

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 because it is mobile and biologically active. Agricultural conservation practices such as native perennial vegetation (NPV) strips will influence carbon cycling of an upland agroecosystem, and could affect how much DOC enters streams in runoff, potentially affecting aquatic ecosystems. In a study conducted in Iowa (USA), four treatments with strips of NPV varying in slope position and proportion of area were randomly assigned among 12 small agricultural watersheds in a balanced incomplete block design. Runoff samples from 2008 to 2010 were analyzed for DOC and correlated with flow data to determine flow weighted DOC concentrations and loads. Data were analyzed for the entire 3 years, annually, seasonally, monthly, by flow event size and for one extreme storm event. Overall we found few differences in DOC

concentration with the exception that concentrations were greater in the 10 % NPV at the footslope watersheds than the 20 % NPV in contours watersheds over the 3 years, and the 100 % agricultural treatment had higher DOC concentrations than all NPV treatments during the one extreme event. Because the NPV treatments reduced runoff, DOC export tended to be highest in the 100 % agricultural watersheds over the 3 years and during high flows. We also compared two watersheds that were restored to 100 % NPV and found decreases in DOC concentrations and loads indicating that complete conversion to prairie leads to less watershed DOC export. Regression results also support the contention that increases in the percentage of NPV in the watershed decreases watershed export of DOC. Further analysis indicated that DOC concentrations were diluted as flow event size increased, independent of any treatment effects. It appears groundwater sources become an important component to flow as flow event size increases in these watersheds.

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Introduction

The benefits of native perennial vegetation (NPV) strips are often associated with influencing sediment and nutrient transport rather than their influence on carbon cycling within a watershed. However, as soil in

buffer strips is not subject to traditional agricultural cultivation practices, it may also accumulate more organic matter and carbon than surrounding row-crop soil (Borin et al. 2010). Because NPV strips have been shown to reduce erosion from agricultural watersheds, they may also be a viable management option to reduce carbon losses.

Loss of dissolved organic carbon (DOC) from agricultural watersheds can decrease the quality of downstream water by its association with the transport and bioavailability of pesticides, heavy metals such as mercury, and organic forms of nutrients (Royer et al. 2007; Avalos et al. 2009; Dittman et al. 2009; Veum et al. 2009; Stanley et al. 2012). DOC influences many ecological processes in aquatic ecosystems including biological respiration and metabolism, nutrient uptake, acidity, light penetration and water temperature (Xenopoulos and Schindler 2001; Stanley et al. 2012). Incorporation of management practices which promote carbon sequestration such as NPV into agricultural watersheds may influence the concentrations, quality and total amount of DOC exported to surface water.

Terrestrial DOC sources and hydrological mobilization of the sources are the two main factors controlling export of DOC from a watershed (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 conversion to agriculture has been shown to change downstream DOC quality towards lower molecular weight, more labile DOC compounds which can fundamentally change aquatic ecosystem productivity (Wilson and Xenopoulos 2009). Land use, organic material and fertilizer applications, conservation tillage, crop rotation, and irrigation influence DOC production in Midwestern US regions (Chantigny 2003; Royer and David 2005; Warrner et al. 2009). These factors can also influence hydrology and flow patterns, and consequently carbon transport to surface waters (Raymond and Saiers 2010) as expressed by the concentrations and total amount of DOC exported from a watershed. Chantigny (2003) suggested that based on the available literature, the trends in DOC from agricultural vs. grassed watersheds have not yet been clearly identified.

Precipitation amount and storm intensity also have a direct correlation to total amount of DOC lost from agricultural watersheds (Royer and 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). Royer and David (2005) and Vidon et al. (2008) found that storm precipitation characteristics had a greater affect on DOC concentrations and export than watershed land use in Midwestern US agricultural regions.

Higher concentrations of carbon in near surface soil than in lower soil horizons suggest that rainfall events that produce overland and near surface flow will have high DOC concentrations (Inamdar et al. 2004; Sanderman and Amundson 2009). McDowell and Likens (1998) reported for forest systems that 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. Farming systems that minimize or eliminate tillage will minimize disruption of the soil A horizon and may decrease the amount of DOC exported through overland runoff (Avalos et al. 2009). Thus, it is important to understand which practices retain the greatest amount of carbon within a watershed to maintain soil quality and diminish negative impacts on downstream surface waters. Moreover, it is critical to determine how certain agricultural practices such as conservation tillage, or establishment of conservation cover as NPV can influence DOC export from row-crop watersheds. Conservation practices such as embedding grass or NPV strips into row-crop agriculture have shown environmental benefits that include higher nutrient retention (Schmitt et al. 1999), lower surface runoff (Veum et al. 2009) and sediment transport (Udawatta et al. 2006), however, little is known on how these conservation practices will affect the hydrologic transport of carbon to surface waters and the possible downstream implications.

To date, we have presented results on the effect of NPV strips on surface runoff (Hernandez-Santana et al. 2013), nutrient concentration and transport (Zhou et al. 2014), and sediment transport (Helmers et al. 2012). Here we characterize the effect of NPV strips on DOC concentrations and loads. The first objective of this study is to determine the effect of varying amounts and slope positions of NPV buffer strips in small agricultural watersheds on concentrations and total amounts of DOC exported in surface runoff. A second objective is to determine whether a relationship exists between event size and DOC concentrations and loads.

Materials and methods

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). NPV cover treatments were randomly assigned to 12 agricultural watersheds ranging in size from 0.47 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 (Fig. 1). Slope varies from 6.1 to 10.5 % in the watersheds. Prior to initiation of the experiment in 2007, all watersheds were planted in brome grass (*Bromus L.*) for at least 10 years. The establishment of a no-till corn-soybean (*Zea mays L./Glycine max (L.) Merr.*) 2-year rotation began in spring 2007 with the planting of soybeans. Crop rotation was identical in all watersheds.

Treatments applied to the watersheds consist of NPV buffer strips varying in location and percentage of the total area within each agricultural watershed. One of four treatments was randomly assigned to each watershed (Fig. 1; Table 1). Three watersheds were planted in 100 % row-crops (100 % agricultural treatment), three with 10 % of the total area planted in NPV only in the footslope position (10 % NPV footslope treatment), three with 10 % of their area in NPV divided into two strips; one on the backslope and one in the footslope position (10 % NPV contour treatment), and three watersheds with 20 % in NPV with strips on the backslope and footslope positions (20 % NPV contour treatment). In July 2007, NPV buffer 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.*). The use of native prairie species in the strips was consistent with the NSNWR goal to re-establish native prairie ecosystems on refuge lands, and the locations for the experiment were scheduled for prairie restoration after 2014.

The NPV strips varied in width from 37 to 78 m in the footslope position, and from 3 to 10 m on the backslopes. Additionally, two watersheds were planted in 2004 with 100 % NPV (i.e. restored to prairie) as described by Tomer et al. (2010). Because these watersheds are not included in the replicated

study design, a paired *t* test statistical analysis is used to present the data and compare DOC concentrations and total export with the results from the twelve study watersheds.

The soils are similar between study watersheds with Mollic Hapludalf and Oxyaquic Argiudolls the two main soil types. Upper soil horizons consist of 7–10 % sand, 63–68 % silt, and 25–28 % clay and have a bulk density of 1.4 g cm⁻³ (Zhou et al. 2010). Total soil organic carbon per hectare was calculated by analysis of percent carbon in soils to a depth of 15 cm. Soil types and textures are similar at the 100 % NPV sites and are classified as Typic Argiudolls, Aquertic Argiudolls, and Mollic Hapludalfs, and have a bulk density of 1.3 g cm⁻³ in the upper soil horizons (Schilling et al. 2007; Tomer et al. 2010).

Sample collection and analysis

Flumes (H-type) were installed below the footslope of each watershed to measure runoff flow volumes, and these flumes were instrumented with automated carousel-type water samplers (ISCO model 6712; ISCO, Inc., Lincoln, NE, USA). The samplers were supplied with pressure transducers (720 Submerged Probe Module) to measure flow stage, from which discharge volumes were calculated based on rating curves published for the H-type flume. The samplers were programmed to collect 300 ml of runoff water for every 1 mm of watershed runoff entering the flume. Sampling occurred from April through October, and the samplers were removed in November and re-installed around April 1 each year to avoid freeze damage. Samples were retrieved within 24 h of each rainfall-runoff event, passed through 0.45 µm glass fiber filter, acidified with 10 % sulfuric acid to a pH of 2.0, and refrigerated at 4 °C until analysis. For the 3 years of this study (2008–2010), a total of 2,121 runoff samples were analyzed for DOC. In the pair of 100 % NPV watersheds, samples were only collected for DOC analysis in 2010.

Runoff samples 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

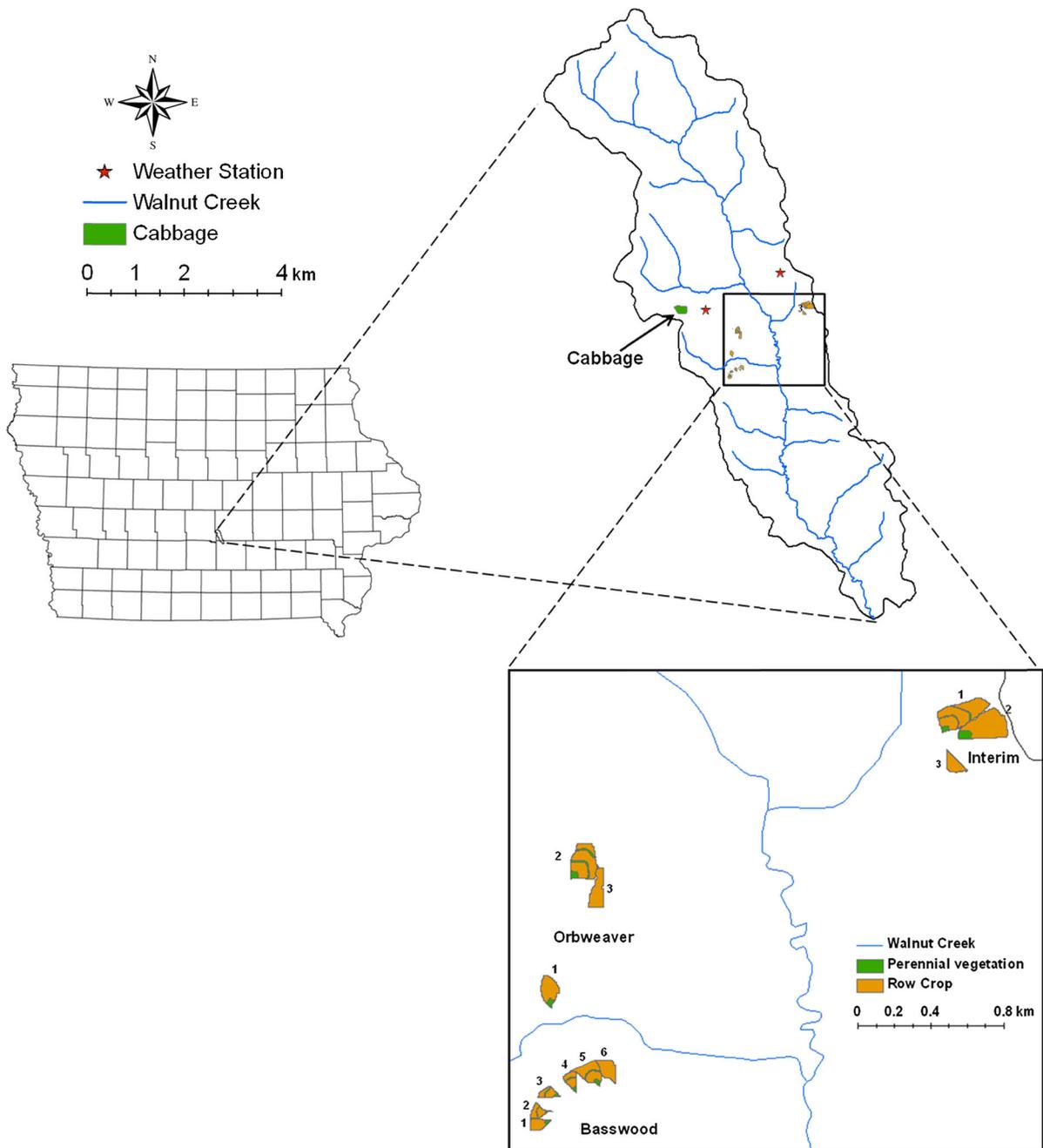


Fig. 1 Location of experimental watersheds at the NSNWR and experimental treatments. One of four treatments were randomly assigned to 12 watersheds. Two additional watersheds

standards and blanks were included as checks, and duplicate analyses were performed every 10 samples to ensure quality control. Ninety-one percent of duplicate results were within 10 % of each other and the mean percent difference between duplicates was

(Cabbage) were planted in 100 % NPV but are not a part of the balanced incomplete block design

4.2 % with a standard error of 0.4 %. Due to mechanical problems with the ISCO sampler in the Basswood-5 watershed in 2009 and in the Orbweaver-1 watershed in 2010, data were not included in statistical analysis for those respective years.

Table 1 Watershed descriptions and assignment of treatments at the NSNWR, Iowa, USA

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 and 5 % upslope
Basswood-3	1	0.47	6.4	10 % at footslope and 10 % upslope
Basswood-4	2	0.55	8.2	10 % at footslope and 10 % upslope
Basswood-5	2	1.24	8.9	5 % at footslope and 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, and 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, and 6.7 % at upslope
Orbweaver-3	4	1.24	6.6	100 % agriculture

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

Runoff was calculated as a flow-weighted volume per event. There were 21, 15, and 24 rainfall-runoff events in 2008, 2009, and 2010 respectively. Occasionally, smaller consecutive events were integrated into one event. Runoff events for 2010 were grouped as large events (producing >10 mm runoff, averaged among all watersheds), mid-size events (2–10 mm runoff) and small events (<2 mm runoff) for further analysis.

Precipitation

Precipitation data were obtained from a National Weather Service Mesonet weather station 1.3–3.6 km from the watersheds, and a US 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.

Calculations and statistical analysis

Daily DOC concentrations (mg l^{-1}) were multiplied by flow (l d^{-1}) to determine total export of DOC (kg). Daily totals were summed to get annual amounts, and normalized by watershed area to allow comparisons of export among the different-sized watersheds on a unit-

area basis. 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, USA) to analyze the data over the full 3-year period (2008–2010), annually, seasonally, monthly, and for a large rainfall event that occurred 8–11 August 2010, to determine how flow weighted DOC concentrations and total loads compared among treatments. The GLM uses the least squares means function followed by a Tukey–Kramer adjustment to determine the difference between treatments. The SAS mixed model for differences in least squares means was used to compare DOC concentrations with 2010 runoff data. Also for 2010, we assessed DOC concentrations and loads by event size using the least squares means function followed by a Tukey–Kramer adjustment to determine the difference between treatments. Linear and nonlinear regression approaches were used to assess relationships between DOC concentration and suspended sediment concentration. Statistically significant differences are reported at an α -level of 0.10.

Flow and DOC measurements from the two watersheds containing 100 % NPV are only available for 2010, and because they are located adjacent to one

another and not randomly assigned to a treatment, they are not part of the balanced incomplete block design. We considered the two watersheds as replicates so for each event we compared the mean DOC concentration and load of the 100 % NPV watersheds to the mean of the treatment watersheds using a paired two-tailed *t* test analysis. Similarly we used a paired two-tailed *t* test to compare 100 % NPV watershed DOC concentrations and loads to the treatment watersheds across our event size categories. We used this approach to determine if DOC export was different between watersheds that had 100 % NPV vs. dominantly agricultural land use. This approach can be used as a guide regarding what could be perceived as differences in concentrations and export of DOC from the two 100 % NPV watersheds and the treatment watersheds.

To further assess the effects of treatment and watershed properties on DOC concentrations we regressed volume weighted DOC concentrations from 2010 (when data was available to include the 100 % NPV) with area of strips, percent area of strips in the watershed, area of strips at the footslope, percent area of strips in the watershed at the footslope, and overall watershed area and slope. We investigated both linear and data transformed single parameter regressions and multiple regressions. One single parameter regression model involving the log of the percent of the watershed area in strips had a statistically significant relationship and is presented. In a second analysis we assessed the relationship between the log of the DOC concentrations and the log of surface runoff volume by treatment to assess if DOC concentrations increase (concentrate) or decrease (dilute) with runoff volume, and if there is an effect of treatment on this relationship (Tomer et al. 2003). Non-overlapping differences in the 95 % confidence interval of relationship's slope and the y-intercept indicate treatment differences.

Results and discussion

Precipitation

Total precipitation exceeded the long term mean precipitation of 682.2 mm during all 3 years of the study (2008–2010). Rainfall during the growing season (April through October) ranged from 811.1 mm in 2009 to 1,220.9 mm in 2010 (Table 2). An extreme

Table 2 Monthly precipitation from April through October for the NSNWR, Iowa, USA

Month	2008 (mm)	2009 (mm)	2010 (mm)	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	1,220.9	682.2

Adapted from Helmers et al. (2012). Normal precipitation represents the 30-year average

Table 3 Mean flow weighted DOC concentrations and total DOC load in surface runoff from experimental watersheds at the NSNWR, Iowa, USA

Year	100 % agriculture	10 % NPV footslope	10 % NPV contours	20 % NPV contours
DOC concentration (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	8.5a	8.4ab	6.6b
DOC load (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

event occurred from 8 to 11 August 2010, with 249 mm of rain received during this four-day period, of which 109 mm fell on 10 August 2010. Rainfall during August 2010 was 373 mm, which was more than half of the mean annual rainfall and more than three times greater than the mean precipitation for August.

Three year flow weighted DOC concentrations

When expressed on a mean flow-weighted basis over the 3-year period (2008–2010), variation in DOC concentrations among the treatments was relatively small, ranging from 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 ($p = 0.07$) (Table 3). Dalzell et al. (2005) found similar concentrations for an agricultural headwater system in Indiana during high flows (6.4 mg l^{-1}) but found concentrations much lower during baseflow conditions (1.3 mg l^{-1}). However, the DOC concentrations we observed were greater than those in stream waters fed by subsurface drained croplands in Minnesota (agricultural ditch = 3.38 mg l^{-1} and stream = 4.78 mg l^{-1} ; Dalzell et al. 2011). Over the 3-year period, runoff from watersheds with 10 % NPV at the footslope had significantly higher DOC concentrations than runoff from watersheds with 20 % NPV placed in contours.

Total runoff during 2008–2010, when compared to the 100 % agricultural watersheds, was decreased by 59 % for watersheds with 10 % NPV at footslope and by 27 % for watersheds with 20 % NPV in contour strips (Hernandez-Santana et al. 2013). The greater relative decrease in runoff volume under the 10 % NPV treatment could explain the relatively high concentrations in 10 % NPV at footslope and low average concentration in the 20 % NPV watersheds as a dilution effect. 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 3-year period were reported from 10 % NPV at footslope watersheds (Helmers et al. 2012), precipitation retention was greatest in those watersheds. Thus, a concentration effect in the runoff water resulted in significantly greater concentrations of DOC than from the 20 % NPV watersheds. The lower water retention in the 20 % NPV watersheds led to lower DOC concentrations primarily due to shorter contact time between precipitation and soil. The closer similarity in runoff between 20 % NPV and 100 % agricultural watersheds when compared to the 10 % NPV at the footslope and 100 % agricultural watersheds could explain the similarity in DOC concentrations. Runoff from 100 % agricultural watersheds was only significantly different than from 10 % NPV at footslope watersheds (Hernandez-Santana et al. 2013). 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 DOC concentrations. Also, differences in flow pathways could influence rate and

source areas of surface runoff which could lead to differences in DOC concentrations.

Annual 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). Annual data analyzed separately showed no significant differences between treatments for any year from 2008 to 2010. 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; Johnson et al. 2009). DOC concentrations were compared with sediment concentrations for 2010. We found no relationship between DOC concentrations and suspended sediment concentrations for individual treatments or all treatments combined (data not shown).

Monthly and seasonal flow weighted DOC concentrations

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. Similar seasonal analyses showed no significant differences (data not shown). The result that DOC concentrations did not significantly differ between treatments on a monthly basis in this study suggests that the nature of plant material supplying leachable carbon (e.g. leftover crop residue, growing or senescing vegetation) has little influence on DOC concentrations in surface runoff. In this study, concentrations did not vary substantially or decline over the growing season implying that the DOC source pools (i.e. above and belowground vegetation and soil carbon) in the watersheds were not depleted during this study period.

Extreme storm event flow weighted DOC concentrations

During the high intensity, lengthy storm event from 8 to 11 August 2010, the presence of NPV treatments in the watersheds significantly decreased DOC concentrations in runoff water. The lowest mean concentration was in the 10 % NPV in footslope watersheds

Table 4 Mean flow weighted DOC concentrations and total DOC load in surface runoff, 8–11 August 2010 from experimental watersheds at the NSNWR, Iowa, USA

100 % agriculture	10 % NPV footslope	10 % NPV contours	20 % NPV contours
DOC concentration (mg l^{-1})			
5.5a	3.3b	4.0b	3.6b
DOC load (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

(3.3 mg l^{-1}), and the highest was in the 100 % agricultural watersheds (5.5 mg l^{-1}) (Table 4).

Soil saturation during this storm event promoted 25 % greater runoff in the 100 % agricultural watersheds when compared to the NPV watersheds (Helmert et al. 2012). The relationship between runoff and DOC concentrations could account for the significantly lower concentrations from the NPV watersheds. Under nearly saturated soil conditions, solute depletion, runoff dilution, increased groundwater seepage with a rising water table (and subsequent dilution), and increased overland flow factor into lower DOC concentrations in surface runoff during large events (Dalzell et al. 2005). Thus, DOC concentrations were notably lower during this single storm than for annual means.

Three year total DOC load exported

Mean DOC exported over the 3-year period 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 (Table 3). DOC exported represents a range of 0.01 % of total soil carbon in 10 % NPV in the footslope position watersheds to 0.03 % of soil carbon in 100 % agriculture watersheds. DOC loads reported in this study are similar to values reported by Royer and David (2005) in an Illinois study (agricultural watershed means range from 8.7 to 10.9 kg ha^{-1}) and our 100 % agricultural watersheds are similar to DOC loads in agricultural watersheds in Indiana (14.1 – 19.5 kg ha^{-1} , Dalzell et al. 2007). Interestingly, average annual precipitation tends to be considerably higher in Indiana (940 mm yr^{-1}) and Illinois ($1,053 \text{ mm yr}^{-1}$) than at the NSNWR (903 mm yr^{-1}), but DOC export is similar. This is

likely a result of the higher than average precipitation years during this study.

From analysis over the 3-year study period, the treatment effect was significant in that the presence of NPV buffer strips (10 % in footslope and 20 % in contours) significantly decreased the mass load of DOC exported in surface runoff as compared to the 100 % agricultural watersheds. 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 presence of NPV buffer strips thus influenced total DOC exported to varying degrees. Compared to the 100 % agricultural watersheds, NPV buffer strips reduced the amount of DOC exported by 64 % from the 10 % NPV at footslope and 48 % from the 20 % NPV in contour strip watersheds. This correlates with a reduction in runoff in watersheds containing NPV buffer strips as compared to 100 % agricultural watersheds (Hernandez-Santana et al. 2013).

The establishment of NPV buffer strips in agricultural watersheds has been shown to effectively reduce surface runoff (Veum et al. 2009; Helmert et al. 2012; Hernandez-Santana et al. 2013). Jacinthe et al. (2004) reported that carbon losses were proportional to runoff. Similarly, Brye et al. (2001) found that leaching volume was responsible for double to quadruple DOC loads leaching from agricultural watersheds when compared with prairies. The overall reduction in export from these NPV treatment watersheds shows the effectiveness of incorporating NPV buffer strips in agricultural watersheds, more convincingly than results from a similar experiment reported by Veum et al. (2009). Veum et al. (2009) had a similar watershed design as this study, though factors associated with hydrology of the Missouri site's claypan soils led to high variability in DOC concentrations and loads. 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 although the grassed buffer treatments did significantly reduce surface runoff from their experimental watersheds.

Placing the 10 % NPV at the footslope position resulted in smaller DOC loads when compared to placing the 10 % NPV in contour strips throughout the watershed. DOC loads were not statistically different between the 10 % NPV in contour strips and 100 % agricultural watersheds. This suggests that a wide

buffer strip in the footslope position will help decrease DOC loads to streams in agricultural watersheds.

Annual 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 28.6 kg ha⁻¹ in the 100 % agriculture watersheds in 2010 (Table 3). There were no significant differences 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, leading to differences in the 3-year mean DOC loads but not in individual years. This result demonstrates the value in multi-year evaluations as single year studies would have led to the interpretation that NPV buffer strips have no effect on DOC loads.

Monthly and seasonal DOC load exported

Significant treatment effects on monthly DOC export were minimal, only observed during May 2009 ($p = 0.06$) and August 2010 ($p = 0.03$) (data not shown). Similar to flow weighted DOC concentrations, it appears that DOC loads are not influenced by carbon availability related to the type and timing of the senescence of plant material but more likely controlled by soil organic matter (SOM) degradation as it affects availability and loss from soils. Also, similar to flow-weighted DOC concentration, few seasonal differences in DOC loads occurred among treatments. The only seasonal difference found was summer 2010 when the extreme 4-day event occurred (see discussion below), and 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).

Extreme storm event DOC load exported

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 load

exported from the 10 % NPV at footslope watersheds differed significantly from that exported from 100 % agricultural watersheds (Table 4). Total DOC exported from watersheds containing 10 % NPV at the footslope position was 76 % less than that exported from 100 % agricultural watersheds. DOC export during this storm showed similar trends with surface runoff greatest from 100 % agricultural watersheds, followed by 20 % NPV in contours, 10 % NPV in contours, and 10 % NPV at footslope (Helmert et al. 2012).

Effects of storm size on DOC loads and concentrations

Flow weighted DOC concentrations and loads did not differ significantly between treatments for small storm events (<2 mm runoff, averaged among all watersheds) or mid-size events (2–10 mm runoff) in 2010. Treatment effects were noted during large events (>10 mm runoff) on DOC loads ($p = 0.0002$) but not concentrations (Table 5). During large runoff events, DOC exported from 100 % agricultural watersheds were greater than from the NPV watersheds.

100 % NPV watersheds

Mean flow weighted DOC concentration (4.0 mg l⁻¹) and annual load (4.2 kg ha⁻¹) from 100 % NPV watersheds in 2010 were statistically less than DOC concentrations and loads from all other watershed treatments. The annual load represented 0.007 % of total soil carbon in the top 15 cm of soil in the 100 % NPV watersheds. It is apparent that conversion of an entire watershed to prairie dramatically decreases DOC concentrations and runoff (by about 50 %, Helmert et al. 2012), leading to much lower loadings of DOC. Although there have been a few studies assessing runoff or stream DOC concentrations in grassland watersheds (e.g. Frank et al. 2000) we found only one study that reported DOC in runoff from native or restored prairie watersheds. For streams draining watersheds on the Konza Prairie in Kansas, median DOC concentrations ranged from 0.90 to 1.6 mg l⁻¹, and annual watershed fluxes ranged from 0.2 to 7.5 kg ha⁻¹ yr⁻¹ over the 10 years of monitoring (Eichmiller 2007). Generally, these concentrations are lower than we found but the loads fall within the range of Eichmiller (2007) indicating more runoff

Table 5 Comparison between the mean flow weighted DOC concentrations and total DOC loads in 100 % NPV watersheds and treatment watersheds across a gradient in event size

Event size	100 % NPV	100 % Agriculture	10 % NPV footslope	10 % NPV contours	20 % NPV contours
DOC concentration (mg l ⁻¹)					
Small	3.4	4.7a	6.0a ^a	4.2a	5.8a ^a
Medium	2.9	7.5a ^a	8.1a ^a	7.0a ^a	7.0a ^a
Large	3.1	5.5a ^a	3.9a	5.1a ^a	4.2a
DOC load (kg ha ⁻¹)					
Small	0.02	0.14a ^a	0.06a ^a	0.07a ^a	0.09a ^a
Medium	0.09	0.76a ^a	0.27a ^a	0.25a ^a	0.28a ^a
Large	0.47	2.22a ^a	0.79b	1.41b ^a	1.45b ^a

Numbers followed by a common letter within a row indicates no significant differences existed between the treatment watersheds (100 % NPV not included)

^a Difference between the 100 % NPV watersheds and the treatment watersheds

during their experiments in Kansas. This is likely due to higher groundwater inputs or lower evapotranspiration than for our 100 % NPV systems because annual precipitation is generally lower at the Konza Prairie (835 mm yr⁻¹) than at the NSNWR (903 mm yr⁻¹).

With a few exceptions, the 100 % NPV watersheds have lower DOC concentrations and loads than any of the treatment watersheds when analyzed by event size (Table 5). While this interpretation must be guarded because it is only based on 1 year of data, prairies appear to reduce transport of DOC when compared to row-crop systems, including those with NPV strips.

Controls on watershed DOC concentrations

When we regressed treatment and watershed parameters with DOC concentrations for 2010, one important relationship became apparent. Our data indicates that the log of the percent of the watershed in NPV is an important control on DOC concentrations at the watershed outlets. We log transformed the percent of the watershed in NPV to normalize the skewness of the data. We found that the log of the percent watershed in NPV had a negative relationship with DOC concentration [DOC (mg l⁻¹) = 6.5 + -1.18 (log percent watershed area in NPV), r² = 0.48] indicating that NPV strips are sinks for watershed level carbon with that sink increasing as NPV percent increases in the watershed. As compared to our *t* test approach above that also included the 100 % NPV watersheds, this novel result even better elucidates

that increasing the area of NPV improves carbon sequestration at the watershed level.

When we assessed if our NPV treatments influenced the log flow volume vs. log DOC concentration relationships (Tomer et al. 2003), we found that the 95 % confidence interval for nearly all the relationship slopes and y-intercepts overlapped indicating few treatment differences. However, the slope in all the relationships was <1 indicating dilution of DOC as event size increases, independent of treatment. The dilution relationships signify that readily transportable dissolved carbon sources become more finite as event size increases. This data supports that presented earlier that DOC concentrations were lower during our extreme storm event in 2010 and our analysis of storm event size where in most cases the DOC concentrations tended to be lower during the large events when compared to the small events (Table 5). Dalzell et al. (2005) found the contrary in streamflow from an agriculturally dominated watershed in Indiana where stormflow DOC concentrations were 5× baseflow concentrations and positive relationships between streamflow and DOC concentrations (Dalzell et al. 2007). Somewhat similar to our study, Royer and David (2005) found higher DOC concentrations during low flows than in high flows in three agricultural watersheds in Illinois. The flow vs. DOC concentration relationship appears to be controlled by variation in source waters over the event period with rising soil water generally leading to higher DOC concentrations with event size and more connection to low DOC groundwater sources leading to lower DOC concentrations with event size. In our study

watersheds it appears that groundwater plays an ever increasing role as event size increases. This result may at least partially explain why we saw few DOC concentration treatment differences.

Conclusions

Results from this study at the NSNWR show that incorporation of varying amounts of NPV into agricultural watersheds led to higher DOC concentrations in the 10 % NPV footslope landscape position. Also, DOC concentrations were highest in the 100 % agricultural watersheds during the extreme event. Differences in watershed DOC concentrations are possibly due to differences in water residence time, flow pathways, and concentration effects. Our flow size vs. DOC concentration analysis revealed that groundwater sources likely become an important component to flow as flow event size increases in these watersheds, independent of our treatments.

Over the 3 years of study, DOC loads in the 10 % NPV footslope and 20 % NPV contour watersheds were 36 and 52 % of that exported from the 100 % agricultural watersheds. The significance in DOC load reduction noted over the 3-year study period highlights the importance of conducting multi-year analyses instead of a singular year study. Also, we found no relationship between DOC concentrations and suspended sediment concentrations. DOC concentrations and loads from the 12 study watersheds were generally greater than from 100 % NPV watersheds in 2010 indicating that watersheds restored to 100 % prairie dramatically decrease export of DOC. Results from our regression analysis also support the assertion that increases in the percentage of NPV in the watershed decreases watershed DOC concentrations and presumably DOC export.

Combined, our results indicate that embedding even a small amount of NPV in agricultural watersheds, particularly in the footslope position, can markedly decrease DOC loads to downstream surface waters. Complete conversion of agricultural systems to restored prairie leads to even greater DOC load reductions. Those decreases in DOC loads will lead to less downstream transport of pesticides, heavy metals and organically bound nutrients, as well as provide the aquatic biological community with carbon substrates that are more similar to pre-settlement conditions.

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