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Dissolved organic carbon in streams from artificially drained and intensively farmed watersheds in Indiana, USA

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Abstract Dissolved organic carbon (DOC) in streams draining hydrologically modified and intensively farmed watersheds has not been well examined, despite the importance of these watersheds to water quality issues and the potential of agricultural soils to sequester carbon. We investigated the dynamics of DOC for 14 months during 2006 and 2007 in 6 headwater streams in a heavily agricultural and tile-drained landscape in the midwestern US. We also monitored total dissolved nitrogen (TDN) in the streams and tile drains. The concentrations of DOC in the streams and tile drains ranged from approximately 1–6 mg L^{-1}, while concentrations of TDN, the composition of which averaged >94% nitrate, ranged from <1 to >10 mg L^{-1}. Tile drains transported both DOC and TDN to the streams, but tile inputs of dissolved N were diluted by stream water, whereas DOC concentrations were generally greater in the streams than in tile drains. Filamentous algae were dense during summer base flow periods, but did not appear to contribute to the bulk DOC pool in the streams, based on diel monitoring. Short-term laboratory assays indicated that DOC in the streams was of low bioavailability, although DOC from tile drains in summer had bioavailability of 27%. We suggest that these nutrient-rich agricultural streams are well-suited for examining how increased inputs of DOC, a potential result of carbon sequestration in agricultural soils, could influence ecosystem processes.

Keywords Agriculture · Algae · Dissolved organic carbon · Indiana · Nitrogen · Stream · Tile drain · SUVA · Allochthonous · Autochthonous · Bioavailability

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Introduction

In aquatic ecosystems, dissolved organic carbon (DOC) is an energy source for microorganisms (Edwards and Meyer 1987), forms complexes with metals (Perdue et al. 1976), absorbs ultraviolet light (Frost et al. 2005), and interacts with inorganic nutrient cycling (Bernhardt and Likens 2002). The DOC pool in a stream is a mixture of recalcitrant substances, such as humic and fulvic acids, together with labile compounds that are respired rapidly (Thurman 1985). Allochthonous DOC is primarily derived from terrestrial plants, soils, and the decomposition of litter, whereas autochthonous DOC includes macrophyte and algal exudates. The source, quality, and fate of DOC in streams have been the subject of much investigation (e.g., Findlay and Sinsabaugh 2003), although mainly in forested or montane environments with relatively little agricultural impact (but see Eckhardt and Moore 1990; Findaly et al. 2001). Streams draining agriculturally-dominated landscapes have received much less attention regarding the biogeochemistry of DOC (Hope et al. 1994).

In the midwestern US, vast areas of poorly drained soils that formerly supported wetlands and wet prairie were drained in the late 19th and early 20th centuries by the installation of tile drains and the land was subsequently converted to intensive row-crop agriculture. Tile drains facilitate the movement of water (and solutes) from the landscape to headwater streams, most of which have been channelized and dredged to prevent overbank flooding from high discharges that occur during storms (Fausey et al. 1995). At present, approximately 20 million hectares of land are tile-drained in the Mississippi River basin, with much of this located in the upper Midwest (Goolsby et al. 1999). These hydrologically-modified and intensively-farmed regions are major contributors of N and other solutes to the Mississippi River and Gulf of Mexico (Royer et al. 2006; Alexander et al. 2008). Because DOC plays an important role in many biogeochemical cycles, a better understanding of DOC in tile-drained agricultural landscapes is needed for addressing both local and continental-scale water quality problems.

DOC concentrations in agricultural streams are often lower than in forested streams or streams influenced by wetlands (Cronan et al. 1999; Royer and David 2005; Jaffé et al. 2008). In the midwestern US, the quality of stream DOC is influenced by antecedent moisture conditions, the interception of natural flow paths by tile drains, and the dominance of terrestrial vegetation by crops (Dalzell et al. 2005, 2007; Vidon et al. 2008). Algal blooms potentially provide an autochthonous source of DOC to agricultural streams (Kaplan and Bott 1982), but the relative importance of autochthonous and allochthonous sources is largely unknown, as is the effect of tile drains on DOC dynamics.

The transport of inorganic nitrogen (N) through tile drains in the midwestern US is understood much more fully than is the case for DOC. The input of N to headwater streams through tile drains occurs mainly as nitrate and displays a strong seasonal pattern in response to precipitation (e.g., Royer et al. 2006). Additionally, antecedent moisture conditions, timing and magnitude of fertilizer application, tillage practices, and soil properties are important controls on N movement through tile drains to streams (e.g., Jaynes et al. 2001; Randall and Goss 2001; Kalita et al. 2006). Because of the greater knowledge base for sources, transport, and fate of inorganic N, we used a comparative approach between DOC and total dissolved N (TDN), the bulk of which is nitrate (see below), to gain insight into the dynamics of DOC in small agricultural watersheds.

The objective of this study was to investigate factors controlling the sources (allochthonous vs. autochthonous) and nature of DOC in headwater streams in a tile-drained, agricultural landscape. Our study focused on periods of low to moderate stream discharge because rates of most biogeochemical processes tend to be high during these periods. Floods represent periods of high solute flux, but with little processing or interaction with sediments (Meyer and Likens 1979). Based on previous work (Royer and David 2005), we expected that tile drains would be a major mechanism for transporting terrestrial DOC to streams and that the DOC would be of low bioavailability. Conversely, we hypothesized that during periods of low discharge, algal blooms would contribute labile DOC that would influence the size and bioavailability of the in-stream DOC pool.

Methods

Study area

The study was conducted in Benton County in northwestern Indiana, a region in which row-crop agriculture (corn-soy bean rotation) accounts for 92% of the land cover (USGS 2001). Six study sites, A through F, were selected on small (1st–3rd order) headwater streams (Fig. 1). Watershed areas ranged from 22 to 125 km^2 and all were dominated by row-

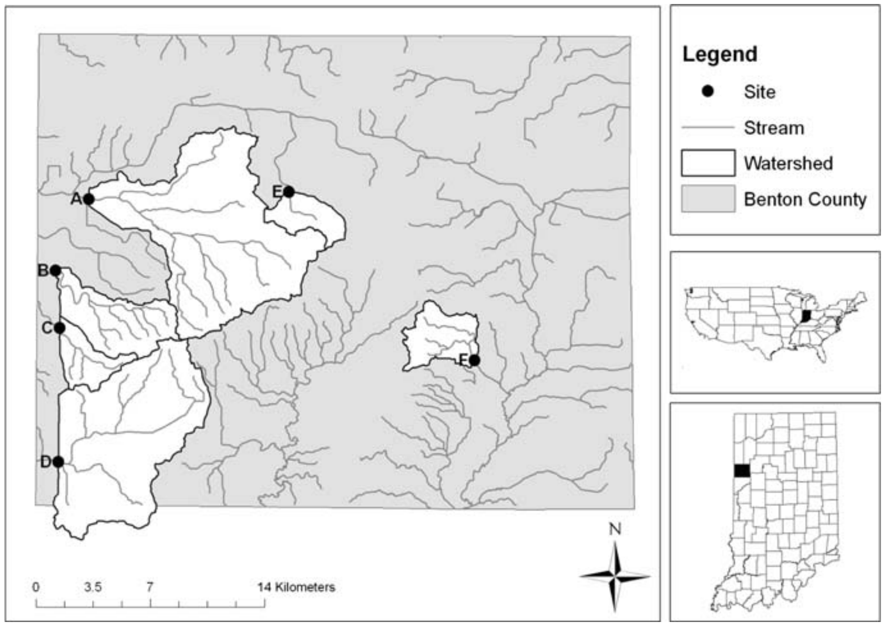


Fig. 1 Map of Benton County, Indiana showing the study streams and their watersheds. *Smaller maps* show location of the study area within Indiana and the contiguous US

Table 1 Site coordinates, drainage area, and land cover for each of the study sites

Watershed	Site coordinates	Area (km^2)	Row crop (%)	Developed (%)	Pasture/hay (%)
A	40°38′43.96″N 87°29′11.55″W	124.8	90.3	5.5	3.6
B	40°36′23.20″N 87°30′38.18″W	32.6	94.2	4.4	0.4
C	40°34′27.59″N 87°30′33.62″W	21.9	96.0	3.9	<0.1
D	40°30′03.05″N 87°30′36.87″W	97.2	96.0	1.5	0.5
E	40°38′58.71″N 87°20′37.41″W	26.7	92.2	5.7	1.4
F	40°33′27.72″N 87°12′33.68″W	25.9	88.5	6.9	3.6

crop agriculture (Table 1). Across the watersheds, somewhat poorly to very poorly drained soils were the prevalent soil classes, representing 64–86 % of the soils (USDA 2007). Despite the poor natural drainage, there were no appreciable wetlands within the study region due to the presence of extensive subsurface tile drains.

Water chemistry, precipitation, and discharge

Water samples were collected from streams and tile drains approximately monthly from July 2006 through September 2007. The total number of tile drains sampled on each date ranged from 3 to 8 depending on how many tiles were flowing on that date. No tiles were flowing from mid-July 2007 through the end of the study. Water samples for DOC were filtered (0.7 μm, Whatman GF/F) and acidified to a pH of <2 in the field and transported to the laboratory on ice. After May 2007, additional water samples were collected for NO_3-N and soluble reactive P (SRP) and filtered with a 0.45 μm membrane filter. In the laboratory, all samples were stored frozen and processed within 1 month of collection. Several duplicate samples were collected at the outset of the study, one duplicate was analyzed immediately while the other was frozen and analyzed 1 month later. There was no significant deterioration of solutes between collection and analysis and Fellman et al. (2008) report that the DOC concentrations observed in our streams are amenable to preservation by freezing. Water temperature and specific conductance were measured on-site using a portable probe (YSI, Inc.).

In the laboratory, DOC and TDN concentrations were determined via high temperature oxidation on a Shimadzu TOC-CPN analyzer with a TNM-1 unit with a detection limit of 0.08 mg L^{-1} for DOC and 0.03 mg L^{-1} for TDN. Bioavailability of DOC is influenced by myriad factors, including the degree to which the DOC is composed of aliphatic versus aromatic compounds (e.g., Sun et al. 1997). Specific Ultra-Violet Absorbance (SUVA) at 254 nm is a reliable indicator of DOC aromaticity, with values <2.0 L mg-C^{-1} m^{-1} indicating low aromaticity (Weishaar et al. 2003). We measured absorbance of the DOC at 254 nm using a scanning spectrophotometer (Shimadzu UV-2101PC) and calculated SUVA by dividing the absorbance (m^{-1}) by DOC concentration (mg C L^{-1}). We used a Lachat QuikChem® 8500 flow injection analyzer to analyze NO_3-N and SRP with detection limits of 10.0 μg L^{-1} for SRP and 0.01 mg L^{-1} for NO_3-N. For solute analyses, blanks and certified commercial standards were routinely analyzed to ensure data quality.

A tipping bucket rain gauge (Onset Computer, Inc.) was located at site C and recorded precipitation throughout the study period. If the streams could be safely waded, instantaneous discharge was measured at the time water samples were collected. Discharge was measured using standard procedures (Platts et al. 1983) with a digital velocity meter (Marsh-McBirney, Inc.). Instantaneous discharge from tile drains was determined by recording the average ($n = 3$) time required to collect a known volume of water at the tile drain outlet.

DOC bioavailability assays

Bioavailability assays using tile water samples were conducted in February and June 2007 when the tiles were flowing at all sites. Assays with stream water were conducted in January and April 2007 following precipitation when stream discharge was elevated, but not to the point of flooding. We assessed bioavailability of stream and tile drain DOC using the approach described by Sobczak et al. (2002) with some modification. Freshly collected, unfiltered stream water was placed into 125 mL acid-washed media bottles ($n = 5$). We assessed potential nutrient limitation on DOC processing by including a treatment with nitrate and SRP ($n = 5$). The amendments were designed to ensure starting concentrations of at least 2.5 mg L^{-1} NO_3-N and 35 μg L^{-1} SRP. A single control bottle containing stream or tile water filtered through a 0.2 μm filter to eliminate bacteria was included with each experiment; no DOC reduction occurred in these control bottles indicating abiotic degradation was not a factor. The change in DOC concentration was followed for 6 days and bioavailability was calculated as the percentage change from initial DOC concentration (DOC concentrations determined as described above). During incubation, all bottles were kept in the dark at approximately 20°C.

All assay bottles, except for the 0.2 μm-filtered controls, contained a source of bacterial inoculum. In the first experiment, 1 cm^3 of stream sediment was added to bottles containing tile water in an attempt to increase bacterial abundance. To eliminate the potential problem of DOC leaching from the sediment, in later experiments we added native biofilm without sediment. Biofilm was established by placing beads of soda-lime glass (5 mm diameter) in mesh bags of plankton netting and anchoring these to each stream bed approximately 30 days prior to the bioavailability assays (a visible biofilm was present after 30 days). Ten colonized beads were added to each bottle at the start of the assay.

Diel patterns in DOC

During July 2007, we assessed the role of algae in contributing to stream DOC pools by collecting DOC samples over a 36-h period in each of 3 streams (sites A, B, and F). Samples were collected at the upstream and downstream ends of a 200-m reach at predawn, mid-morning, early afternoon, late-afternoon, and after dusk. All samples were collected and analyzed for DOC concentration and SUVA as described above. Photosynthetically active radiation (PAR) was monitored during the diel study at each site to indicate periods when autochthonous DOC was expected to contribute to total stream DOC load. At the end of the monitoring period, filamentous algal coverage of the stream bed was determined by establishing cross-sectional transects every 10 m throughout the study reach. At each transect, the wetted width of the stream was recorded and the substrate type was recorded at approximately 10 points across each transect. To determine algal biomass, we collected 5 cores, targeting areas of 100% filamentous algal coverage, at each site using an 11.5 cm diameter tube. The material was dried, combusted at 550°C and the ash-free dry mass (AFDM) measured. Filamentous algal biomass and coverage were then calculated for the entire 200 m reach. Finally, a bioavailability assay was conducted during each diel study using the approach outlined above. Stream water was collected at predawn (no sunlight) and early afternoon (peak sunlight), transported to the laboratory and placed into bottles containing 10 glass beads as described above.

Data analysis

Differences in DOC and TDN concentrations between streams and tile drains were assessed with two-sample *t*-tests. The relationships for DOC, TDN, and SUVA in streams versus tile drains were examined with simple linear regression. The relationship between DOC yield and TDN yield was analyzed with Pearson product-moment correlation. The normality of the concentration data was verified with the Kolmogorov–Smirnov test. All statistical tests were performed using Minitab 15 (Minitab Inc.) with $\alpha = 0.05$.

Results

DOC and TDN concentrations and fluxes

Based on 107 samples for which both TDN and nitrate were determined, nitrate-N represented 94.6 ± 1.5 % of the TDN. The dominance of the dissolved N pool by nitrate suggests that ammonium and dissolved organic N, while certainly present, did not comprise a significant fraction of TDN. Concentrations of TDN were generally high (>2 mg L^{-1}) except during periods of low discharge when concentrations often declined to <1 mg L^{-1}. Most SRP concentrations were less than the detection limit of 10 µg L^{-1}, but a few SRP concentrations exceeded 40 µg L^{-1}. Water temperatures were >25°C for much of the summer growing season, likely due to the lack of riparian shading, and median stream water temperatures during the study were >17°C. The streams contained hard water, with median specific conductivity (25°C) of 578–666 µS cm^{-1} across the sites. Mean stream DOC concentrations ranged between 2 and 5 mg L^{-1} in this agricultural landscape and water from tile drains usually contained between 1 and 4 mg L^{-1} DOC. Precipitation was more or less evenly distributed throughout the study period (Fig. 2). SUVA values for stream water DOC ranged from approximately 0.8–2.8 L mg-C^{-1} m^{-1} but did not display a seasonal pattern (data not shown).

During dry periods (run-off <0.5 mm d^{-1}) there was a large range in stream DOC concentrations and the range appeared to narrow as conditions became wetter and run-off increased (Fig. 3). Individual stream loads during the study ranged from <1 to 1,022 kg d^{-1} for DOC and from <1 to 10,335 kg d^{-1} for TDN. The largest individual tile drain input of DOC we documented was 2 kg d^{-1} and occurred in March 2007, but 79 of a total 83 measured tile drain loads were <1 kg d^{-1}. The input of TDN from individual tile drains ranged from <1 to 12 kg d^{-1}. We quantified inputs from only 1–2 tiles per site, but headwater streams in this area can receive inputs from numerous tile drains with a large cumulative effect (e.g., Stone and Wilson (2006) reported >15 tile drains along a 400-m reach of headwater stream in central Indiana). When expressed as a watershed yield, there was a strong correlation between DOC and TDN (Fig. 4) suggesting similar mechanisms for watershed fluxes of DOC and dissolved N.

Tile drains were a conduit to streams for both DOC and dissolved N, but the effect of tile drains on stream concentrations differed between DOC and dissolved N. For TDN samples, mean concentrations in tile drains were significantly greater than in the receiving streams (two sample *t*-test, $p < 0.001$; Fig. 5), suggesting stream dilution of the N input from tile drains. In contrast, the tile drain concentrations of DOC were significantly less than in-stream DOC concentrations (two sample *t*-test, $p < 0.001$; Fig. 5), suggesting there were other DOC sources to the streams. Tile drain DOC concentrations explained 79% of the variation in stream DOC concentrations ($p < 0.001$, $r^2 = 0.790$), with the slope of the relationship nearly equal to 1 and all points occurring above the 1:1 line (Fig. 6a). For TDN, there was no statistical relationship between tile drain and stream concentrations and all points fell below the 1:1 line (Fig. 6b). There was an inverse relationship between mean DOC concentration and mean SUVA in water from tile drains ($p = 0.015$, $r^2 = 0.35$; Fig. 7a) but no such relationship existed for stream water (Fig. 7b).

Diel patterns in DOC and SUVA

During the diel studies (July 2007), the nitrate concentrations in sites A, B, and F were >1 mg L^{-1}

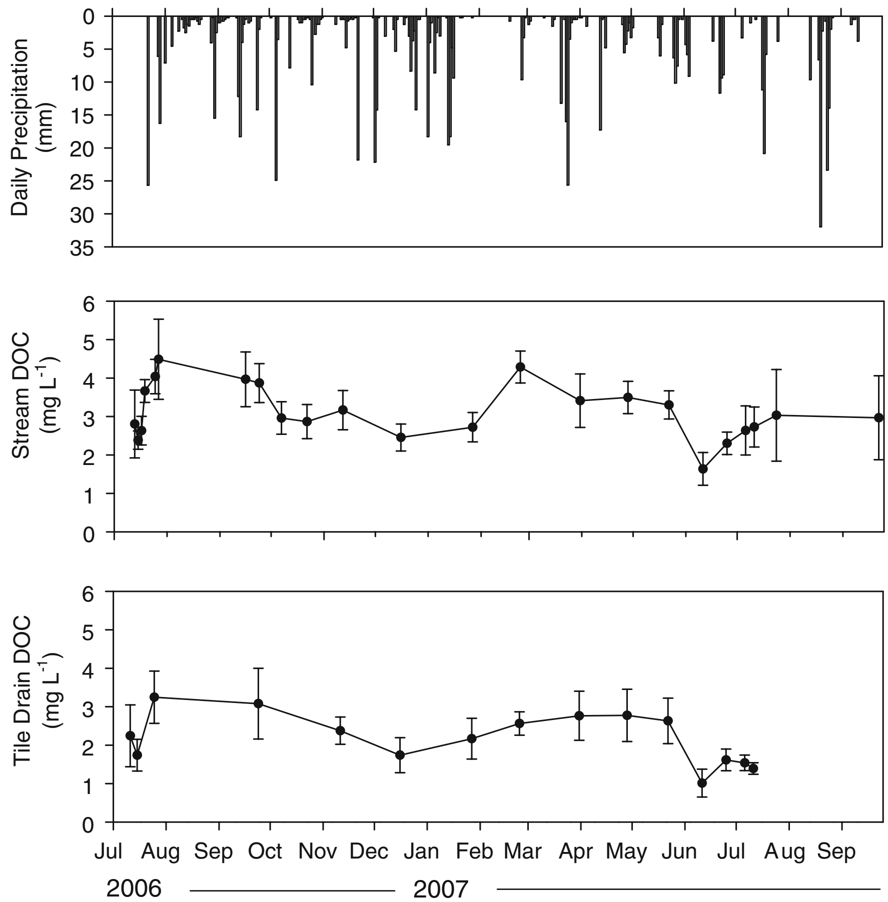


Fig. 2 Daily precipitation and the concentration of DOC in streams and tile drains during the study period. DOC concentrations are the mean value ± one SD ($n = 6$ for streams, $n = 3$–8 for tile drains)

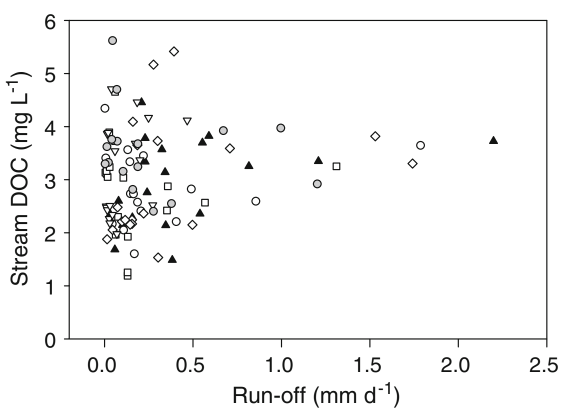


Fig. 3 Relationship between run-off and DOC concentration in streams during the study period. *Different symbols* indicate different streams

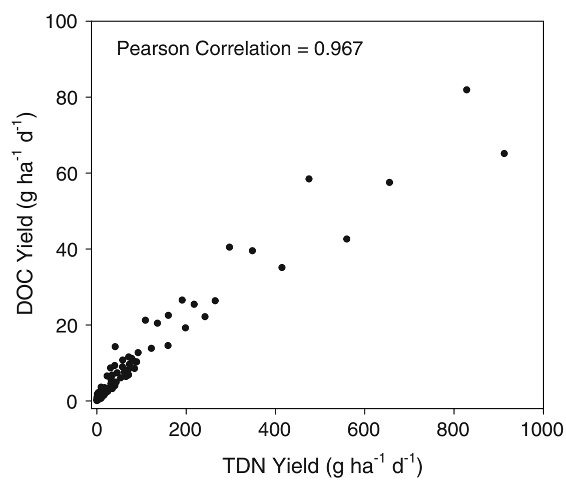


Fig. 4 Relationship between instantaneous yields of TDN and DOC across all stream sites ($n = 101$)

NO_3-N while SRP concentrations were below 10.0 μg L^{-1}. Each stream supported filamentous algal blooms that covered 28–53% of stream bed area (Table 2), which equated to an average algal biomass of 27, 27, and 63 g AFDM m^{-2} at sites A, B, and F, respectively. Site B also contained bryophytes that covered 7% of the stream bed. All sites were super-

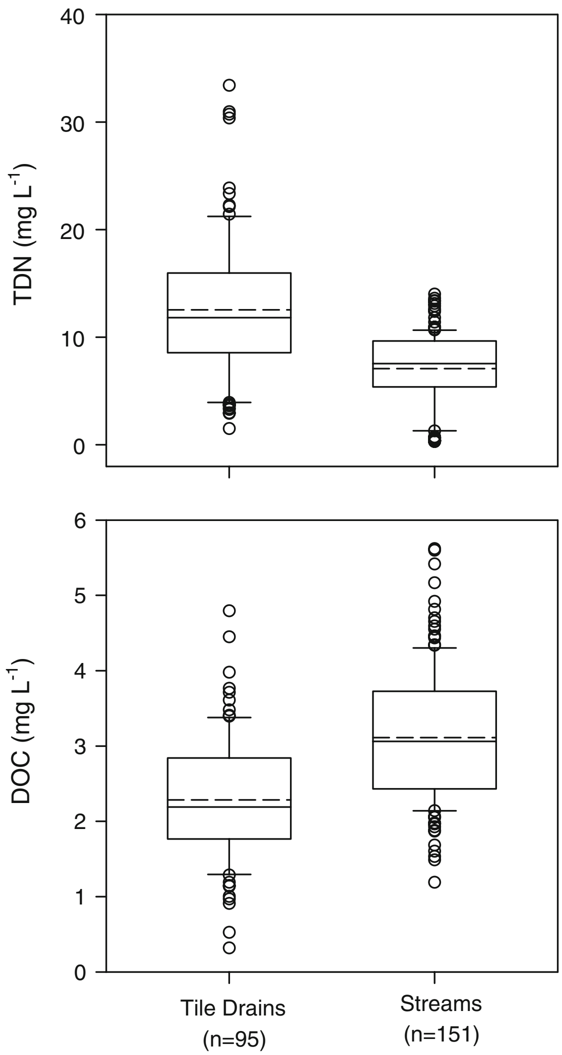


Fig. 5 *Box plots* showing the difference in TDN and DOC concentrations between tile drains and streams during the study. *Dashed line* is the mean and *open circles* are samples outside the 10th or 90th percentile

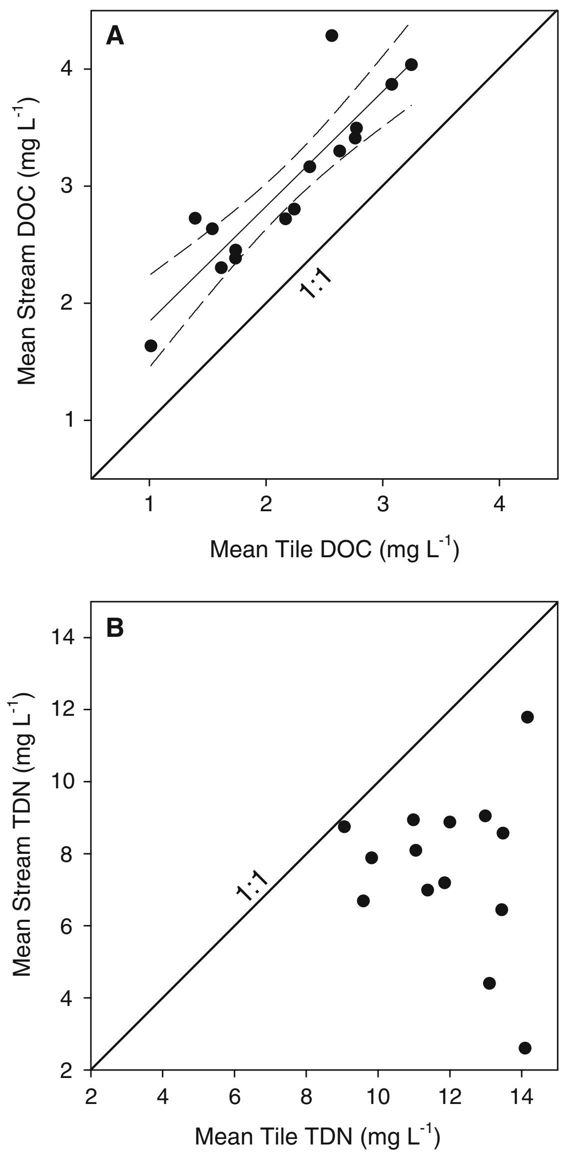


Fig. 6 Relationships between tile drains and streams in **a** DOC concentration and **b** TDN concentration. The regression between tile drain and stream DOC includes the 95% confidence intervals; this relationship was significant ($p < 0.0001$, $r^2 = 0.79$), with a slope of 0.982

saturated with dissolved O_2 during the afternoon, but declined to <80% saturation at night indicating the streams were highly productive. Despite the abundance of primary producers in the streams, DOC concentrations varied by less than 0.5 mg L^{-1} between the upstream and downstream ends of the 200-m study reaches. Over a diel cycle, DOC concentrations at the downstream end of the reaches varied by about 1 mg L^{-1} or less at each site while SUVA varied by about 1 L mg-C^{-1} m^{-1}, but in neither case were the trends related to PAR in a consistent fashion. For example, SUVA increased while DOC decreased during peak PAR at site A, but the opposite pattern occurred at site F (Fig. 8). At site B, SUVA declined during peak PAR while DOC did not vary (Fig. 8).

Bioavailability of DOC

Water collected from 3 tile drains in June 2007 had a mean bioavailability of about 27 % (Table 3). The

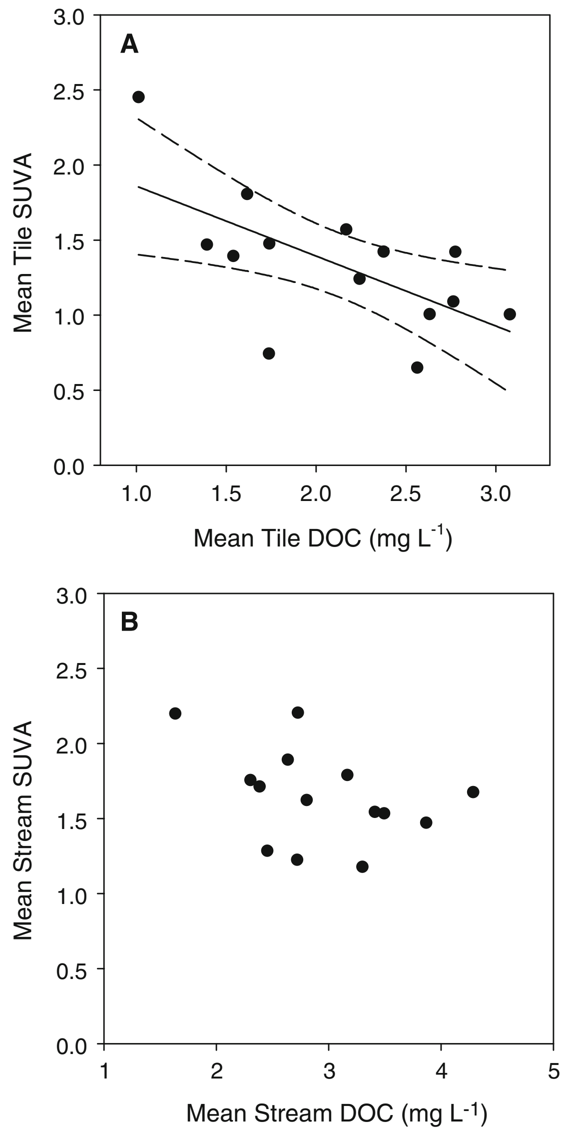


Fig. 7 Relationship between mean DOC concentration and mean SUVA for **a** tile drains and **b** streams. The regression ($p = 0.015$, $r^2 = 0.35$) between DOC and SUVA in tile drains includes the 95% confidence intervals

mean SUVA of the tile water was 1.0. At the time of the assays, SRP concentrations in the tile water were below detection, but the addition of inorganic nutrients did not stimulate consumption of DOC. All other bioavailability assays indicated no reduction of DOC over the 6-day incubation, despite mean SUVA values of 1.7 or less (Table 3). Stream water collected during peak sunlight versus pre-dawn had similar SUVA values and neither had detectable bioavailability.

Table 2 Algal and macrophyte coverage of the stream beds and channel characteristics during diel studies at sites A, B, and F in July 2007

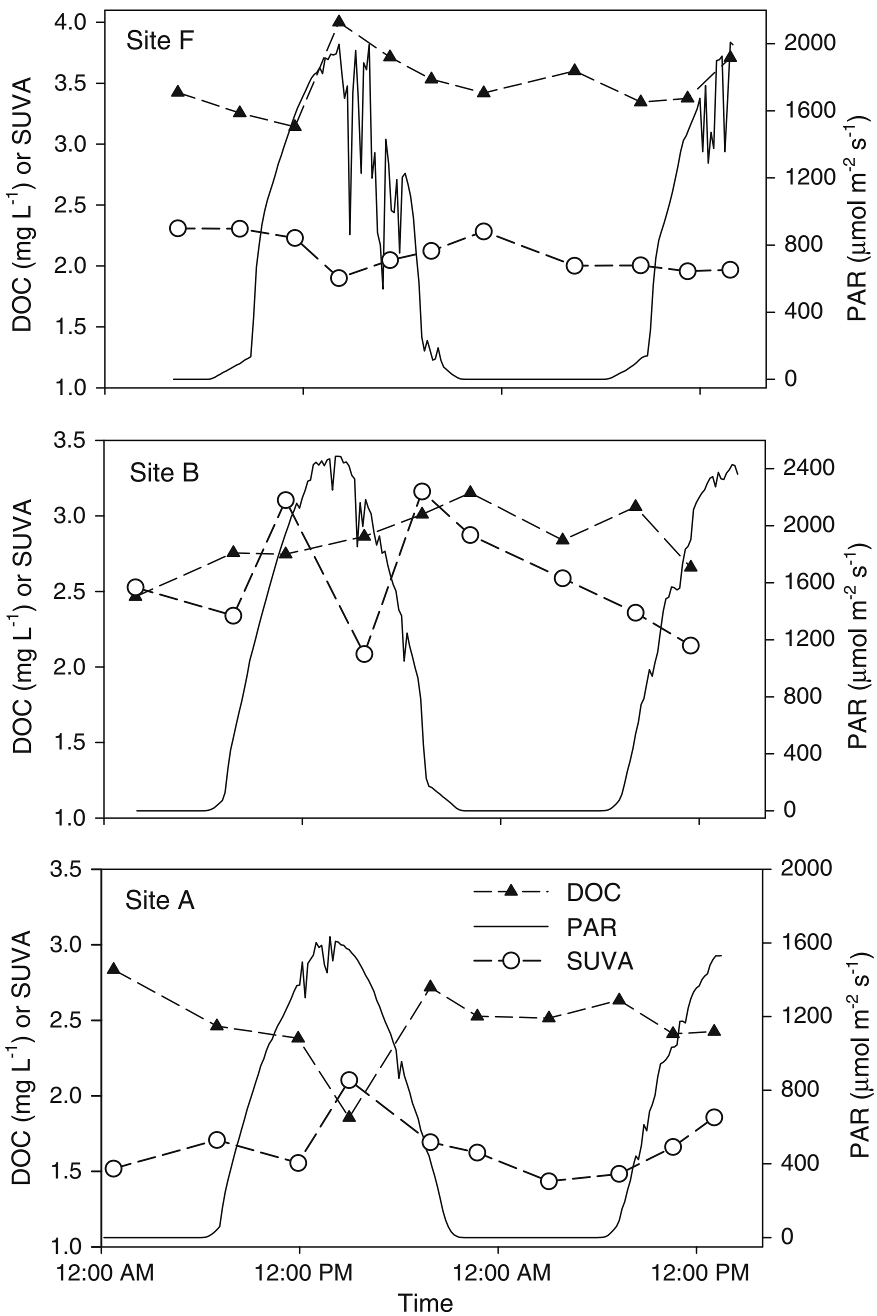
	Site A	Site B	Site F
Stream bed coverage			
Filamentous algae (%)	41	28	53
Bryophytes (%)	0	7	0
Channel characteristics			
Mean width (cm)	760	250	260
Mean depth (cm)	17	8	7
Mean discharge (L s^{-1})	180	9.3	6.2

Discussion

DOC and dissolved N concentrations and fluxes

Our study focused on low to moderate flow conditions when there is the greatest interaction between solutes and benthic processes and the greatest likelihood of significant autochthonous DOC inputs from algae. We were not able to capture several large storm flows that occurred during the study period and our results therefore do not represent the dynamics of DOC or dissolved N during storm flows. The DOC concentrations in streams and tile drains ranged from approximately 1–6 mg L^{-1}, which is within the ranges reported by other studies in similar landscapes (Royer and David 2005; Dalzell et al. 2005, 2007; Vidon et al. 2008). Previous studies that included storm sampling have reported DOC concentrations as high as 10–15 mg L^{-1} in Midwest agricultural streams (Royer and David 2005; Vidon et al. 2008). Despite the lack of storm sampling, we observed an approximately 5-fold range in DOC concentrations, but without any distinct seasonal pattern. Streams often exhibit seasonal patterns in DOC, with autumnal peaks generally attributed to leaching from deciduous leaf litter (Tate and Meyer 1983; McDowell and Likens 1988; Mulholland and Hill 1997), but the watersheds we studied contained no significant forest cover and there was no source of deciduous leaf litter to the streams. Lack of a seasonal pattern in DOC concentrations has been observed in other studies of both forested and mixed land-use watersheds (Eckhardt and Moore 1990; David et al. 1992; Inamdar and Mitchell 2006),

Fig. 8 Changes in stream DOC concentration, SUVA, and PAR during July 7–8, 2007 (*sites A* and *B*) and July 12–13, 2007 (*site F*)



suggesting that the lack of seasonality in DOC is not unique to intensively farmed watersheds nor due solely to the absence of deciduous forest.

Even during times of low to moderate discharge, hydrology was a strong control on the flux of DOC and dissolved N from the watersheds. During dry periods, DOC concentrations were highly variable and there was a tendency for concentrations to become less variable as run-off increased (see Fig. 3). The effect of soil characteristics on DOC concentrations in streams varies with changes in hydrological connectivity (Wilson and Xenopoulos 2008). Tile drains create a high degree of connectivity between soils and streams and are a well-documented mechanism for the rapid transport of DOC (Royer and David 2005; Vidon et al. 2008) and

Table 3 Mean bioavailability and SUVA of DOC collected from tile drains and streams during 2007

	Mean bioavailability (%)	Mean SUVA (L mg-C^{-1} m^{-1})
Tiles		
February 2007 ($n = 4$)	Undetectable	1.7 (0.6)
June 2007 ($n = 3$)	26.8 (11.1)	1.0 (0.3)
June 2007-N + P enriched ($n = 3$)	27.3 (10.8)	1.0 (0.2)
Streams		
January 2007 ($n = 3$)	Undetectable	1.2 (0.1)
April 2007 ($n = 3$)	Undetectable	1.4 (0.3)
July 2007-day ($n = 3$)	Undetectable	1.6 (0.1)
July 2007-night ($n = 3$)	Undetectable	1.7 (0.1)

Values in parentheses are one SD. Undetectable indicates no decrease in DOC concentration during the 6-day incubation (see text for details)

inorganic nitrogen (e.g., David et al. 1997) to agricultural streams. The streams we examined received inputs from multiple tile drains throughout their watersheds and the strong correlation between TDN and DOC yields (Fig. 4) indicates similar processes were responsible for the flux of these solutes from the watersheds. We suggest that tile drainage is responsible for the similarity in DOC and dissolved N fluxes during non-storm flows in these agricultural watersheds. When tile drains cease flowing (typically during late summer and autumn), natural processes, such as groundwater flow, likely become important to solute flux from these watersheds, although the absolute flux of solutes would be low during these times (Royer et al. 2006).

Although tile drains transported both DOC and dissolved N (mainly as nitrate), dissolved N inputs from tile drains were diluted upon entering the stream, whereas DOC concentrations were generally greater in the streams than in the tile drains. This suggests a consistent, but relatively small, additional source of DOC. In this region, shallow groundwater typically enters streams though tile-drains but streams continue to flow after tile-drains stop flowing, indicating diffuse groundwater inputs not associated with tile drains. Groundwater is a potential source of DOC to tile-drained streams (Vidon et al. 2008), but the relative importance of groundwater, tile drain, and in-stream sources is unknown. Given the abundance of filamentous algae in the streams we examined, we thought algae to be a likely source for in-stream production of DOC (Kaplan and Bott 1982, 1989). However, we found no consistent increase in DOC concentrations during daylight hours when the streams contained abundant algal biomass (see Fig. 8), nor did the bioavailability of the DOC differ between daylight versus nighttime hours. This unexpected result may be explained if the (presumably) labile algal exudates were rapidly respired within the benthic zone and therefore did not contribute to the bulk DOC in the water column. The idea that most terrestrially-derived DOC is transported downstream while autochthonous DOC is respired locally has been proposed for the Hudson River (del Giorgio and Pace 2008) and our results suggest a similar process may be occurring in headwater agricultural streams.

Benthic sediments and eroded soil that enters streams can contribute DOC to the water column, particularly if exposed to ultra-violet radiation (Kaplan and Bott 1989; Mayer et al. 2006). This source of DOC was not explicitly investigated in the present study, but preliminary leaching trials suggest the potential for significant DOC input from these sources (Royer, *unpublished data*). We believe that benthic sediments, including recently eroded soil, may be an important, but as yet unquantified, in-stream DOC source. Because these agricultural streams generally lack riparian shading and receive full sunlight, photodissolution of particulate organic matter could play a large role in these streams and warrants further investigation.

SUVA and DOC bioavailability

The fate of DOC that enters streams from the surrounding landscape is determined in part by the ease with which heterotrophic microorganisms can use the material as a source of reduced carbon. Aromaticity, as indicated by SUVA, provides an indication of the bioavailability of the DOC with low SUVA values generally reflecting higher bioavailability. The SUVA values of the DOC from stream and tile drain samples in the present study were consistently <2.0 L mg-C^{-1} m^{-1} indicating low aromaticity (Weishaar et al. 2003). Vidon et al. (2008) reported similar SUVA values for DOC during non-storm flows in a tile-drained agricultural watershed in central Indiana. The SUVA values measured in the present study and those reported for similar streams (Vidon et al. 2008) are lower than SUVA values from less disturbed ecosystems across North America (Jaffé et al. 2008). Our results suggest that allochthonous DOC in the streams was relatively low in aromatic compounds and may have originated in mineral soils (Hood et al. 2006). High densities of tile drains are found in glaciated landscapes where mineral soils from glacial till are common, suggesting that DOC with low aromaticity observed here and by Vidon et al. (2008) may be a general characteristic of tile-drained watersheds in the midwestern US.

We found no relationship between DOC concentration and SUVA in stream water, but an inverse relationship between DOC and SUVA in water from tile drains. As tile flow increased, DOC that was low in aromaticity likely was mobilized and transported to the streams. Tile drains are typically installed at a depth of 80–150 cm below the soil surface, therefore DOC in tile drains must have originated in these soil layers. Because the watersheds in our study area have been in agricultural production for many decades, crop residue is the most likely precursor material for the DOC in tile water. Unlike in the tile drains, the DOC pool in the streams was probably a mixture of DOC from a variety of precursor materials, which resulted in the lack of relationship between DOC concentration and SUVA in the streams during non-storm flows. During storm flows in an agricultural stream, Vidon et al. (2008) reported sharp increases in both DOC concentration and SUVA which they attributed to mobilization of a different pool of DOC than that which was responsible for DOC during base flow. Intensively farmed and artificially-drained landscapes are simplified in terms of land cover, but the combination of natural and modified hydrology of these ecosystems appears to maintain complex temporal patterns in the sources and optical properties of DOC.

Despite low SUVA values, DOC in the streams we examined was of low bioavailability, based on short-term (6 days) assays. A few of the assays were followed for 30 days but no additional change in DOC occurred following day 6 (data not shown). In most cases, we detected no loss of DOC during the incubations and in some cases the DOC concentration actually increased slightly, raising the possibility that the biofilm we added as an inoculum actually contributed some DOC to the assay bottles. It is unlikely, however, that the biofilm contributed enough DOC to obscure significant DOC consumption and we believe the DOC in the streams was indeed of very low bioavailability. In a similar landscape in Illinois, stream DOC had a bioavailability of approximately 18% (Royer and David 2005), based on 30-day assays. DOC from streams in tile-drained, agricultural watersheds appears to vary in its bioavailability, but at present there are too few assessments of DOC bioavailability from these types of landscapes to draw any general conclusions.

Nitrogen-rich conditions may allow for rapid metabolism of bioavailable DOC leaving the bulk DOC pool composed mainly of refractory compounds. In the tile-drained midwestern US, precipitation that drives DOC inputs (Dalzell et al. 2005; Vidon et al. 2008) also transports large inputs of N and P (Royer et al. 2006). Therefore, periods during which labile DOC is mobilized from the landscape and transported to the streams tend also to be periods of high inorganic-nutrient availability within the streams. This situation likely contributes to rapid metabolism of labile DOC and the generally low bioavailability of DOC in the streams.

Broader biogeochemical implications

Tile drains serve to facilitate the vertical movement of labile organic carbon within the soil profile (Jacinthe et al. 2001), but the extent to which tile drains flush organic carbon from watersheds is unknown. Our results indicate that the DOC from tile drains ranged in bioavailability from undetectable to 27%, whereas the bulk DOC in streams was consistently of low bioavailability. Photodegradation could potentially enhance the bioavailability of the DOC during in-stream transport, increasing the likelihood of the headwater-derived DOC fueling downstream microbial processes (e.g., denitrification). This upstream-downstream linkage, mediated by photodegradation, remains a hypothesis to be tested.

Agricultural watersheds in the midwestern US have lost about 40% of their original soil organic carbon since conversion from native vegetation to cropland in the early 20th century (Donigian et al. 1994; Lal et al. 1998; Grace et al. 2006). Carbon sequestration in agricultural soils could contribute to offsetting increasing atmospheric CO_2 levels (Kern and Johnson 1993; Lal 2002), however considerable uncertainty remains regarding the magnitude and fate of soil organic matter lost to surface waters in tile-drained watersheds (Lal et al. 1998). Restoring soil organic carbon levels could result in greater transport of labile DOC to streams in tile-drained watersheds, with subsequently higher rates of microbial respiration and biogeochemical cycling in headwater, agricultural streams. Nutrient-rich agricultural streams are useful systems for examining how changes in labile DOC loading may impact ecosystem functioning.

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