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ORIGINAL RESEARCH

Storm Dissolved Organic Carbon Dynamics in an Artificially Drained Watershed of the US Midwest

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Abstract: This study investigates changes in the nature, concentrations, and fluxes of dissolved organic carbon (DOC) in tile drains (aka subsurface drains), overland flow, and stream flow for 6 spring storms in an artificially drained agricultural watershed. For moderate size storms, DOC concentrations are primarily affected by variations in antecedent moisture conditions. Generally, DOC concentrations and aromaticity increase with flow, especially for storms associated with high antecedent moisture conditions. A shift in the source of DOC to the stream and tile drains from low aromaticity DOC at baseflow, to more aromatic DOC during storms was observed. Data indicates that increases in the frequency and intensity of large precipitation events as well as wetter conditions in spring would likely lead not only to an increase in DOC fluxes (simply because of higher discharge) but also to an increase in the amount of DOC exported for every unit of flow.

Keywords: organic carbon, storm, UV absorbance, subsurface drainage, stream

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Introduction

Fluxes of dissolved organic carbon (DOC) in streams are important in regulating the transfer of organic matter from the terrestrial environment to estuaries and oceans.[1,2] The timing, quantity, and refractivity of DOC exported to streams impact stream metabolism by affecting heterotrophic microbial activity, respiration in small streams, and short term CO_2 outgasing.[3] A thorough understanding of the timing, quantity, and refractivity of DOC exports to streams is therefore of primary importance in order to better predict how ecosystems might respond to changes in land use and climate in the coming years. To this end, many studies have focused on DOC dynamics across a range of scale (plot scale to continental scale).[2,4–7] In most cases, studies report annual DOC losses and show a good positive correlation between DOC losses and flow.[4,6,8–11] Studies in a variety of settings across the nation also indicate that the DOC exported during storms is generally less biodegradable or more refractive than at baseflow.[7,9,10] For instance, Royer and David (2005) report that only 18% of stream DOC was readily available in a study in Illinois,[6] and Vidon et al. (2008) report a strong increase in DOC refractivity as stream flow increases in Indiana streams.[7] Hood et al. (2006) also report changes in DOC refractivity as a function of flow in a forest watershed in Oregon, USA.[9] Changes in DOC composition as reported in the literature are generally associated with the mobilization of DOC pools of different composition and aromaticity during storms (ie, wetland soil water, litter leachate, throughfall, mineral soil DOC, surficial soil DOC).[7,12]

Although these studies provide critical insight into DOC dynamics in artificially drained landscapes of the US Midwest and elsewhere (eg, Oregon, Maryland), they do not provide a clear understanding of how tile drains (aka subsurface drains) and/or overland flow (if any) contribute to stream DOC losses. Neither do they explain to what extent DOC concentrations and fluxes measured in tile drains at the plot scale can be used to estimate DOC exports at the whole watershed scale. This lack of integration between soil DOC distribution, DOC concentrations and fluxes in tile drains, and stream DOC losses strongly limits our ability to scale up knowledge obtained at the plot scale to the whole watershed scale. There is also a lack of high temporal resolution data during storms for DOC concentrations, fluxes, and composition across a variety of scales (tile drain, overland flow, and stream). This hinders one's ability to predict how changes in precipitation dynamics (bulk precipitation, soil antecedent moisture conditions) might affect DOC losses to streams in artificially drained landscapes of the US Midwest in the coming years. With many climate change models predicting a change in the intensity and frequency of precipitation events in numerous regions around the globe, including the US Midwest, it is critical to address this issue.[13] Interestingly, most of the DOC studies referenced above take place in the United States. However, it should be noted that the results of these studies ought to be applicable to many areas around the world where tile drainage and heavy soils are common.

In this study, we provide direct measurements of DOC concentrations, fluxes, and specific UV absorbance (SUVA) in tile drains, overland flow, and stream flow for 6 spring storms in a tile-drained watershed that typifies much of agricultural lands in the US Midwest. DOC concentrations and SUVA in riparian groundwater before each storm, tile drain base flow, stream base flow, and soil water extracts between 0 cm and 110 cm (approximate tile drain depth) are also provided. The objectives of this study are (1) to better understand the processes regulating the timing, quantity, and quality of DOC exported to streams for a variety of storms in spring; (2) to provide a framework to extrapolate knowledge obtained at the plot scale to the whole watershed scale; and (3) to ultimately better understand how DOC exports, both in terms of quantity and quality, might change in the coming years in response to changes in precipitation characteristics and antecedent moisture conditions. We use SUVA as an indicator of DOC refractivity because SUVA has been shown to be significantly positively correlated to aromaticity—a key component in controlling DOC availability and degradability.[14,15] We focus on spring storms because most solute losses do occur during high flow conditions in spring in the US Midwest.[16]

Site Description

Leary Weber Ditch (LWD) is a small watershed (7.2 km^2) located in the larger Sugar Creek watershed, approximately 20 km east of Indianapolis, Indiana (Fig. 1). Climate at the site is classified as temperate continental and humid. The average annual

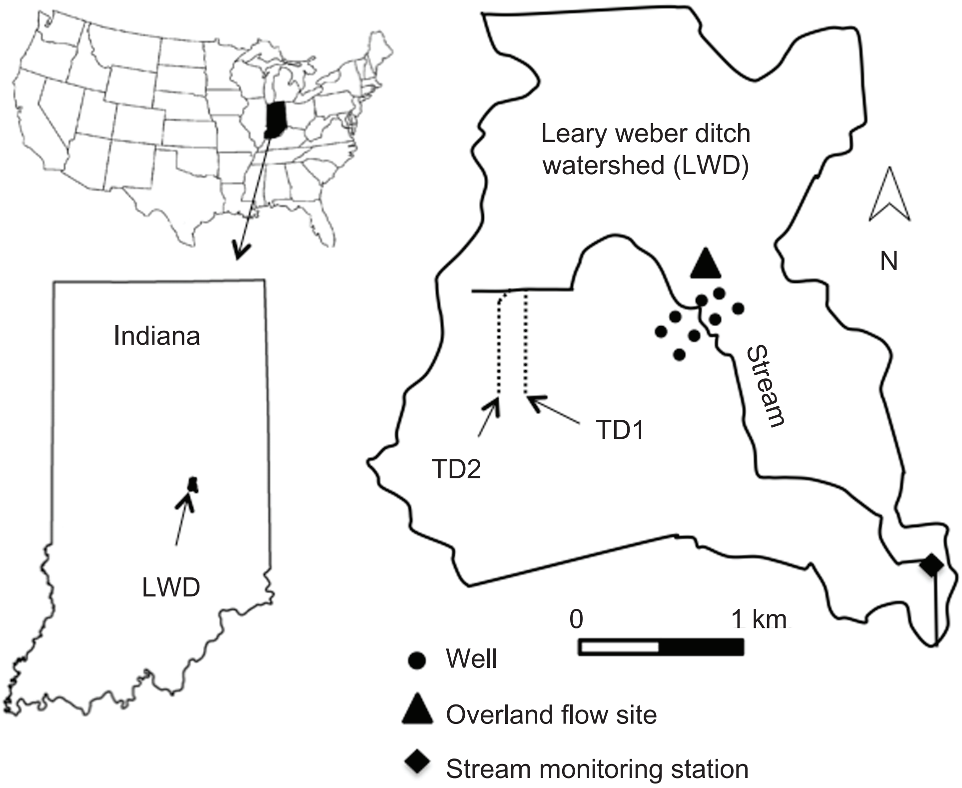

Figure 1. Experimental site location. TD1 and TD2 correspond to the two tile drains monitored for this study in 2009 and 2010.

temperature for central Indiana is 11.7 °C with an average January temperature of −3.0 °C and an average July temperature of 23.7 °C. The long-term average annual precipitation (1971–2000) is 100 cm.[17] Soils in the watershed are dominated by well-buffered poorly drained loams or silt loams, and typically belong to the Crosby-Brookston association. Crosby-Brookston soils are generally deep, very poorly drained to somewhat poorly drained, and have a silty clay loam texture in the first 30 cm of the soil profile. Soils in LWD are suited for row crop agriculture such as corn and soybean but require artificial drainage to lower the water table, removing ponded water, adding nutrients, and ensuring good soil tilth. Conventional tillage and a corn/soybean rotation have been implemented consistently for the last 20 years in LWD. Each year, approximately 50% of the watershed is planted with corn with the remaining portion planted with soybean. Soybean is generally planted early May and glyphosate applied mid-May. Phosphorus application on soybean generally averages 112 kg $ha^{-1}yr^{-1}$. For corn, fertilizer such as anhydrous ammonia is generally applied at a rate of 180 kg N $ha^{-1}yr^{-1}$ and herbicides atrazine and acetochlor are generally applied mid-May. Potash (K_2O) is applied post-harvest on soybean fields at a rate of approximately 220 kg $ha^{-1}yr^{-1}$. The LWD watershed (87% row crop, 6% pasture, 7% non-agricultural land use) is representative of many watersheds in the US Midwest where poorly drained soils dominate, and where artificial drainage is commonly used to lower the water table.[18]

Field and laboratory measurements

A total of 7 storms were monitored between February and June during 2009 and 2010. Bulk precipitation for the storms was measured using a network of 7 rain gages distributed throughout the watershed. The two tile-drains monitored for this study (TD1 and TD2) are located in the headwaters of the watershed (Fig. 1). Each tile-drain is 20.3 cm in diameter and located approximately 120 cm below the ground surface. TD1 extends 660 m from the stream and drains an area approximately 8.1 ha in size. TD2 extends 710 m from the stream and drains an area approximately 6.1 ha in size. Each tile drain was equipped with a Doppler velocity meter (ISCO 2150) for continuous discharge measurements, and an In-Situ LTC probe (level-temperature-conductivity) (In-Situ Inc.).

Whenever possible (ie, when the stream water level was below the tile drain), discharge was also measured by hand using the bucket method to validate discharge measurements obtained with the Doppler velocity meters. No significant differences between manual and automated discharge measurements were found. The occurrence of overland flow was measured using a H-flume inserted into the ground, equipped with an In-Situ LT (level-temperatue) logger (In-Situ Inc.). Stream stage at the outlet of the watershed was measured using an In-Situ LTC probe (In-Situ Inc.). Discharge was measured biweekly using a handheld Doppler velocity meter (Sontek) so a rating curve could be established. A total of 8 riparian zone wells were also installed between the field edge and the stream to capture antecedent water table depth at the field edge before each storm, in addition to riparian groundwater quality. Following a preliminary analysis of results in Fall 2009, a level logger (In-Situ Inc.) was installed at the field edge in winter 2010 to continuously monitor the water table depth during the 2010 field season (ie, storms 5, 6, and 7).

Water samples for dissolved organic carbon (DOC) analysis were collected in tile drains 1 and 2 (TD1 and TD2), in overland flow (if any), and in the stream using auto samplers (ISCO 6712) for storms 2 through 7. In tile drains, the sample collection line from each ISCO sampler was located at least 1 m into the tile-drains, and Doppler velocity measurements confirmed that no flow reversals occurred in the tile-drains during the storms studied, therefore indicating that tile samples were not contaminated by stream water when the tiles were submerged during storms. Samplers used to collect water samples in the stream and the two tile drains were triggered manually before the beginning of each storm, and generally set to collect water samples every 20 minutes during the rising limb of the hydrograph or the first 24 hours of the storm. Each 1 L sample was a composite of 3 samples taken 20 minutes apart (1 bottle per hour for 24 hours). Sampling interval was extended to 2 hours (3 samples taken 40 minutes apart per bottle) on the falling limb of the hydrograph. Although all water samples collected on the rising limb of the hydrograph and around peak flow were analyzed, not all samples were necessarily analysed on the falling limb of each hydrograph in order to limit cost. Additional water samples were also collected in riparian groundwater wells (immediately before each storm) to measure riparian water chemistry before each of the storms studied.

Soil samples at three locations randomly selected in the section of the field between TD1 and TD2 were analyzed (in triplicate) for DOC and SUVA distribution in the vertical dimension. At each location, a soil pit was established and soil samples were collected at the following depth ranges: 0–5 cm; 10–15 cm; 20–50 cm; 60–80 cm; 90–110 cm (5 depths x 3 locations x triplicate analyses = 45 analyses). After collection, the soil samples were air dried for a week, and subsequently sieved through a 2 mm mesh sieve. The DOC concentration and the SUVA characteristics of soil water extracts were measured for all samples. Extracts were obtained by mixing 50 g of soil with 100 mL of deionized water. Samples were shaken for 1 hour and centrifuged for 30 minutes, at 4,000 rpm.[19]

All samples (soil water extract, and water samples collected in the field) were filtered using Whatman GF/F 0.7 μm filters within a few hours of collection and frozen until analysis. Triplicate analysis of 10% of all samples and the analysis of check standards every 10 samples were performed to determine measurement error. DOC samples were analyzed using a persulfate oxidation to CO_2 and an OI Analytical DOC/DIC analyzer. SUVA was determined following the method described by Weishaar et al. (2003) using a UV spectrometer (Ocean Optics Inc.) and a quartz cell of 1 cm path length.[14] SUVA was obtained by dividing the UV absorbance of each water sample at 254 nm (measured in m^{-1}) by the DOC concentration and is reported in units of $L \cdot mg \cdot C^{-1} \cdot m^{-1}$. 14 Although freezing samples before SUVA analysis is not recommended, tests in the laboratory did not show any significant "freezing effect" on either SUVA or DOC results for our water samples.

Hydrological data analysis and flux calculations

For this study, the start of each event was defined when a perceptible rise in discharge in the stream was observed. The end of the event was defined when flow in the stream returned to pre-event flow values or when a new event started, which never occurred first. Seven and fourteen day antecedent discharges (7dQ and 14dQ, respectively) in the stream were calculated as the mean discharge during the 7 and 14 days preceding each event.

Solute fluxes in gram per storm were calculated for each storm by first multiplying the concentration of the sample for each sampling interval (mg/L) by the average discharge for that interval (L/s) and a unit conversion factor. Fluxes reported here in g/ha/storm were obtained by dividing the solute flux for each storm (g/storm) by the contributing area to each tile-drain (m^2) or the stream (m^2) and a unit conversion factor. Solute export yields (g/ha/hr) before each storm were calculated as the flux in the hour preceding the commencement of the storm. Solute export yields (g/ha/hr) during storms were calculated as the average hourly solute fluxes over the duration of the storm. We used double mass curves of cumulated stream flow (mm) vs. cumulated DOC export (kg) during storms to investigate the temporal variability of DOC exports (kg C/mm of stream flow) to the stream over the course of each event. Significant differences between groups were established using student *t*-tests. Significance was established at $P < 0.05$.

Results

Stream flow was continuously monitored from November 2008 to May 2010. During this period, a total of 7 storms were investigated for a suite of water quality parameters, with DOC measured in stream water, overland flow, riparian water, and tile flow for storms 2 through 7 (Fig. 2). Storms 2 through 7 ranged from 1.02 cm to 4.45 cm in bulk precipitation. Storm 3, 5, and 6 were the three storms for which overland flow was observed. For these storms, maximum daily storm flow, 7 and 14 day antecedent discharges (7dQ and 14dQ), and antecedent water table levels were higher than for any of the other storms. However, precipitation was not consistently higher for these storms (1.02–4.45 cm range) than for storms 2, 4, and 7 (2.29–2.67 cm). The maximum water levels reached during storms 5, 6, and 7 were 60 cm, 49 cm and 108 cm below ground surface, respectively (no continuous water level measurements were made for storms 2, 3 and 4—see materials and methods) (data not shown).

Mean DOC concentrations in the stream ranged from 2.63 mg/L to 5.39 mg/L for storms 2–7 with highest stream DOC values observed for storms 3, 5, and 6 (Table 1). When storm and pre-storm mean DOC concentrations were compared, storm DOC concentrations were generally greater (by an average of 33%) during storms (2.63–5.39 mg/L) than at baseflow (2.02–3.10 mg/L). Differences were

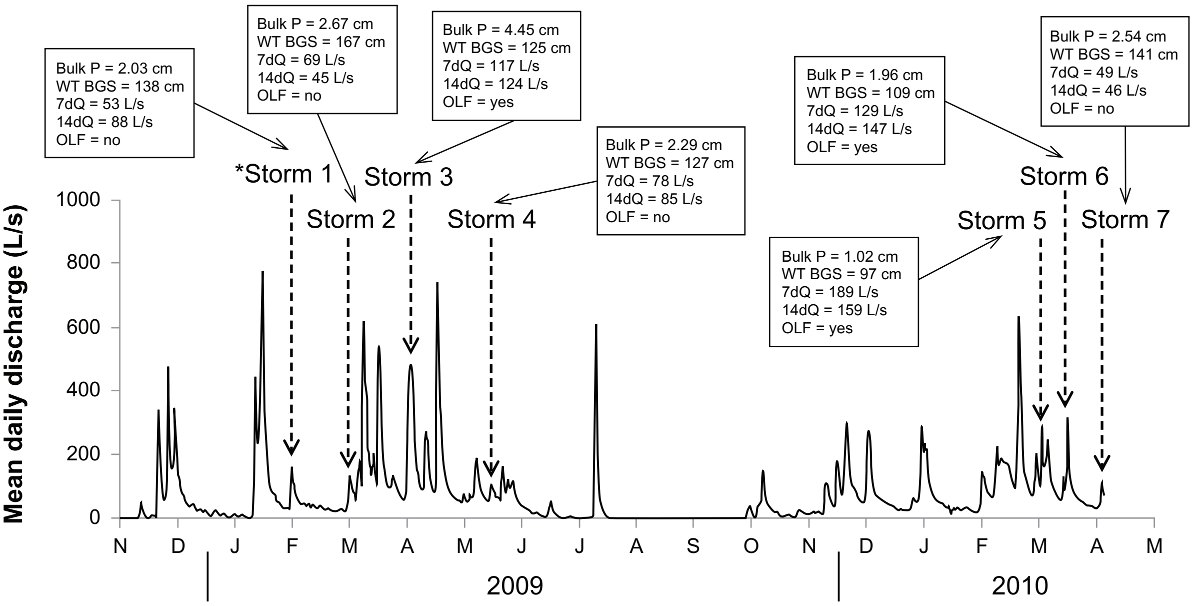

Figure 2. Mean daily discharge (L/s) in the stream at the outlet of the study watershed (Leary Weber Ditch) between November 2008 and May 2010. Storm 1 (February 26, 2009), storm 2 (April 1, 2009), storm 3 (April 29, 2009), storm 4 (June 11, 2009), storm 5 (March 29, 2010), storm 6 (April 8, 2010), and storm 7 (April 26, 2010) are the storms during this period for which water samples were collected in the watershed. Bulk precipitation amounts (Bulk P), antecedent water table depth below ground surface (WT BGS), 7-day antecedent discharge (7dQ), 14-day antecedent discharge (14dQ), and the occurrence of overland flow (OLF) are also indicated for each storm.
Note: *No dissolved organic carbon data for storm 1.

Table 1. Mean dissolved organic carbon (DOC) concentration (mg/L) before storm 2 (April 1, 2009), storm 3 (April 29, 2009), storm 4 (June 11, 2009), storm 5 (March 29, 2010), storm 6 (April 8, 2010), and storm 7 (April 26, 2010) in the stream, tile drain 1 (TD1), tile drain 2 (TD2), and riparian groundwater.

Mean DOC (mg/L)	Pre-storm				During storm			
	Stream	TD1	TD2	RZ	Stream	TD1	TD2	OLF
Storm 2	3.10 (0.39)	2.16 (0.21)	n/a	2.65 (0.51)	3.55 (0.73)	2.44 (0.62)	n/a	–
Storm 3	2.79 (0.41)	2.14 (0.56)	2.27 (0.39)	n/a	5.39 (1.82)	3.52 (1.05)	4.94 (2.02)	9.00 (2.00)
Storm 4	2.72 (0.52)	1.61 (0.10)	2.08 (0.22)	4.96 (2.09)	2.81 (0.39)	2.18 (0.43)	2.10 (0.31)	–
Storm 5	2.27 (0.19)	2.51 (0.69)	n/a	2.61 (1.21)	3.86 (0.94)	2.95 (0.63)	2.72 (0.51)	16.23 (3.28)
Storm 6	2.02 (0.27)	2.13 (1.01)	No flow	2.58 (0.91)	5.06 (1.74)	3.89 (1.48)	4.09 (1.27)	20.02 (1.39)
Storm 7	2.65 (0.30)	No flow	No flow	2.46 (0.20)	2.63 (0.46)	2.28 (0.64)	2.36 (0.20)	–

Notes: Mean DOC concentrations during storms 2–7 in the stream, TD1, TD2, and overland flow (OLF) are also indicated. Values in parenthesis indicate one standard deviation.
Abbreviation: n/a, not available.

especially large for storms 3, 5, and 6, where mean DOC concentrations in the stream during storms were 4.77 mg/L, but only 2.36 mg/L in the stream at baseflow. For these three storms (the only storms with measurable overland flow amounts), DOC concentrations in overland flow (15.08 mg/L) were significantly higher ($P < 0.05$) than at any other location in the watershed where DOC was measured. Although the differences in storm DOC concentrations in tile drains (3.06 mg/L) and in the stream (3.89 mg/L) were not always statistically significant, mean storm DOC concentrations in tile drains were always lower than in the stream (by an average of 21%). Like in the stream, storm DOC concentrations in tile drains was higher for storms 3, 5, and 6 (3.69 mg/L) than for the other storms (2.27 mg/L). When available (ie, when tile drains were flowing before each storm), baseflow DOC concentrations in tile drains were generally lower than during the storms. In the riparian zone, groundwater DOC concentrations immediately before the storms varied between 2.46 mg/L and 4.96 mg/L.

The mean SUVA value in the stream and in tile drains during storms 2–7 were 3.00 $\mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$ and 3.39 $\mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$, respectively (Table 2). Highest SUVA values were observed in both tile drains and the stream for storms 3 and 6. Although differences were not always statistically significant ($P > 0.05$), SUVA values were generally higher during storms than at baseflow, especially in the stream. In the riparian zone and in overland flow, SUVA values varied between 1.29–2.77 $\mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$, and 4.17–4.48 $\mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$, respectively.

Figures 3 and 4 show patterns of DOC and SUVA in the stream and each tile drain (TD1 and TD2) during storms 2–7. With the exception of storm 7, for which DOC concentrations showed a decreasing trend in TD1, TD2, and the stream as the storm progressed, DOC concentrations generally increased with stream

Table 2. Mean specific UV absorbance (SUVA) ($\mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$) before storm 2 (April 1, 2009), storm 3 (April 29, 2009), storm 4 (June 11, 2009), storm 5 (March 29, 2010), storm 6 (April 8, 2010), and storm 7 (April 26, 2010) in the stream, tile drain 1 (TD1), tile drain 2 (TD2), and riparian groundwater.

Mean SUVA	Pre-storm				During storm			
	Stream	TD1	TD2	RZ	Stream	TD1	TD2	OLF
Storm 2	2.96 (1.03)	1.64 (0.60)	n/a	2.33 (0.42)	2.40 (0.53)	2.12 (0.47)	n/a	–
Storm 3	1.94 (0.49)	3.46 (0.35)	3.22 (0.85)	n/a	3.82 (1.14)	4.63 (1.38)	4.94 (2.02)	4.17 (1.68)
Storm 4	1.49 (0.66)	2.96 (0.87)	2.45 (2.53)	1.29 (0.40)	2.04 (0.35)	2.78 (0.50)	2.53 (0.35)	–
Storm 5	2.04 (0.26)	2.92 (0.59)	n/a	2.77 (1.23)	2.76 (0.30)	2.58 (0.56)	3.15 (0.85)	4.48 (3.25)
Storm 6	3.78 (1.35)	2.88 (0.46)	No flow	2.34 (0.94)	4.15 (0.49)	4.58 (0.97)	4.11 (0.63)	4.22 (0.53)
Storm 7	2.74 (0.29)	No flow	No flow	2.74 (0.73)	2.79 (0.35)	3.14 (0.61)	2.77 (0.28)	–

Notes: Mean SUVA during storms 2–7 in the stream, TD1, TD2, and overland flow (OLF) are also indicated. Values in parenthesis indicate one standard deviation.
Abbreviation: n/a, not available.

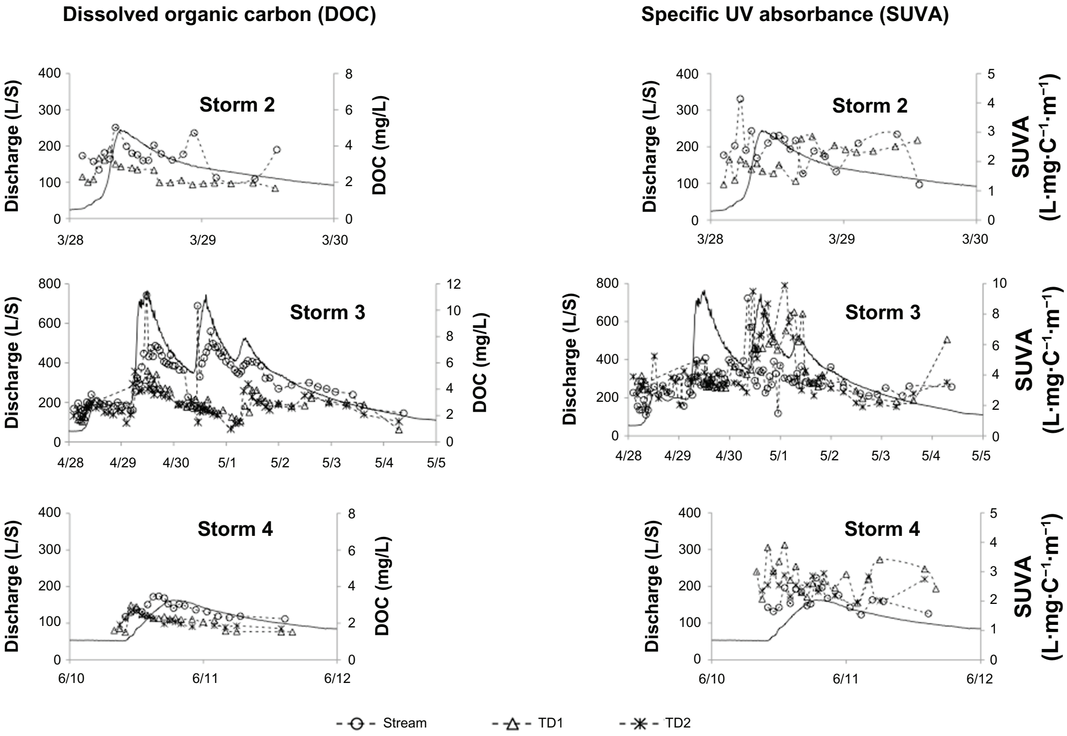

Figure 3. Stream discharge (L/s) (solid line), and dissolved organic carbon (DOC) concentration (left panel) and DOC specific UV absorbance (SUVA) (right panel) in the stream (watershed outlet) and in tile drain 1 (TD1) and tile drain 2 (TD2) for storm 2 (April 1, 2009), storm 3 (April 29, 2009), and storm 4 (June 11, 2009).

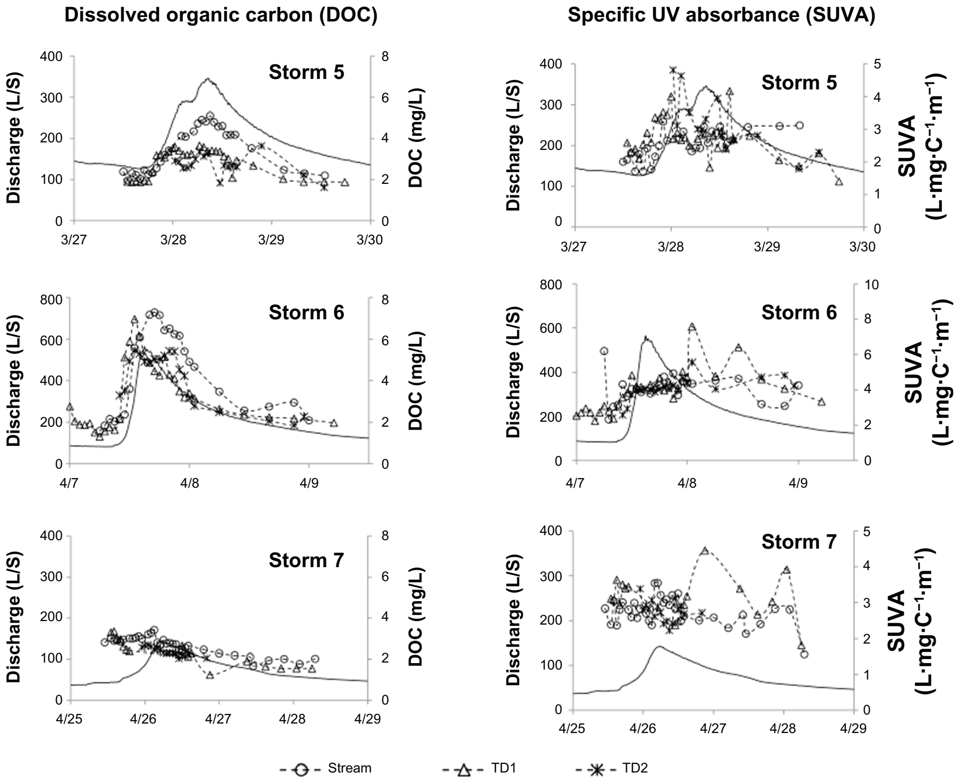

Figure 4. Stream discharge (L/s) (solid line), and dissolved organic carbon (DOC) concentration (left panel) and DOC specific UV absorbance (SUVA) (right panel) in the stream (watershed outlet) and in tile drain 1 (TD1) and tile drain 2 (TD2) for storm 5 (March 29, 2010), storm 6 (April 8, 2010), and storm 7 (April 26, 2010).

flow for storms 2–6. For these storms, DOC concentrations in tile drains consistently peaked before the peak in DOC concentration in the stream. Tile drain flow (not shown) generally peaked before stream flow, with the peak in DOC in tile drains corresponding to the peak in tile flow. Unlike DOC, SUVA values measured in either tile drains or the stream did not show a clear and consistent increase as a function of flow, although, on average, SUVA was generally higher during the storms than immediately before (Table 2).

The DOC concentration and SUVA characteristics of soil water extracts at select depths (0–5 cm; 10–15 cm; 20–50 cm; 60–80 cm; 90–110 cm) showed a progressive decline in DOC concentration as a function of depth with mean DOC concentrations in soil water extracts decreasing from 20.1 mg/L near the soil surface (0–5 cm) to 6.9 mg/L in the 90–110 cm depth range where most tile drains are located (Fig. 5). Contrary to DOC, SUVA values showed a clear peak in the 20–50 cm depth range with a mean SUVA value of 6.18 $L \cdot mg \cdot C^{-1} \cdot m^{-1}$ at that depth. Lowest SUVA values in soil extracts were observed in the 90–110 cm depth range (1.48 $L \cdot mg \cdot C^{-1} \cdot m^{-1}$).

When DOC flux data were analyzed, mean storm DOC fluxes were 291 g/ha/storm in the stream and 307 g/ha/storm in TD1 and TD2 for storms 2–6 (Table 3). Tile flow was not available for storm 7, so DOC fluxes and yields in tile drains for this storm were not calculated. Clearly, higher DOC fluxes were observed in both the stream and tile drains during storms 3, 5 and 6, than for storms 2 and 4. Yield data allowed for the comparison of DOC losses between baseflow and storm flow. On average, storm DOC yield in the stream (4.73 g/ha/hr) was approximately 5 times greater than at baseflow (0.94 g/ha/hr). When tile drain DOC yields are compared to those calculated in the stream, storm DOC yields in tile drains for storms 2–6 (6.27 g/ha/hr) are, on average, 7.9% larger than in the stream for these storms.

Double mass curve analysis of cumulated stream flow (mm) vs. cumulated DOC export (kg) indicated that the export rates of DOC (ie, the slope of the double mass curves) did not vary significantly over the course of storms 2, 3, and 4 (linear curves) (Fig. 6). However, for storms 5 and 6, a progressive decline of the DOC export rate was observed over time (logarithmically shaped double mass curves). Mean export rates, or the overall amount of DOC (kg) exported per millimeter of stream flow also varied from storm to storm, from an average export rate of 39.5 kg of C per mm of stream flow at the outlet of the watershed for storm 3, to only 19.0 kg of C per mm of stream flow for storm 4. Over the course of storms 2–6, the average export rate was 30.1 kg of C per mm of flow, or 41.9 g of C per hectare per millimeter of stream flow at the outlet of the watershed.

Discussion

In tile drains, mean DOC concentrations for storms 2–7 (3.06 mg/L) are consistent with those reported by Kovacic et al. (2000) in Illinois (2.6–3.6 mg/L).[20] They are however a bit higher than those reported by Ruark et al. (2005) in Indiana (<2 mg/L)[4] and McCarty and

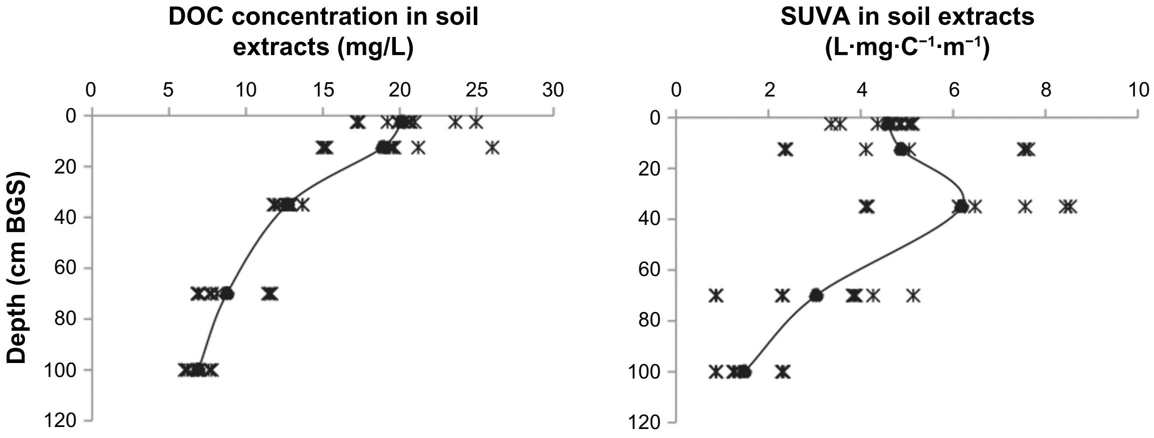

Figure 5. Dissolved organic carbon (DOC) concentration (left) and DOC specific UV absorbance (SUVA) (right) in soil water extracts at 0–5 cm; 10–15 cm; 20–50 cm; 60–80 cm; 90–110 cm below ground.
Note: Solid line indicates mean values.

Table 3. Dissolved organic carbon (DOC) fluxes (kg/ha/storm) and yields (g/ha/hr) for storm 2 (April 1, 2009), storm 3 (April 29, 2009), storm 4 (June 11, 2009), storm 5 (March 29, 2010), storm 6 (April 8, 2010), and storm 7 (April 26, 2010) in tile drain 1 (TD1), tile drain 2 (TD2), and the stream (watershed outlet).

	DOC flux in g/ha/storm				**DOC yield in g/ha/hr**			
	Stream (base flow)	**Stream (storm flow)**	**TD1**	**TD2**	**Stream (base flow)**	**Stream (storm flow)**	**TD1**	**TD2**
Storm 2	n/a	87.2	66.3	n/a	0.53	2.57	1.72	n/a
Storm 3	n/a	863.8	603.0	681.9	1.32	12.66	10.91	12.12
Storm 4	n/a	70.0	71.7	78.4	0.62	1.33	1.55	1.69
Storm 5	n/a	185.3	164.6	213.0	1.49	4.10	3.58	5.16
Storm 6	n/a	251.4	335.2	494.4	1.02	6.66	5.68	12.44
Storm 7	n/a	64.4	n/a	n/a	0.66	1.09	n/a	n/a

Note: Fluxes in TD1 and TD2 for storm 7 were not calculated because discharge data in these tile drains were not available for this storm.

Bremmer (1992) in Iowa (range: <0.3 to 2.9 mg/L).[21] These differences are likely due to the fact that these two studies focus on DOC concentrations throughout the year in tile drains, instead of focusing primarily on storm DOC concentrations. In the stream, mean storm DOC concentrations (2.63–5.39 mg/L) for storms 2–7 (1.02 to 4.45 cm in bulk precipitation) are consistent with those reported by Wagner et al. (2008) in a nearby agricultural watershed (4.55–8.80 mg/L) for a series of storms ranging from 2.8 cm to 5.8 cm in bulk precipitation.[22] With respect to DOC fluxes, Dalzell et al. (2005) report DOC loads of 3.43×10^7 $g \cdot C \cdot d^{-1}$ or 0.41 kg/ha/day at the outlet of Big Pine Creek watershed.[3] If converted into a yield, as in Table 3, this equates to 17 g/ha/hr, which is of the same order of magnitude as DOC yields reported for our storms. Several studies report that although some of the surface soil DOC is quickly decomposed, a large fraction of it also sorbs to soils.[21,23,24] This is consistent with the higher DOC concentration in surface soil extracts (0–5 cm and 10–15 cm) and the peak in aromaticity in the 20–50 cm depth reported here (Fig. 5). Indeed, as surficial DOC is decomposed and progressively moves downward, its aromaticity increases. However, over long periods of time (hundreds of years), even aromatic substances are degraded, which leads to low DOC aromaticity at depth. Hood et al. (2006) also observed DOC poor in aromatic substances in deep mineral soils.[9]

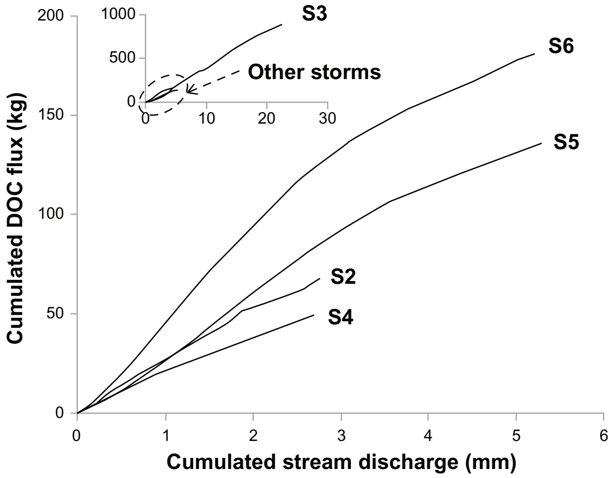

Figure 6. Double mass curves showing cumulated stream discharge (mm) versus cumulated dissolved organic carbon (DOC) flux (kg) in the stream (watershed outlet) for storm 2 (April 1, 2009), storm 3 (April 29, 2009), storm 4 (June 11, 2009), storm 5 (March 29, 2010), and storm 6 (April 8, 2010).

Aside from the comparison of our study results with those of other studies, the comparison of DOC dynamics in tile drains, overland flow, and the stream, in relation to change in SUVA with depth in the soil profile and throughout the watershed during storms, also sheds light on the processes regulating DOC losses (both concentrations and fluxes) to streams in tile drained dominated watersheds of the US Midwest. Data indicate that DOC concentrations in tile drains peak slightly before DOC concentrations in the stream, and that peak flow in tile drains (not shown) occur slightly before peak flow in the stream, suggesting that the timing of DOC losses (both concentrations and fluxes) is primarily driven by changes in flow.

Highest stream DOC concentrations during storms are associated with storms 3, 5, and 6, which are the storms with the highest antecedent moisture conditions, highest mean daily discharges, and overland flow. Significantly higher DOC concentrations in overland flow (15.08 mg/L) than anywhere else in the watershed suggests that overland flow likely contributes to the higher DOC concentrations observed in stream for storms with overland flow (ie, storms 3, 5 and 6) than for storms without overland flow. However, DOC concentrations are also higher in tile drains for storms 3, 5 and 6 (3.69 mg/L) than for other storms (2.27 mg/L). Therefore, although overland flow certainly contributes to the higher DOC concentrations in the stream for these three storms, this indicates that overland flow is likely not the only mechanism leading to higher DOC concentrations in the stream during storms. Previous work has shown that macropore flow can contribute between 11%–15% of total tile drain flow during storms in this watershed.[25,26] It is likely that near surface soil water (rich in DOC) is therefore quickly moved to tile drains, and ultimately to the stream, via soil macropores, during storms. For storms 3, 5 and 6 in particular, the water table before the storm was closer to the surface (97 cm $<$ water table depth $<$ 125 cm) than for storms 2, 4, and 7 (127 cm $<$ water table depth $<$ 167 cm) (Fig. 2). In addition, the water table reached a maximum level of 60 cm below ground surface (BGS) for storm 5, 49 cm BGS for storm 6, but only reached 108 cm BGS for storm 7. Although continuous water table level measurements were not available for storms 2–4, continuous water level data for storms 5, 6 and 7, higher antecedent water table depths for storms 3, 5 and 6, and higher mean daily discharges for storms 3, 5 and 6 (Fig. 2) suggest that the water table likely rose closer to the soil surface where soil water extractable DOC is higher for storms 3, 5 and 6 than for the other storms (ie, 2, 4, and 7) (Fig. 5). This is clearly shown for storms 5, 6 and 7 for which continuous water level measurements are available. We therefore hypothesize that the increase in DOC concentration with flow in tile drains during storms (Figs. 3 and 4), and overall higher DOC concentrations in both the stream and tile drains for storms 3, 5, and 6 than for the other storms, are primarily due to the mobilization of near surface soil water rich in DOC as the water table rises during storms (Fig. 5), and to its quick transfer to tile drains during storms via macropore flow.

SUVA data are consistent with this hypothesis and indicate a shift in the source of DOC during storms, especially for storms 3, 5 and 6. Indeed, data indicates a clear peak in SUVA in the soil profile between 20 and 50 cm below ground surface ($6.18\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$) (Fig. 5). The mean SUVA value in the stream and in tile drains during storms 2–7 were $3.00\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$ and $3.39\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$, respectively. For storms 3, 5 and 6 in particular, when the water table was at minimum within 60 cm of the ground surface (at least for storms 5 and 6), mean SUVA values in the stream and the tile drains were $3.58\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$, and $4.00\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$, respectively. These values are higher than the SUVA values of either riparian zone water ($2.29\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$) or deep (90–110 cm) soil water ($1.48\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$). This suggests that these water sources are not large DOC contributors to the stream or tile drains during storms. This was particularly noticeable during storms 3, 5 and 6.

At baseflow, the mean SUVA in the stream or tile drains before each storm (Table 2) were $2.49\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$ and $2.79\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$, respectively. This suggests that baseflow DOC is likely a combination for riparian water ($2.29\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$), 90–110 cm soil water ($1.48\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$), and 60–80 cm soil water ($3.04\ \mathrm{L \cdot mg \cdot C^{-1} \cdot m^{-1}}$). This is consistent with relatively deep soil water ($<$ 60 cm) being the main source of water to the stream and tile drains (when flowing) at baseflow. During storms, and particularly during storms 3, 5 and 6 which are associated with high antecedent moisture conditions compared to the other storms (Fig. 2), the water table rises towards the surface (within 60 cm of the ground surface), and mobilizes near surface soil water rich in DOC and with high SUVA values (Fig. 5). These results confirm the results of a previous study in a nearby agricultural watershed where Vidon et al. (2008) used the fluorescence properties of DOC and SUVA to characterize the processes regulating DOC exports to streams.[7] They concluded that the increase in DOC concentration in the stream during storms most likely corresponded to a shift in the source of DOC from DOC originating from mineral soil layers of the soil profile at baseflow, to DOC originating from surficial soil layers richer in aromatic substances and lignin during storms (high SUVA).

Additionally, our results provide a better understanding of the relationship between bulk DOC losses in tile drains and in streams, and of their relationships with precipitation characteristics and antecedent moisture conditions. As previously discussed, higher DOC concentrations and fluxes occurred for storms 3, 5, and 6 than for the other storms.

Storms 3, 5, and 6 are not consistently associated with higher bulk precipitation amounts (1.02–4.45 cm) than storms 2, 4, and 7 (2.03–2.67 cm). Antecedent moisture conditions (water table level, 7dQ, 14dQ) were, however, higher for storms 3, 5 and 6. Although only 6 storms are considered, this suggests that at least in spring, when the soil is bare and antecedent moisture conditions minimally variable, high DOC concentrations and high DOC fluxes are primarily related to antecedent moisture conditions for storms ranging from 1.02 to 4.45 cm in bulk precipitation.

When DOC fluxes in the stream and in tile drains are compared, data indicate that on average, DOC fluxes in tile drains are 5.5% higher per storm than in the stream. DOC yields in tile drains are on average 7.9% larger per hour than in the stream. These slight differences between tile drain and stream losses, either on a storm or hourly basis, are likely explained by the fact that the mean flow path length is by definition shorter at the field scale (tile drain) than at the whole watershed scale. This would generate a higher drainage density at the plot scale than at watershed scale, and therefore slightly higher DOC losses (per hectare) in tile drains than at the whole watershed scale. Interestingly, when DOC fluxes and yields in tile drains and the stream are compared for storms with overland flow only (storms 3, 5, and 6), DOC fluxes in the stream are 4.2% higher than in tile drains. Differences of less than 10% are not significant, primarily because the error on flow measurements is generally between 10% and 15% (Vidon 2008, unpublished data). These results therefore suggest that although tile drain DOC concentrations are on average 21% lower than in the stream, tile drain DOC fluxes (on an area basis) are not significantly different from those in the stream. Based on these results, DOC fluxes estimated in tile drains could therefore potentially be scaled up at the watershed scale, and vice-versa. However, the observed trend of lower fluxes in the stream than in tile drains for storms without overland flow, and higher fluxes in the stream than in tile drains for storms with overland flow, suggest that DOC contributions via overland flow potentially impact DOC losses to the stream, albeit in a very limited manner ($<10\%$). This is consistent with the observation previously made that overland flow likely contributes to higher DOC concentrations in the stream for storms 3, 5 and 6 than for other storms. This also confirms that its impact is limited ($<10\%$), and that the primary mechanism by which DOC is exported to the stream is by subsurface/macropore flow, and by the mobilization of near surface soil water rich in DOC and with high SUVA, especially for storms associated with high antecedent moisture conditions.

From a watershed management perspective, this suggests that if the predictions of climate change models hold true, and that the frequency and the intensity of large storm events increase in the future, we will see an increase in the amount of DOC (both concentration and flux) exported to streams. This is assuming land use practices remain the same. Further, if wet periods become wetter and dry periods dryer, late winter and spring storms associated with high antecedent moisture conditions will become more common.[13] For storms associated with wet antecedent moisture conditions, our data suggest that the SUVA of the exported DOC will increase. SUVA is highly positively correlated to the aromaticity of DOC,[14] and highly aromatic substances are not as easily degraded as less complex organic molecules. Consequently, although it is difficult to determine with certainty how climate will change, and whether other variables (eg, land use) will remain the same, it is likely that the coming years will not only see an increase in the quantity of DOC exported to streams, but also a change in the quality of DOC toward DOC molecules richer in aromatic substances, and therefore less bioavailable to stream organisms.

Finally, the analysis of the double mass curves of cumulated stream flow (mm) vs. cumulated DOC export (kg) indicates that a progressive decline (logarithmically shaped double mass curve) of the rate of export of DOC over the duration of a storm (ie, the amount of DOC exported with each unit volume of stream flow) was observed for storms 5 and 6, but not for other storms (Fig. 6). This suggests a progressive exhaustion of the pool of DOC available for leaching over the duration of these storms. Conversely, a linear shaped double mass curve for storms 2, 3, and 4 indicates a constant DOC export rate over the duration of these storms. The DOC pool available for leaching was therefore not limiting for DOC exports in these storms. Together, this means that for 3 of the 5 storms with DOC flux data available, the DOC pool available for leaching did not appear to be a limiting factor, and that cumulated flow was the primary driver.

Regardless of the shape of the double mass curves, the mean export rates (ie, the mean slopes of the double mass curves) nevertheless varied from one storm to the next. Highest export rates were observed for storms 3, 5, and 6, with a highest value of 39.5 kg of C per mm of stream flow at the outlet of the watershed for storm 3. For storm 4, the export rate was only 19.0 kg of C per mm of stream flow. Overall, data indicated that higher export rates (kg/mm of flow) tend to occur for storms associated with high antecedent moisture conditions (ie, storms 3, 5 and 6), or storms capable of mobilizing near surface soil water rich in DOC. This positive feedback mechanism (more storms > wetter conditions > higher flow and higher DOC export rate per volume of flow) is likely to exacerbate the effect of changes in climate in the coming years on DOC exports. Within this context, should minimizing DOC losses to streams become a management need in the near future, lowering the average water table depth through management might help achieve this goal.

Conclusions

This study, documenting dissolved organic carbon (DOC) dynamics in a heavily tile-drained watershed representative of many watersheds of the US Midwest, is the first to simultaneously document the concentrations, nature, and fluxes of DOC in tile drains, stream flow, and overland flow at a high temporal resolution in spring; a critical time of year for all solute exports to streams in the US Midwest. It revealed that overland flow has only a limited impact on DOC losses to streams and that for precipitation events between 1.02 cm and 4.45 cm of bulk precipitation, antecedent moisture conditions are likely more important than bulk precipitation in regulating the occurrence of overland flow and DOC concentrations in streams and tile drains during storms. As DOC concentrations in the stream and tile drains increase during storms, DOC also becomes more aromatic, especially for storms with wet antecedent moisture conditions. This corresponds to a shift in the source of DOC from low aromaticity DOC located in the mineral soil layer of the soil profile at baseflow, to more aromatic DOC located closer to the soil surface during storms. When DOC fluxes and yields between the stream and tile drains are compared, no clear differences (<10%) were observed, suggesting that DOC fluxes estimated in tile drains could potentially be scaled up at the watershed scale, and vice-versa.

From a management perspective, results suggest that any increase in the frequency and intensity of large precipitation events, and wetter conditions in spring, would lead not only to an increase in DOC flux (simply because of higher discharges during storms) but also to an increase in the amount of DOC (kg) exported with every unit of flow. This positive feedback mechanism between flow and antecedent moisture conditions could exacerbate the effect of climate change on DOC fluxes in the coming years. As indicated above, our data also suggest that DOC exported during storms associated with wet antecedent moisture conditions would likely be more aromatic, and therefore less bioavailable to stream organisms. Although replicating these observations in other regions of the globe, as well as for a larger number of storms is needed, this study stresses the potential large impact that future changes in climate might have on DOC quality and quantity in streams, and ultimately on stream metabolism as a whole.

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Competing Interests

Author(s) disclose no potential conflicts of interest.

Author Contributions

Conceived and designed the experiments: PV. Analyzed the data: PV, HH, PC, MH. Wrote the first draft of the manuscript: PV. Contributed to the writing of the manuscript: PV. Agree with manuscript results and conclusions: PV, HH, PC, MH. Jointly developed the structure and arguments for the paper: PV, HH, PC, MH. Made critical revisions and approved final version: PV. All authors reviewed and approved of the final manuscript.

Disclosures and Ethics

As a requirement of publication author(s) have provided to the publisher signed confirmation of compliance with legal and ethical obligations including but not limited to the following: authorship and contributorship, conflicts of interest, privacy and confidentiality and (where applicable) protection of human and animal research subjects. The authors have read and confirmed their agreement with the ICMJE authorship and conflict of interest criteria. The authors have also confirmed that this article is unique and not under consideration or published in any other publication, and that they have permission from rights holders to reproduce any copyrighted material. Any disclosures are made in this section. The external blind peer reviewers report no conflicts of interest.

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