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ORIGINAL PAPER

Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses

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Abstract Dissolved organic carbon (DOC) dynamics in streams is important, yet few studies focus on DOC dynamics in Midwestern streams during storms. In this study, stream DOC dynamics during storms in two Midwestern watersheds with contrasting land uses, the change in character of stream DOC during storms, and the usability of DOC as a hydrologic tracer in artificially drained landscapes of the Midwest are investigated. Major cation/DOC concentrations, and DOC specific UV absorbance (SUVA) and fluorescence index (FI) were monitored at 2–4 h intervals during three spring storms. Although DOC is less aromatic in the mixed land use watershed than in the agricultural watershed, land use has little impact on stream DOC concentration during storms. For both watersheds, DOC concentration follows discharge, and SUVA and FI values indicate an increase in stream DOC aromaticity and lignin content during storms. The comparison of DOC/major cation flushing dynamics indicates that DOC is mainly exported via overland flow/macropore flow. In both watersheds, the increase in DOC concentration in the streams during storms corresponds 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. Results also suggest that DOC, SUVA and FI could be used as hydrologic tracers in artificially drained landscapes of the Midwest. These results underscore the importance of sampling streams for DOC during high flow periods in order to understand the fate of DOC in streams.

Keywords Dissolved organic carbon character · Midwest · Storm · Stream · Watershed

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Introduction

A thorough understanding of carbon cycling in the environment is critical in order to predict the effects of climate change in a world where biogeochemical cycles are increasingly influenced by human activities. Carbon dynamics in streams is a critical component of the carbon cycle and acidification processes (Wigington et al. 1996). For instance, organic carbon dynamics in streams during high flow periods influences heterotrophic productivity and respiration in small streams, which is important in influencing rates of C cycling and short term CO_2 outgasing (Dalzell et al. 2005). Understanding the processes controlling the delivery of organic carbon to streams is therefore important in order to be able to predict the impact of changes in land use and precipitation patterns on C cycling in streams, assist in the development of better water quality criteria for the future (e.g. total maximum daily load criteria), and assist modelers in developing better algorithms linking precipitation, discharge, landscape characteristics, and organic carbon concentration in streams.

It is well established that most carbon export occurs during precipitation events when large quantities of solutes (including dissolved organic carbon (DOC)) are flushed from the soil profile (Boyer et al. 1997). Nevertheless, recent research on DOC dynamics at the watershed scale suggests that considerable uncertainties still remain on the processes controlling DOC delivery to streams during storms. For instance, in forested mountainous catchments of Colorado, stream DOC concentration typically peaked prior to discharge, on the rising limb of the snowmelt hydrograph, and then quickly decreased as snowmelt continued (Hornberger et al. 1994; Boyer et al. 1997). To the contrary, Inamdar et al. (2004) indicate that DOC typically peaked with or slightly after the peak in discharge during summer storms in a forested catchment of the Adirondack Mountains, NY. Research in H.J. Andrews experimental forest in Central Oregon has also shown that the character of DOC (aromaticity, relative abundance of humic–non humic substances) in streams varies during storms, indicating a change in the source of DOC to the stream as a function of discharge (Hood et al. 2006). In that study, Hood et al. (2006) used the fluorescence properties of DOC and the changes in the specific UV absorbance of DOC (SUVA) during storms to show the change in character of stream DOC during flushing in three small watersheds (<100 ha). High SUVA is related to a high amount of aromatic substances (Weishaar et al. 2003; Mladenov et al. 2005) and the fluorescence properties of DOC are related to the presence of lignin and can be used to distinguish between aquatic autochthonous material that lacks lignin and allochthonous (terrestrial) material containing lignin (McKnight et al. 2001).

Research therefore suggests complex delivery flowpaths for DOC in mountainous catchments, including variations in the sources of DOC to streams during storms. In addition, recent research has also suggested that DOC can be employed as a useful hydrologic tracer in a watershed context (Katsuyama and Ohte 2002; McGlynn and McDonnell 2003; Hood et al. 2006). For instance, in a forested mountainous catchment of New Zealand, McGlynn and McDonnell (2003) indicate that DOC could potentially be used to identify the mixing of spatially distinct streamflow source waters at the catchment outlet. Similarly, Katsuyama and Ohte (2002) successfully used the fluorescence properties of DOC as a hydrologic tracer in forested headwater catchments in Japan.

Over the past 10 years, many studies have therefore investigated the processes controlling the delivery of DOC to streams, the change in the character of stream DOC during storms, and the usability of DOC as a hydrologic tracer in forested mountainous catchments (Katsuyama and Ohte 2002; McGlynn and McDonnell 2003; Inamdar et al. 2004; Hood et al. 2006). However, there is a lack of similar studies in agricultural and urban Midwestern watersheds, despite the importance of many Midwestern watersheds as nutrient and carbon sources to the Mississippi River and eventually the Gulf of Mexico (Goolsby et al. 2000; Royer et al. 2006). Dalzell et al. (2005) investigate the quantity, source, and relative degradation state of total organic carbon in an agricultural watershed of the Midwest by collecting aquatic organic matter during flood and baseflow conditions, but did not investigate the progressive change in the character of DOC in streams during storms as a function of discharge at a high temporal resolution. The objectives of this study are therefore threefold: (1) develop a better understanding of stream DOC dynamics (concentration, timing of delivery to streams) across land uses in glaciated landscapes of the Midwest during storms; (2) determine the change of character of stream DOC during storms in an agricultural and a mixed urban/agricultural land use watershed, and (3) assess the usability of DOC as a hydrologic tracer in artificially drained landscapes of the Midwest. The research approach chosen in this study is similar to the one used by Hood et al. (2006) in a forested watershed in Central Oregon. It consists in monitoring the change in the quantity and character of DOC in the stream during storms, and in comparing the flushing behavior of DOC to major cation flushing characteristics. This approach allows for the determination of the flowpath associated with the flushing of DOC from the soil profile, and for the determination of the usability of DOC as a hydrologic tracer at the watershed scale.

Study area

The two first order watersheds used in this study are located in Central Indiana near Indianapolis, IN, USA. Indiana has a temperate continental and humid climate. The average annual 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) in the watersheds studied is 105 cm (NOAA 2005). Highest stream discharge is observed in March while the lowest discharge typically occurs in September (Clark 1980). Topography in the area is nearly flat with slope angles mainly between 1 and 2% despite steeper areas of 2–6% slopes (Waldrip and Roberts 1972). Sediments are mainly composed of till, outwash and patchy thin loess. These unconsolidated glacial deposits may be several hundred feet thick and are dominated by till. Soil profiles in Central Indiana and in the watersheds studied in particular are poorly drained, deep, and nearly level to gently sloping silt loams and silty clay loams (USDA 1974).

Study Watershed A (Fig. 1) is a 10.9 km^2 agricultural watershed with a stream length of 5.7 km and an average slope of 0.08%. Artificial tile drainage is widely used in this watershed and land use is approximately 85% agricultural (corn-soybean rotation) with small percentages of residential, forest, and other land uses (roads, open water). Study Watershed M (Fig. 1) is a 6.7 km^2 mixed land use watershed with a stream length of 4.6 km and an average slope of 0.4%. This watershed consists of residential neighborhoods (33%), agriculture (tile drained fields with corn-soybean rotation) (33%), pasture (17%), forest (13%) and other land uses (roads, open water) (4%). Single-family residential dwellings built in the 1980 s-to-present dominate development in the residential areas. New neighborhoods in the headwaters of watershed M contains at least three artificial wet retention ponds that feed into the stream.

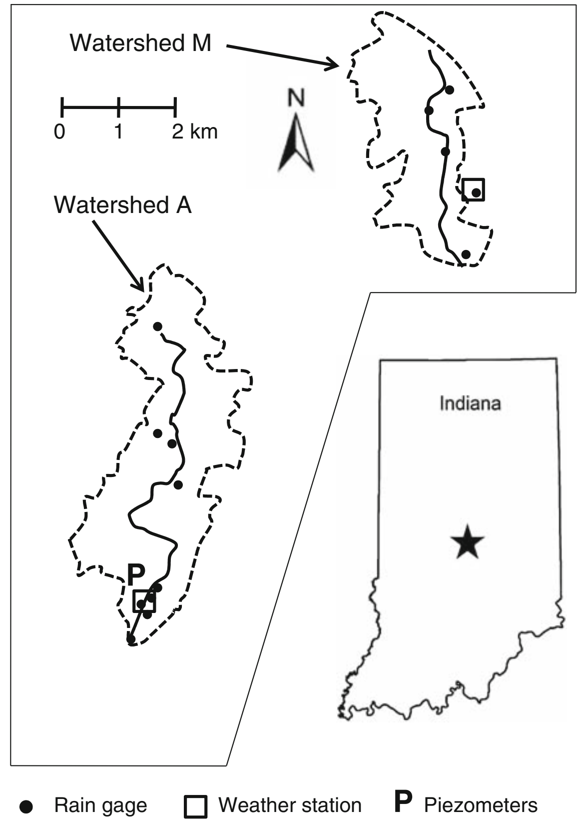

Fig. 1 Experimental site locations

Methods

Three storm events were monitored between May 2006 and July 2006 (Fig. 2). Precipitation timing and intensity was recorded at 15-min intervals in each watershed by two Vaisala WXT510 Multi-Parameter Transmitter weather stations. In addition, graduated rain gages were distributed throughout each watershed (10 in Watershed A; 5 in Watershed M) to capture variability in bulk precipitation and chemistry of precipitation (Fig. 1). Stream stage was recorded at 15-min intervals using a levelogger (Solinst 3001) at each watershed outlet. A Doppler acoustic velocity meter (Sontek Argonaut-SW) was installed in rotation at the outlet of each watershed to develop a rating curve for discharge estimation. A simple mixing model using oxygen-18 of water was also used to separate event (direct precipitation/overland flow/preferential flow) from pre-event water (water stored in the watershed prior to the storm event) in the streams during the storms studied (Sklash, 1990; Hill and Waddington 1993). A detailed description of the methodology and results of this hydrograph separation is presented in details in Wagner et al. (2008). Soil characteristics were determined using a combination of field observation and USDA soil maps. In addition, a total of 20 piezometers were installed in watershed A to characterize groundwater chemistry under agricultural land use. All piezometers were

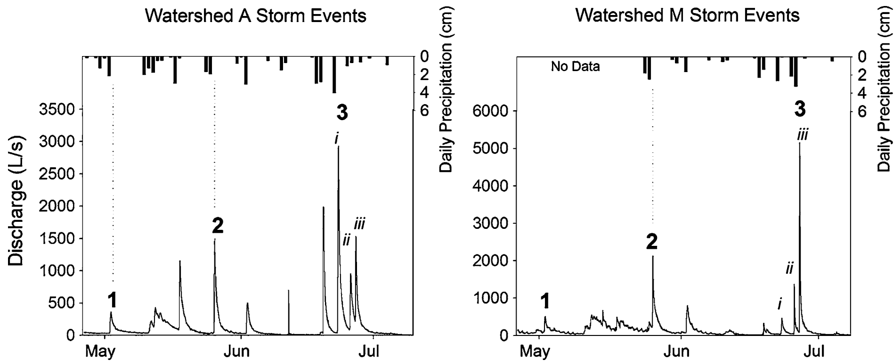

Fig. 2 Daily precipitation (cm) and stream discharge (L/s) (15 minute intervals) between May 2006 and July 2006. Numbers 1, 2 and 3 indicate the storms studied. The first, second and third pulses in discharge during storm 3 are indicated by *i*, *ii*, and *iii*

installed using a hand auger and constructed of 1.27 cm diameter PVC pipe with a 20 cm screen length. In watershed A, ten of these piezometers were installed at 90 cm depth and ten at 150 cm depth at the boundary between an agricultural field (corn/soy rotation) and a riparian zone along a deeply incised (3 m deep) section of the stream channel to capture the groundwater chemistry under agricultural conditions. A total of six tile drain outlets draining agricultural fields were also sampled to further characterize groundwater chemistry under agricultural conditions in the watersheds studied. Finally, three residential water retention ponds were sampled before each storm in watershed M to characterize water chemistry originating from residential areas. Stream samples were collected during storms using four ISCO brand auto-samplers, with two samplers located at the outlet of each watershed. One sampler per watershed contained bottles with 8 mL of 11 N sulfuric acid to preserve the DOC (Standard Method SM 5310C). ISCO brand auto-samplers were triggered manually and samples were taken every two hours on the rising limb of the hydrograph and every four hours on the falling limb. Each stream sample is a composite of 4 sub-samples taken every 30–60 min. Field blanks (Milli-Q water) were collected to insure the integrity of field sampling methods.

All water samples were filtered using Whatman GF/F 0.7 μm filters within a few hours of collection and frozen until analysis for DOC and major cations (generally within a few weeks of collection). Although freezing samples with high DOC concentrations (>15 mg/L) may affect DOC, SUVA and FI values, freezing typically does not affect these parameters if DOC concentrations are less than 15 mg/L (Hood 2007, oral communication).Triplicate analysis of 10% of all samples and the analysis of check standards every 10 samples were performed to assess measurement error. DOC samples were analyzed using a persulfate oxidation to CO_2 and an OI Analytical DOC/DIC analyzer interfaced to an IRMS. 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. 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 mg C^{-1} m^{-1} (Weishaar et al. 2003). The fluorescence index of each DOC sample was measured using a full range fluorometer (Gilford Fluoro IV spectrofluorometer) and is expressed as the ratio of the emission intensity at 450 nm to that of the emission intensity at 500 nm, with an excitation wavelength of 370 nm (McKnight et al. 2001). Major cation concentrations were determined using a Dionex DX500 Ion Chromatograph with a CS15 column and an 11 N sulfuric acid eluent.

Results

Storm characteristics and stream hydrology

Stream hydrographs (15 min intervals) for watersheds A and M between May 2006 and July 2006 are shown on Fig. 2. Average discharges for the study period in watersheds A and M were 139 L/s and 147 L/s, respectively. For the three spring storms studied in each watershed, bulk precipitation, average intensity, maximum intensity and 7-day antecedent precipitation are shown in Table 1. In both watersheds, storm 1 is the smallest and storm 3 is the largest, both in terms of bulk precipitation and in terms of the increase in discharge generated in each watershed. In watershed

Table 1 Seven-day antecedent precipitation (cm), bulk precipitation (cm), and average and maximum precipitation intensities (cm/h) for storms 1, 2, and 3 in watersheds A and M

	7-day antecedent precipitation (cm)	Bulk precipitation (cm)	Average intensity (cm/h)	Maximum intensity (cm/h)
Watershed A				
Storm 1	1.7	2.8	0.51	1.80
Storm 2	1.9	3.6	1.31	2.84
Storm 3	5.9	5.8	0.76	5.26
Watershed M				
Storm 1	n/a	2.7	n/a	n/a
Storm 2	1.9	3.4	2.96	4.55
Storm 3	3.8	8.0	0.96	6.22

Table 2 Average event water contribution (average % event) as a % of total discharge for each storm, and maximum event (% max event) and maximum pre-event (% max pre-event) water contributions as percentage of instantaneous discharge for storms 1, 2, and 3 for Watershed A and Watershed M

	Watershed A			Watershed M		
	Average % event	% max event	% max pre-event	Average % event	% max event	% max pre-event
Storm 1	11	32	97	44	77	99
Storm 2	23	34	99	23	48	95
Storm 3	33	61	88	23	96	97

A, storm 3 contained 3 pulses with the first pulse being the largest. To the contrary, the third pulse in discharge is the largest in watershed M for storm 3. Overall, discharge increased in watershed A from less than 50 L/s to 360 L/s for storm 1, 1,500 L/s for storm 2, and 2,900 L/s for storm 3 (Fig. 2). In watershed M, discharge increased from less than 100 L/s to 470 L/s for storm 1, 2,100 L/s for storm 2 and 5,200 L/s for storm 3. The average water table depth below ground surface (BGS) as measured in piezometers before each storm was 90 cm BGS for storm 1, 80 cm BGS for storm 2 and 52 cm BGS for storm 3. As indicated earlier, a thorough analysis of each storm using a simple hydrograph separation technique based on oxygen-18 of water was also conducted to determine the proportion of event and pre-event water in the stream for each storm. Briefly, although hydrograph separations indicate that streamflow was dominated by pre-event water for all storms in both watersheds, the proportion of event and pre-event water in the stream varied during the storms studied and between land uses (Table 2). Average contributions of event water were larger in watershed M than watershed A for storm 1, similar for storm 2, and smaller than in watershed A for storm 3 (Table 2). However, maximum instantaneous contributions of event water to stream flow were consistently higher in watershed M (77% for storm 1; 48% for storm 2, 96% for storm 3) than in watershed A (32% for storm 1; 34% for storm 2, 61% for storm 3). In all cases, maximum event water contribution coincided with maximum discharge (data not shown).

Concentration and spectroscopic characteristics of DOC

The average DOC concentration, and SUVA and FI values in shallow (90 cm) and deep (150 cm) piezometers, in tile drains, in residential ponds and in the streams before each storm are shown in Table 3. Stream DOC concentration at baseflow in watershed A (4.78 mg/L) is higher than in tile drains (2.28 mg/L) but similar ($p < 0.05$) to groundwater (4.34 mg/L at 90 cm and 3.60 mg/L at 150 cm). In watershed M, DOC is highest in retention ponds (6.11 mg/L). In watershed A, SUVA in the stream at baseflow is similar to SUVA of DOC in piezometers ($p < 0.05$), but is higher than in tile drains. In watershed M, SUVA of stream DOC at baseflow (1.09 L mg C^{-1} m^{-1}) is similar to SUVA of wet residential ponds (1.04 L mg C^{-1} m^{-1}). The fluorescence index (FI) of stream at baseflow ranges between the FI of deep piezometers

Table 3 Average dissolved organic carbon concentration (DOC), DOC specific UV absorbance (SUVA) and DOC fluorescence index (FI) in shallow (90 cm) and deep (150 cm) piezometers, in tile drains, in residential water retention ponds, and in the stream in watersheds A and M for baseflow conditions in Spring 2006. Values in parenthesis indicate standard deviation

	DOC (mg/L)	SUVA (L mg C^{-1} m^{-1})	Fluorescence index
Shallow Piezometer (90 cm) (n = 9)	4.34 (±1.30)	1.04 (±0.69)	1.36 (±0.09)
Deep Piezometer (150 cm) (n = 28)	3.60 (±1.30)	1.33 (±1.47)	1.34 (±0.13)
Tile drains (n = 17)	2.28 (±1.04)	0.72 (±0.58)	1.39 (±0.07)
Residential water retention ponds (n = 9)	6.11 (±1.22)	1.04 (±0.49)	1.38 (±0.03)
Stream in watershed A (n = 12)	4.78 (±1.39)	1.35 (±0.39)	1.37 (±0.03)
Stream in watershed M (n = 12)	4.85 (±1.10)	1.09 (±0.22)	1.36 (±0.02)

and tile drains in both watersheds. Nevertheless, less variation within each group (lower standard deviation) is observed in the fluorescence index in both streams at baseflow than in any other group (except when compared to the retention pond water group).

Changes in DOC, SUVA, and FI in the stream in watersheds A and M during the three storms studied are shown on Fig. 3 (storm 1), Fig. 4 (storm 2) and Fig. 5 (storm 3). With the exception of storm 3 in watershed A where DOC peaks slightly after the peak in discharge during the first and largest peak of the storm, DOC peaks with discharge in both watersheds. Maximum DOC concentrations in watershed A during storms 1, 2, and 3 reach 5.0 mg/L, 7.6 mg/L and 11.1 mg/L, respectively. In watershed M, maximum DOC concentration during storms 1 and 2 are higher than in watershed A, but lower for storm 3 (6.5 mg/L for storm 1, 8.9 mg/L for storm 2, 9.5 mg/L for storm 3). Average DOC concentrations in watershed A during storms 1, 2, and 3 are 4.55 mg/L, 6.02 mg/L and 8.80 mg/L, respectively. In watershed M, average DOC concentrations during the storms studied are 4.63 mg/L for storm 1, 6.38 mg/L for storm 2, and 6.95 mg/L for storm 3. However, when all samples are combined, DOC concentration is higher ($p < 0.01$) in watershed A (6.6 mg/L) than in watershed M (6.0 mg/L).

Similarly to DOC, SUVA quickly increases and decreases with discharge for all storms in both watersheds. In watershed A, maximum SUVA values are 3.4 L mg C^{-1} m^{-1} for storm 1, 3.9 L mg C^{-1} m^{-1} for storm 2, and 4.4 L mg C^{-1} m^{-1} for storm 3, with average SUVA values for storms 1, 2, and 3 of 2.8 L mg C^{-1} m^{-1}, 2.1 L mg C^{-1} m^{-1}, and 2.9 L mg C^{-1} m^{-1}, respectively. In watershed M, maximum SUVA values for storm 1 is 1.9 L mg C^{-1} m^{-1}, 3.8 L mg C^{-1} m^{-1} for storm 2, and 5.2 L mg C^{-1} m^{-1} for storm 3. Average SUVA values in watershed M are significantly lower ($p < 0.01$) than in watershed A with average SUVA values of 1.3 L mg C^{-1} m^{-1}, 1.8 L mg C^{-1} m^{-1}, and 1.9 L mg C^{-1} m^{-1}, for storms 1, 2, and 3, respectively.

Although FI appears to follow discharge in watershed M when it is less than 200 L/s (Fig. 3), FI is inversely correlated to discharge during all storms in both watersheds and drops quickly at the onset of the storm as discharge and DOC concentration start increasing in the streams (Figs. 3–5). Minimum FI reached during the peak in discharge in watershed A are 1.32, 1.19, and 1.19 for storms 1, 2, and 3, respectively. Minimum values for FI in watershed M are 1.33 (storm 1), 1.24 (storm 2), and 1.19 (storm 3). Average FI values for the entire duration of the storms are generally slightly higher in watershed M (1.36 for storm 1, 1.32 for storm 2, 1.31 for storm 3) than in watershed A (1.36 for storm 1, 1.28 for storm 2, 1.26 for storm 3).

DOC and major cation hysteresis

The flushing dynamics of DOC and major cations is presented using hysteresis analysis for storms 1, 2, and 3 in each watershed in Fig. 6 (DOC) and Fig. 7 (cations). The hysteresis patterns for calcium and sodium were similar to magnesium, suggesting a similar flushing behavior. Consequently, only the hystereses for magnesium and potassium are shown on Fig. 7 to minimize the number of figures. In watershed A, the analysis of DOC hystereses (Fig. 6) indicates a clockwise rotation for storms 1, 2, and 3 with the exception of the first pulse in storm 3. This indicates a higher concentration of DOC on the rising limb of the storm hydrograph than on the falling limb, except during the largest increase in discharge of all

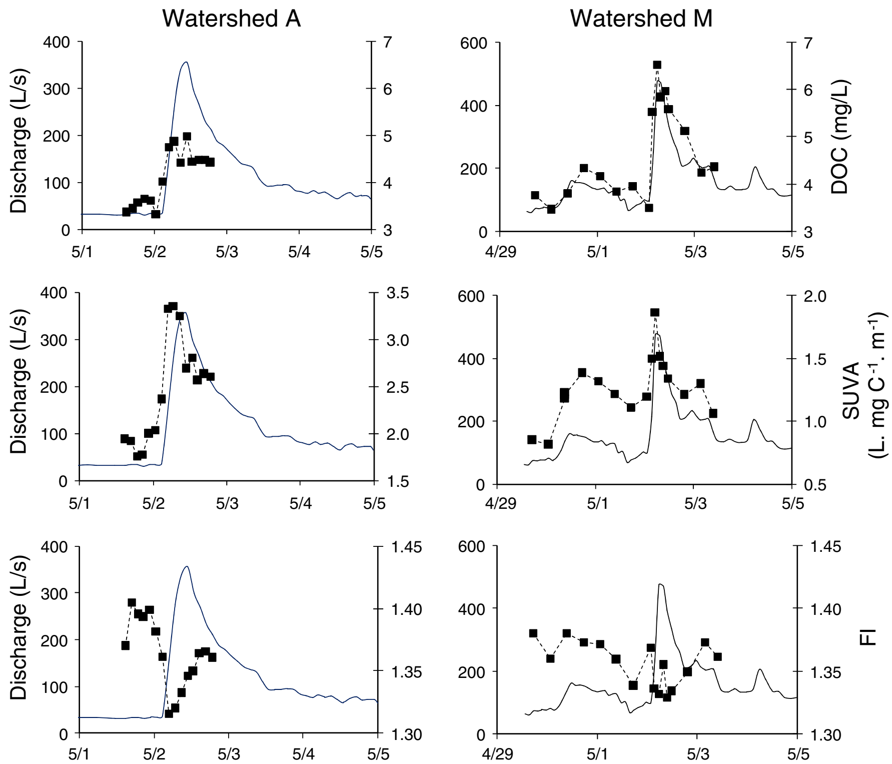

Fig. 3 Discharge, stream dissolved organic carbon concentration (DOC) (mg/L), specific UV absorbance of stream DOC (SUVA) (L mgC^{-1} m^{-1}), and fluorescence index of stream DOC (FI) in watersheds A and M during storm 1

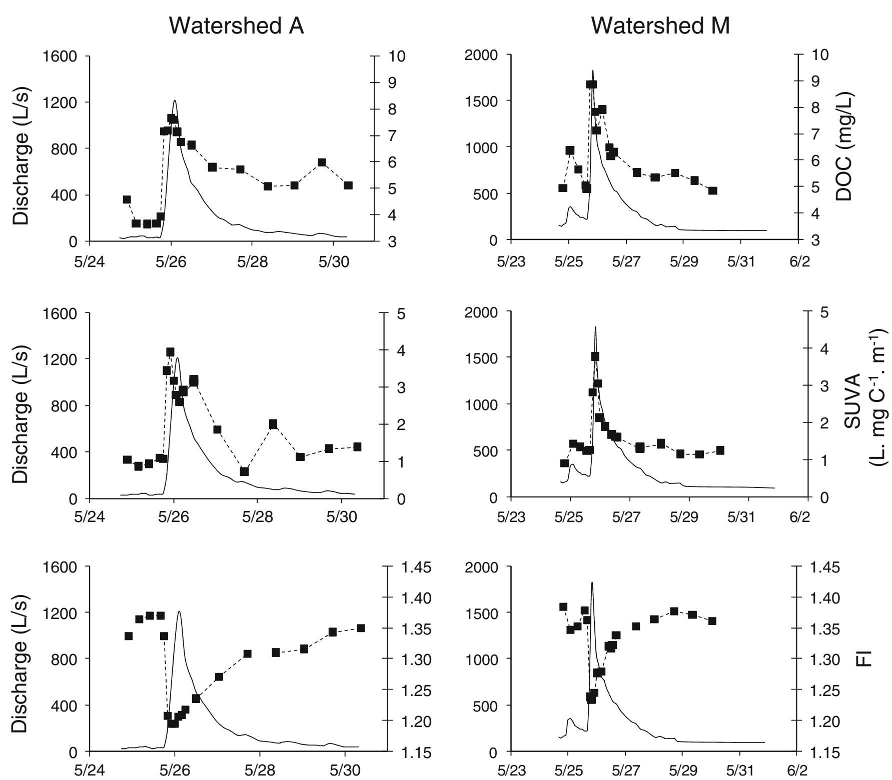

Fig. 4 Discharge, stream dissolved organic carbon concentration (DOC) (mg/L), Specific UV absorbance of stream DOC (SUVA) (L mgC^{-1} m^{-1}), and fluorescence index of stream DOC (FI) in watersheds A and M during storm 2

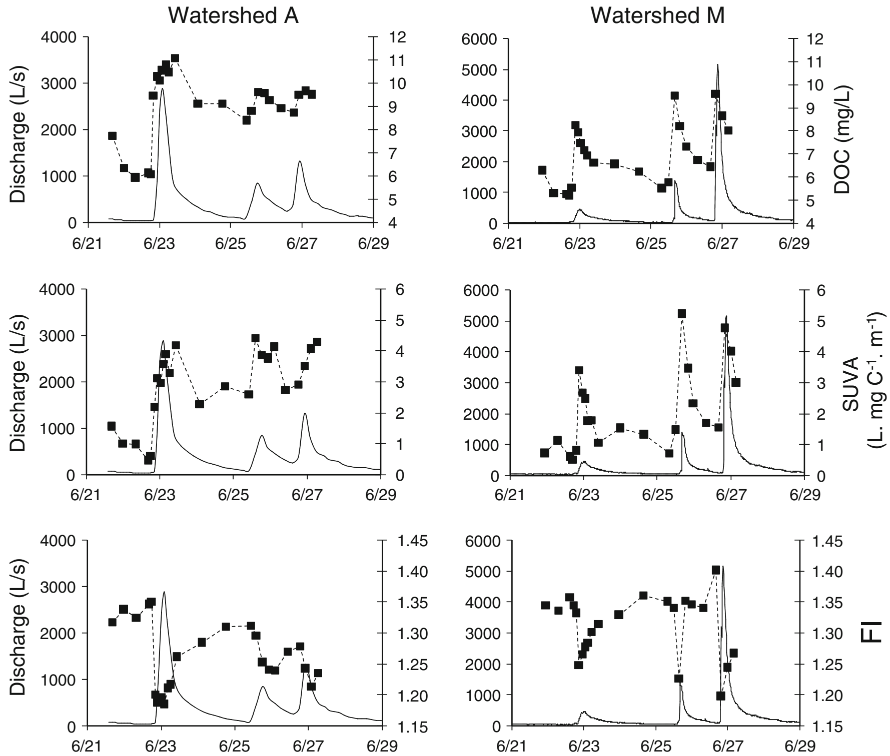

Fig. 5 Discharge, stream dissolved organic carbon concentration (DOC) (mg/L), Specific UV absorbance of stream DOC (SUVA) (L mgC^{-1} m^{-1}), and fluorescence index of stream DOC (FI) in watersheds A and M during storm 3

storms (first peak of storm 3) where the DOC hysteresis rotates in a counterclockwise motion, suggesting higher DOC concentration on the falling limb of the hydrograph than on the rising limb. In watershed M, DOC flushing dynamics for storm 1 and 2 was very similar to DOC behavior in watershed A with hystereses of similar shapes and rotations in a clockwise direction. For storm 3, DOC hystereses all rotated in a clockwise motion, whereas a counterclockwise rotation was observed for the first and largest peak in watershed A.

For storm 2 and the second and third pulses of storm 3 in watershed A, the shape and rotation of potassium hystereses are similar to the one of DOC, which indicates a similar flushing behavior. Both show an increase in concentration with discharge and higher concentration on the rising limb than the falling limb (clockwise rotation). Although data also indicate an increase in concentration with discharge for both potassium and DOC for the first and largest peak in storm 3 in watershed A, the potassium hysteresis rotates in the clockwise direction and presents a figure eight shape, whereas the DOC hysteresis rotates in a counterclockwise direction and presents a single loop. In watershed M, potassium data also indi-

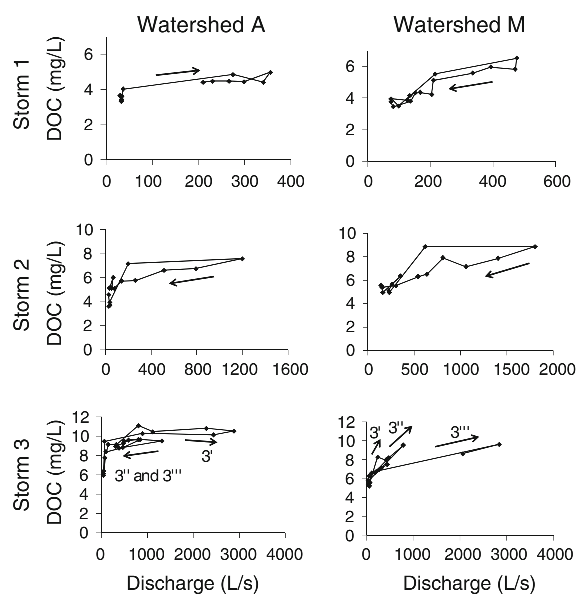

Fig. 6 Concentration/discharge plots for DOC in watersheds A and M for storms 1, 2, and 3. Numbers 3′, 3′′, and 3′′′ indicate the 1st, 2nd, and 3rd peaks in discharge during storm 3 for both watersheds A and M

cate an increase in concentration with discharge for all storms but hysteresis loops in the counterclockwise direction, except for the largest and third peak in

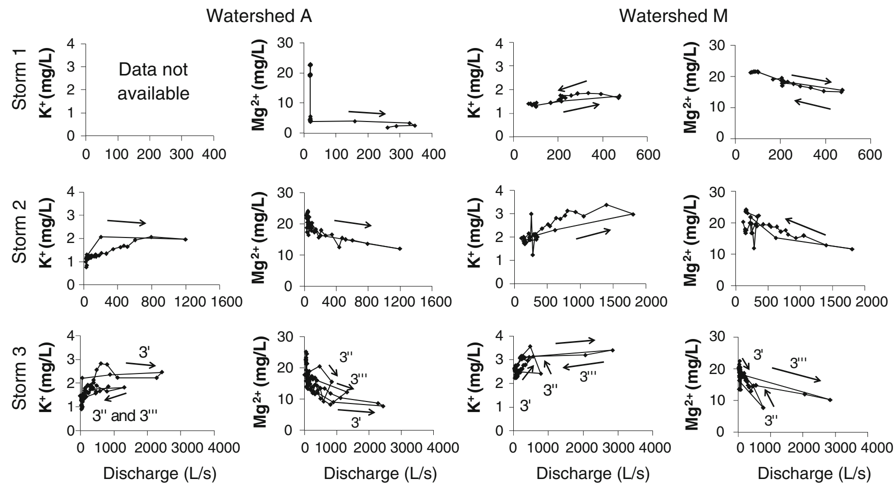

Fig. 7 Concentration/discharge plots for potassium (K^+) and magnesium (Mg^{2+}) in watersheds A and M for storms 1, 2, and 3. Numbers 3′, 3′′, and 3′′′ indicate the 1st, 2nd, and 3rd peaks in discharge during storm 3 for both watersheds A and M. Because of initial equipment malfunction, potassium hysteresis data for storm 1 in watershed A are not shown

discharge for storm 3. When compared to DOC hysteresis loops, DOC and potassium in watersheds A and M both increase with discharge, suggesting a similar flushing behavior.

In watershed A, hysteresis for magnesium indicates a dilution trend as discharge increases, and shows a clockwise rotation for all storms, except the first and largest peak in discharge for storm 3 for which a counterclockwise rotation is observed. For watershed M, magnesium hysteresis loops also indicate a dilution trend for storms 1, 2, 3, with lower concentrations at high discharge than at baseflow. When DOC flushing behavior is compared to magnesium flushing dynamics, shapes are different and hysteresis rotations are not consistently the same, suggesting overall different flushing behavior for DOC and magnesium in both watersheds.

Discussion

As indicated on Figs. 3–5, DOC concentration increases and decreases quickly with discharge regardless of land use, and DOC concentration typically peaks with discharge. This suggests a quick transfer of DOC to the stream as soon as discharge increases due to precipitation. This behavior is similar to the flushing behavior of DOC reported by Inamdar et al. (2004) in the Adirondack Mountains of New York, where DOC peaks with or slightly after the peak in discharge. When looking at DOC dynamics in the streams studied, it does not appear that land use is a strong control on stream DOC concentration or dynamics. Indeed, DOC typically peaks with discharge regardless of land use. In addition, although when all storms are grouped together average DOC concentration is slightly higher in watershed A (6.6 mg/L) than M (6.0 mg/L), a detailed analysis of each storm revealed that average DOC concentrations for storms 1 and 2 were higher in watershed M than A. On the other hand, precipitation characteristics / discharge appear to be the primary control on stream DOC concentration during storms. For both watersheds, DOC concentration is strongly positively correlated to discharge (Pearson correlation coefficient $\rho_{xy} = 0.65$ in watershed A ($n = 50$); $\rho_{xy} = 0.69$ in watershed M ($n = 56$)). In addition, when the data from watersheds A and M are grouped together, the Pearson correlation coefficient between discharge and DOC concentration remains almost the same ($\rho_{xy} = 0.65$, $n = 106$). This suggests that precipitation characteristics and stream response to precipitation (discharge) are the primary controls on stream DOC concentration during storms in spite of differences in hydrological functioning between the two watersheds. Indeed, although surficial geology is the same in both watersheds, artificial drainage is commonly used in watershed A, whereas artificial wet retention ponds that feed into the stream are present in watershed M. In spite of these differences, land use appears to be only a secondary control on DOC concentration in the watersheds studied.

Another point of interest is that although hydrograph separation data indicate that the proportion of event/pre-event water changes over the course of the storms (Table 2), event water peaks with maximum discharge (data not shown). The fact that event water contribution is maximum when discharge is maximum and therefore when DOC concentration is at its highest, suggests that high DOC concentrations are associated with high contributions of event water (direct precipitation/overland flow/preferential flow). This is consistent with DOC being exported mainly as overland flow or preferential flow through soil macropores.

Overall, data suggest that the differences in precipitation event characteristics and associated response in terms of discharge for each storm is directly related to DOC concentration patterns, with DOC concentration showing a strong positive correlation with discharge. Bulk precipitation, maximum precipitation intensity and 7-day antecedent precipitation nevertheless all increase from storms 1 to 3, so although these variables certainly affect DOC exports, it is not possible to determine which of these precipitation characteristics has the most impact on DOC concentration in the streams studied.

Data also indicate that the increase in concentration of DOC in the streams studied during storms is not simply due to an increased mobilization of a given pool of DOC, but rather to the mobilization of a different pool of organic carbon than the organic carbon pool contributing to baseflow. The increase in the specific UV absorbance of DOC (SUVA) during storms 1, 2, and 3 across land use indicates a change in the character of stream DOC during storms. Using the regression model developed by Weishaar et al. (2003), where SUVA is directly linked to the percent of aromaticity of DOC, the aromaticity of stream DOC in watershed A increases from 15% to 25% during storm 1, from 9% to 29% for storm 2, and from 7% to 32% for storm 3. Similarly, in watershed M, the aromaticity of stream DOC increases from 9% to 16% for storm 1, from 10% to 28% for storm 2, and from 7% to 38% for storm 3. It is important to note here that DOC aromaticity was not directly measured in this study and that the Weishaar model was not developed for artificially drained landscapes of the Midwest. Although this does not affect the validity of the patterns of aromaticity observed in this study, caution should be used in interpreting the absolute values of aromaticity estimates presented here. Regardless, data indicate an increase in stream DOC aromaticity during storms regardless of land use, which is consistent with the mobilization of near surface soil DOC rich in aromatic substances (Hood et al. 2006). This is also consistent with the model of DOC flushing presented by McGlynn and McDonnell (2003) in forested mountainous catchments of New Zealand, which suggests that DOC early in the storm likely originates from shallow organic soils which have high concentrations of aromatic DOC.

Low SUVA values at baseflow in watersheds A and M, and low SUVA values in tile drains and piezometers at baseflow (Table 3) are also consistent with stream DOC at baseflow originating from mineral soils poor in aromatic substances (Hood et al. 2006). Indeed, mineral soils such as soil derived from glacial till are common in the watersheds studied. The water table was also always below 50 cm deep before each storm, indicating that during baseflow, the surficial soil rich in organic carbon and in aromatic substances was hydrologically disconnected from the stream. SUVA data therefore suggest that DOC originating from mineral soils in the watersheds studied (low SUVA) is likely the main source of DOC to the stream at baseflow. As precipitation starts and stream discharge increases, DOC richer in aromatic substances located near the soil surface is mobilized and quickly reaches the stream (high SUVA).

For our watersheds, we believe that the presence of tile drains offers a quick transfer mechanism for near surface soil DOC to the stream. We did not directly measure the relative importance of overland flow relative to the flushing of near surface soil DOC to tile drain via preferential flow through soil macropores during storms; however, many studies have shown the importance of macropores in solute transport to tile drains in artificially drained landscapes of the Midwest (Kladivko et al. 1991; Kung et al. 2000a, b; Stone and Wilson, 2006). In particular, Stone and Wilson (2006) indicate that for two storms in an agricultural watershed East of Indianapolis, IN, preferential flow through soil macropores can represent up to 15% of total tile drain flow, with maximum instantaneous contribution of 81%. This suggests that the transport of near surface soil water to tile drains through soil macropores can be an important transfer mechanism in artificially drained landscapes. On the other hand, many studies have also shown that the mobilization of near surface soil DOC by overland flow could be an important transport mechanism for DOC to streams (Stottlemyer and Toczydlowski 1991; Stevens et al. 1999; Hyer et al. 2001; Johnson et al. 2006). Consequently, we believe that in the watersheds studied, the increased contribution of DOC rich in aromatic substances to the streams during storms is likely due to the mobilization of near surface soil DOC rich in aromatic substances, and that this DOC is transported to the streams via either overland flow or preferential flow through soil macropores. These results indicate that the increase in DOC concentration in the stream during storms in the watersheds studied is not simply due to an increased mobilization of a given pool of DOC, but rather to a shift in the dominant source of DOC from mineral soil DOC poor in aromatic substances at baseflow, to near surface soil DOC rich in aromatic substances during storms. More investigations are underway to characterize the nature and concentration of DOC in tile drains during storms and the relative importance of overland flow and tile flow in DOC export at the watershed scale.

Average SUVA values in watersheds A and M also indicate that on average, DOC is more aromatic in the agricultural watershed (watershed A) than in the mixed land use watershed (watershed M). Indeed, the average percent of aromatic substances in stream DOC as estimated using the Weishaar model (Weishaar et al. 2003) in watershed A is 22% for storm 1, 17% for storm 2, and 23% for storm 3; whereas it is 12% for storm 1, 15% for storm 2 and 16% for storm 3 in watershed M. The higher aromaticity of stream DOC during storms in watershed A could simply be due to the larger availability of crop residues rich in aromatic substances near the soil surface in watershed A, and to the widespread use of artificial drainage in this watershed, which can facilitate the transfer of near surface soil DOC rich in aromatic substances to the stream via macropore flow to tile drains. SUVA data also indicate that in addition to land use, precipitation characteristics and stream discharge influence the nature of DOC in the stream. There are highly significant ($p < 0.001$) correlations between SUVA values and discharge in both watersheds ($\rho_{xy} = 0.44$ in watershed A, $\rho_{xy} = 0.77$ in watershed M). This suggests that although discharge cannot explain all variations in SUVA values, high SUVA values tend to be associated with high discharges. It is difficult to dissociate the impact of antecedent moisture conditions (7 day antecedent precipitation), bulk precipitation and maximum precipitation intensity on SUVA or DOC values as all increase from storms 1 to 3; however, there is a clear relationship between discharge and SUVA suggesting that as discharge increases, DOC in the stream becomes more aromatic (higher SUVA). Although the total and maximum contribution of new water to the stream increases from storms 1 to 3 in watershed A, there are no clear relationships between event water contributions and discharge or precipitation characteristics in watershed M (Table 1, 2). Higher event water contributions (direct precipitation/overland flow/preferential flow) therefore appear to be related to higher SUVA and DOC values in watershed A, but no clear relationships between event water contributions and SUVA or DOC values are observed in watershed M.

Overall, inter-storm comparison clearly indicates that variability in SUVA values during the storms studied is directly related to discharge; however, no clear relationships could be identified between specific precipitation characteristics and event water contributions on one hand, and DOC concentrations and SUVA values on the other.

In addition to SUVA data, the fluorescence index data (FI) are consistent with an influx of terrestrial DOC more aromatic and containing more lignin than DOC at baseflow to both streams during storms. As indicated by McKnight et al. (2001), the fluorescence index (FI) of filtered whole water samples is related to the presence or absence of lignin in organic matter, and to aromaticity. Hood et al. (2006) indicate that the FI of filtered whole water samples can therefore be used to differentiate between aquatic autochthonous material that lacks lignin (high FI around 1.8) and terrestrial material that contains lignin (low FI around 1.3). In our streams, FI values range between 1.18 and 1.40 suggesting that most of the DOC in the streams studied is terrestrial (allochthonous) in origin. This is consistent with results reported by McKnight et al. (2001), which indicate that most organic carbon in US rivers is terrestrial in origin. It is nevertheless important to note here that direct comparison of FI values between studies is always difficult as FI values tend to be extremely sensitive to instrument type. Triplicate analysis of 10% of all samples allowed us to determine a standard error on all measurements of 0.01. Although the accuracy of our measurement was not determined relative to other studies, the high precision of our measurements suggest that variations in FI along the hydrograph reported in this study are significant. Although data suggest that most of the carbon in our streams is likely terrestrial in origin, the sharp decrease in FI as discharge increases during storms in both watersheds is consistent with an input of terrestrial organic carbon rich in aromatic substances and containing a higher amount of lignin than the DOC present in the stream at baseflow (McKnight et al. 2001; Hood et al. 2006). FI values between 1.34 and 1.39 in piezometers and tile drains before the storms (Table 3) are also consistent with DOC present in groundwater before each storm having less lignin and a lower aromaticity than DOC present in the stream during storms ($1.18 < FI < 1.32$). These results are consistent with SUVA data and with a change in the source of DOC to the streams during storms from terrestrial DOC originating from mineral soil layers and containing low amounts of lignin at baseflow, to near surface soil DOC with a higher aromaticity and containing a higher amount of lignin during storms.

Finally, the comparison of DOC flushing hystereses with the flushing trajectories of major cations revealed that DOC was not exported along with magnesium, but had a flushing trajectory relatively similar to potassium. As indicated by many studies, magnesium is typically exported via groundwater flow and dilution trends in magnesium concentration are often observed as discharge increases (Reid et al. 1981; Elwood and Turner 1989; Kahl et al. 1992; Hill 1993; Hood et al. 2006). On the other hand, as indicated by Hood et al. (2006), potassium concentration in streams is likely to have precipitation contributions, whereas magnesium is likely to have only weathering contributions. It is also usual for potassium to be applied to the soil surface in agricultural fields along with nitrogen. This suggests that magnesium is likely exported with groundwater in the watersheds studied, whereas potassium is more likely to be exported from the soil surface via overland flow or preferential flow through soil macropores. The similarity of DOC and potassium flushing trajectories in both watersheds is therefore consistent with DOC being exported mainly as overland flow or preferential flow through soil macropores in the watersheds studied. These results are also consistent with results reported by Hood et al. (2006) for a forested mountainous watershed in Oregon, where DOC and potassium often had similar flushing trajectories.

Another interesting aspect of this study is that it is consistent with studies in forested mountainous landscapes in that it indicates that DOC could be used as a hydrological tracer to identify the mixing of various water sources at the watershed scale (Katsuyama and Ohte 2002; McGlynn and McDonnell 2003; Hood et al. 2006). For instance, sharp changes in DOC concentration, and SUVA and FI values of stream DOC during storms suggest that different pools of water contribute DOC to the stream in different ways as storms progress. More research needs to be conducted to better identify the chemical signature of surface soil DOC vs. deeper soil DOC (90–150 cm); however, our results suggest that the analysis of the specific UV absorbance and fluorescence properties of DOC could be used in artificially drained landscapes of the Midwest to quickly separate water originating from the near soil surface from water originating from deeper soil horizons.

Conclusion

This study investigates the changes in concentration and character of stream DOC in an agricultural and a mixed agricultural/urban land use watershed during three spring storm events ranging from 2.8 to 8.0 cm near Indianapolis, IN, USA. Although DOC is less aromatic in the mixed land use watershed than in the agricultural watershed, results indicate that land use has little influence on DOC concentration or DOC delivery to the streams studied. Instead, data indicate that discharge/precipitation characteristics are the primary controls on stream DOC concentration. The spectroscopic analysis of stream DOC (SUVA and FI) reveal a clear shift in the source of DOC to the streams during storms. In particular, results suggest that the increase in DOC concentration in the streams during storms is not simply due to the increased mobilization of a given pool of DOC during storms, but rather to the mobilization of near surface soil DOC with higher aromaticity and lignin content than the DOC derived from mineral layers of the soil profile and contributing DOC to the stream at baseflow. Together, SUVA and FI data, and the comparison of DOC flushing trajectories with major cations flushing behavior all point to DOC being exported via overland flow or tile drains via preferential flow through soil macropore during storms, regardless of land use. Results also suggest that DOC, SUVA and FI could be used as hydrologic tracers to determine the mixing of various water reservoirs at the watershed scale in artificially drained landscapes of the Midwest.

Overall, these results have significant implications regarding the fate of DOC in streams, as organic carbon containing high amounts of lignin is typically less easily degraded than organic carbon containing low amounts of lignin (Melillo et al. 1982). This study also indicates that since most DOC is exported during episodic precipitation events (Boyer et al. 1997; Dalzell et al. 2007), it is essential to characterize the nature of DOC in streams during high flow periods, as opposed to baseflow, in order to fully comprehend the fate of DOC in streams. Additional research is underway to further characterize the relative contribution of overland flow and preferential flow through soil macropores in DOC transport across land uses in glaciated landscapes of the Midwest, as well as variations in the character of DOC in tile drains during storms.

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