOC load n	P
2008-2010	35	0.09	34	0.04
2008	12	0.63	11	0.49
2009	11	0.18	11	0.43
2010	12	0.11	11	0.09
Spring 2008	NA*	NA	11	0.74
Summer 2008	NA*	NA	11	0.39
Fall 2008	NA*	NA	11	0.48
April 2008	11	0.16	12	0.42
May 2008	10	0.26	12	0.68
June 2008	11	0.58	12	0.28
July 2008	11	0.70	12	0.52
August 2008	7	0.002	12	0.48
September 2008	11	0.50	12	0.39
October 2008	NA**	NA	12	0.51
Spring 2009	NA*	NA	11	0.33
Summer 2009	NA*	NA	11	0.64
Fall 2009	NA*	NA	11	0.14
April 2009	9	0.31	12	0.25
May 2009	10	0.13	12	0.06
June 2009	11	0.14	12	0.47
July 2009	10	0.51	12	0.62
August 2009	NA**	NA**	NA**	NA**
September 2009	NA**	NA**	NA**	NA**
October 2009	10	0.38	12	0.24
Spring 2010	NA*	NA	11	0.12
Summer 2010	NA*	NA	11	0.21
Fall 2010	NA*	NA	11	0.06
April 2010	9	0.46	12	0.10
May 2010	11	0.99	12	0.27
June 2010	11	0.76	12	0.19
July 2010	11	0.85	12	0.39
August 2010	11	0.41	12	0.03
September 2010	11	0.55	12	0.17
October 2010	NA**	NA**	NA**	NA**

*PROC GLM was not performed on seasonal DOC concentrations as no treatment effects on monthly DOC concentrations were noted.
**No runoff data recorded or samples collected due to low precipitation during these months
Spring months are April and May, Summer months are June and July,
Fall months are August, September, and October

Table A.9 Seasonal DOC load exported in surface runoff

Treatments	Spring	Summer	Fall
	---------------------------------kg ha^{-1}----------------------------		
2008			
100% Agriculture	1.79	11.03	0.37
10% NPV footslope	0.58	4.75	0.17
10% NPV contours	1.95	8.58	1.16
20% NPV contours	1.37	5.36	0.50
2009			
100% Agriculture	5.24	2.98	1.36
10% NPV footslope	1.26	0.95	0.65
10% NPV contours	3.43	2.74	0.64
20% NPV contours	1.19	1.84	0.85
2010			
100% Agriculture	8.21	7.46	12.90
10% NPV footslope	2.02	3.51	3.81
10% NPV contours	1.67	4.91	7.80
20% NPV contours	1.59	5.43	8.37

Spring months are April and May, Summer months are June and July,
Fall months are August, September, and October

Table A.10 Total DOC load exported in surface runoff

	100% Agriculture	10% NPV at footslope	10% NPV contours	20% NPV contours
	---kg ha^{-1}---------------------------------------			
Fall 2010	12.9a	4.2b	7.8ab	8.4ab
May 2009	0.55a	0.15ab	0.12b	0.06b
August 2010	12.4a	3.4b	7.6b	8.1a

Numbers followed by a common letter within a row indicates no significant differences existed between those treatments.

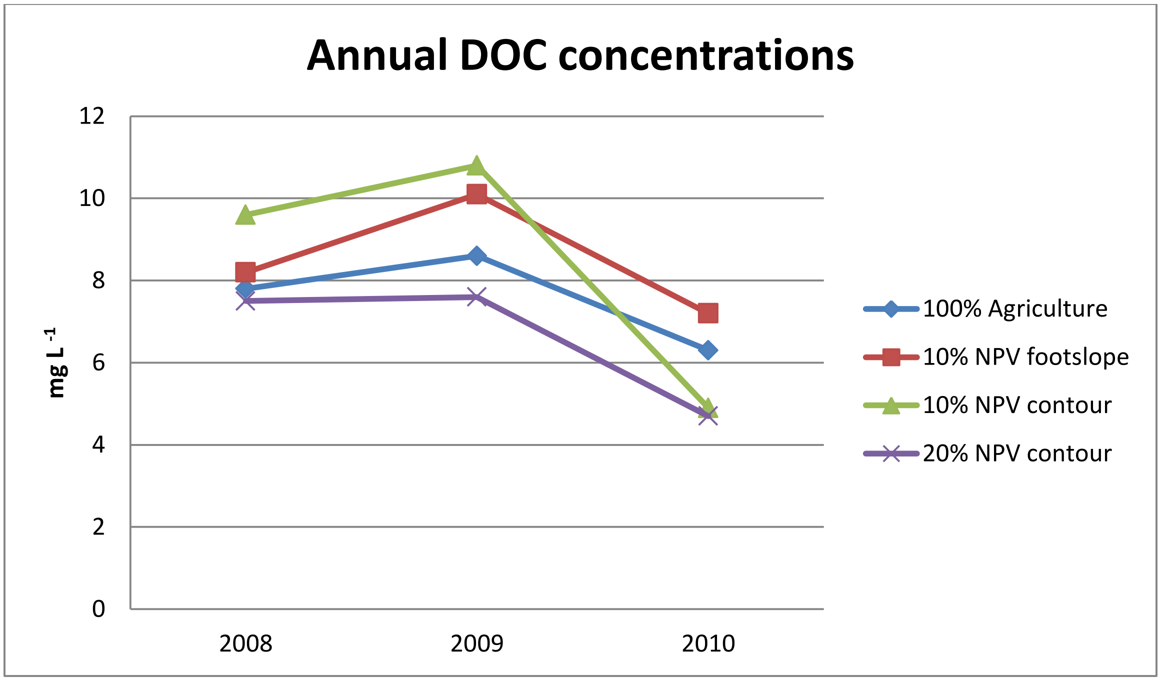

Figure A.1 Annual flow weighted DOC concentrations (2008-2010)

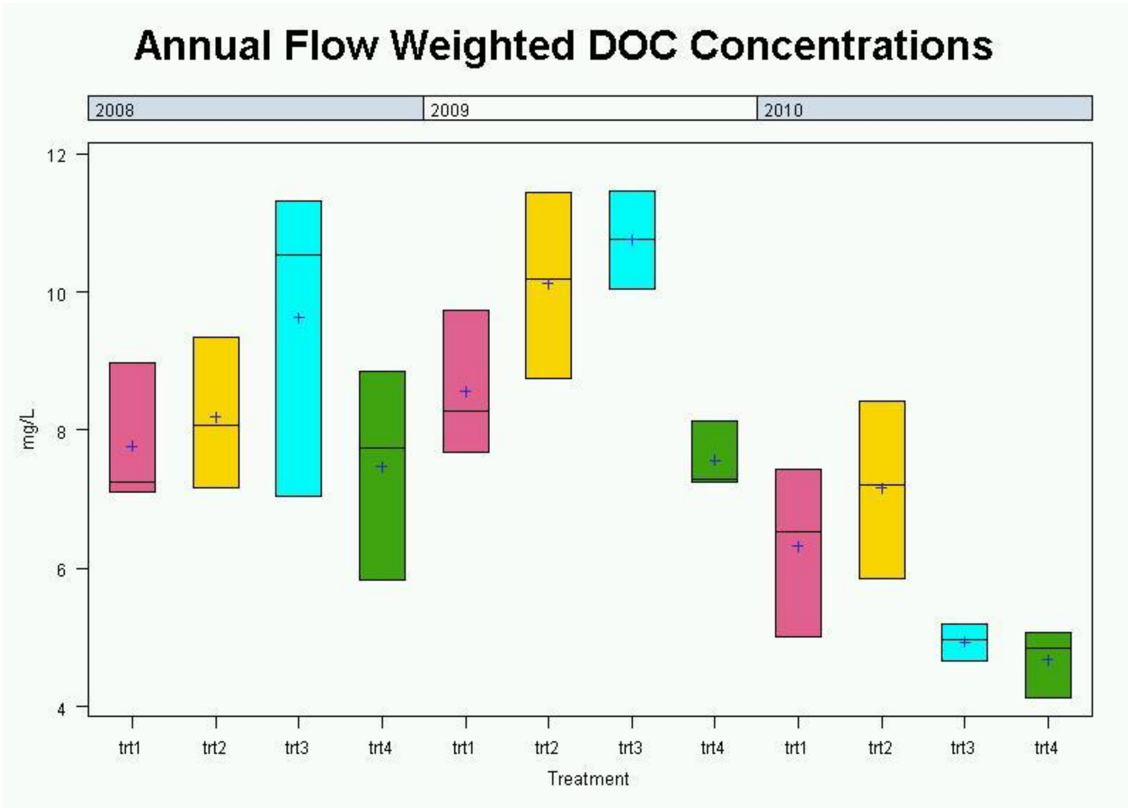

Figure A.2 Annual flow weighted DOC concentrations: Box plots (2008-2010). Treatment (trt) 1: 100% agriculture, trt 2: 10% NPV at footslope, trt 3: 10% NPV in contours, trt 4: 20% NPV in contours
This figure shows the variability in DOC concentration means for the three watersheds assigned to the same treatment.

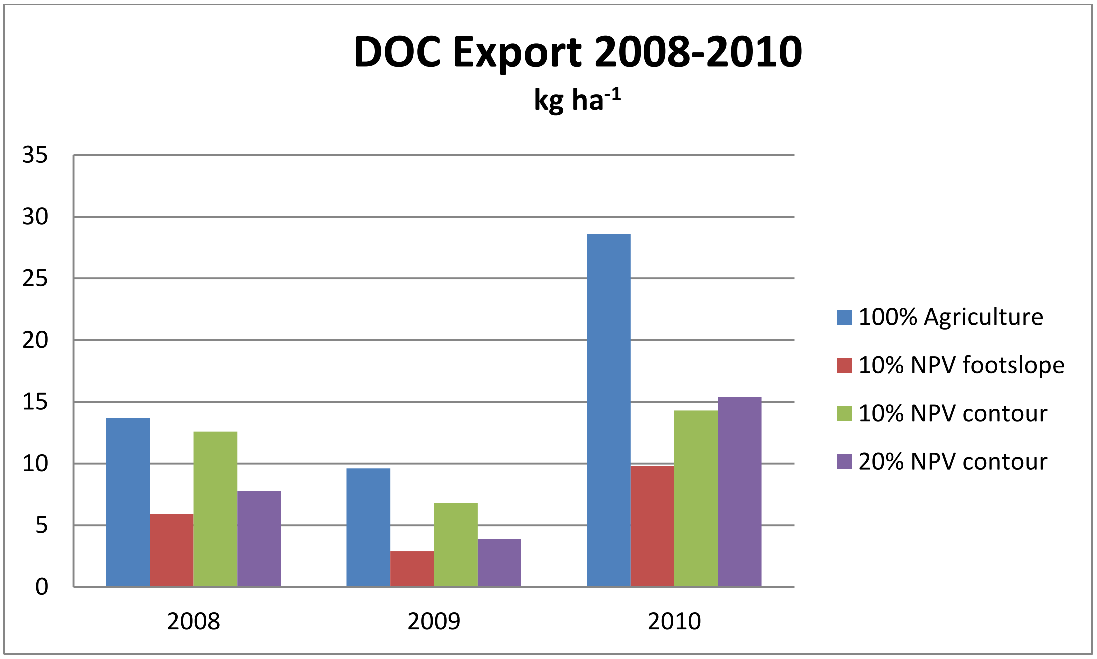

Figure A.3 Total DOC load exported in surface runoff over the study period (2008-2010)

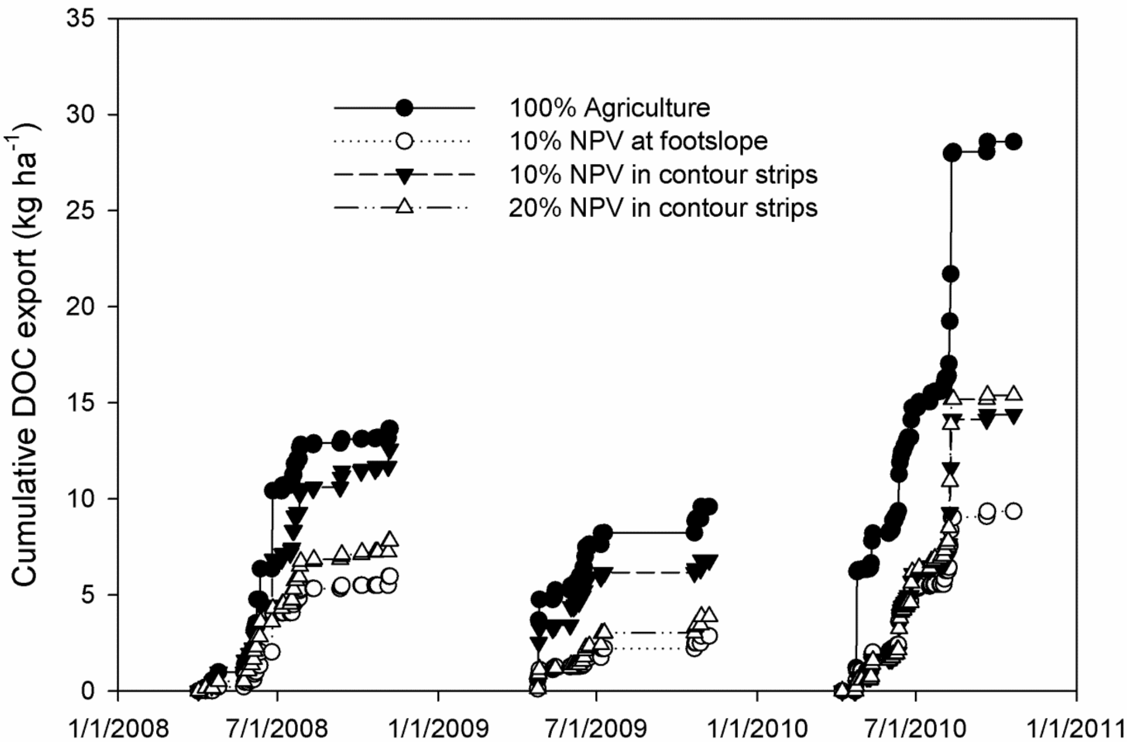

Figure A.4 Cumulative DOC export from the four treatments 2008-2010

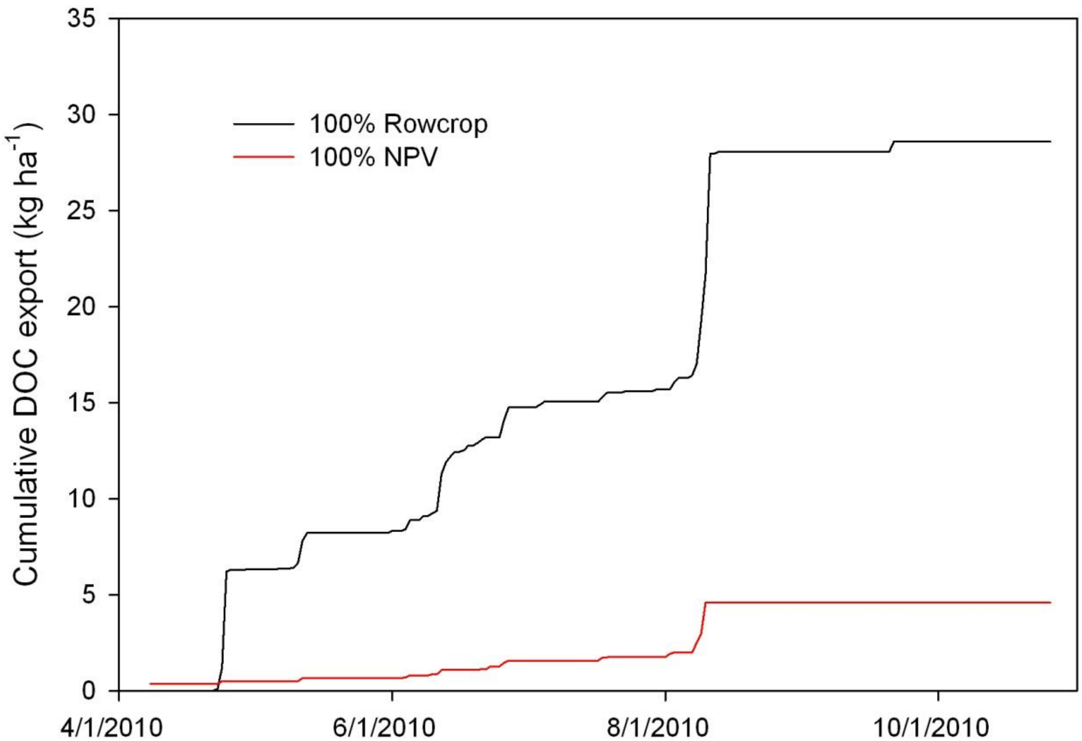

Figure A.5 Cumulative DOC export from 100% agricultural (row-crop) and 100% NPV watersheds (2010)

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