**Research Article**

# Export of dissolved organic carbon from agricultural streams in Illinois, USA

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**Abstract.** In the Midwestern USA, agricultural soils contain a large pool of organic carbon, yet little is known about carbon export in agriculturally-influenced streams. We studied DOC in three streams draining intensively farmed areas in Illinois, all draining Mollisols with large organic matter pools. Water quality samples were collected (weekly to daily) for 3–10 years and discharge was monitored continuously at each site. In-stream DOC concentrations ranged from 1–16 mg $L^{-1}$, and high concentrations of DOC occurred both during floods and periods of low discharge. Among sites, average flow-weighted DOC concentrations varied from 3.1 to 3.9 mg $L^{-1}$. DOC in the streams appeared to originate from two sources: allochthonous DOC from drainage of cropland in late winter through early summer, and autochthonous DOC from algal blooms in late summer through autumn. Inputs of allochthonous DOC were under hydrological control, with most of the allochthonous DOC entering streams during floods. Watershed export of DOC ranged from 3–23 kg $ha^{-1}$ $yr^{-1}$. The mass of C exported from watersheds as DOC was strongly related to water yield (r = 0.98), and by inference to precipitation. Bioassays indicated that on average 18% of the native DOC was bioavailable. Stream export of DOC from the agricultural watersheds was a small flux relative to the pool of soil organic C. However, increases in soil organic C could lead to greater inputs of DOC to streams and increased rates of microbial respiration.

**Key words.** DOC; DOM; organic matter; agriculture.

## Introduction

Dissolved organic carbon (DOC) is an abundant form of organic matter in streams and rivers, and represents a large flux of organic matter from watersheds (e.g., Mulholland, 1997, 2003). DOC in streams fuels bacterial production, and the addition of labile DOC can stimulate the productivity of multiple trophic levels in streams (Warren, 1964). Natural DOC in streams ranges from labile forms, such as simple sugars and organic acids, to highly refractory forms, such as humic acids (David and Vance, 1991). The composition of the DOC pool is determined largely by DOC sources. Allochthonous sources of DOC in streams include soil leachates and the breakdown of particulate organic matter, and this DOC can vary widely in chemical characteristics (Dahm, 1980; David and Vance, 1991; Aitkenhead-Peterson et al., 2003). Autochthonous sources of DOC can also be substantial (Minshall, 1978; Kaplan and Bott, 1982; Bertilsson and Jones, 2003) and often include labile forms of DOC that are readily used by heterotrophic bacteria.

The dynamics and biogeochemistry of DOC have been widely studied in upland forested streams (e.g., Mulholland, 1997; David et al., 1999). We are aware of no

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published studies that have directly examined the inputs and fate of DOC in headwater agricultural streams. A better understanding of DOC biogeochemistry in agricultural streams is needed because the cycling of other important nutrients is linked to the quantity and quality of DOC (Hedin et al., 1998; Baker et al., 1999). Additionally, increases in atmospheric $CO_2$ have led to interest in ways to sequester carbon within the biosphere. One suggested approach involves altering agricultural practices in ways that will increase soil organic matter (e.g., Kern and Johnson, 1993). Although this approach shows promise for sequestering C, a better accounting of all C fluxes is needed (Schlesinger, 2000).

Because of concerns about nitrogen loading to the Mississippi River and hypoxia in the Gulf of Mexico, much of our previous work in Illinois streams focused on nitrogen (David et al., 1997; David and Gentry, 2000; Royer et al., 2004). In this paper, we examine DOC in headwater agricultural streams using long-term records on discharge and in-stream DOC concentrations, monitoring of agricultural drainage water, and recent experiments to determine the bioavailability of DOC in streams. Our goals in this paper are to: (1) examine seasonal and annual patterns in DOC concentrations in three agricultural streams in east-central Illinois; (2) identify major sources of DOC to the streams, and (3) begin to assess the bioavailability and fate of DOC in the streams.

## Materials and methods

### Study sites

Sampling stations were established on three streams in east-central Illinois, USA: the Embarras River (EMC), the Lake Fork of the Kaskaskia River (LFK), and Big Ditch (BDO), a tributary to the Sangamon River (Table 1). An additional site Black Slough (BLS) was used only for bioavailability assays. Land use upstream of the sites is 80 to >90% row-crop agriculture, mainly corn and soy bean. At LFK, BDO, and BLS, riparian vegetation consists primarily of grasses and the streams are open canopied. At EMC, a narrow corridor of forest creates a closed canopy, although most upstream areas are open. Due to the flat topography of east-central Illinois, stream channel slopes are 0.1% or less and streambeds are composed mostly of gravel, sand, and fine organic sediments (Royer et al., 2004). The streams flow through areas that were mainly wetlands and mesic prairie prior to settlement (Rhoads and Herricks, 1996). During the late 19th century and early 20th century, streams and wetlands in east-central Illinois were extensively channelized and dredged to facilitate drainage, and this practice has been maintained (Rhoads and Herricks, 1996). Additionally, extensive networks of underground drain tiles were installed throughout east-central Illinois in the late 19th century to lower the water table and provide unsaturated conditions in the upper soil horizons. The drain tiles have been maintained and enhanced and now serve as effective conduits for removing excess water and associated solutes from the landscape directly to headwater streams. The streams are rich in both nitrogen and phosphorus, with $NO_3$-N concentrations ranging annually from 0.5 to >12 mg $L^{-1}$ and total phosphorus ranging from 80 to 500 µg $L^{-1}$ (Royer et al., 2004). The study streams and their watersheds are described further elsewhere (David et al., 1997; Rhoads and Herricks, 1996).

### Monitoring DOC

Stream discharge was monitored continuously at each site by the US Geological Survey or the Illinois State Water Survey. Water samples for analysis of DOC were

**Table 1.** Abbreviations, coordinates, and channel and watershed descriptors for each stream used in the study. All sites are located in east-central Illinois, USA.

| Site | Site name | Coordinates | Order | Channel slope (%) | Watershed area (km²) | Row-crop agriculture (% land cover) | Study period (water years) |
|------|-----------|-------------|-------|-------------------|----------------------|-------------------------------------|----------------------------|
| EMC | Embarras River | 39° 47′ 29″ N 88° 11′ 08″ W | 4 | <0.1 | 481 | 91 | 1994−2003 |
| LFK | Lake Fork Kaskaskia River | 39° 50′ 09″ N 88° 29′ 18″ W | 3 | <0.1 | 365 | 91 | 1998−2003 |
| BDO | Big Ditch (Sangamon River) | 40° 16′ 06″ N 88° 19′ 35″ W | 2 | 0.1 | 101 | 86 | 2001−2003 |
| BLS | Black Slough (Embarras River) | 39° 57′ 07″ N 88° 10′ 10″ W | 1 | 0.1 | 25 | 85 | used only for bioavailability assays |

collected from the center of the channel manually or with automated samplers during periods of rapidly changing discharge. Sampling frequency was determined by precipitation and discharge patterns, with more intensive sampling during periods of high discharge. All sites were sampled at least 40 times per water year (October 1 through September 30 of the following year). Samples collected prior to 1999 were filtered through 1.2 µm glass fiber filters (Whatman GF/C). Samples collected during and after 1999 were filtered through 0.45 µm membranes (Fisherbrand). All samples were acidified to $pH < 2$ with high-grade $H_2SO_4$ and stored at 4°C in acid-washed HDPE bottles until analysis. DOC concentrations were determined by persulfate oxidation using a Dohrmann TOC analyzer equipped with a Horiba infrared gas analyzer (Model PIR-2000). The method detection limit for DOC was 0.5 mg $L^{-1}$. Both internal and external quality-control standards were analyzed routinely throughout the study.

Discharge in the study streams arises in large part from agricultural drainage (David et al., 1997). During 2002, we monitored DOC concentrations in water from two drain tiles in the Sangamon River watershed. Water samples were collected either manually or with automated samplers. Precipitation near the tile monitoring sites was also recorded. Samples were treated as described above.

### Bioavailability of DOC

In June and October of 2003 we conducted experiments to assess the bioavailability of the DOC from two sites in the Embarras River watershed: EMC and BLS (Table 1). At the start of each assay, 200 mL of unfiltered stream water from each site were placed in acid-washed, 250-mL Nalgene HDPE bottles (n = 3). Initial DOC concentration was determined from samples collected from the bottles at the outset of the experiment. All bottles were kept in a refrigerated incubator at stream temperature and were not shaken during the assay except prior to sampling. DOC samples were collected from each bottle usually after 6, 15, and 30 days. Bioavailability of the DOC was assessed as the % decline in initial DOC concentration during the 30-day incubation.

### Data analysis

Water yields were calculated by converting the mean daily discharge values to water volume and summing for each water year. For days when DOC samples were not collected, concentrations were determined by interpolating between dates on which DOC was measured. Daily DOC loads were calculated by multiplying the daily DOC concentration (mg $L^{-1}$) by the daily water volume (L). Watershed yields of DOC were determined by summing the daily DOC loads for each water year. Using SAS version 8.2, daily DOC concentrations were estimated with linear interpolation and the annual flow-weighted DOC concentrations were determined. The relationship between water yield and DOC export was examined using a Pearson product-moment correlation. For the bioavailability assays, ANOVA was used to test for differences in DOC loss between sites and dates. Percentage data were arcsine transformed prior to ANOVA (Zar, 1999).

## Results

Across sites, in-stream concentrations of DOC ranged during the study period from 1 to nearly 18 mg $L^{-1}$. The lowest in-stream DOC concentrations occurred during intermediate values of discharge, and this pattern was consistent across the three watersheds (Fig. 1). High concentrations of DOC occurred both during floods and periods of low discharge. Although floods increased DOC concentrations, the highest DOC concentration from each site occurred during relatively low discharge. Annual flow-weighted DOC concentrations varied by <2 mg $L^{-1}$ within any site, and average values across sites ranged from 3.1 to 3.9 mg $L^{-1}$ (Table 2). DOC concentrations in tile water ranged from 1 to 14 mg $L^{-1}$, and increased sharply following rainfall (Fig. 2). In general, inputs of DOC from tile drains occurred in pulses that corresponded to rainfall. In-stream DOC concentrations responded quickly to inputs from tile drains, with changes in DOC related to the flood hydrograph (Fig. 3).

During the study period, water export from sites varied considerably. For example, at EMC water yield varied nearly 6-fold between the driest and wettest years (Table 2). At the same site, annual DOC yield ranged from 164 Mg C (Mg = $10^6$ g) in 2000, the driest year, to 1,071 Mg C in 2002, the wettest year. Annual DOC yield decreased with decreasing watershed area. On an areal basis (kg C $ha^{-1}$), however, watershed yields within any particular year were usually similar among sites (Fig. 4). For EMC, the site with the longest record, areal yields ranged from approximately 3 to 23 kg C $ha^{-1}$ $yr^{-1}$ during the 10 years of study. Across the three sites, the areal yield of DOC averaged 9.5 kg $ha^{-1}$ $yr^{-1}$. The mass of C exported from the watersheds as DOC was strongly related to water yield (r = 0.98; Fig. 5), and by inference to precipitation.

Bioavailability assays conducted in June and October 2003 showed that an average of 18% of the ambient DOC was respired by microbes within 30 days. There were no statistical differences between dates or sites (ANOVA, $p > 0.05$) in bioavailability of DOC, suggesting a similar composition of DOC between 1st and 4th order locations within the Embarras River watershed (Table 3).
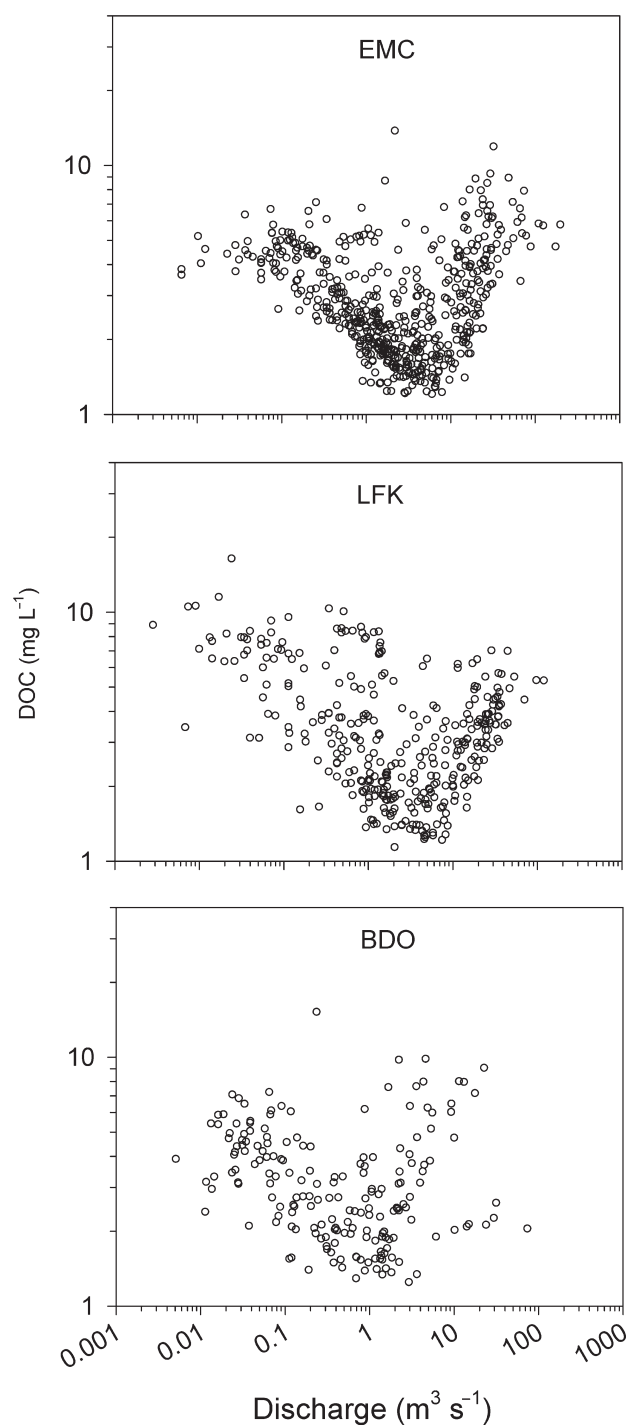
**Figure 1.** Log-log relationship between stream discharge and DOC concentration for three agricultural streams in east-central Illinois, USA. The duration of sampling for each site given in Table 1.

## Discussion

The concentration of DOC in streams can range from <1 to about 50 mg L$^{-1}$ (Mulholland, 2003). The agricultural streams we examined fell within this range, with most measurements <8 mg L$^{-1}$. Although the drainage areas of
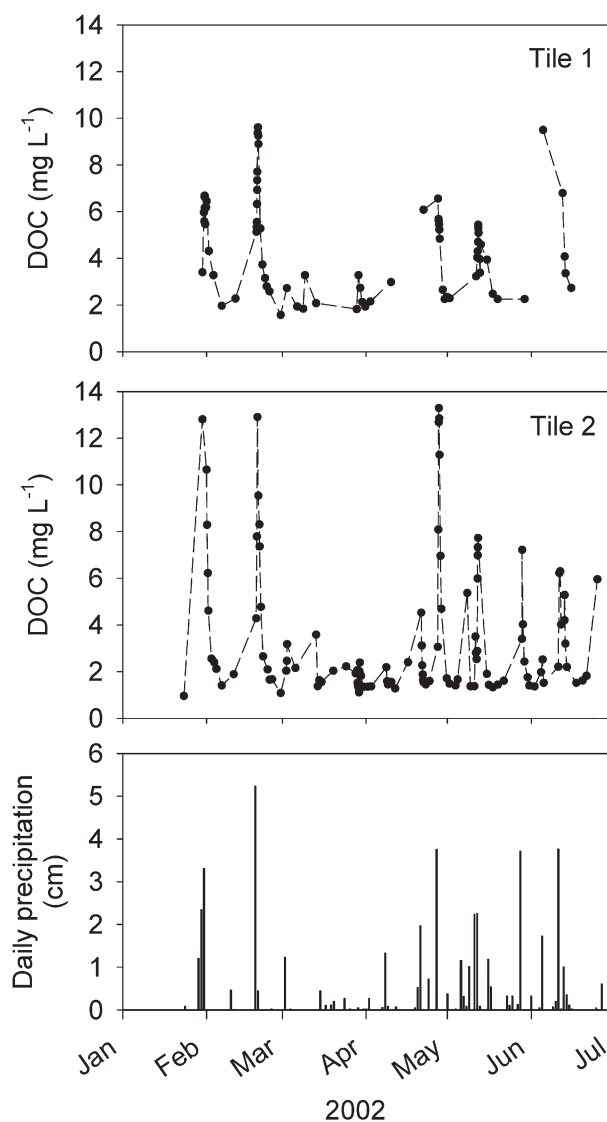


**Figure 2.** Daily precipitation in an agricultural watershed from January to July 2002 (lower graph) and corresponding DOC concentrations in two agricultural drain tiles in the same watershed (upper graphs).
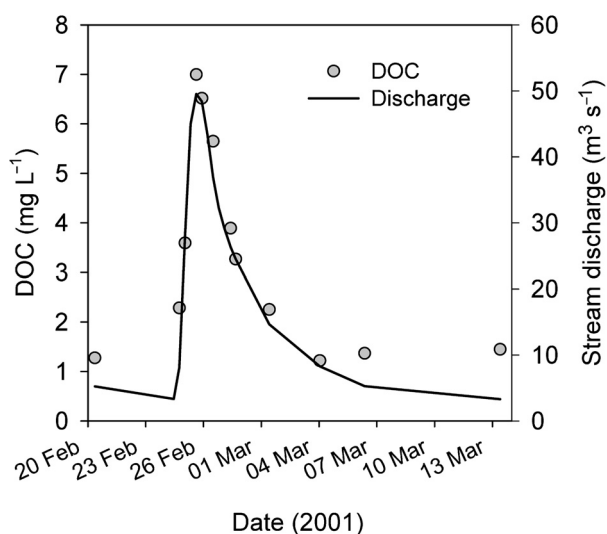
the sites varied from 101 to 481 km$^2$, the average flow-weighted DOC concentrations were remarkably similar among sites, varying by <1 mg L$^{-1}$ (see Table 2). The main determinants of in-stream DOC concentrations are precipitation, the presence of wetlands within the watershed, and the flowpath of water as it moves toward the stream (Mulholland, 1997; 2003). The watersheds in our study have similar topography, geology and land-use histories; thus the similarity in DOC dynamics was not unexpected.

The abundance of wetlands within a watershed has a strong influence on in-stream DOC concentrations (Eckhardt and Moore, 1990). Quantitatively, Eckhardt and Moore (1990) showed that mean DOC concentration in
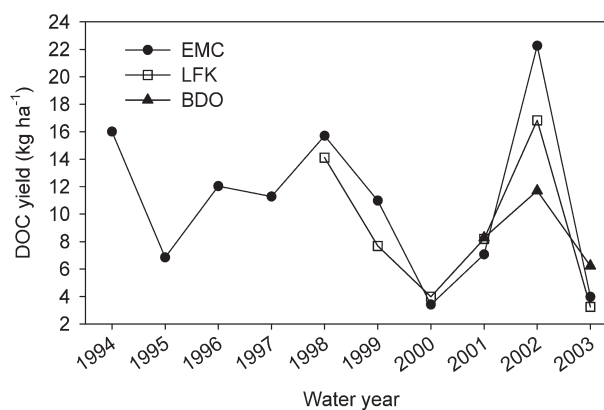
**Table 2.** Water yield, DOC export, and annual flow-weighted DOC concentration for each study stream. Mean (1 SD) values in the final row are average across the study period for each site.

| Water Year | Water Yield ($10^6$ $m^3$) | | | DOC Export (Mg C $yr^{-1}$) | | | DOC Concentration (mg $L^{-1}$)* | | |
|---|---|---|---|---|---|---|---|---|---|
| | EMC | LFK | BDO | EMC | LFK | BDO | EMC | LFK | BDO |
| 1994 | 235 | | | 770 | | | 3.3 | | |
| 1995 | 125 | | | 329 | | | 2.6 | | |
| 1996 | 186 | | | 579 | | | 3.1 | | |
| 1997 | 137 | | | 543 | | | 4.0 | | |
| 1998 | 228 | 179 | | 756 | 515 | | 3.3 | 2.9 | |
| 1999 | 132 | 96 | | 528 | 280 | | 4.0 | 2.9 | |
| 2000 | 52 | 46 | | 164 | 145 | | 3.2 | 3.1 | |
| 2001 | 92 | 100 | 18 | 340 | 299 | 84 | 3.7 | 3.0 | 4.3 |
| 2002 | 290 | 187 | 34 | 1071 | 615 | 118 | 3.7 | 3.3 | 3.5 |
| 2003 | 53 | 33 | 16 | 191 | 118 | 63 | 3.6 | 3.5 | 3.8 |
| Mean (1 SD) | 153 (80) | 107 (65) | 23 (10) | 527 (284) | 329 (199) | 88 (28) | 3.4 (0.4) | 3.1 (0.3) | 3.9 (0.4) |

* Flow-weighted concentration.



**Figure 3.** Relationship between stream water DOC concentration and discharge during a typical early spring flood at site LFK (see Table 1).



**Figure 4.** DOC yield (kg $ha^{-1}$) for the three agricultural watersheds. Yields were calculated on a water year basis (01 October through 30 September of the following calendar year).

streams of southern Québec was related to wetland abundance by the equation: ln(DOC) = 2 + (0.025)(% wetland). This equation also held for a range of streams throughout North America (Mulholland, 1997). Approximately 90% of the original wetlands in Illinois have been drained, and wetlands were nearly absent from the watersheds we studied. However, it is estimated that these watersheds were at least 50% wetland prior to European settlement (Rhoads and Herricks, 1996). Applying this wetland % to the above equation gives an expected average DOC concentration of about 26 mg $L^{-1}$. This value is substantially higher than concentrations we measured during the study, suggesting that wetland drainage has reduced in-stream DOC concentrations in agricultural regions of Illinois.

Both allochthonous and autochthonous sources contributed to DOC load in the streams. During periods of low discharge, streams supported dense growths of filamentous algae (mainly *Cladophora*) that can exceed 200 g $m^{-2}$ of dry mass (Schaller et al., 2004). We believe high DOC values that occurred during low discharge were the result of algal exudates (e.g., Kaplan and Bott, 1982). Minshall (1978) showed that for streams with open canopies, autochthonous production could exceed allochthonous inputs as a source of organic matter. Autochthonous production in open-canopied streams in east-central Illinois can exceed 15 g C $m^{-2}$ $d^{-1}$ during summer (Wiley et al., 1990) and represents a potentially large source of DOC to streams. For the sites we examined, the fraction of the DOC load that originated from autochthonous production is unknown, but we suspect it could be large during late summer and autumn when agricultural drainage has ceased and algal blooms are com-
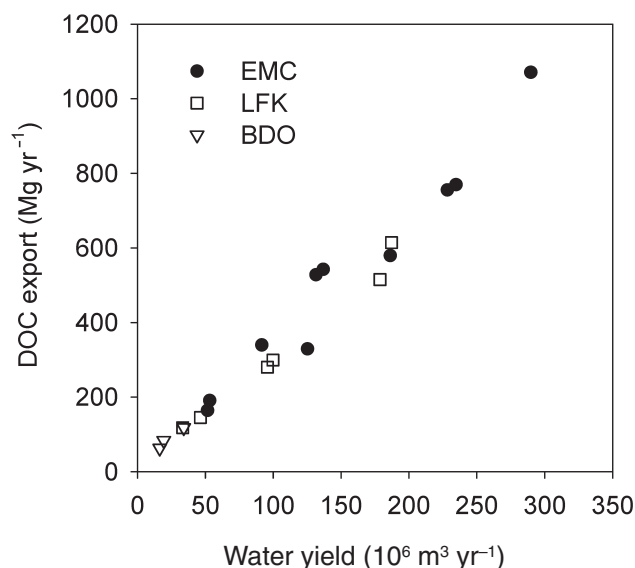
**Figure 5.** Relationship between water yield and DOC export for the three agricultural watersheds; r = 0.98 using Pearson product-moment correlation.

mon. In central Illinois, water from tile drains consists primarily of shallow groundwater that is drained in order to maintain unsaturated soil for farming. Discharge from tiles increases quickly following rainfall or snowmelt (David et al., 1997; Gentry et al., 2000), and tiles are a major source of water for streams from late winter through mid summer. During that time, allochthonous DOC from the upper soil horizon enters streams via tile water (see Fig. 2). The concentration of DOC in this water can approached 14 mg L$^{-1}$ during heavy rainfall. In the present study, we were not able to calculate areal yields of DOC from tile drains. However, a previous study conducted in the Embarras River watershed monitored DOC and discharge for three years from three tiles that drained areas of 5, 15, and 25 ha (Kovacic et al., 2000). Using those data, we calculate an average input of allochthonous DOC to the streams of 9.4 kg ha$^{-1}$ yr$^{-1}$, with a range of 4 to 18 kg ha$^{-1}$ yr$^{-1}$.

The average export of DOC from the watersheds was 9.5 kg ha$^{-1}$ yr$^{-1}$, or about the same as the average input of allochthonous DOC estimated from Kovacic et al. (2000). DOC export from agricultural watersheds in Illinois was generally lower than that in forested watersheds (e.g.,

Mulholland, 1997), but was greater than that reported for Kings Creek, a relatively undisturbed prairie stream in Kansas (Gray, 1997). For many biomes, soil characteristics are a good predictor of DOC export from watersheds. For example, Aitkenhead and McDowell (2000) constructed a linear model that related DOC export to soil C:N ratio using forested, grassland, and peat biomes from tropical to boreal regions; no agricultural ecosystems were included. The model performed well when soil C:N ratios were >12.5 (mass:mass), but the model predicted negative DOC export for watersheds with soil C:N ratios <12.5, suggesting a second-order polynomial relationship if examined across a wider range of soil C:N ratios (Aitkenhead and McDowell 2000). Watersheds in central Illinois have an average soil C:N ratio of 11.4 (M. B. David, unpublished data) with average DOC export of 9.5 kg ha$^{-1}$ yr$^{-1}$. Therefore, our results support the suggestion by Aitkenhead and McDowell (2000) that a second-order function might actually describe the relationship between soil C:N ratio and DOC export when low C:N ratio soils from agricultural areas (or other low C:N ratio soils) are included.

Precipitation had a strong influence on the amount of DOC exported from agricultural watersheds (see Fig. 4), as previously reported for less disturbed systems in North America (Mulholland, 1997). Hydrology and flowpaths in agricultural watersheds have been greatly modified to facilitate farming, but DOC concentrations responded to floods in the same manner as observed in smaller, forested streams (Hinton et al., 1997). Thus, although the landscape is artificially drained and dominated by agriculture, inputs of allochthonous DOC appeared to be under hydrological control, with much of this material entering streams during floods. At present, we cannot determine what fraction of the DOC exported from the watersheds was allochthonous or autochthonous, or how much of each type was respired within each stream. However, bioassays were conducted when DOC concentrations and algal densities were relatively low. Thus, the assays assessed primarily allochthonous DOC, and showed that on average 18% of this DOC was bioavailable. If glucose was added to the assays, it was respired quickly (data not shown), suggesting a microbial demand for DOC that was not met by the native DOC in the stream water. This pattern is the same as that described by Sobczak et al. (2002)

**Table 3.** Results of bioavailability assays conducted in 2003. All values are means (n = 3) ± one standard deviation.

| Site | Date | Initial DOC (mg L$^{-1}$) | | Final DOC (mg L$^{-1}$) | | DOC loss (%) | |
|------|------|------|------|------|------|------|------|
| BLS | June | 1.64 | ±0.05 | 1.33 | ±0.07 | 19.0 | ± 6.6 |
|     | October | 1.63 | ±0.32 | 1.28 | ±0.05 | 19.5 | ±14.0 |
| EMC | June | 1.83 | ±0.07 | 1.56 | ±0.04 | 14.7 | ± 2.7 |
|     | October | 2.79 | ±0.14 | 2.24 | ±0.03 | 19.5 | ± 4.6 |

for a forested stream in New York. The bioavailability of autochthonous DOC in the streams is unknown, but we assume that it would be greater than allochthonous DOC.

The export of DOC from the agricultural watersheds was a small flux relative to the pool of organic C in soil. Soils in the watersheds studied contain 150,000 to 220,000 kg C ha$^{-1}$ in the upper 1 m of soil (M. B. David, unpublished data). However, because the landscape is artificially drained, increases in soil organic C could lead to increased inputs of allochthonous DOC to streams and, depending on the bioavailability of DOC inputs, increased microbial respiration and rates of biogeochemical cycles.

## Acknowledgments

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