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EFFECTS OF LAND USE ON WATER QUALITY OF COLD-WATER STREAMS IN  
THE DRIFTLESS AREA OF THE MIDWESTERN U.S.

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By Rachel Marie Olmanson

We recommend acceptance of this thesis in partial fulfillment of the candidate's requirements for the degree of Master of Science in Biology

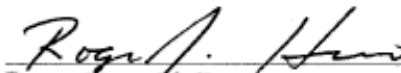
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## ABSTRACT

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Streams are important ecosystems that affect the dynamics of downstream ecosystems. Increased nutrient input and changes to land cover have altered the natural functioning of streams. The purpose of our study was to examine the seasonal and spatial relationships between land cover and nutrients in streams across the Driftless Area. We hypothesized that streams dominated by agricultural land use would have higher N, dominated by nitrate. We investigated if a threshold occurred as N changed in response to land cover and as percent  $\text{NO}_3^-$ -N changed in response to TDN. We sampled 77 streams in fall 2012, and winter, spring, and summer 2013. TDN ranged from 0.145 to 25.0 mg/L with higher concentrations in agricultural streams. Nitrate dominated the TDN pool in most streams. Land use was not a strong predictor of TDP or DOC, and concentrations were variable across seasons. A threshold occurred at 49.15% forested and 80.55% agricultural land use in response to TDN. We estimated water quality criteria to be between 1.7 to 2.1 mg/L TDN based on these results. Our results suggest that N saturation is likely occurring in streams in the DA, which could lead to an increase in export of N to downstream ecosystems.

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## INTRODUCTION

Small headwater streams are important and valuable ecosystems because they provide many benefits and ecosystem services. For example, headwater streams mitigate flooding, provide habitat for plants and animals, regulate transport of sediment, cycle nutrients, and recharge groundwater (Meyer *et al.* 2007a; Lowe and Likens 2005). Headwater streams also support diverse populations of flora and fauna, which contribute to the maintenance and enhancement of biological diversity within the entire river network (Meyer *et al.* 2007b). Headwater streams supply water and nutrients to downstream ecosystems; therefore, these systems are important in maintaining the natural functioning of streams, rivers, lakes, wetlands, and estuaries located downstream. The small size of these systems also makes them vulnerable to disturbances, which are often caused by human activities. For example, anthropogenic increases in nutrient input and altering land use and land cover are threatening the natural functioning of stream ecosystems. Since small streams affect entire river networks, it is important to understand how human caused disturbances impact stream ecosystems.

Changes in land use and land cover can be detrimental to stream ecosystems. The conversion of forested land to agricultural or urbanized land can be particularly damaging. Agricultural runoff often contains high concentrations of nutrients and pesticides. Many studies have shown that streams in agricultural watersheds typically contain high levels of nitrogen (N) and phosphorus (P) (Johnson *et al.* 1997; Robertson *et*

*al.* 2006). Urban runoff, including pet waste, construction site debris, and lawn fertilizer also can contribute significant amounts of N and P to aquatic ecosystems (Carpenter *et al.* 1998). Natural streams are often diverted or channelized in urbanized areas, which consequently changes the natural hydrologic patterns of streams (Meyer *et al.* 2007a). Additionally, urbanized catchments have high percentages of impervious surfaces. This ubiquity of impervious surfaces has long been known to lead to an increase in the volume and velocity of storm water runoff to streams (Leopold 1994). These changes in flow can cause flooding, sedimentation, altered temperature regimes, decreased rates of nutrient cycling, and diminished water quality.

All organisms require N and P for production. In pristine nutrient-poor systems, most nutrients are cycled very tightly and added nutrients are quickly assimilated into organisms. However, excessive nutrient additions can directly and often adversely affect the biological and chemical functions of surface waters. An increase in nutrients, specifically N and P, to aquatic ecosystems can lead to higher rates of heterotrophic or autotrophic metabolism, also known as eutrophication (Dodds 2006). Eutrophication can have deleterious consequences to aquatic ecosystems, including fish kills, a decrease in biodiversity, oxygen depletion, toxic algal blooms, and changes in biogeochemical processes (Carpenter *et al.* 1998; Bernhardt and Likens 2002; Woodward *et al.* 2012). The longitudinal transport of nutrients from riverine ecosystems results in nutrient increases in marine ecosystems, otherwise known as coastal eutrophication.

Eutrophication can cause anoxic and hypoxic conditions, or dead zones, in estuaries and oceans. Globally, dead zones are increasing at an exponential rate. Since the 1960s, the number of dead zones reported has roughly doubled every ten years (Diaz and Rosenberg

2008). Monitoring nutrient concentrations in aquatic ecosystems can help elucidate ecosystem health, identify trends in stream water chemistry, and determine how human land use impacts water quality.

Nitrogen is present in different forms in headwater streams. In healthy streams, N is quickly cycled and assimilated by microbes, plants, and animals. This results in relatively low concentrations of nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) in most small headwater streams. However, streams receiving water from agricultural or urban landscapes may contain higher levels of these two forms of nitrogen, especially  $\text{NO}_3^-$  (Galloway *et al.* 2003). Chronic inputs of N to streams can result in a condition of saturation. Nitrogen saturation can be defined as nitrogen concentrations large enough to maximize nitrification rates and decrease efficiency of nitrogen uptake and denitrification, potentially leading to an increase in export of N to downstream ecosystems (Bernot and Dodds 2005; Earl *et al.* 2006; Arango *et al.* 2008; Mulholland 2008). Mulholland *et al.* (2009) suggest that optimal efficiency of N removal by denitrification occurs in streams where  $\text{NO}_3^-$  concentrations are below 1 mg N/L. In a study of Wisconsin streams, those with total dissolved nitrogen (TDN) concentrations greater than 3 mg/L and dominated by  $\text{NO}_3^-$ , or streams in which  $\text{NO}_3^-$  exceeded 2 mg N/L, were labeled nitrogen hypersaturated (Stanley and Maxted 2008).

Elevated concentrations of different fractions of N in aquatic ecosystems can be harmful or toxic to plants and animals. Ammonia ( $\text{NH}_3$ ) can be particularly harmful to plants and organisms at high pH levels, where ammonium hydroxide forms. Nitrite ( $\text{NO}_2^-$ ) is a potent toxin that can affect growth, respiration, and reproduction of aquatic plants and animals. These toxic effects are not isolated to aquatic organisms. Blue baby

syndrome, or methemoglobinemia, is a condition that can affect infant children after consuming water containing elevated concentrations of  $\text{NO}_3^-$ . Nitrate binds to hemoglobin, resulting in a loss in the oxygen carrying capacity of the blood. The World Health Organization drinking water standard for  $\text{NO}_3^-$  is 11 mg N/L (2011) and the US EPA has a maximum contaminant level of 10 mg N/L. These standards are in place to protect infants from this condition, which can cause serious illness or death, if untreated.

Phosphorus can be an important driver of primary production in low-nutrient headwater streams (Steinman and Mulholland 2006). For example, Hill and Knight (2008) used nutrient-diffusing substrates to demonstrate that light and phosphorus limited periphyton growth in two California streams. Similarly, primary production and leaf decomposition increased as a result of P additions in Walker Branch stream in Tennessee (Elwood *et al.* 1981). Erosion, agricultural and urban runoff, and industrial effluent have all been linked to increased P concentrations in streams (Carpenter *et al.* 1998). Elevated concentrations of P in lotic ecosystems can lead to reductions in the quality of benthic communities in streams (Miller *et al.* 2006). The seasonal dynamics of P in Midwestern streams is not well established; Robertson *et al.* (2006) found that P concentrations in WI streams were highest in June and July and lowest in October; whereas, Miller *et al.* (2006) observed highest dissolved P concentrations in fall in streams in western WI.

Streams are also important in the transformation of terrestrial organic matter to usable sources of carbon. The transformation of carbon in headwater streams results in healthy downstream ecosystems. Dissolved organic carbon (DOC) makes up the majority of the organic carbon pool in headwater streams (Chapin *et al.* 2011). In forested headwater streams, much of the DOC originates from allochthonous sources and is

assimilated into microbial biomass and subsequently incorporated into the lotic food web (Wilcox *et al.* 2005). The availability of DOC in aquatic systems also can directly affect the biogeochemical cycles of other important nutrients, such as N and P (Oviedo-Vargas *et al.* 2013). Because bacteria and fungi are often limited by carbon, the availability and/or the quality of carbon can affect the availability of other nutrients in ecosystems. For example, as C:N ratios increase in streams, N can become limiting to heterotrophic bacteria. This results in higher competition for N between heterotrophs and nitrifying bacteria, thereby influencing rates of nitrification (Strauss and Lamberti 2002). Previous research suggests that increases in organic C availability in streams reduce rates of nitrification (Strauss and Lamberti 2000, 2002; Strauss *et al.* 2002; Bernhardt and Likens 2002). Furthermore, the quality of organic C may affect nitrification rates in streams. Carbon of higher quality may have more of an influence on nitrification rates than refractory C (Strauss and Lamberti 2002). However, research on the dynamics of DOC concentrations and nitrogen cycling has generally been limited to forested streams (Pellerin *et al.* 2006, Bernhardt and Likens 2002, and Brookshire *et al.* 2005). Moreover, few studies have examined the seasonal patterns of N and C dynamics in stream ecosystems. Understanding how nutrients, such as N and C, are coupled in headwater streams is imperative in elucidating nutrient dynamics in these important ecosystems.

### **Objectives and Hypotheses**

The overall objective of this study was to examine the seasonal relationships between land use/land cover and dissolved nutrients (C, N, and P) in cold-water streams in the Driftless Area (DA) of the upper Midwestern United States. As part of this study, we sought to determine if a threshold (*sensu* Dodds *et al.* 2010) occurred as N

concentrations changed in response to changes in land cover. Additionally, we wanted to determine if a threshold occurred at which the TDN pool was dominated by  $\text{NO}_3^-$ . If so, the threshold value could potentially be used as a metric to identify N saturating conditions.

We hypothesized that streams located in agricultural and developed basins would have higher concentrations of N. Additionally, we hypothesized that  $\text{NO}_3^-$  would dominate the TDN pool in agricultural streams, and  $\text{NH}_4^+$  and  $\text{NO}_2^-$  would make up a smaller percentage of the TDN pool across all streams. It was also anticipated that the concentrations of dissolved organic nitrogen (DON),  $\text{NO}_2^-$ , and  $\text{NH}_4^+$  would be higher in agricultural and developed streams compared to forested streams. We expected that  $\text{NO}_3^-$  and DOC concentrations would be correlated due to the tight coupling of N and C in streams. It was anticipated that agricultural and developed streams would have higher concentrations of total dissolved phosphorus (TDP) compared to forested streams as a result of urban and agricultural runoff and erosion.

To test these hypotheses, we collected water samples from 77 streams distributed across the DA. Stream locations were chosen based on accessibility and dominant land cover in the stream basin, and represent four categories of land use: agricultural, forested, developed, and mixed. We analyzed samples for different fractions of N, TDP and DOC. Although recent research has examined how land use influences water quality of streams (Stanley and Maxted 2008; Robertson *et al.* 2006; Arango *et al.* 2008), further research is needed to understand how land use influences C, N, and P dynamics in headwater streams in the DA.

We hypothesized that concentrations of C, N, and P would be seasonally variable in cold-water streams in the DA. It was expected that N and P concentrations would be highest in spring and summer as a result of snowmelt and rain events that occur during these seasons, and would be lowest in the winter when stream discharge is driven by ground water contributions. Additionally, it was expected that concentrations of DOC would be highest in fall and spring, concurring with fall leaf litter and spring soil thaw. To test these hypotheses, we collected samples at each site in fall 2012, and winter, spring, and summer 2013. Previous studies have examined seasonal variation of N and P in WI streams (Robertson *et al.* 2006; Miller *et al.* 2006); however, there has been limited research on the seasonal dynamics of C, N, and P in streams located in the DA.

## **METHODS**

### **Study Area and Site Selection**

The Driftless Area (DA) level III ecoregion, is located in the Upper Mississippi Basin (UMB) and includes southeast Minnesota (MN), southwest Wisconsin (WI), northeast Iowa (IA) and extreme northwest Illinois (IL) (Figure 1). This unique geological region is approximately 62,000 km<sup>2</sup> and was bypassed by the last continental glacier, resulting in a landscape dominated by rolling hills, sinkholes, caves, and cold-water streams. Cold-water streams are abundant in the DA, totaling about 5,800 km, and many support trout populations (Trout Unlimited 2005).

The DA is dominated by agricultural land use, about 60% of the area is classified as cultivated or pasture. Forests (maple/basswood/oak) cover approximately 25% of the DA, and 6% is considered developed. The region is characterized by karst topography, consisting of soluble carbonate bedrock, such as limestone, sandstone, shale or dolomite covered with silty loess soils. Due to the porous nature of the geology of this ecoregion, water quickly infiltrates to groundwater or surface water, reducing time for filtration and/or nutrient cycling processes. Karst topography along with the high percentage of agricultural land makes the DA particularly susceptible to pollutants.

The ecoregion is environmentally and economically valuable. Trout fishing alone brings in about \$1.1 billion annually to the region (WI DNR 2012). The DA is home to numerous threatened and endangered species such as whooping cranes, Higgins eye pearly mussels, Iowa Pleistocene snails, and eastern prairie fringed orchids. However,

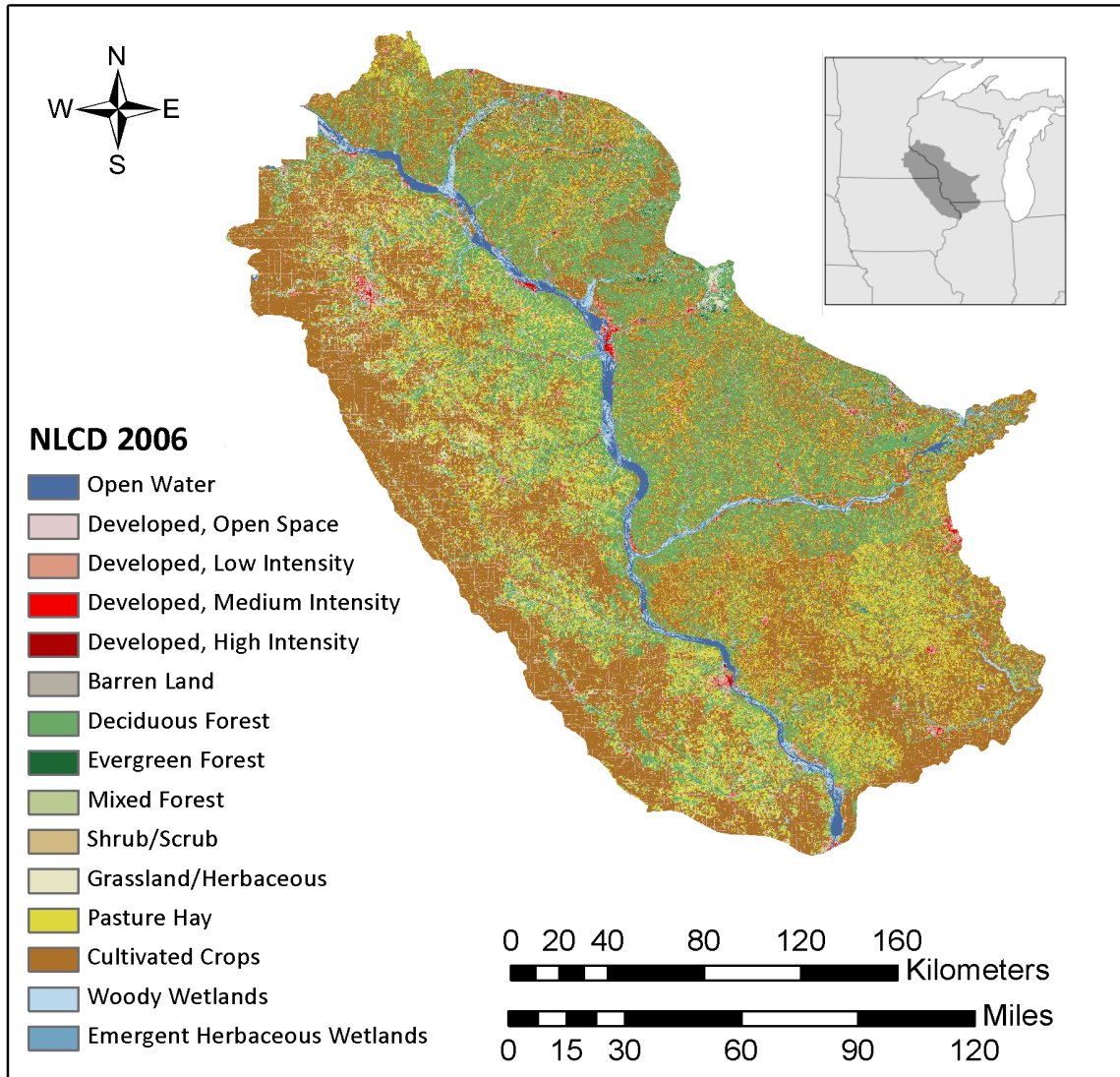


Figure 1. Land use in the Driftless Area, based on the 2006 National Land Cover Database for the Conterminous United States (Fry *et al.* 2011).

increased changes in land use across the region continue to threaten the DA. Changing agricultural practices and a shift to hillside farming may be particularly damaging. Thousands of acres of land protected by the federal Conservation Reserve Program (CRP) are shifting back to agricultural land use. Many organizations such as Trout Unlimited, the Driftless Area Restoration Effort, the Driftless Area Landscape Conservation Initiative, and the Driftless Area Initiative value the natural history of the

DA and are dedicated to protecting and restoring this region. Research on streams in the DA has been limited to the southwest WI region (Robertson *et al.* 2006; Miller *et al.* 2006; Stanley and Maxted 2008). Few studies, if any, have focused on the seasonal dynamics of C, N and P concentrations in streams throughout the DA.

This study encompassed the entire DA and included cold-water streams throughout the region (Fig. 2). We chose 77 sampling locations based on stream order, accessibility, land cover, drainage-network independence, and distribution (Table 1). The stream sites were limited to first through third-order streams as determined with the National Hydrography Dataset (NHD) high-resolution flowline data (1:24,000-scale). We delineated watershed basins manually from a 30-m digital elevation model (DEM) and ArcMap v. 10.0 geographic information system (GIS) software (Environmental Systems Research Institute Redlands, California, USA). Watershed basin size ranged from 0.9 to 338.7 km<sup>2</sup>, with a median size of 24.3 km<sup>2</sup>.

### **Land Cover Classification**

We analyzed land cover for each catchment basin with the 2006 National Land Cover Database (NLCD) (Fig. 1) (Fry *et al.* 2011). We classified agricultural land as hay/pasture and cultivated crops; forested land as evergreen, deciduous, and mixed forest; and developed land as: high, medium, low intensity, and open space. We classified shrub/scrub, herbaceous, barren, emergent and woody wetlands, and open water as other. We sampled streams within forested ( $n=24$ ), agricultural ( $n=30$ ) and developed ( $n=9$ ) watersheds. Land cover within the watershed was categorized based on the dominant (>50%) land use for forested and agricultural streams. Since the DA is fairly undeveloped, we classified streams as developed if at least 30% of the direct catchment

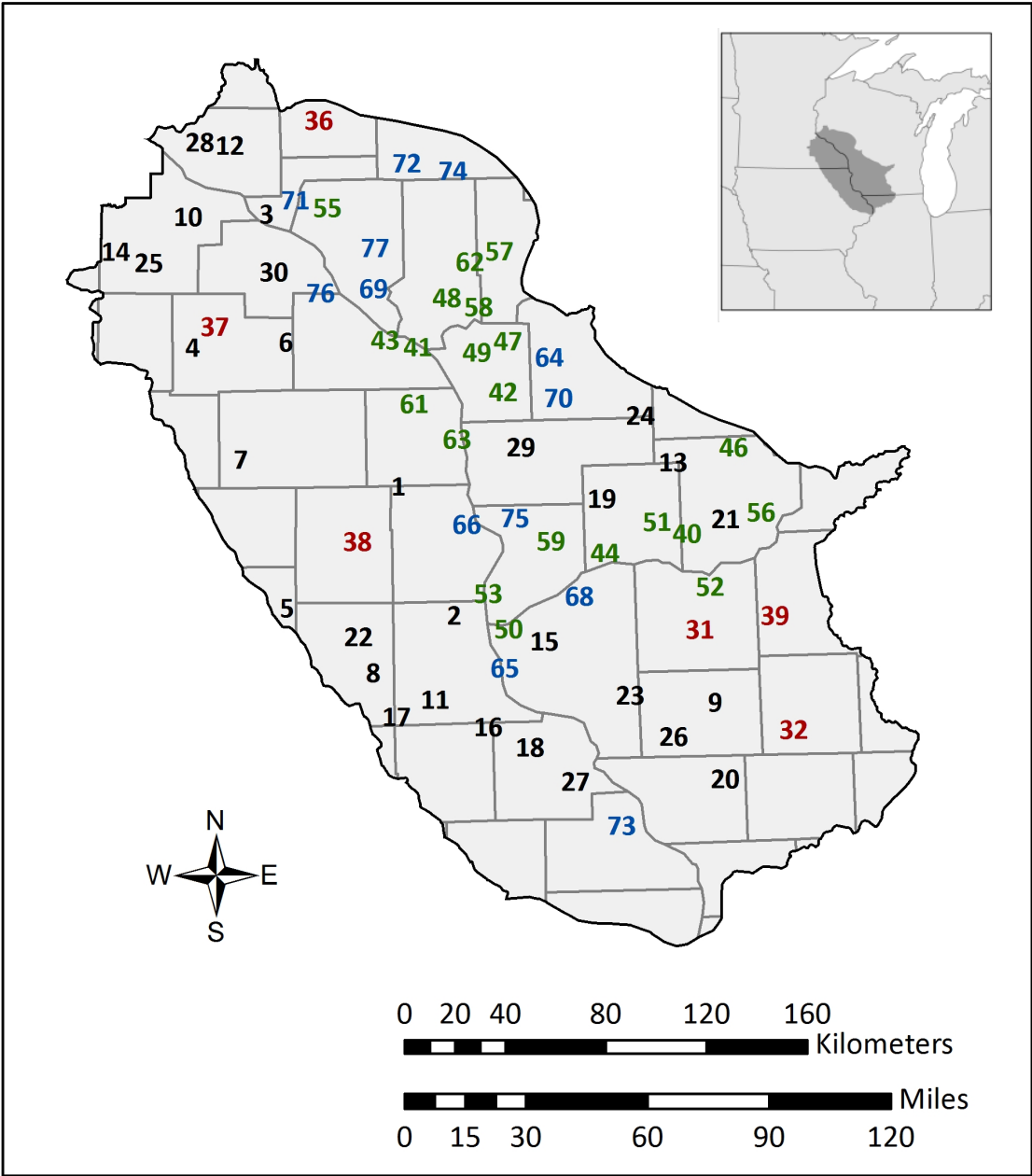


Figure 2. Stream site locations in the Driftless Area, USA. [black text, agricultural; red text, developed; green text, forested; blue text, mixed]. Numbers correspond to site ID numbers listed in Table 1.

Table 1. Identification information (ID), land cover, watershed area, and location information for streams ( $n=77$ ) in the Driftless Area. Location of streams is shown in Figure 2. [Cr, Creek; R, River; Trib, Tributary]

ID	Stream	Land cover classification	Land Cover (%)				Watershed area (km <sup>2</sup> )	Latitude	Longitude
			Agriculture	Developed	Forested	Other			
1	Bee Cr	Ag	72.1	4.4	16.3	7.2	47.5	43.49971	91.57065
2	Bloody Run	Ag	82.2	7.0	4.3	6.6	26.0	43.03364	91.30915
3	Bogus Cr	Ag	52.4	3.7	43.2	0.6	20.7	44.48002	92.20602
4	Cascade Cr	Ag	74.1	15.2	2.0	8.8	34.9	44.00488	92.57821
5	Crane Cr	Ag	81.7	6.0	3.7	8.6	338.7	43.07034	92.14530
6	Crow Spring	Ag	83.2	3.7	5.3	7.8	21.2	44.02089	92.11558
7	Etna Cr	Ag	82.7	7.5	2.2	7.6	14.6	43.60257	92.34348
8	Grannis Cr	Ag	60.8	4.8	16.1	18.3	14.3	42.83446	91.70935
9	Gravel Run Cr	Ag	91.4	3.5	4.9	0.2	18.6	42.69876	90.05442
10	Hay Cr	Ag	65.8	4.0	0.2	30.1	51.1	44.47241	92.59722
11	Honey Cr-IA	Ag	58.9	2.7	31.2	7.2	26.5	42.73462	91.40968
12	Isabelle Cr	Ag	59.6	22.7	17.7	0.0	7.9	44.72628	92.45707
13	Little Baraboo R	Ag	72.3	4.9	22.3	0.6	48.5	43.56178	90.21807
14	Little Cannon R	Ag	82.3	6.7	5.7	5.3	32.7	44.34880	92.95720

Table 1. Cont.

ID	Stream	Land cover classification	Land Cover (%)				Watershed area (km <sup>2</sup> )	Latitude	Longitude
			Agriculture	Developed	Forested	Other			
15	Little Grant R	Ag	87.6	6.7	5.2	0.5	21.3	42.93446	90.87121
16	Little Turkey R	Ag	65.0	4.9	23.0	7.1	18.5	42.63410	91.15444
17	Maquoketa R	Ag	88.8	4.6	0.9	5.7	44.9	42.67606	91.59774
18	Middle Fork Little Maquoketa R	Ag	67.2	5.7	14.8	12.3	32.8	42.55783	90.95515
19	Mill Cr-WI	Ag	59.3	3.8	35.1	1.9	10.9	43.43898	90.57424
20	Mud Run	Ag	82.7	6.5	9.6	1.3	23.5	42.42284	90.01858
21	N Branch Honey Cr	Ag	53.7	3.6	41.6	1.1	31.9	43.35132	89.96897
22	Otter Cr-IA	Ag	78.6	11.8	1.8	7.8	39.4	42.94454	91.77649
23	Rountree Branch	Ag	88.1	10.3	1.2	0.3	18.3	42.73255	90.46203
24	Seymour Cr	Ag	66.0	4.1	28.7	1.2	24.3	43.73239	90.36971
25	Shingle Cr	Ag	83.7	8.1	2.3	5.8	19.3	44.30857	92.79380
26	Shullsburg Branch	Ag	87.6	9.7	2.2	0.5	22.7	42.58104	90.26010
27	Swiss Valley Cr	Ag	52.4	5.2	34.9	7.4	34.9	42.43061	90.73874
28	Trimbelle R	Ag	67.5	5.0	25.9	1.5	49.2	44.78460	92.53535

Table 1. Cont.

ID	Stream	Land cover classification	Land Cover (%)				Watershed area (km <sup>2</sup> )	Latitude	Longitude
			Agriculture	Developed	Forested	Other			
29	Unnamed Trib N Fork Bad Axe R	Ag	79.4	6.4	13.1	1.1	13.1	43.63113	90.96426
30	W Indian Cr	Ag	65.8	4.2	13.9	16.1	57.4	44.27182	92.17064
31	Dodge Branch	Developed	22.0	74.1	3.9	0.0	2.5	42.95996	90.11457
32	Honey Cr-WI	Developed	42.8	55.1	1.5	0.6	11.8	42.58996	89.67789
33	N Fork Catfish Cr	Developed	5.7	93.5	0.4	0.3	8.1	42.49314	90.70808
34	Unnamed Trib Little Platte R-2	Developed	0.0	100.0	0.0	0.0	1.3	42.73107	90.47603
35	Unnamed Trib Little Platte R-3	Developed	61.9	32.3	5.8	0.0	31.2	42.73096	90.50437
36	Unnamed Trib Red Cedar R	Developed	30.6	38.7	24.4	6.4	6.9	44.87002	91.93548
37	Unnamed Trib S Fork Zumbro R	Developed	49.3	37.5	2.7	10.5	20.2	44.07928	92.50434
38	Unnamed Trib Upper Iowa R	Developed	16.6	64.5	11.2	7.7	3.7	43.30471	91.77466
39	W Branch Sugar R	Developed	10.4	89.1	0.0	0.5	0.9	43.00066	89.74593

Table 1. Cont.

ID	Stream	Land cover classification	Land Cover (%)				Watershed area (km <sup>2</sup> )	Latitude	Longitude
			Agriculture	Developed	Forested	Other			
40	Bear Cr	Forested	41.9	4.0	52.8	1.3	73.5	43.30677	90.19214
41	Big Trout Cr	Forested	34.1	4.2	54.4	7.2	53.7	43.99616	91.46074
42	Bostwick Cr	Forested	34.6	2.9	59.2	3.3	30.9	43.82875	91.04332
43	Burns Valley Cr	Forested	25.9	9.4	56.2	8.5	37.7	44.02377	91.62208
44	Byrds Cr	Forested	25.9	4.6	68.0	1.6	10.2	43.24514	90.56609
45	Center Cr	Forested	20.4	2.0	73.4	4.1	9.0	44.49566	91.96301
46	Dell Cr	Forested	40.1	3.7	53.5	2.7	46.0	43.60974	89.91768
47	Fleming Cr	Forested	33.9	3.6	61.5	1.0	39.2	44.01229	91.05194
48	French Cr	Forested	28.3	3.5	60.3	7.8	27.0	44.20329	91.31152
49	Halfway Cr	Forested	26.5	2.9	69.7	0.9	11.4	43.97294	91.16999
50	Lane Cr	Forested	35.5	6.1	58.0	0.4	28.8	42.99448	91.04460
51	Little Willow Cr	Forested	41.8	4.2	52.3	1.7	30.5	43.35112	90.30507
52	Lowery Cr	Forested	28.5	3.7	66.7	1.2	16.7	43.11362	90.05800
53	Mill Coulee Cr	Forested	33.4	3.5	62.9	0.2	17.7	43.11143	91.14158
54	N Branch Douglas Cr	Forested	30.9	2.3	63.5	3.3	7.8	44.18502	91.02626

Table 1. Cont.

ID	Stream	Land cover classification	Land Cover (%)				Watershed area (km <sup>2</sup> )	Latitude	Longitude
			Agriculture	Developed	Forested	Other			
55	N Branch Little Bear Cr	Forested	32.2	3.9	61.7	2.2	7.4	44.50021	91.90086
56	Otter Cr-Sauk Co, WI	Forested	2.5	1.5	95.3	0.8	10.4	43.37248	89.79614
57	Pine Cr	Forested	17.4	3.7	68.1	10.7	28.0	44.33513	91.08801
58	S Fork Beaver Cr	Forested	28.2	3.2	65.6	3.0	31.3	44.13612	91.15686
59	Sand Cr	Forested	34.9	4.2	59.5	1.3	21.3	43.29226	90.82942
60	Spring Branch	Forested	35.6	8.2	53.5	2.7	5.4	43.69101	91.28647
61	Storer Cr	Forested	33.3	1.7	60.0	5.1	16.4	43.79368	91.48387
62	Tappen Coulee Cr	Forested	38.1	4.0	55.4	2.5	25.3	44.29764	91.19459
63	Unnamed Trib Mississippi R	Forested	22.4	5.3	71.5	0.7	1.5	43.66384	91.27671
64	Beaver Cr	Mixed	45.0	7.9	45.9	1.2	44.9	43.95006	90.81357
65	Chase Cr	Mixed	49.5	2.1	48.3	0.1	10.4	42.84325	91.06879
66	Clear Cr	Mixed	35.4	5.1	47.1	12.5	32.2	43.35931	91.23832
67	Coon Cr	Mixed	49.2	3.6	46.3	0.9	47.7	43.72190	90.97678

Table 1. Cont.

ID	Stream	Land cover classification	Land Cover (%)				Watershed area (km <sup>2</sup> )	Latitude	Longitude
			Agriculture	Developed	Forested	Other			
68	Crooked Cr	Mixed	42.7	6.0	48.8	2.5	28.5	43.09204	90.69640
69	Eagle Cr	Mixed	45.5	3.7	49.5	1.3	36.7	44.20929	91.67816
70	Little La Crosse R	Mixed	48.2	6.9	43.4	1.5	45.3	43.80427	90.77181
71	Little Plum Cr	Mixed	45.8	4.3	48.8	1.2	26.0	44.52945	92.06065
72	Lowes Cr	Mixed	46.9	5.2	39.4	8.5	22.8	44.65533	91.49906
73	Mill Cr-IA	Mixed	47.9	3.6	34.8	13.7	33.4	42.26959	90.52367
74	Otter Cr-Eau Claire Co, WI	Mixed	45.2	10.6	36.8	7.4	7.3	44.62557	91.26970
75	Sugar Cr	Mixed	49.5	5.7	44.3	0.5	20.4	43.37767	91.00034
76	Trout Cr	Mixed	38.5	2.0	49.4	10.0	45.2	44.19639	91.94070
77	Waumandee Cr	Mixed	45.2	3.4	49.5	1.9	48.0	44.35430	91.66503

basin was developed. Streams lacking a dominant land cover were categorized as mixed ( $n=14$ ). The number of streams sampled within each land use category generally represents the overall percentages of these land uses in the ecoregion. We verified land cover class in each catch basin by ground-truthing the GIS analysis with aerial photography. We recorded exact sampling locations at each site with global-positioning system (GPS) equipment and used the GPS coordinates to further analyze and verify land cover classification and watershed basin size with GIS for each site after sample collection.

### **Sample Collection**

We followed standard quality assurance and quality control procedures during sample preparation, collection, and laboratory analyses. Grab samples were collected at most site locations four times to determine seasonal baseflow nutrient concentrations. We sampled the streams in fall (September 29-November 1, 2012), winter (January 5-February 9, 2013), spring (April 27-May 16, 2013), and summer (July 15-August 2, 2013). Specific sampling times varied depending on weather and hydrologic conditions. For example, we only collected samples during baseflow conditions, or periods of minimal flow (>48 hours since previous rain or melt event). Throughout the sampling period we were unable to sample all 77 streams every season for various reasons. We did not sample three streams in fall, one stream in spring, and three streams in summer due to a lack of positive baseflow. Eight streams were not sampled in winter as a result of inaccessibility to site locations because of hazardous winter road conditions, or because the sampling site was completely frozen.

At each site, specific conductance, dissolved oxygen (DO), pH, water temperature, and redox potential (ORP) were measured with a Hydrolab DataSonde DS5 multi-parameter probe. Representative water quality grab samples were collected from well-mixed areas with uniform flow near the thalweg of each stream. Grab samples consisted of one field-filtered (Whatman GF/F, 0.7- $\mu\text{m}$  nominal pore size) and one unfiltered sample placed into acid-washed polyethylene bottles. Field duplicates at a predetermined number of sites were also collected.

### **Water Quality Analyses**

All samples were kept on ice or refrigerated to 4 °C immediately after collection until analyzed. We preserved TDN,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and TDP samples immediately with  $\text{H}_2\text{SO}_4$  to pH less than 2. Samples to be analyzed for DOC were preserved with HCl to pH less than 2. We analyzed  $\text{NO}_2^-$  for each sample within 48 hours of sample collection and all other analytes were measured within 28 days of sample collection. All nutrient concentration determinations were made using a Lachat QuikChem 8500 Series 2 Flow Injection Analysis System. We analyzed samples for  $\text{NH}_4^+$  (QuikChem® Method 10-107-06-1-J),  $\text{NO}_2^- + \text{NO}_3^-$ ,  $\text{NO}_2^-$  alone (QuikChem Method 10-107-04-1-C), TDN (QuikChem® Method 10-107-04-4-B), and TDP (QuikChem® Method 10-115-01-1-E). We determined TDN and TDP concentrations with the autoanalyzer following a persulfate digestion (APHA 2005; Patton and Kryskalla 2003). The concentration of DON in each sample was calculated by subtracting  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_2^-\text{-N}$ , and  $\text{NO}_3^-\text{-N}$  from TDN. Dissolved inorganic nitrogen (DIN) was determined as the sum of  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_2^-\text{-N}$ , and  $\text{NO}_3^-\text{-N}$ . We analyzed DOC with a Shimadzu TOC analyzer. Turbidity was measured for each sample with a Hach 2100 Turbidimeter within 48 hours of sample

collection and total suspended solids (TSS) were determined gravimetrically for each sample within seven days of collection (APHA 2005). Refer to Appendix B for all raw data.

### **Statistical Analyses**

We used data from all stream locations in the statistical analyses, with the exception of data collected from Isabelle Creek (ID number 12; Figure 2; Table 1). We removed Isabelle Creek from all statistical analyses because we discovered the sampling location was directly downstream (ca. 0.5 km) from a wastewater treatment facility. Additionally, we used a substitution value of one-half the detection limit for sample concentrations that were below the detection limit (Table 2).

We used a Kruskal Wallis non-parametric test followed by a multiple comparison test on ranks to analyze differences in nutrient concentrations across land cover types as well as to detect seasonal differences in nutrients (Helsel and Hirsch 2002). Additionally, we used spearman correlation coefficients to examine relationships among variables.

We used a non-parametric change point analysis (nCPA) to analyze thresholds between the response of percent N to changes in TDN and to determine thresholds in the response of N to changes in percent agricultural and forested land cover. This statistical approach uses a deviance reduction method to determine the point at which the maximum difference occurs in the sum of the deviances of two groups, which are defined as the values above and below this point respectively, along a stressor gradient (e.g. % Ag, % Forest, TDN (mg/L)) compared to the overall deviance of the data set (Qian *et al.* 2003; King and Richardson 2003). The nCPA R 2.9.3 package, which uses a bootstrap

simulation that recalculates the thresholds 1000 times, was used for all threshold analyses (King and Richardson 2003).

We considered differences to be statistically significant at  $p$ -values less than 0.05 for all statistical tests. All statistical analyses were done with R statistical software 3.0.2 (R Development Core Team 2006) or SPSS statistical software 20.0 (SPSS Inc. 2011).

Table 2. Method detection limits of constituents analyzed in stream samples.

Constituent	Method detection limit (mg/L)
Ammonia as nitrogen, dissolved	0.003
Nitrate plus nitrite, as nitrogen, dissolved	0.0006
Nitrite, as nitrogen, dissolved	0.001
Total dissolved nitrogen	0.006
Total dissolved phosphorus	0.0006
Dissolved organic carbon	0.004

## RESULTS

### Nitrogen

We observed a wide range of N concentrations across streams in the DA (Table 3; Table 4). TDN concentrations were significantly higher in agricultural streams compared to forested streams for all seasons (Kruskal Wallis test,  $p < 0.0001$ ; Fig. 3). The median TDN concentration in forested streams was 1.39 mg/L, compared to 5.85 mg/L in agricultural streams across all seasons (Table 4). In winter and spring, developed streams also had significantly higher TDN concentrations compared to forested streams (Kruskal Wallis test,  $p < 0.0001$ ; Fig. 3). TDN concentrations were widely variable in developed streams, ranging from 0.145 to 25.0 mg/L (Table 4).

Median TDN concentrations were not significantly different across seasons, ranging from 2.26 to 2.88 mg/L (Table 3). However, the median TDN concentration was nearly 30% higher in both spring and summer in agricultural streams compared to fall and winter (Fig. 3). Similar to TDN, we observed significantly higher  $\text{NO}_3^-$  concentrations in agricultural streams compared to forested streams across all seasons (Kruskal Wallis test,  $p < 0.0001$ ) (Appendix A, Fig. 13). We found highly variable  $\text{NO}_3^-$  concentrations in developed streams, ranging from 0.003 to 23.3 mg/L. There were not significant differences in  $\text{NO}_3^-$  across seasons; however, the median concentration of  $\text{NO}_3^-$  in agricultural streams was highest in spring (5.96 mg/L) and lowest in fall (4.06 mg N/L).

Table 3. Seasonal mean, median, and minimum-maximum concentrations of nutrients in streams across all land use types.  
 [All values in mg/L;  $\bar{x}$ , mean;  $M$ , median]

N Fraction	Fall			Winter			Spring			Summer		
	$\bar{x}$	$M$	Range	$\bar{x}$	$M$	Range	$\bar{x}$	$M$	Range	$\bar{x}$	$M$	Range
NO <sub>3</sub> <sup>-</sup> -N	3.45	2.13	0.003-23.3	3.55	2.39	0.599-20.7	4.01	2.10	0.255-16.8	3.62	2.44	0.096-11.8
NO <sub>2</sub> <sup>-</sup> -N	0.020	0.014	0.001-0.181	0.015	0.012	0.003-0.130	0.025	0.019	0.008-0.129	0.026	0.020	0.001-0.222
NH <sub>4</sub> <sup>+</sup> -N	0.062	0.046	0.002-0.419	0.050	0.030	0.002-0.360	0.023	0.011	0.002-0.381	0.027	0.016	0.002-0.390
DON	0.562	0.273	0.000-2.71	0.249	0.071	0.000-2.13	0.440	0.113	0.000-3.08	0.412	0.266	0.000-2.35
TDN	4.09	2.26	0.145-25.0	3.83	2.36	0.741-20.6	4.48	2.42	0.368-18.15	4.08	2.88	0.356-11.9
TDP	0.084	0.049	0.007-0.808	0.074	0.035	0.000-0.831	0.037	0.014	0.000-0.264	0.043	0.015	0.000-0.316
DOC	2.50	1.91	1.09-9.48	2.21	1.75	1.01-7.50	2.87	2.88	1.42-6.15	2.26	2.02	1.24-7.15

Table 4. Mean, median, and minimum-maximum concentrations of nutrients in agricultural, developed, forested, and mixed streams across all seasons. [All values in mg/L;  $\bar{x}$ , mean;  $M$ , median]

N Fraction	Agricultural			Developed			Forested			Mixed		
	$\bar{x}$	$M$	Range	$\bar{x}$	$M$	Range	$\bar{x}$	$M$	Range	$\bar{x}$	$M$	Range
NO <sub>3</sub> <sup>-</sup> -N	5.79	4.94	0.364-16.8	4.30	2.91	0.003-23.3	1.40	1.21	0.026-4.25	2.58	2.21	0.370-7.42
NO <sub>2</sub> <sup>-</sup> -N	0.027	0.021	0.001-0.222	0.035	0.016	0.006-0.181	0.014	0.011	0.001-0.080	0.016	0.016	0.003-0.045
NH <sub>4</sub> <sup>+</sup> -N	0.034	0.019	0.002-0.390	0.050	0.027	0.002-0.323	0.045	0.031	0.002-0.419	0.038	0.029	0.002-0.381
DON	0.667	0.320	0.000-3.08	0.496	0.262	0.000-2.04	0.156	0.079	0.000-1.19	0.288	0.106	0.000-2.71
TDN	6.511	5.850	0.718-18.2	4.87	3.25	0.145-25.0	1.60	1.39	0.174-5.50	2.90	2.35	0.663-10.2
TDP	0.067	0.029	0.000-0.831	0.073	0.039	0.000-0.579	0.048	0.033	0.000-0.223	0.052	0.027	0.000-0.286
DOC	2.418	2.268	1.09-7.08	3.72	3.18	1.33-7.50	2.12	1.77	1.05-9.48	2.05	1.76	1.01-7.15

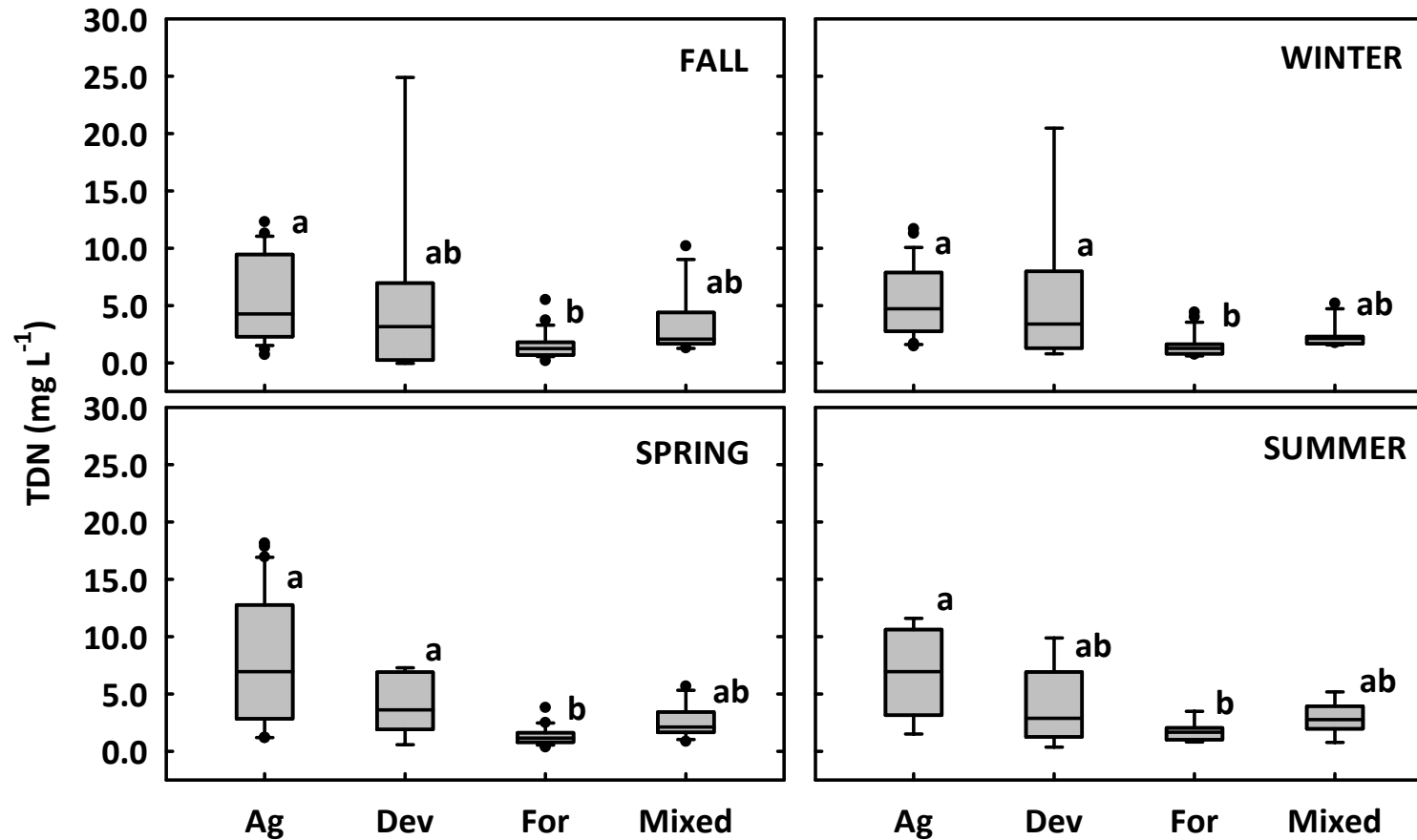


Figure 3. Seasonal concentrations of total dissolved nitrogen (TDN) (mg/L) in streams in the Driftless Area. Significant differences were identified with a Kruskal Wallis test: fall  $n=73$ , winter  $n=68$ , spring  $n=75$ , summer  $n=73$ ;  $p < 0.0001$  for all seasons. Lowercase letters adjacent to boxes indicate significant differences among land use categories identified with a multiple comparison test on ranks ( $p < 0.05$ ).

[Box plots display 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles, and data points outside the 10<sup>th</sup> and 90<sup>th</sup> percentiles. Agr, agricultural; Dev, developed; For, forested; Mix, mixed]

We observed relatively low  $\text{NO}_2^-$  concentrations across all streams and seasons, ranging from 0.001 to 0.22 mg N/L. However,  $\text{NO}_2^-$  concentrations were significantly higher in agricultural streams compared to forested streams across all seasons (Kruskal Wallis test,  $p < 0.05$ ; Appendix A, Fig. 16). We also observed seasonal differences in  $\text{NO}_2^-$ . We observed significantly higher  $\text{NO}_2^-$  concentrations in spring and summer compared to fall and winter (Kruskal Wallis test,  $p < 0.0001$ ).

Ammonium was variable across streams, ranging from 0.002 to 0.419 mg N/L. In winter, we observed significantly higher  $\text{NH}_4^+$  concentrations in developed streams, compared to agricultural, forested, and mixed streams (Kruskal Wallis test,  $p = 0.003$ ; Appendix A, Fig. 15). Ammonium concentrations were also significantly higher in agricultural streams compared to forested streams in spring (Kruskal Wallis test,  $p = 0.015$ ). We did not observe significant differences in  $\text{NH}_4^+$  concentrations across land use types in fall or summer. Ammonium concentrations were significantly different across seasons (Kruskal Wallis test,  $p < 0.0001$ ); higher concentrations occurred in fall and winter compared to spring and summer.

DON concentrations typically made up a smaller portion of the TDN pool across DA streams, ranging from 0.00 to 3.08 mg/L. In fall and spring, we observed significantly higher DON concentrations in agricultural streams compared to forested streams (Kruskal Wallis test,  $p < 0.05$ ; Appendix A, Fig. 14). DON concentrations were not significantly different across land use types in winter or summer. DON was also seasonally variable, spring and winter concentrations were lower compared to fall and summer (Kruskal Wallis test,  $p < 0.0001$ ).

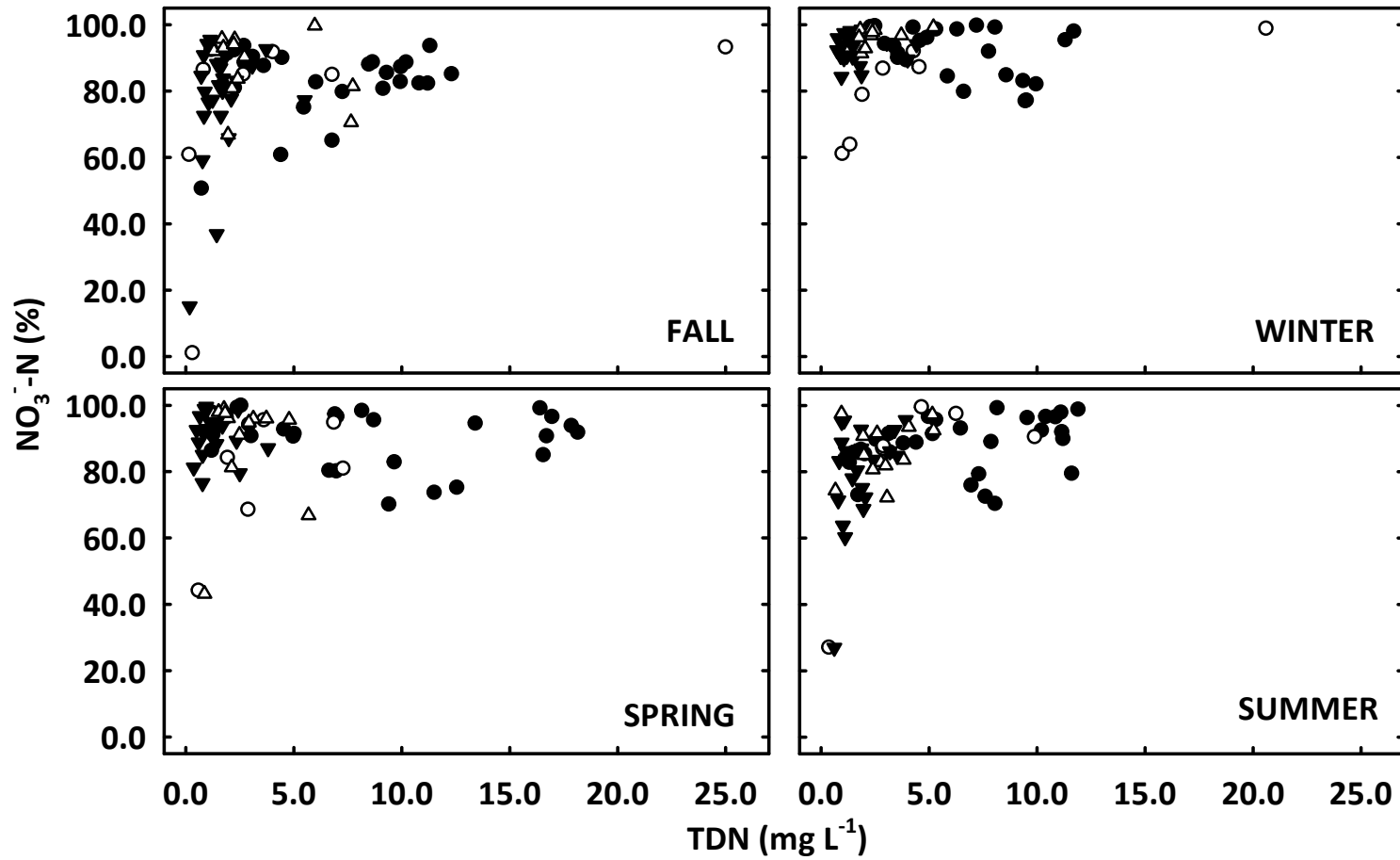


Figure 4. Percent nitrate-nitrogen ( $\text{NO}_3^- \text{-N}$ ) in relation to total dissolved nitrogen (TDN mg/L) across all seasons. [ ● , agricultural; ○ , developed; ▼ , forested; △ , mixed streams. ]

### **TDN Pool**

The TDN pool was dominated by  $\text{NO}_3^-$  in most streams (Fig. 4). Nitrate-nitrogen accounted for between 60 and 98% of the TDN pool in agricultural streams across all seasons. Ammonium and  $\text{NO}_2^-$  made up a smaller percentage of the TDN pool in most streams, generally less than 10% (Appendix A; Figs. 18 and 19). However,  $\text{NH}_4^+$  made up a slightly larger percentage of the TDN pool in fall (up to 28%), specifically in forested and developed streams. The contribution of DON to the TDN pool was variable. Dissolved organic nitrogen accounted for a higher percentage of the TDN pool in fall and spring compared to winter and summer (Appendix A; Fig. 17). In winter,  $\text{NO}_3^-$  was the dominant fraction of N across all streams (Fig. 4).

### **Total Dissolved Phosphorus**

We observed a wide range of TDP concentrations across all land use types, ranging from below detection to 0.831 mg/L (Table 2). TDP concentrations were not significantly different across land use types (Fig. 5). However, TDP concentrations were significantly different across seasons (Kruskal Wallis test,  $p < 0.0001$ ). Similar to  $\text{NH}_4^+$ , we observed higher concentrations in fall and winter compared to spring and summer. Median TDP concentrations were approximately two times higher in fall and winter compared to spring and summer (Table 3).

### **Dissolved Organic Carbon**

Throughout our study DOC concentrations ranged from 1.09 to 9.48 mg/L (Table 2). DOC concentrations were not significantly different across land cover types in fall. However, in winter, DOC concentrations were significantly higher in agricultural and

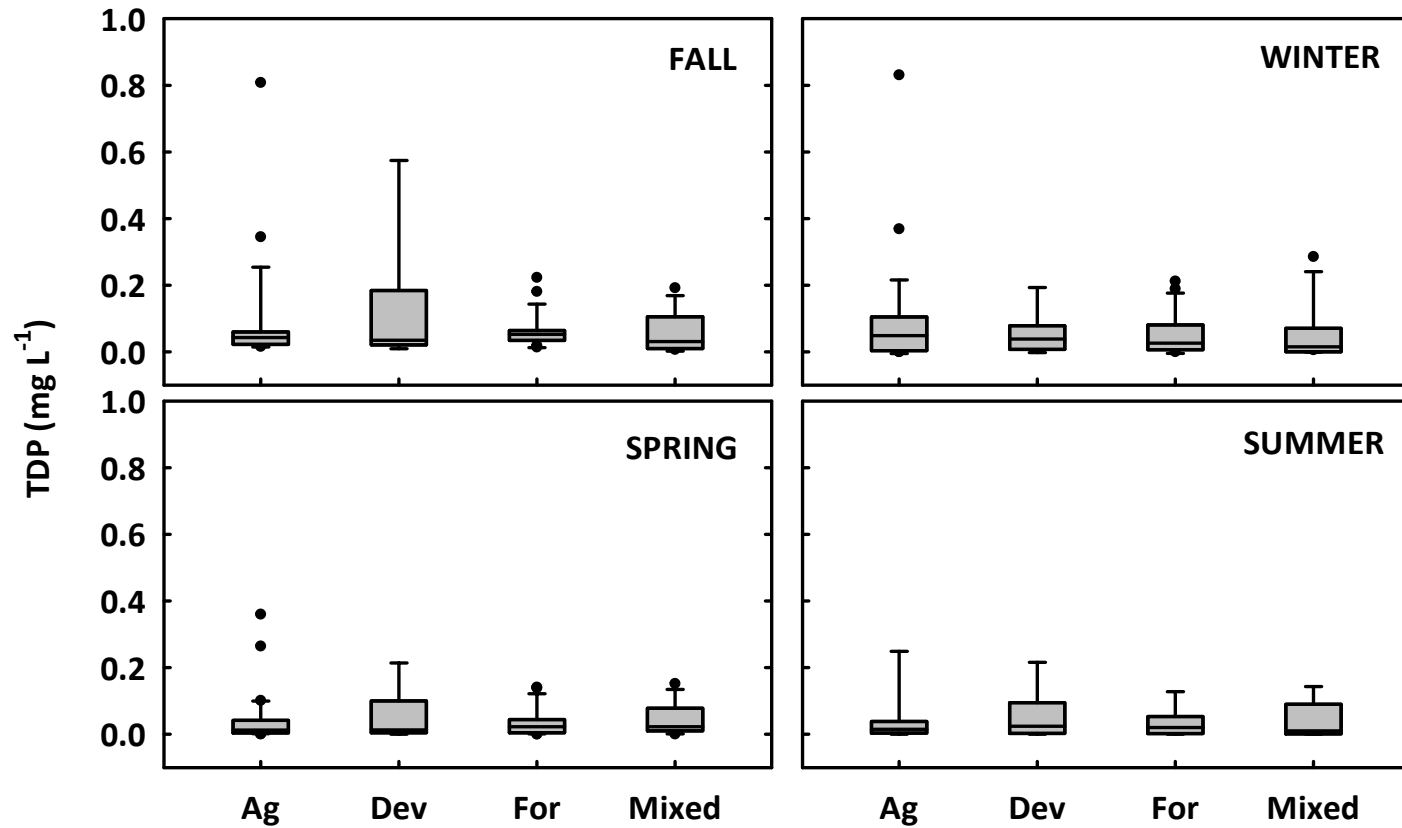


Figure 5. Seasonal concentrations of total dissolved phosphorus (TDP) (mg/L) in streams in the Driftless Area. Significant differences among land use categories were identified with a Kruskal Wallis test: fall  $n=73$ , winter  $n=68$ , spring  $n=75$ , summer  $n=73$ ;  $p > 0.05$  for all seasons.

[Box plots display 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles, and data points outside the 10<sup>th</sup> and 90<sup>th</sup> percentiles. Agr, agricultural; Dev, developed; For, forested; Mix, mixed]

developed streams compared to forested streams (Kruskal Wallis test,  $p < 0.0001$ ; Fig. 6). We also observed significantly higher DOC concentrations in developed streams compared to forested and mixed streams in summer (Kruskal Wallis test,  $p = 0.006$ ). DOC concentrations were significantly higher in spring compared to fall, winter, and summer across all land use types (Kruskal Wallis test,  $p < 0.0001$ ). However, the analysis was performed on a limited number of streams ( $n=32$ ), due to equipment malfunctions. Seasonal differences were analyzed only for DOC data available for all seasons ( $n=128$ ).

### **Correlations**

The percentage of land use within each catchment was correlated with many of the nutrient concentrations and chemical water quality parameters (Table 5). Nitrate,  $\text{NO}_2^-$ , DON, and TDN fractions were significantly ( $p < 0.05$ ) correlated with percent developed (+), agriculture (+), and forested (-) land use. Nitrate and TDN were strongly correlated with percent total agriculture (+) and percent forest (-). DON was most strongly correlated with percent forest, with an  $r_s$  value of -0.653. TDP was not significantly correlated with any of the land use characteristics. DOC was correlated with percent developed (+), and forested (-) land use. Conductivity was strongly correlated with percent forested (-) land use.

There also were significant correlations between different nitrogen fractions (Table 6). We found weak correlations between TSS and all N fractions, with the exception of  $\text{NH}_4^+$  ( $r_s$  values ranging from -0.232 to -0.362). Conductivity was correlated with N fractions, and weakly correlated with DOC and DO. DOC was also correlated with  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , DON and TDP ( $r_s$  values ranging from 0.292 to 0.401).

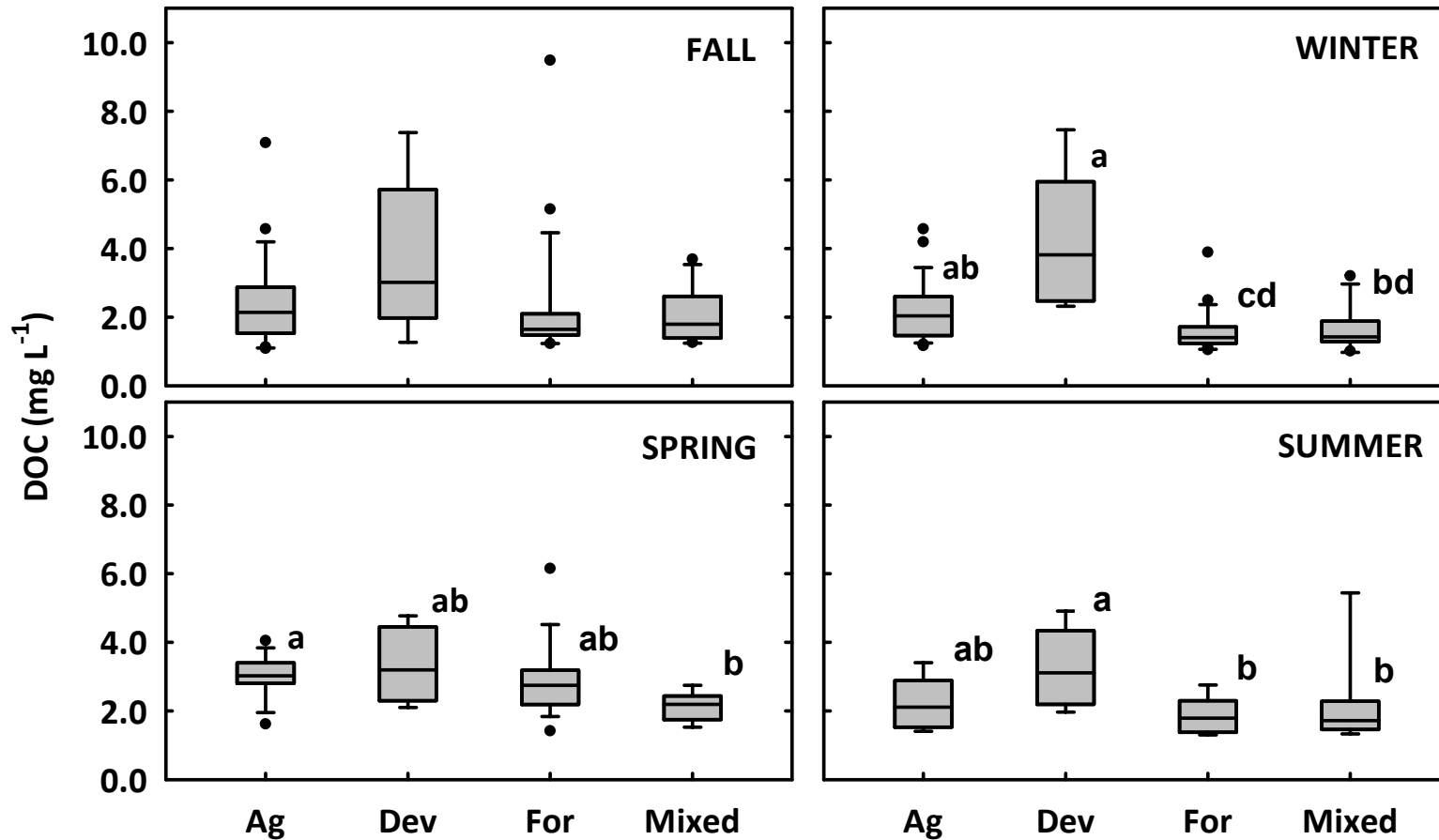


Figure 6. Seasonal concentrations of dissolved organic carbon (DOC) (mg/L) in streams in the Driftless Area. Significant differences among land use categories were identified with a Kruskal Wallis test: fall  $n=73$ , winter  $n=68$ , spring  $n=75$ , summer  $n=73$ ;  $p < 0.05$  in winter, spring, and summer. Lowercase letters adjacent to boxes indicate significant differences among categories identified with a multiple comparison test on ranks ( $p < 0.05$ ).

[Box plots display 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles, and data points outside the 10<sup>th</sup> and 90<sup>th</sup> percentiles.

Ag, agricultural; Dev, developed; For, forested; Mix, mixed]

Table 5. Spearman rank correlations between mean nutrient concentrations across seasons and percent land use in each catchment basin. [Values are Spearman's rho ( $r_s$ ); the values in bold text represent significant correlations ( $p < 0.05$ )]

Land Use Characteristic	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	DON	TDN	TDP	DOC	DO	Cond	pH	ORP	TSS
% Ag	<b>0.668</b>	<b>0.568</b>	<b>-0.315</b>	<b>0.501</b>	<b>0.656</b>	0.036	0.149	<b>0.366</b>	0.213	<b>0.347</b>	-0.192	<b>-0.322</b>
% Developed	<b>0.354</b>	<b>0.429</b>	0.092	<b>0.356</b>	<b>0.372</b>	0.086	<b>0.414</b>	0.133	<b>0.498</b>	-0.016	0.043	-0.127
% Forest	<b>-0.656</b>	<b>-0.611</b>	0.145	<b>-0.653</b>	<b>-0.673</b>	-0.044	<b>-0.428</b>	<b>-0.268</b>	<b>-0.563</b>	-0.183	0.031	<b>0.340</b>

Table 6. Spearman rank correlations between mean nutrient concentrations and selected water quality parameters across seasons. [Values are Spearman's rho ( $r_s$ ); the values in bold text represent significant correlations ( $p < 0.05$ )]

Constituent	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	DON	TDN	TDP	DOC	DO	Cond	pH	ORP	TSS
NO <sub>3</sub> <sup>-</sup>	1.000											
NO <sub>2</sub> <sup>-</sup>	<b>0.655</b>	1.000										
NH <sub>4</sub> <sup>+</sup>	-0.162	0.008	1.000									
DON	<b>0.806</b>	<b>0.551</b>	-0.087	1.000								
TDN	<b>0.994</b>	<b>0.657</b>	-0.141	<b>0.843</b>	1.000							
TDP	<b>0.247</b>	0.195	<b>0.408</b>	<b>0.279</b>	<b>0.261</b>	1.000						
DOC	0.196	<b>0.401</b>	<b>0.323</b>	<b>0.354</b>	0.215	<b>0.292</b>	1.000					
DO	0.201	<b>0.252</b>	-0.105	0.112	0.184	0.086	-0.018	1.000				
Cond	<b>0.501</b>	<b>0.557</b>	-0.107	<b>0.482</b>	<b>0.510</b>	0.017	<b>0.260</b>	<b>0.247</b>	1.000			
pH	<b>0.230</b>	<b>0.404</b>	-0.176	0.194	0.223	0.071	0.166	<b>0.354</b>	<b>0.319</b>	1.000		
ORP	-0.012	-0.061	-0.064	-0.039	-0.026	-0.149	-0.139	0.118	0.139	-0.028	1.000	
TSS	<b>-0.329</b>	<b>-0.232</b>	0.079	<b>-0.362</b>	<b>-0.322</b>	-0.153	<b>-0.258</b>	-0.128	-0.156	-0.036	<b>0.253</b>	1.000

### Threshold Analyses

A statistically significant threshold occurred at 0.76 mg/L TDN, in response to percent NO<sub>3</sub><sup>-</sup>-N in the TDN pool ( $p < 0.001$ ; threshold  $\leq$  value 50% time; Table 7.; Fig. 7). We also found significant thresholds in response of TDN to total agricultural land use at 60.05% and forested land use in the catchment basin at 35.30% ( $p < 0.001$ ; threshold  $\leq$  value 50% time; Table 7; Figs. 8 and 9).

Table 7. Estimates of nonparametric changepoint analysis thresholds (nCPA) (50% = threshold  $\leq$  value 50% time, 95% = threshold  $\leq$  value 95% of the time) for median total dissolved nitrogen concentrations and median NO<sub>3</sub><sup>-</sup>-N as a percentage of the TDN pool across all seasons in Driftless Area streams.

Independent variable	Dependent variable	Threshold	
		50%	95%
% Forest	TDN (mg/L)	35.30	49.15
% Total Ag	TDN (mg/L)	60.05	80.55
TDN (mg/L)	NO <sub>3</sub> <sup>-</sup> -N (%)	0.76	1.03

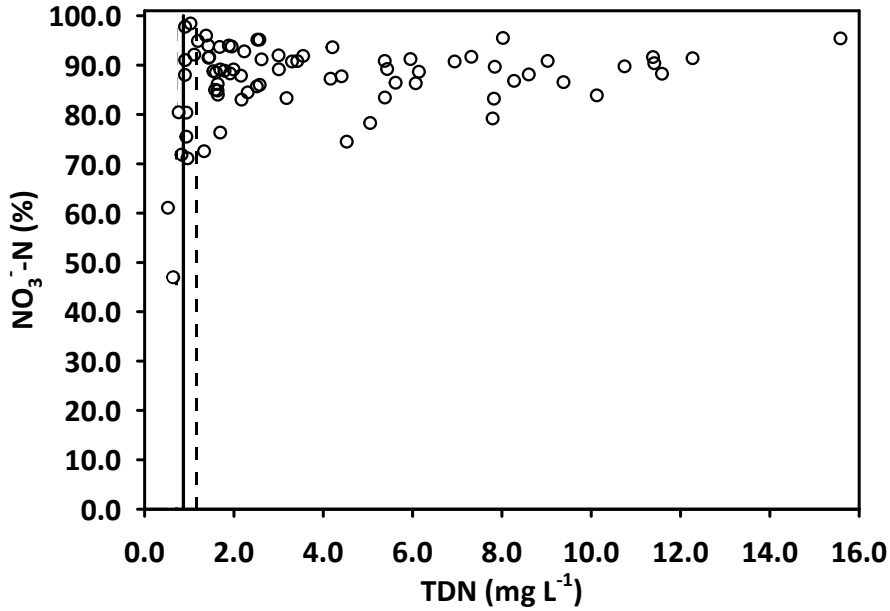


Figure 7. Median nitrate (NO<sub>3</sub><sup>-</sup>-N) as a percentage (%), across total dissolved nitrogen (TDN, mg/L) for samples collected from all seasons. Solid vertical line represents the nonparametric changepoint analysis (nCPA) 50% threshold estimate. Dotted vertical line represents nCPA 95% threshold estimate.

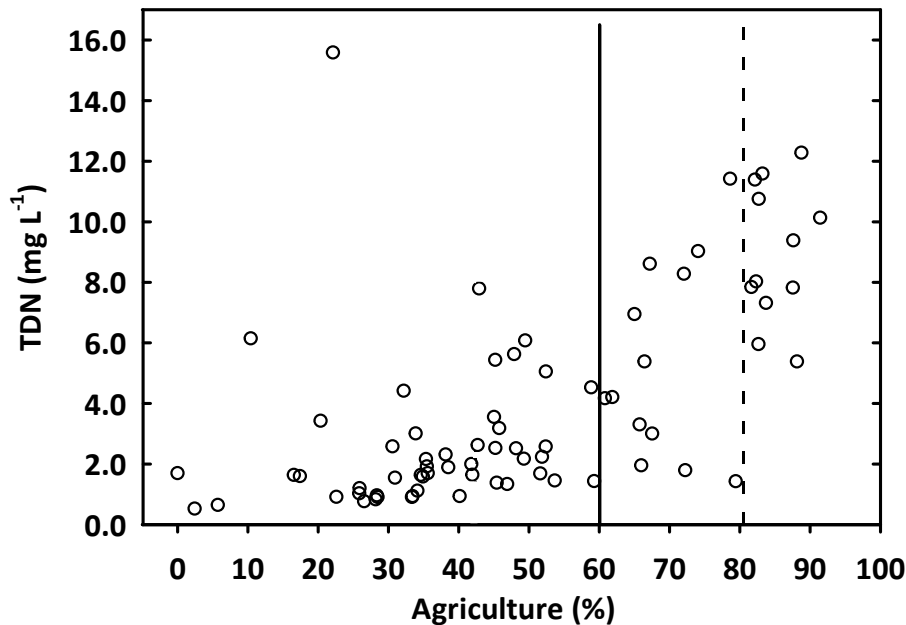


Figure 8. Median total dissolved nitrogen (TDN, mg/L) across percent agriculture (%) for samples collected from all seasons. Solid vertical line represents the nonparametric changepoint analysis (nCPA) 50% threshold estimates. Dotted vertical line represents nCPA 95% threshold estimate.

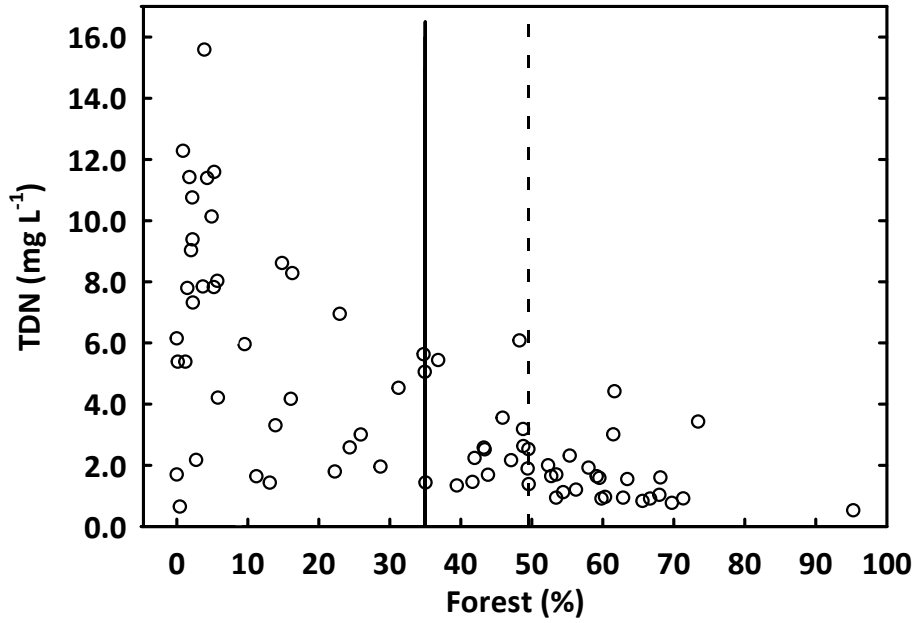


Figure 9. Median total dissolved nitrogen (TDN, mg/L) across percent forest (%) for samples collected from all seasons. Solid vertical line represents the nonparametric changepoint analysis (nCPA) 50% threshold estimate. Dotted vertical line represent nCPA 95% threshold estimate.

## DISCUSSION

In this study we measured various water quality parameters in 77 streams to examine the seasonal relationships between land use/land cover and dissolved nutrients (C, N, and P) in cold-water streams in the Driftless Area (DA) of the upper Midwest United States. We also determined if a threshold occurred as N concentrations changed in response to change in land cover, as well as if a threshold occurred as percent  $\text{NO}_3^-$ -N increased in response to increasing total dissolved nitrogen (TDN) concentrations.

### Effects of Land Use on Nitrogen

As we expected, land use was a major driver of N concentrations in DA streams (Fig. 10). In particular, TDN and  $\text{NO}_3^-$ -N concentrations were strongly correlated to land use (Table 4). Our results are similar to other studies conducted in the Midwest (Schilling and Libra, 2000; Stanley and Maxted, 2008; Robertson *et al.* 2006), where streams in agricultural areas had higher N concentrations.

We found a significant threshold response of median TDN concentrations in relation to percent forested and agricultural land use (Figs. 8 and 9). We are 95% confident that a threshold occurs at 49.15% forested land use and 80.55% agricultural land use. In other words, TDN concentrations remain relatively low when percent forest cover is greater than 49.15% or when percent agriculture is less than 80.55%. Based on these results, we estimated water quality criteria for TDN, similar to the methods utilized by Chambers *et al.* (2012). We determined a threshold for TDN by calculating the

median TDN concentration below the detected changepoint (Chambers *et al.* 2012). For our analysis, we used the 95% C.I. threshold for both agricultural and forested land use. The determined threshold for TDN was 2.1 mg/L using the agricultural threshold and 1.7 mg/L TDN using the forested threshold. Based on these results, nutrient criteria for TDN was estimated to be between 1.7 to 2.1 mg/L TDN. The US EPA uses the 25<sup>th</sup> percentile approach to determine suggested water quality criteria. Similar to Evans-White *et al.*

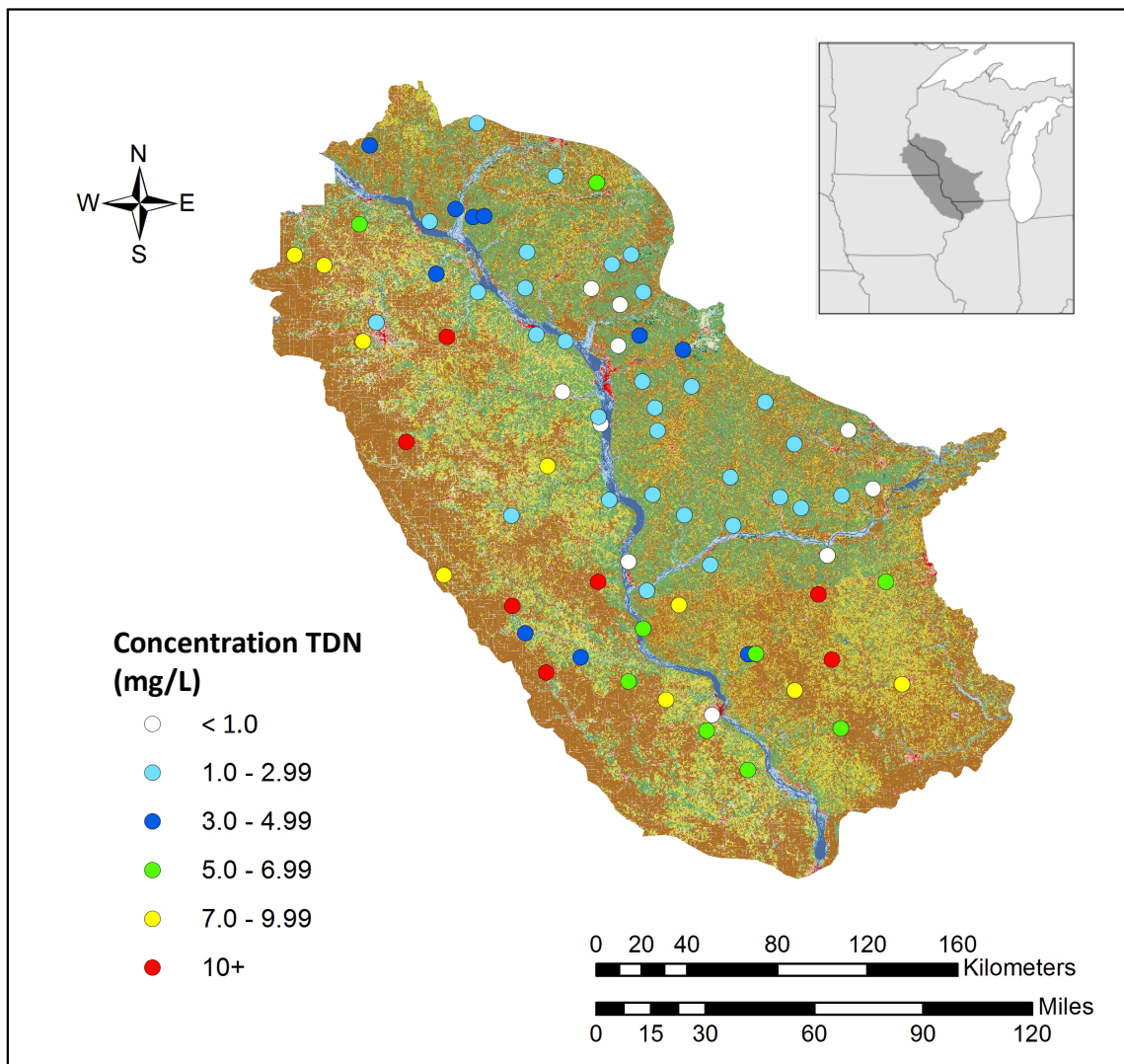


Figure 10. Mean total dissolved nitrogen (TDN) concentrations (mg/L) in relation to land use across all seasons for all samples collected from 2012-2013 in the Driftless Area of the Midwestern USA. Refer to Fig. 1 for land use categories.

(2014), when we assessed our data with the EPA approach, a more conservative estimate of N criteria was determined, 1.5 mg/L TDN, compared to the threshold analysis. Our analysis is based solely on chemical thresholds. It may also be important to look at biological thresholds as well as other stressors: suspended sediments, pesticides and climate change to establish nutrient criteria in streams (Chambers *et al.* 2012).

Our hypothesis that agricultural streams have higher N concentrations for all N fractions was supported, with the exception of  $\text{NH}_4^+$ . Ammonium concentrations may be driven more by in-stream processes such as, nitrification, assimilation, and sorption to sediments, rather than by land use characteristics in these streams. High  $\text{NO}_3^-$  in agricultural streams is likely a result of excess N from fertilizer application entering groundwater. Karst topography along with the mobile nature of  $\text{NO}_3^-$  leads to high concentrations in groundwater that eventually contribute to surface water baseflow. Atmospheric deposition, overland runoff, and in-stream processes (mineralization) are also sources of N to streams in the DA.

We hypothesized that streams in developed basins would have higher concentrations of all N fractions. Unexpectedly, we only observed higher concentrations of  $\text{NO}_2^-$  in developed streams in winter and spring and  $\text{NH}_4^+$  concentrations in winter. Although developed land use was correlated with N, it is difficult to determine the extent of the effects of urbanized land use due to the limitations of our study: small sample size ( $n = 9$ ) due to limited urbanized areas, limited sampling frequency, and the occurrence of agricultural land use in the developed stream catch-basins. Targeted, more frequent sampling in larger urbanized areas in the DA is needed to evaluate the effects of developed land on N concentrations in these streams.

## Seasonal Variation in Nitrogen

Unexpectedly, TDN and  $\text{NO}_3^-$  concentrations were not seasonally variable. Our hypothesis that N concentrations would be higher in spring and summer as a result of rain and snowmelt events was generally not supported by our data. Many of the streams in our study are fed by groundwater year round. Our results suggest that subsurface flow rather than overland flow is likely contributing a larger portion of the inorganic N to DA streams throughout the year during baseflow conditions. Furthermore, we only collected samples during near-baseflow conditions; collecting samples during rain and melt events may provide different results. Furthermore, our fall sampling period overlapped with a moderate to severe drought in the region (NOAA 2013); therefore our results may not reflect average seasonal N concentrations.

Higher DON concentrations were observed in fall and summer, suggesting that rain and melt events may be contributing DON to streams through overland and subsurface flow. This could be a result of run-off from farm fields following manure application that generally occurs during this time of year.

We observed lower  $\text{NO}_2^-$  concentrations in fall and winter. Since  $\text{NO}_2^-$  is an intermediate product of nitrification and denitrification, its presence may be a result of the rate of these processes in streams. Denitrification and nitrification rates are limited by temperature, among other factors (Strauss *et al.* 2006); as such, lower concentrations during fall and winter could be associated with lower rates of N transformation occurring during the colder seasons.

Ammonium concentrations were lower in spring and summer. Warmer water temperature and increased light availability stimulate production and assimilation in

spring and summer, lowering concentrations in stream water. Higher concentrations of  $\text{NH}_4^+$  in winter and fall are likely a result of colder water temperatures and limited light availability, resulting in decreased assimilation by primary producers. Furthermore, temperature, pH, and the availability of DOC and  $\text{NH}_4^+$  regulate nitrification rates (Strauss *et al.* 2004). As such, lower  $\text{NH}_4^+$  concentrations in spring and summer may be a result of higher nitrification rates, due to warmer water temperatures.

### **TDN Pool and N Saturation**

Our hypothesis that  $\text{NO}_3^-$  would be the dominant form of nitrogen in agricultural streams was supported by our data but we also found that  $\text{NO}_3^-$  generally made up the majority of the TDN pool across all streams, not only agricultural streams, particularly in winter when subsurface groundwater is the only contributor of water to these streams. Similar to Stanley and Maxted (2008), land use appears to be influencing the TDN pool in Midwestern streams. In winter and spring,  $\text{NO}_3^-$  generally made up at least 80% of the TDN pool. Fall and summer did show more variation; however, in general, the TDN pool of agricultural streams was dominated by  $\text{NO}_3^-$  year round.

Our results differ from Stanley and Maxted's study where a wider range of the percentage of DON in terms of the TDN pool was observed across WI streams (0-100%). Stanley and Maxted suggested that leaching of organic matter from wetlands was the driver of DON concentrations in streams where DON made up a larger percentage of the TDN pool (2008). Wetlands are likely not a major source of DON to DA streams, as they make up a small percentage of the land use in the ecoregion, ranging from 0-5%. Four streams in our study had wetland cover >1%. DON made up a larger portion of the TDN pool seasonally (13-49%) in these streams.

Under N saturation conditions, reduced efficiency of uptake and denitrification may occur, leading to an increase in export of N to downstream ecosystems (Bernot and Dodds 2005; Mulholland 2008). An increased export of N downstream could negatively affect downstream ecosystems and exacerbate hypoxia conditions in the Gulf of Mexico. Stanley and Maxted suggest that N saturation occurs when TDN concentrations are greater than 3 mg/L and dominated by  $\text{NO}_3^-$  (2008). Using this metric of saturation, in our study, on average nearly one-half (46%) of the streams, mostly agricultural and developed, would be considered to be N saturated. Using a statistical threshold analysis on the relationship between TDN concentration and percent  $\text{NO}_3^-$  of TDN, for the data presented here, we found that when TDN concentrations are above 1.03 mg/L, the TDN pool is dominated by  $\text{NO}_3^-$ . We argue that this threshold value can be considered an N saturation benchmark metric because  $\text{NO}_3^-$  dominance of the TDN pool is a consequence of high N loading and nitrification coupled with a decreased efficiency in  $\text{NO}_3^-$  uptake and denitrification. Using 1.03 mg N/L TDN as a metric of N-saturation, approximately 87% of the streams in this study would be considered N saturated (Fig. 7). This pattern may be different in areas where wetlands and/or pristine forest land cover are more dominant, where DON may make up a larger percentage of the TDN pool.

### **Effects of Land Use and Total Dissolved Phosphorus**

Unexpectedly, TDP concentrations were not correlated with land use in our study. Our results contrast with results from Robertson *et al.* (2006), where percent agriculture in the basin explained 44% of the variation in TP concentrations in WI streams. Spatially, the northeastern and southern regions of the DA generally had higher TDP concentrations compared to central areas (Fig. 11). Non-anthropogenic factors, such as soil

characteristics, bedrock geology, and slope, may be important drivers of TDP concentrations in DA streams. Robertson *et al.* found that the percentage of loam deposits in catch basins explained 44% of the variability in TP concentrations when eliminating anthropogenic factors (2006). Further research is needed to understand the anthropogenic and non-anthropogenic drivers of TDP concentrations in DA streams.

### **Seasonal Variation in Total Dissolved Phosphorus**

Our results did not support our hypothesis that TDP concentrations would be higher in spring and summer. Similar to  $\text{NH}_4^+$ , higher concentrations of TDP were observed in fall and winter. Again, this is likely due to lower rates of biological uptake as a result of lower temperatures and light availability during these months. Furthermore, we only sampled during baseflow events, making it difficult to assess the effects of overland flow on TDP concentrations. Sampling during variable flow conditions may further elucidate TDP dynamics in DA streams.

### **Effects of Land Use on Dissolved Organic Carbon**

We hypothesized that DOC concentrations would be higher in agricultural streams and developed streams. Spatially, we did not observe any clear patterns in DOC concentrations in DA streams (Fig. 11). We observed a seasonal pattern of DOC concentrations, with higher concentrations in agricultural streams in winter compared to forested streams. We also found higher DOC concentrations in developed streams in winter and summer compared to forested and mixed streams. We are uncertain as to what the source of DOC is in developed streams. A study conducted in Ontario, Canada found that factors other than land use, such as soil drainage conditions, slope, and wetland cover are strong predictors of stream DOC concentrations (Wilson and Xenopoulos, 2008).

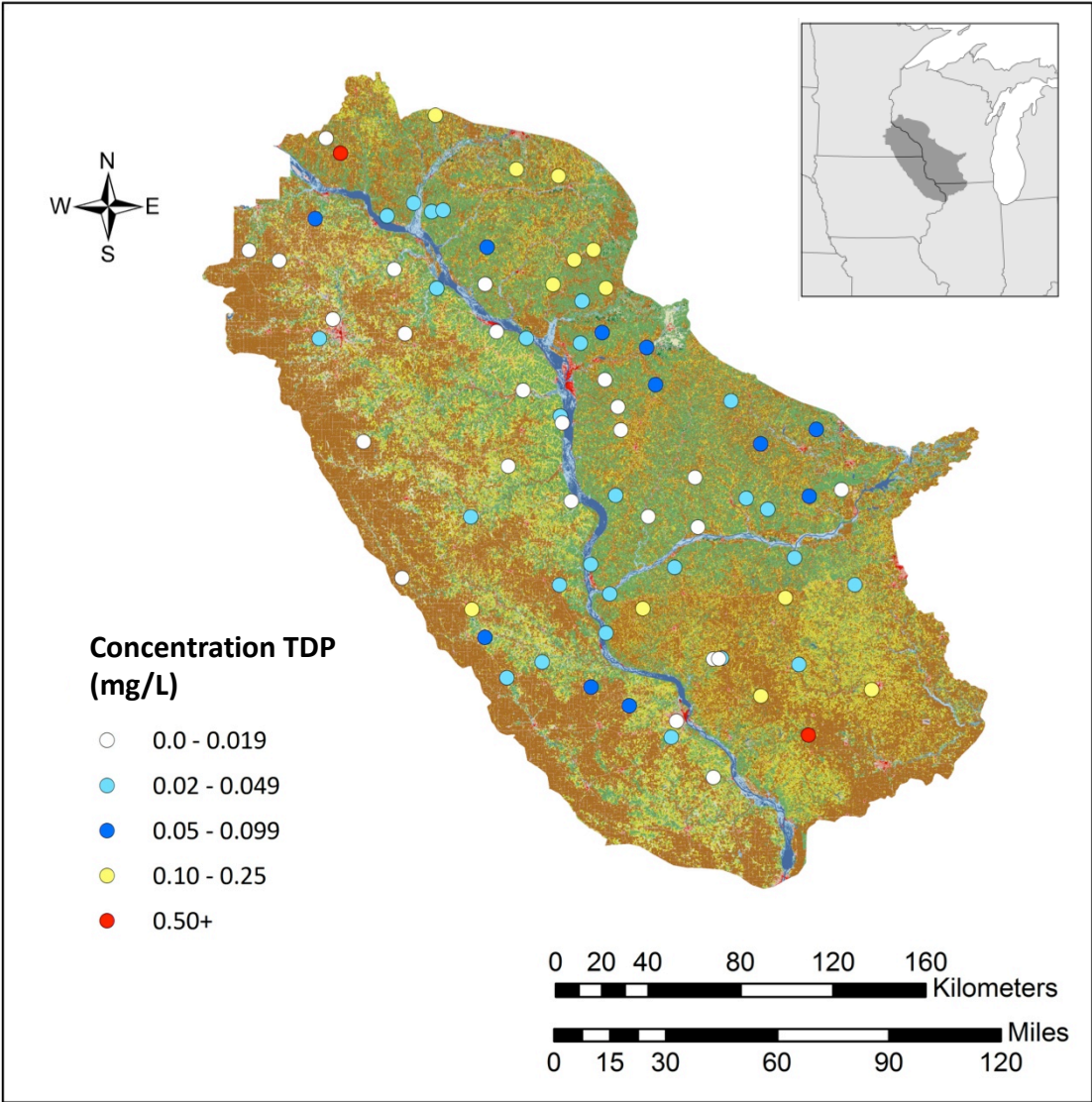


Figure 11. Mean total dissolved phosphorus (TDP) concentrations (mg/L) in relation to land use across all seasons for all samples collected from 2012-2013 in the Driftless Area of the Midwestern USA. Refer to Fig.1 for land use categories.

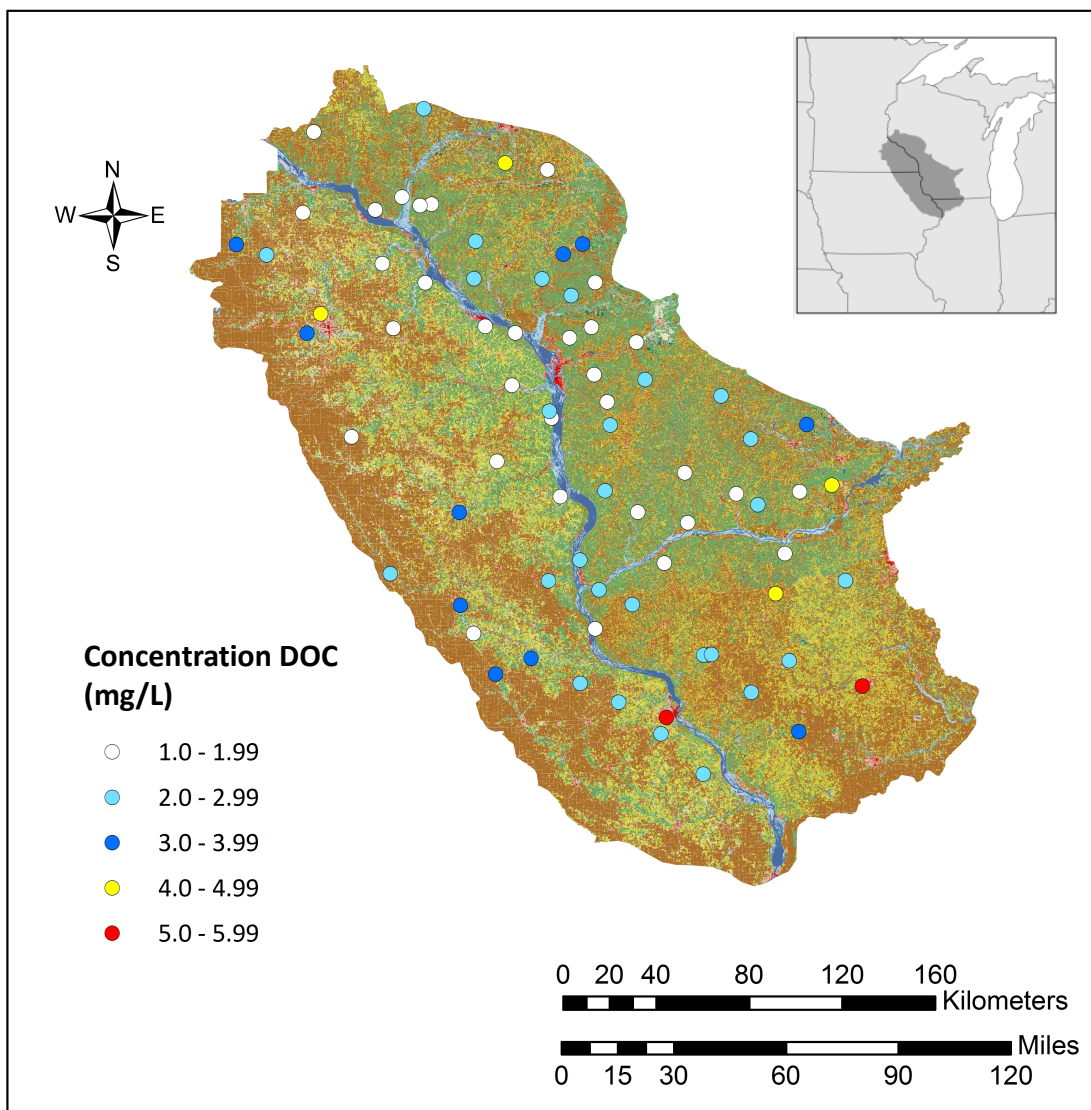


Figure 12. Mean dissolved organic carbon (DOC) concentrations (mg/L) in relation to land use across all seasons for all samples collected from 2012-2013 in the Driftless Area of the Midwestern USA. Refer to Fig.1 for land use categories.

### Seasonal Variation in Dissolved Organic Carbon

Our hypothesis that DOC concentrations would be higher in fall and spring was partially supported by our data. In spring, higher DOC concentrations were observed, most likely a result of spring soil thaw. Fall DOC concentrations were similar to spring and summer. Leaf litter does not appear to be a major driver of DOC in streams in the

ecoregion. However, sampling more frequently in fall or immediately after leaf fall events may provide different results. Due to resources, our fall sampling was spread out over a month, so it is difficult to make generalizations on the seasonal drivers of DOC.

### **Consequences of Increased Nutrient Loading to Stream Ecosystems**

Elevated  $\text{NO}_3^-$  concentrations can potentially have negative effects on biological communities in stream ecosystems. Approximately 55% of the streams in our study had average  $\text{NO}_3^-$ -N concentrations exceeding 2 mg/L, surpassing the suggested criteria for protecting sensitive freshwater animals (Camargo *et al.* 2005). Five streams in our study exceeded the US EPA criteria of 10 mg/L  $\text{NO}_3^-$ -N for drinking water.

Nitrite can be toxic to freshwater taxa, even at low levels. Levels of 0.1 mg N/L may slow growth and development of invertebrates (Neumann *et al.* 2001), and may also increase toxic effects of other pollutants (Shailaja *et al.* 2006). Five streams in our study had concentrations greater than 0.1 mg/L of  $\text{NO}_2^-$ -N at least once during the four sampling seasons; however, the mean  $\text{NO}_2^-$ -N concentration was below 0.1 mg/L for all streams.

Wisconsin has developed a state water quality criterion for P of 0.1 mg/L for most rivers and streams in the state. Minnesota has also adopted river eutrophication criteria, which include P criteria. The proposed standard for the Central Region of MN, which includes the Driftless Area is 0.1 mg/L (Heiskary *et al.* 2013). Iowa and Illinois currently do not have N or P criteria in place for rivers and streams. Throughout our study, nearly 32% of streams exceeded TDP concentrations of 0.1 mg/L at least once during the sampling period. Of those streams, the majority exceeded this standard more than once. The criteria that has been established in WI and MN is based on TP concentrations, so

our results are likely a conservative estimate of the number of streams exceeding 0.1 mg/L TP, as our data are based on TDP concentrations, rather than TP.

### **Conclusions**

Changes in land use from forested/prairie to more intensive agriculture are a major driver of stream N concentrations in the DA. Streams in the ecoregion are particularly vulnerable to anthropogenic changes due to the karst geological features and the large contribution of groundwater to these streams. Regional climate change predictions also make streams in the DA vulnerable. Predictions of more extreme flood and drought conditions are expected in the Midwest (Melillo *et al.* 2014). These changes could deliver more nutrients in flood seasons, and cause increased concentrations in drought years as a result of lower flows.

Water quality standards for TP have been established in WI and MN. Currently only Florida and New Jersey have developed N criteria for streams and rivers. States need to continue establishing nutrient criteria for streams and rivers, as directed by the Clean Water Act. Best management practices (BMPs), such as proper fertilizer application rates and timing, manure management, conservation tillage, cover crops, livestock exclusion, and buffers along stream banks need to be implemented to reduce the loading of N and P, particularly from agricultural landscapes to DA streams. Research has already been conducted on the effectiveness of agricultural BMPs, and resources have been developed, such as The Agricultural BMP Handbook for Minnesota (Miller *et al.* 2012). These resources should be utilized in the ecoregion to protect the water quality and quantity of stream ecosystems.

Five of the streams sampled in this study exceeded the EPA recommended drinking water criteria of 10 mg/L NO<sub>3</sub><sup>-</sup>-N. High NO<sub>3</sub><sup>-</sup> in surface waters could indicate potential groundwater and well contamination in these areas. The increased anthropogenic N loading to streams will decrease the biological integrity, alter biogeochemical processes (Carpenter *et al.* 1998; Woodward *et al.* 2012), and as a result, reduce the ecosystem services provided by stream ecosystems. Anthropogenic influences on stream ecosystems could potentially cause major changes in the functioning of stream ecosystems and increase the downstream transport of N to the Gulf of Mexico.

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APPENDIX A

FIGURES 13-19: SEASONAL NUTRIENT CONCENTRATIONS ACROSS LAND  
COVER TYPES AND SEASONAL COMPOSITION OF THE TDN POOL

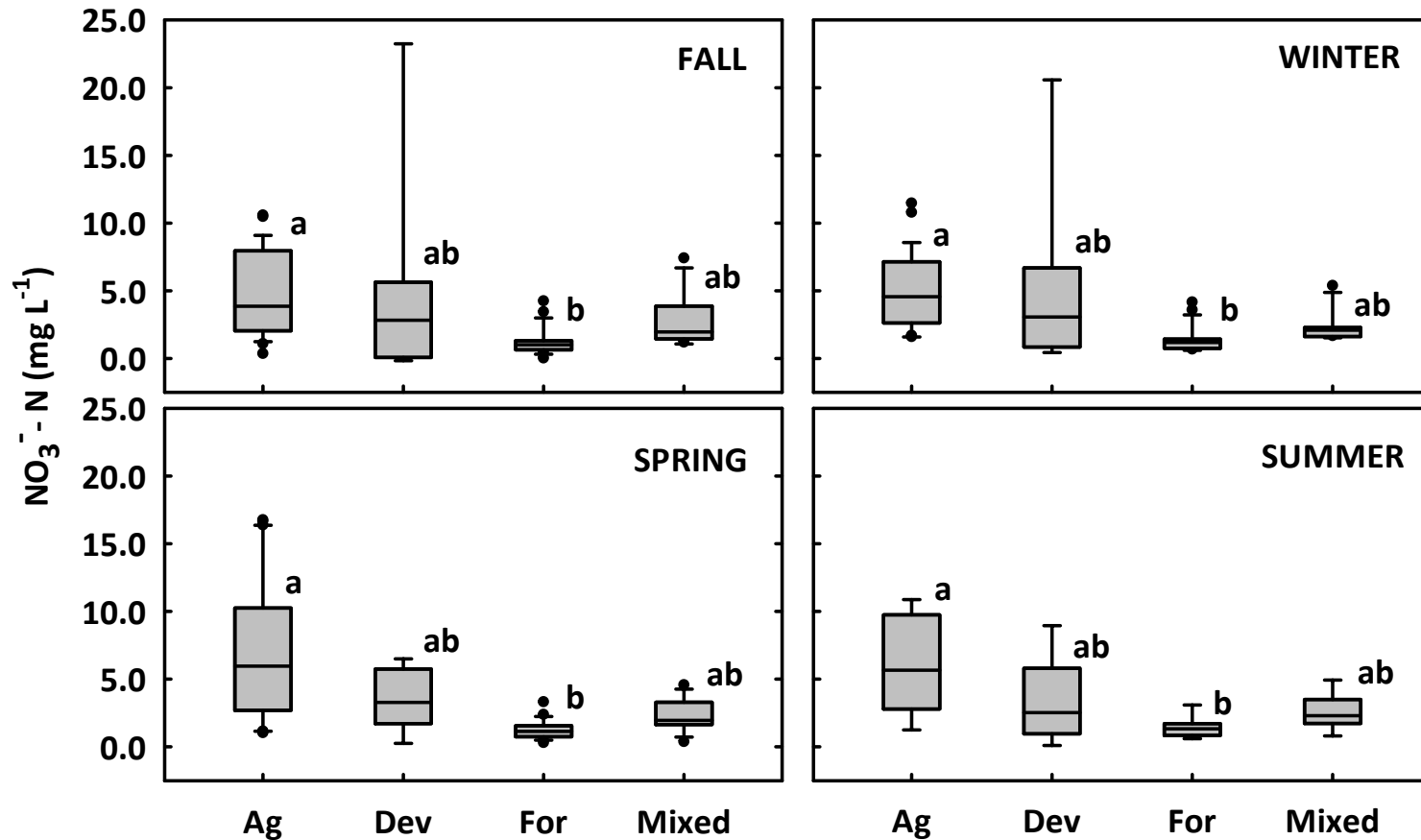


Figure 13. Seasonal concentrations of nitrate-nitrogen ( $\text{NO}_3^-$ -N) (mg/L) in streams in the Driftless Area. Significant differences among land use categories were identified with a Kruskal Wallis test: fall  $n=73$ , winter  $n=68$ , spring  $n=75$ , summer  $n=73$ ;  $p < 0.0001$  across all seasons. Lowercase letters adjacent to boxes indicate significant differences among categories identified with a multiple comparison test on ranks ( $p < 0.05$ ).

[Box plots display 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles, and data points outside the 10<sup>th</sup> and 90<sup>th</sup> percentiles. Agr, agricultural; Dev, developed; For, forested; Mix, mixed]

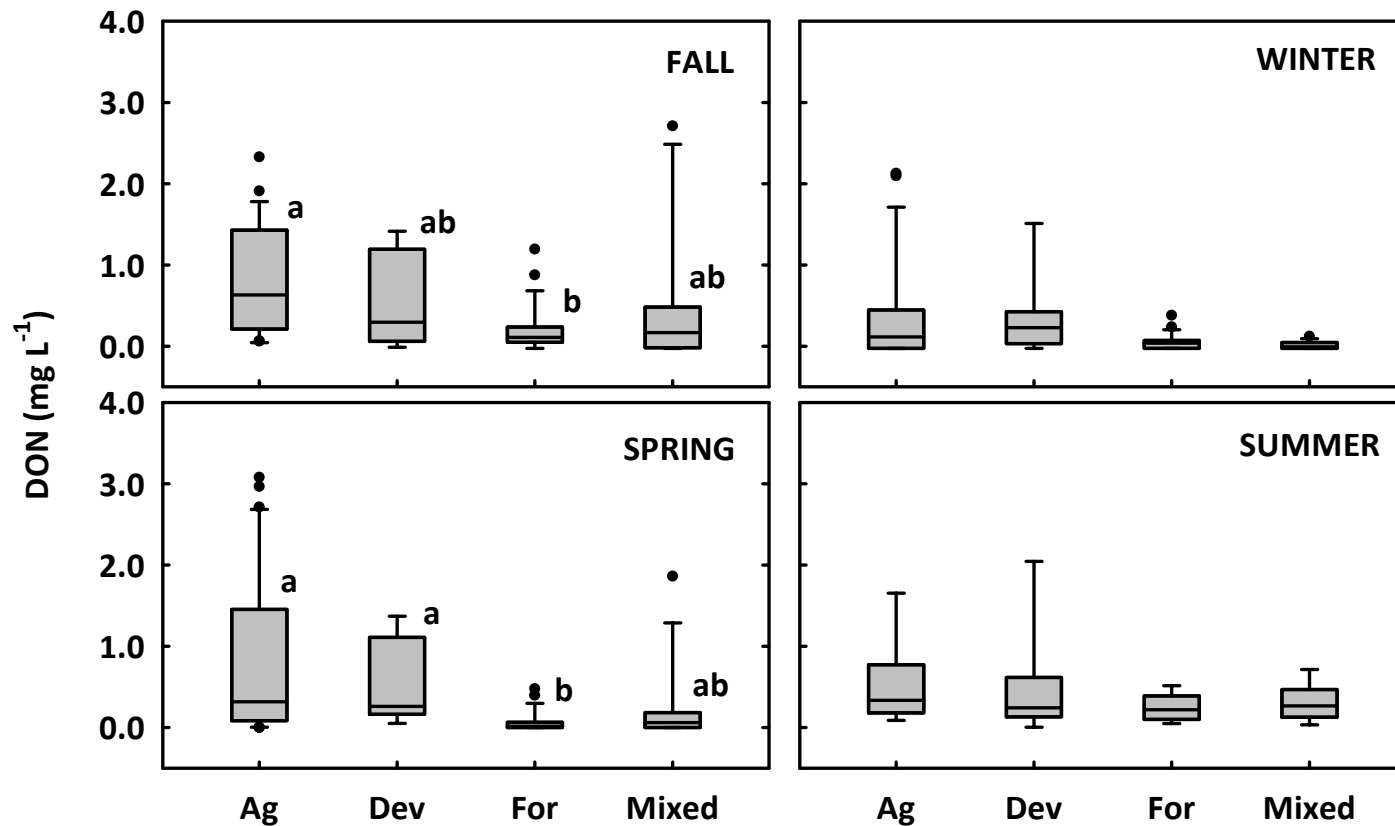


Figure 14. Seasonal concentrations of dissolved organic nitrogen (DON) (mg/L) in streams in the Driftless Area. Significant differences among land use categories were identified with a Kruskal-Wallis test: fall  $n=73$ , winter  $n=68$ , spring  $n=75$ , summer  $n=73$ ;  $p < 0.05$  in fall and spring. Lowercase letters adjacent to boxes indicate significant differences among categories identified with a multiple comparison test on ranks ( $p < 0.05$ ). [Box plots display 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles, and data points outside the 10<sup>th</sup> and 90<sup>th</sup> percentiles. Agr, agricultural; Dev, developed; For, forested; Mix, mixed]

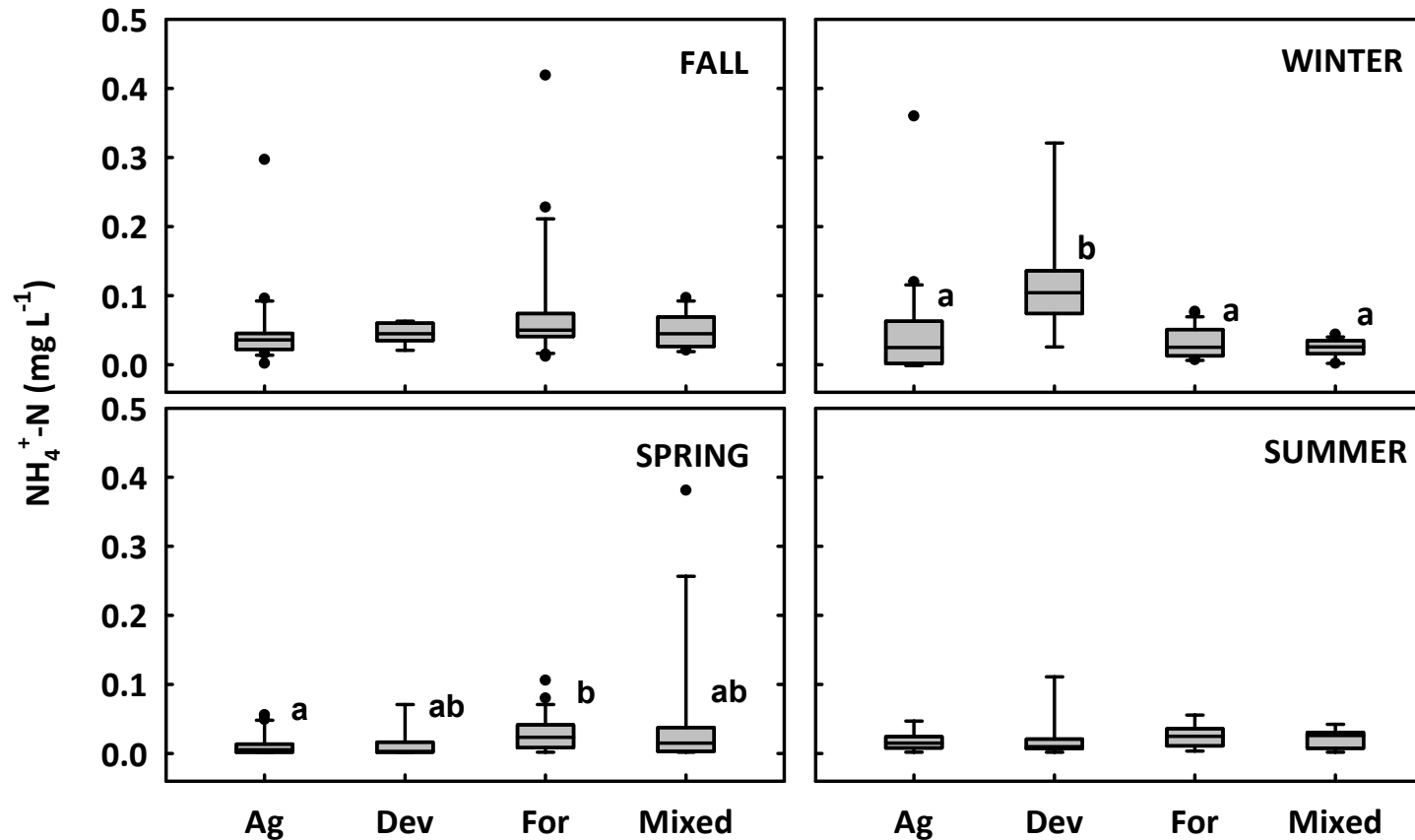


Figure 15. Seasonal concentrations of ammonium-nitrogen ( $\text{NH}_4^+\text{-N}$ ) (mg/L) in streams in the Driftless Area. Significant differences among land use categories were identified with a Kruskal-Wallis test: fall  $n=73$ , winter  $n=68$ , spring  $n=75$ , summer  $n=73$ ;  $p < 0.05$  in winter and spring. Lowercase letters adjacent to boxes indicate significant differences among categories identified with a multiple comparison test on ranks ( $p < 0.05$ ).

[Box plots display 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles, and data points outside the 10<sup>th</sup> and 90<sup>th</sup> percentiles. Agr, agricultural; Dev, developed; For, forested; Mix, mixed.

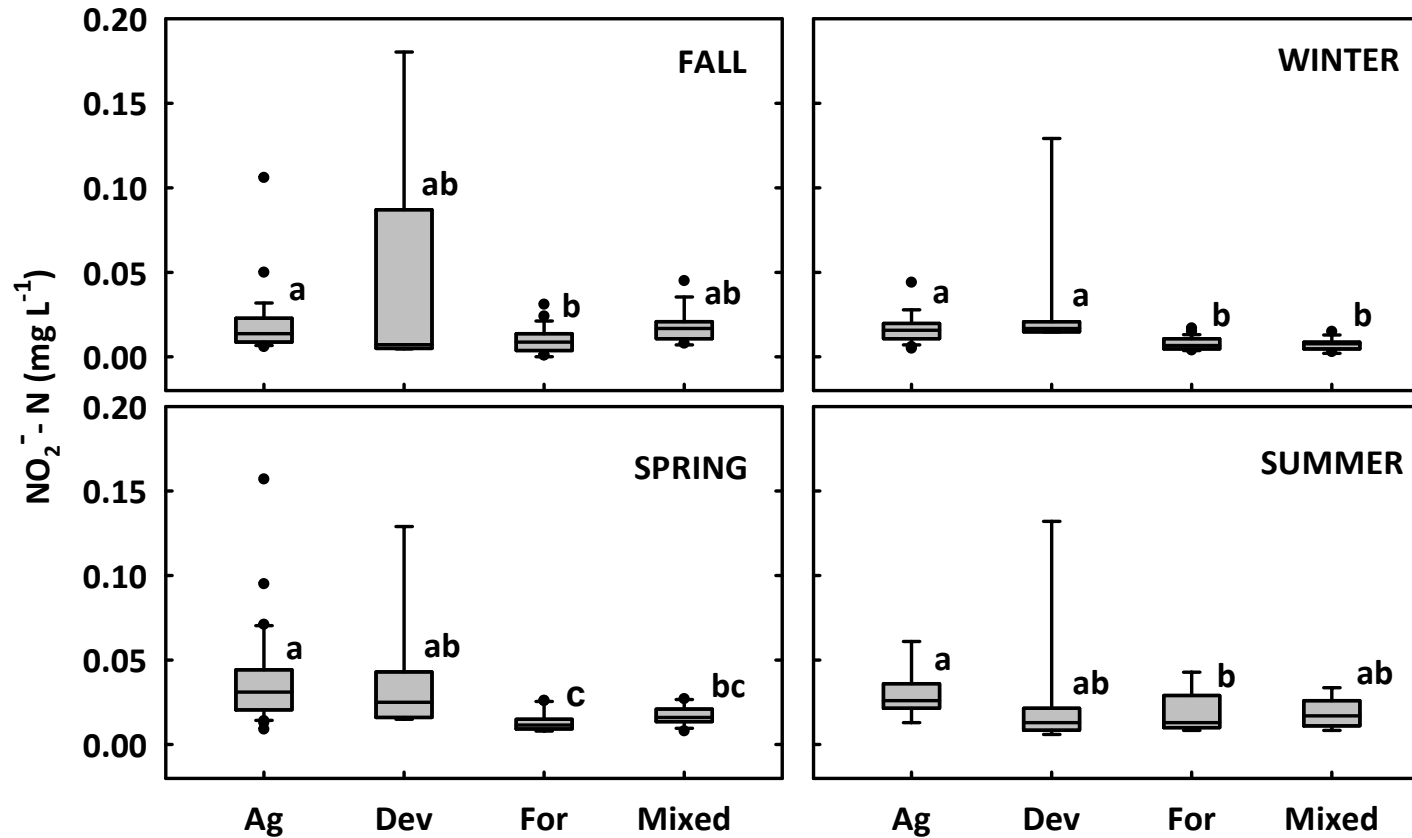


Figure 16. Seasonal concentrations of nitrite-nitrogen ( $\text{NO}_2^-$ -N) (mg/L) in streams in the Driftless Area. Significant differences among land use categories were identified with a Kruskal-Wallis test: fall  $n=73$ , winter  $n=68$ , spring  $n=75$ , summer  $n=73$ ;  $p < 0.05$  across all seasons. Lowercase letters adjacent to boxes indicate significant differences among categories identified with a multiple comparison test on ranks ( $p < 0.05$ ).

[Box plots display 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles, and data points outside the 10<sup>th</sup> and 90<sup>th</sup> percentiles. Agr, agricultural; Dev, developed; For, forested; Mix, mixed]

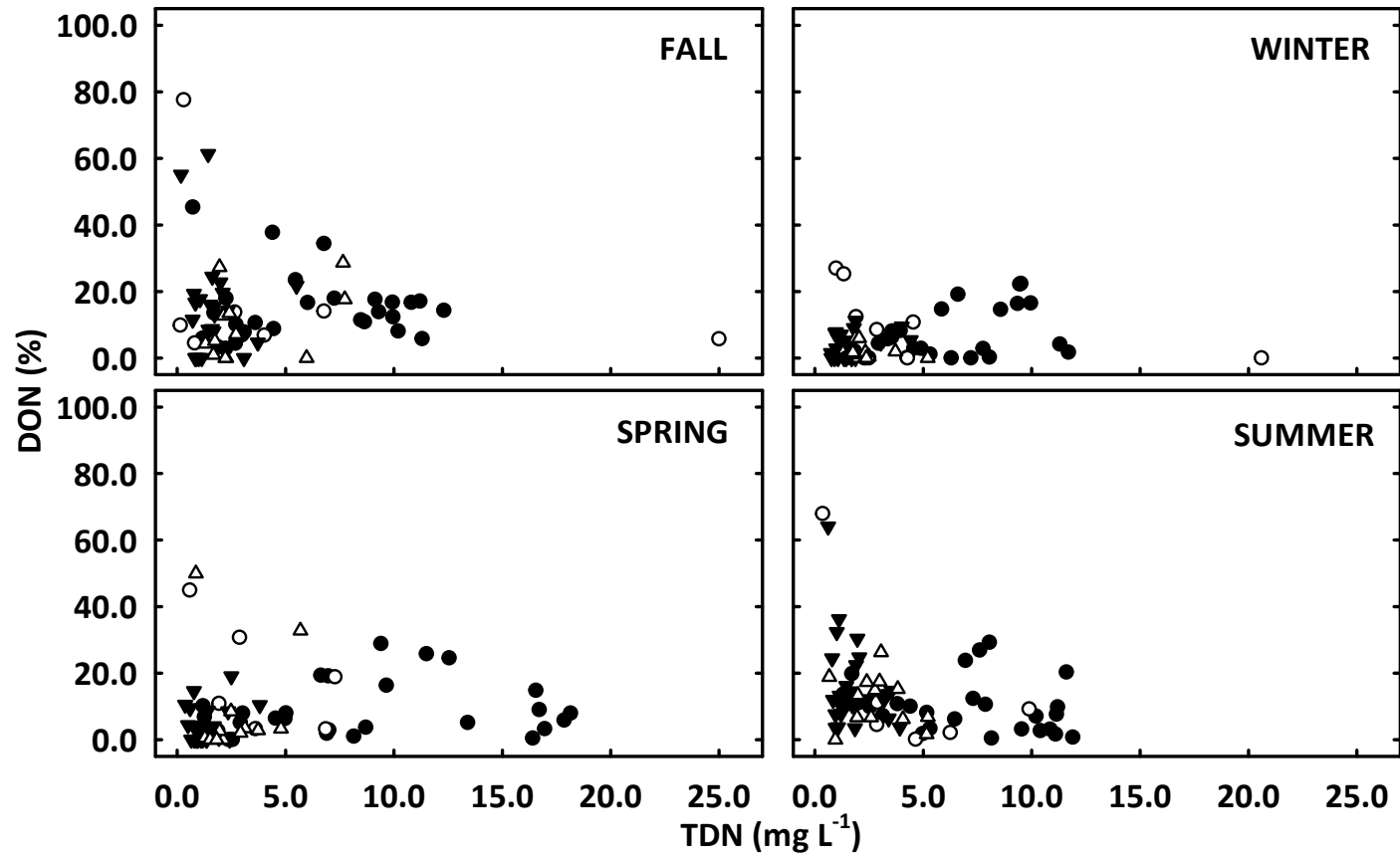


Figure 17. Percent dissolved organic nitrogen (DON) in relation to total dissolved nitrogen (TDN mg/L) across all seasons. [●, agricultural; ○, developed; ▼, forested; △, mixed streams.]

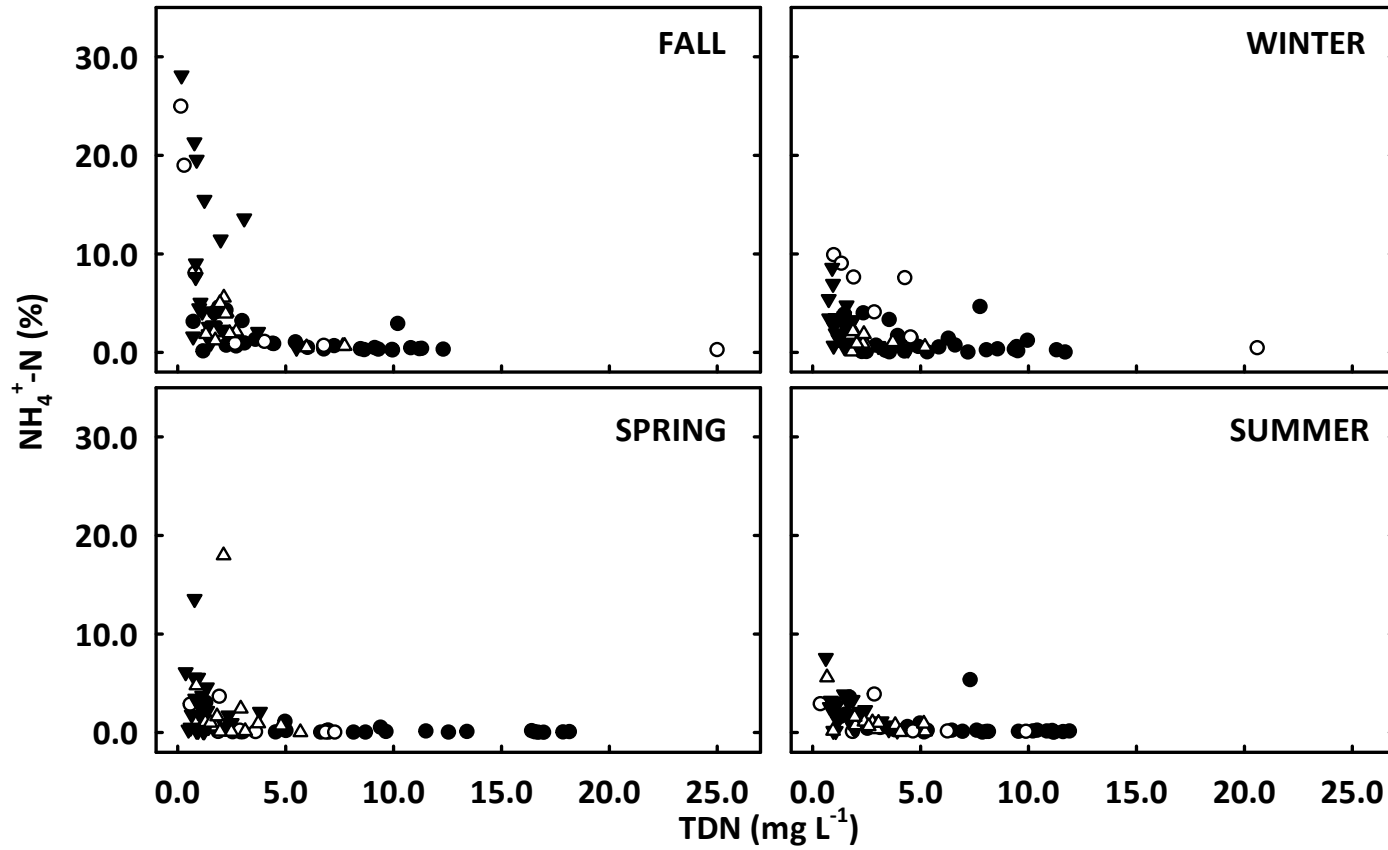


Figure 18. Percent ammonium-nitrogen ( $\text{NH}_4^+-\text{N}$ ) in relation to total dissolved nitrogen (TDN  $\text{mg/L}$ ) across all seasons. [ ● , agricultural; ○ , developed; ▼ , forested; △ , mixed streams. ]

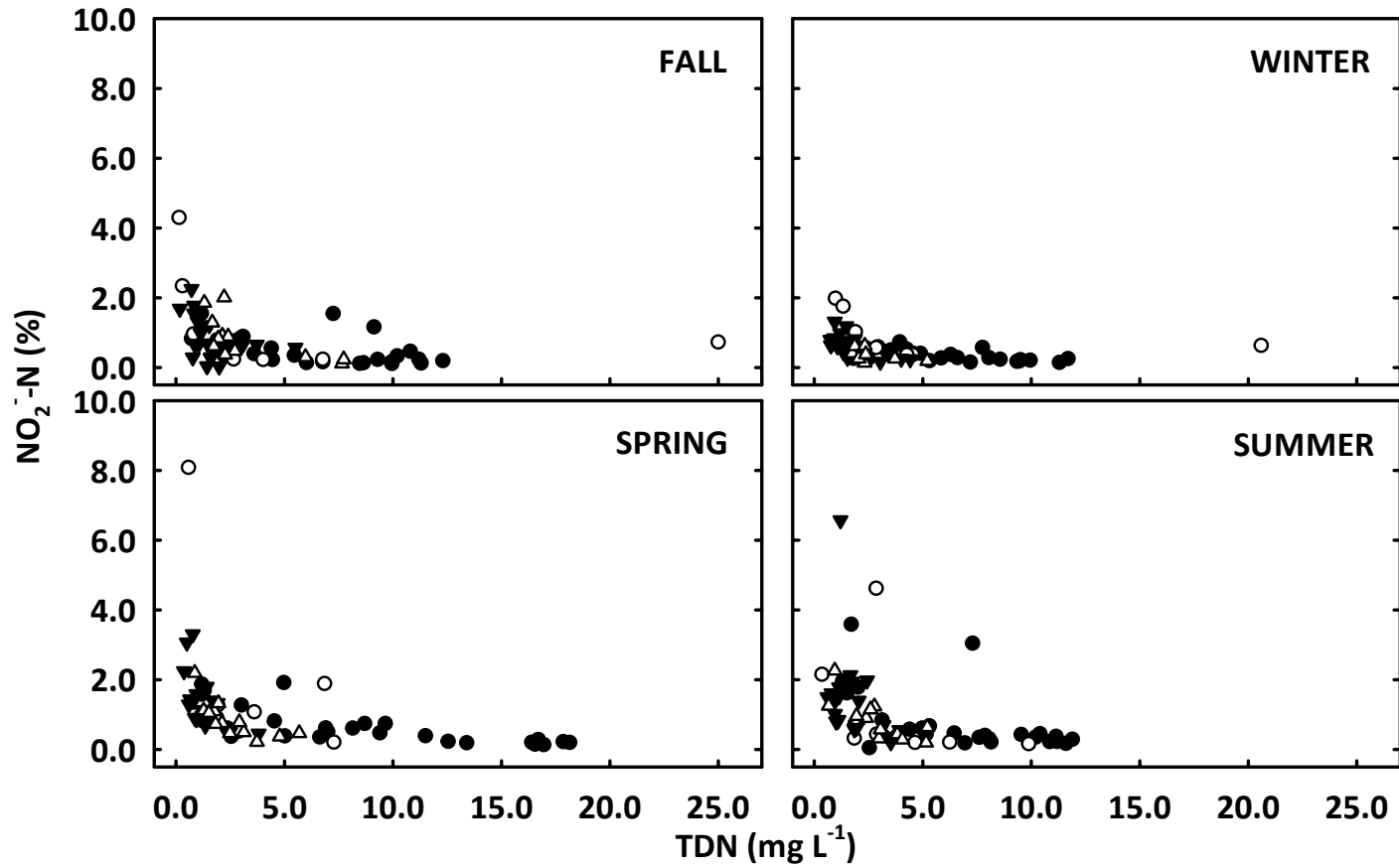


Figure 19. Percent ammonium-nitrogen ( $\text{NH}_4^+\text{-N}$ ) in relation to total dissolved nitrogen (TDN  $\text{mg/L}$ ) across all seasons. [●, agricultural; ○, developed; ▼, forested; △, mixed streams.]

APPENDIX B

TABLES 8-11: WATER QUALITY PARAMETERS MEASURED IN STREAMS  
IN THE DRIFTLESS AREA, 2012-2013

Table 8. Sampling dates, times and physical and chemical water-quality parameters in agricultural streams ( $n=30$ ) in the Driftless Area of the Midwestern U.S. in fall 2012 and winter, spring and summer 2013. [ $^{\circ}\text{C}$ , degrees Celsius; mg/L, milligrams per liter;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter; ppt, parts per trillion; mV, millivolts; NTU, nephelometric turbidity units]

ID	Date	Time	Temp ( $^{\circ}\text{C}$ )	Dissolved $\text{O}_2$ (mg/L)	Dissolved $\text{O}_2$ (% saturation)	Specific conductance ( $\mu\text{S}/\text{cm}$ )	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
1	16-Oct	9:06	8.43	10.15	89.2	608.8	0.31	7.76	434	0.49	4.33
	12-Jan	10:15	5.65	12.04	98.5	586.3	0.30	8.16	695	0.50	0.00
	14-May	9:48	9.45	12.37	110.6	589.2	0.30	7.82	479	0.52	0.00
	23-Jul	8:30	10.37	10.33	93.7	579.0	0.30	7.39	527	1.13	0.33
2	16-Oct	16:24	11.52	10.04	95.4	699.5	0.36	7.78	373	1.28	2.33
	8-Feb	12:30	6.31	13.49	111.0	655.0	0.34	7.88	427	1.70	0.60
	30-Apr	14:50	18.18	13.18	144.0	572.6	0.28	8.12	451	4.04	4.33
	17-Jul	9:44	16.94	9.00	93.2	590.0	0.30	7.90	411	9.37	6.11
3	29-Sep	16:00	11.78	9.91	93.4	563.4	0.29	7.84	389	2.24	0.67
	5-Jan	12:35	4.63	11.80	93.5	573.4	0.29	8.03	441	4.70	12.00
	27-Apr	11:50	10.99	10.91	101.4	557.5	0.28	7.79	582	10.20	7.89
	2-Aug	11:45	11.79	10.23	94.6	537.0	0.27	7.66	412	5.90	12.00
4	6-Oct	16:00	7.84	14.35	124.0	432.5	0.22	8.20	339	6.17	9.67
	19-Jan	11:31	0.22	12.22	87.6	613.9	0.31	7.80	422	0.60	1.00
	8-May	14:30	11.89	9.22	87.3	543.3	0.28	7.31	428	6.52	16.67
	30-Jul	10:45	15.99	9.35	94.9	582.0	0.30	7.71	448	5.27	28.33

Table 8. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
1	16-Oct	7.67	0.012	0.022	7.70	0.938	8.64	0.0533	1.21
	12-Jan	7.45	0.011	<0.003	7.46	0.000	7.20	0.0230	1.48
	14-May	6.60	0.044	0.049	6.69	2.711	9.40	<0.0006	1.62
	23-Jul	7.01	0.031	<0.003	7.04	0.830	7.87	<0.0006	1.24
2	16-Oct	10.48	0.024	0.039	10.54	1.761	12.30	0.0670	1.50
	8-Feb	11.47	0.029	<0.003	11.50	0.200	11.70	0.0653	1.95
	30-Apr	8.00	0.071	0.008	8.08	1.572	9.65	0.0114	3.06
	17-Jul	11.77	0.034	0.015	11.81	0.085	11.90	0.0394	2.04
3	29-Sep	2.40	0.019	0.017	2.44	0.273	2.71	0.0422	1.17
	5-Jan	2.55	0.006	<0.003	2.56	0.000	2.49	0.1110	1.86
	27-Apr	2.55	0.009	<0.003	2.56	0.000	2.55	0.0161	—
	2-Aug	2.28	0.001	0.010	2.29	0.250	2.54	0.0091	1.26
4	6-Oct	4.01	0.010	0.039	4.06	0.391	4.45	0.0248	2.76
	19-Jan	4.23	0.022	0.005	4.25	0.005	4.26	0.0331	2.79
	8-May	14.08	0.024	0.008	14.11	2.442	16.55	0.0173	—
	30-Jul	10.48	0.024	0.015	10.51	0.335	10.85	0.0149	4.42

Table 8. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (μS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
5	16-Oct	11:47	11.92	10.50	100.3	455.9	0.23	7.92	328	1.09	7.33
	12-Jan	12:30	0.13	13.01	91.9	399.2	0.21	8.02	600	2.10	1.70
	14-May	11:15	13.14	10.10	98.1	473.7	0.24	7.66	463	7.51	11.00
	23-Jul	11:00	20.59	8.94	101.1	449.8	0.23	7.90	429	5.58	10.33
6	6-Oct	14:57	8.92	12.59	112.1	581.6	0.30	8.10	330	2.84	4.67
	19-Jan	12:26	7.60	12.33	107.4	559.5	0.29	7.84	410	2.10	8.00
	8-May	13:15	15.02	16.05	162.5	525.9	0.27	8.26	417	1.12	2.00
	30-Jul	15:40	13.41	10.97	105.2	443.0	0.28	7.59	435	3.47	3.00
7	6-Oct	13:00	7.09	10.90	92.1	517.5	0.26	7.76	321	1.02	0.33
	12-Jan	14:00	2.57	14.05	106.1	487.2	0.25	8.33	568	0.40	1.30
	8-May	12:45	12.69	10.39	99.9	428.8	0.22	7.61	428	3.25	5.67
	30-Jul	9:45	12.23	9.29	86.8	470.0	0.24	7.46	459	3.49	10.67
8	16-Oct	13:32	10.48	10.93	101.1	610.6	0.31	8.05	385	3.98	8.33
	3-Feb	12:30	0.27	12.56	88.8	550.1	0.28	8.03	560	1.10	1.00
	14-May	13:15	16.02	18.44	190.7	468.0	0.24	8.80	423	5.00	9.33
	23-Jul	12:15	15.71	10.40	106.3	556.0	0.28	7.92	371	2.87	3.00
9	20-Oct	15:00	13.74	13.78	134.8	713.1	0.37	8.43	350	3.11	5.00
	2-Feb	15:50	2.16	12.69	94.4	632.4	0.32	8.08	375	1.60	1.67
	15-May	14:10	20.19	13.31	150.3	611.3	0.31	8.43	430	2.45	5.67
	24-Jul	12:57	17.96	12.46	133.6	647.0	0.33	7.94	474	10.10	16.00

Table 8. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
5	16-Oct	2.66	0.025	0.095	2.78	0.205	2.98	0.0221	2.75
	12-Jan	3.52	0.029	0.067	3.62	0.323	3.94	<0.0006	2.58
	14-May	16.27	0.033	0.028	16.33	0.072	16.40	0.0231	3.48
	23-Jul	5.67	0.025	0.007	5.70	2.353	8.05	<0.0006	2.84
6	6-Oct	10.59	0.014	0.045	10.64	0.655	11.30	0.0363	1.58
	19-Jan	10.78	0.016	0.028	10.83	0.472	11.30	0.0100	1.47
	8-May	9.44	0.029	0.003	9.47	3.077	12.55	0.0058	—
	30-Jul	10.07	0.025	0.003	10.10	1.097	11.20	0.0020	1.49
7	6-Oct	8.69	0.011	0.023	8.72	1.227	9.95	0.0360	1.13
	12-Jan	7.99	0.022	0.019	8.03	0.021	8.05	0.0101	1.64
	8-May	12.67	0.025	0.012	12.71	0.688	13.40	0.0018	3.20
	30-Jul	9.22	0.020	0.009	9.25	2.351	11.60	<0.0006	1.41
8	16-Oct	2.52	0.020	0.032	2.57	0.118	2.69	0.0803	2.03
	3-Feb	2.77	0.017	0.021	2.81	0.129	2.94	0.1190	2.10
	14-May	5.33	0.023	<0.003	5.35	1.280	6.63	0.0141	—
	23-Jul	3.90	0.025	0.026	3.96	0.439	4.40	0.0046	1.70
9	20-Oct	7.96	0.021	0.028	8.01	1.292	9.30	0.0501	3.55
	2-Feb	7.27	0.020	0.029	7.32	1.251	8.57	0.0552	2.75
	15-May	8.48	0.045	0.016	8.54	2.964	11.50	0.0060	3.13
	24-Jul	10.26	0.041	<0.003	10.30	0.850	11.15	0.0289	2.49

Table 8. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (μS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
10	7-Oct	8:40	6.97	10.35	87.1	520.8	0.26	7.56	379	1.03	1.00
	18-Jan	17:05	5.31	12.70	101.9	495.6	0.25	8.01	388	0.60	1.67
	8-May	17:30	13.32	12.49	121.9	487.5	0.25	8.15	414	2.96	4.00
	30-Jul	13:45	12.45	11.94	112.1	486.0	0.25	7.85	437	1.88	2.33
11	16-Oct	15:30	12.01	10.66	102.2	567.9	0.29	8.26	367	3.03	6.67
	—	—	—	—	—	—	—	—	—	—	—
	14-May	15:00	19.64	10.59	119.1	484.8	0.24	8.27	448	6.38	6.00
—	—	—	—	—	—	—	—	—	—	—	
12	29-Sep	17:00	20.60	3.82	43.2	2,780.0	1.50	8.10	404	1.76	4.00
	18-Jan	16:00	9.56	8.18	73.5	2,881.8	1.55	8.09	383	10.10	25.00
	9-May	8:30	12.81	7.54	73.0	1,581.2	0.84	7.97	403	2.59	4.00
	2-Aug	12:40	23.85	11.50	137.3	2,606.0	1.40	8.34	407	1.24	11.33
13	28-Oct	9:05	4.21	9.95	77.9	437.9	0.22	7.92	327	3.23	3.33
	9-Feb	12:30	0.40	13.72	97.1	413.9	0.21	8.10	362	4.51	6.67
	5-May	16:30	18.76	12.14	132.1	328.4	0.16	8.26	420	7.40	15.33
	19-Jul	16:00	28.70	10.59	138.1	411.0	0.21	8.25	400	6.73	5.33
14	6-Oct	18:10	7.65	12.78	110.6	644.4	0.39	8.12	351	3.63	5.67
	19-Jan	9:33	0.12	11.98	85.7	717.2	0.34	7.85	421	2.10	2.67
	8-May	18:00	12.03	9.11	86.3	555.9	0.28	7.95	426	6.32	9.89
	30-Jul	13:00	18.95	9.97	107.6	604.0	0.31	7.97	435	4.63	3.67

Table 8. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
10	7-Oct	4.98	0.008	0.029	5.02	1.001	6.02	0.0522	1.09
	18-Jan	5.24	0.010	<0.003	5.25	0.060	5.31	0.0570	1.17
	8-May	4.59	0.019	0.009	4.62	0.401	5.02	0.0866	2.29
	30-Jul	4.72	0.023	<0.003	4.74	0.420	5.16	0.0052	1.55
11	16-Oct	2.34	0.016	0.029	2.39	0.441	2.83	0.0272	2.80
	—	—	—	—	—	—	—	—	—
	14-May	4.39	0.017	<0.003	4.41	1.810	6.22	0.0142	4.05
—	—	—	—	—	—	—	—	—	
12	29-Sep	18.19	1.310	0.648	20.15	3.452	23.60	1.1400	8.36
	18-Jan	13.91	1.390	2.870	18.17	4.930	23.10	0.4620	14.01
	9-May	3.36	0.157	4.490	8.01	0.340	8.35	0.3600	—
	2-Aug	12.81	0.193	0.037	13.04	0.264	13.30	0.9170	7.49
13	28-Oct	1.74	0.015	0.088	1.85	0.063	1.91	0.0417	2.90
	9-Feb	2.34	0.013	0.094	2.44	0.000	2.35	0.1052	1.34
	5-May	1.03	0.022	0.019	1.07	0.121	1.19	0.0220	—
	19-Jul	1.25	0.061	0.061	1.37	0.339	1.71	0.1050	2.73
14	6-Oct	0.36	0.006	0.022	0.39	0.326	0.72	0.0260	3.73
	19-Jan	4.71	0.020	0.029	4.76	0.141	4.90	<0.0006	3.33
	8-May	16.38	0.023	<0.003	16.40	0.550	16.95	0.0042	—
	30-Jul	9.19	0.040	0.009	9.24	0.301	9.54	0.0116	2.93

Table 8. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (µS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
15	21-Oct	12:30	9.40	12.88	114.1	792.1	0.41	8.40	305	1.86	1.33
	—	—	—	—	—	—	—	—	—	—	—
	30-Apr	12:45	19.05	15.60	154.8	547.5	0.28	8.51	429	3.74	5.67
	17-Jul	12:10	13.32	10.72	102.5	530.0	0.27	7.46	401	13.50	17.33
16	21-Oct	9:55	8.32	10.13	87.3	675.3	0.35	7.94	353	0.63	0.00
	3-Feb	10:00	0.25	12.72	89.7	605.6	0.31	8.05	646	3.50	3.00
	14-May	15:45	18.29	15.55	168.7	545.8	0.28	8.53	440	5.02	7.00
	23-Jul	14:45	10.42	11.22	126.2	600.2	0.31	7.95	417	12.80	17.00
17	16-Oct	14:30	12.48	10.24	99.1	541.7	0.28	7.71	378	0.59	4.67
	3-Feb	11:45	2.78	10.90	82.0	492.4	0.25	7.74	598	2.60	9.00
	14-May	14:15	15.95	15.71	162.3	473.0	0.24	7.42	477	1.31	0.33
	23-Jul	13:10	17.10	9.74	102.5	507.0	0.26	7.46	431	1.79	0.33
18	21-Oct	9:00	8.00	9.87	84.4	669.4	0.34	7.89	352	1.25	0.00
	3-Feb	9:10	0.97	12.21	87.7	591.5	0.30	8.06	723	5.40	10.67
	14-May	16:15	20.13	15.37	178.7	503.5	0.25	8.74	413	4.85	6.67
	23-Jul	15:50	20.01	11.53	129.0	586.0	0.30	8.08	408	2.95	5.67
19	28-Oct	16:47	8.98	9.24	81.6	477.5	0.24	8.08	344	2.10	8.33
	8-Feb	15:30	6.48	12.31	101.8	446.4	0.22	8.08	413	3.20	9.67
	5-May	9:30	10.54	10.68	97.3	425.1	0.21	7.50	474	2.80	6.33
	19-Jul	8:50	16.89	9.12	94.9	452.0	0.23	7.75	312	10.80	19.00

Table 8. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
15	21-Oct	9.22	0.026	0.041	9.29	1.910	11.20	0.1070	2.85
	—	—	—	—	—	—	—	—	—
	30-Apr	4.50	0.095	0.056	4.66	0.315	4.97	0.0511	—
	17-Jul	5.79	0.222	0.390	6.40	0.900	7.30	0.2490	3.00
16	21-Oct	7.46	0.010	0.030	7.50	0.970	8.47	0.0628	1.77
	3-Feb	4.94	0.016	0.031	4.99	0.859	5.85	0.1690	1.96
	14-May	6.76	0.035	<0.003	6.80	0.200	7.00	0.0010	—
	23-Jul	6.01	0.030	0.013	6.05	0.397	6.45	0.0598	3.22
17	16-Oct	9.05	0.033	0.297	9.38	0.823	10.20	0.0658	7.08
	3-Feb	8.17	0.021	0.120	8.31	1.640	9.95	0.0909	2.89
	14-May	16.76	0.039	0.006	16.81	1.044	17.85	0.0053	2.99
	23-Jul	10.87	0.030	0.021	10.92	0.179	11.10	0.0034	2.02
18	21-Oct	8.22	0.015	0.028	8.27	1.662	9.93	0.0655	1.73
	3-Feb	7.28	0.017	0.054	7.35	2.096	9.45	0.1230	2.64
	14-May	6.72	0.042	0.011	6.77	0.129	6.90	0.1010	3.38
	23-Jul	8.09	0.017	0.007	8.12	0.033	8.15	0.0347	—
19	28-Oct	1.44	0.009	0.044	1.49	0.226	1.72	0.0158	1.62
	8-Feb	1.70	0.011	0.024	1.73	0.000	1.69	0.0029	1.21
	5-May	1.12	0.013	<0.003	1.13	0.050	1.18	0.0047	—
	19-Jul	0.98	0.017	0.017	1.02	0.123	1.14	0.0064	2.21

Table 8. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (µS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)		
71	20	20-Oct	17:55	10.65	13.36	122.1	1,027.8	0.54	8.31	347	4.06	2.33	
		2-Feb	18:00	0.01	13.62	95.4	933.7	0.49	8.30	391	3.30	1.00	
		15-May	12:10	17.03	13.79	135.9	672.8	0.35	8.13	408	2.86	4.00	
		24-Jul	10:40	17.74	8.31	88.7	867.0	0.45	7.74	491	8.78	5.33	
		21	28-Oct	11:00	5.85	9.93	81.1	353.0	0.17	7.83	356	1.61	4.00
		9-Feb	11:50	2.77	12.97	97.8	329.5	0.16	8.05	439	4.30	7.00	
		5-May	14:15	17.29	11.66	123.2	317.5	0.15	8.17	425	2.06	5.00	
		19-Jul	13:30	21.08	10.80	122.3	338.0	0.17	8.11	408	2.99	2.67	
		22	16-Oct	12:42	12.19	10.01	96.4	755.4	0.39	8.03	394	3.06	6.00
		18-Jan	12:10	3.40	12.50	95.3	301.7	0.15	7.68	353	1.30	3.33	
		3-Feb	13:00	0.04	12.20	85.6	760.0	0.39	8.16	572	1.40	1.00	
		23-Jul	11:45	19.64	9.57	106.1	668.0	0.34	7.98	428	3.23	1.67	
	23	20-Oct	13:25	9.00	10.63	93.0	936.7	0.49	7.81	321	1.58	1.67	
	2-Feb	14:00	1.20	12.32	89.7	843.9	0.40	7.86	323	2.90	1.00		
	15-May	15:30	20.15	12.62	142.3	825.6	0.43	8.19	434	3.41	2.00		
	24-Jul	14:35	17.82	9.90	105.9	820.0	0.43	7.76	460	5.00	7.33		
	24	28-Oct	7:58	4.52	9.68	76.3	444.3	0.22	8.07	363	5.08	9.00	
	9-Feb	13:30	0.55	14.77	104.8	410.3	0.20	8.26	417	1.09	0.00		
	5-May	17:15	17.00	12.34	130.7	375.4	0.19	8.49	406	1.66	3.00		
	19-Jul	17:00	24.70	9.98	121.1	421.0	0.21	8.32	401	3.36	2.00		

Table 8. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
20	20-Oct	2.68	0.024	0.040	2.74	1.660	4.40	0.8080	4.57
	2-Feb	6.21	0.023	0.090	6.32	0.000	6.29	0.8310	4.57
	15-May	8.02	0.049	<0.003	8.07	0.080	8.15	0.2640	2.99
	24-Jul	4.81	0.030	0.047	4.89	0.088	4.98	0.3160	2.83
21	28-Oct	1.40	0.010	0.069	1.48	0.231	1.71	0.2600	1.67
	9-Feb	1.61	0.009	0.057	1.68	0.000	1.47	0.0329	1.53
	5-May	1.21	0.022	0.040	1.27	0.030	1.30	0.0388	2.83
	19-Jul	1.08	0.026	0.021	1.13	0.179	1.31	0.0176	1.49
22	16-Oct	8.90	0.050	0.050	9.00	1.800	10.80	0.3450	1.74
	18-Jan	7.14	0.044	0.360	7.54	0.220	7.76	0.3690	4.19
	3-Feb	15.15	0.047	<0.003	15.20	1.500	16.70	0.0715	—
	23-Jul	10.05	0.047	0.022	10.12	0.278	10.40	0.1960	3.41
23	20-Oct	4.10	0.019	0.057	4.18	1.283	5.46	0.0655	3.06
	2-Feb	4.35	0.018	0.066	4.44	0.134	4.57	0.0247	2.66
	15-May	4.21	0.037	<0.003	4.25	0.290	4.54	0.0031	2.88
	24-Jul	5.28	0.013	0.007	5.30	1.653	6.95	0.0367	2.04
24	28-Oct	2.07	0.010	0.096	2.18	0.064	2.24	0.0412	2.50
	9-Feb	2.37	0.012	<0.003	2.38	0.000	2.28	0.0989	1.34
	5-May	1.15	0.021	0.004	1.17	0.086	1.26	0.0081	3.63
	19-Jul	1.72	0.036	0.037	1.80	0.223	2.02	0.0374	2.38

Table 8. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (µS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
25	6-Oct	17:25	7.94	13.06	112.7	602.3	0.31	8.29	345	1.07	1.00
	19-Jan	10:20	0.44	13.34	96.3	612.2	0.31	7.91	410	1.00	0.67
	8-May	16:20	14.27	9.12	91.0	563.7	0.29	7.81	432	2.50	6.33
	30-Jul	12:10	18.33	9.54	101.6	587.0	0.30	8.07	433	6.35	6.67
26	20-Oct	15:45	11.72	11.57	108.3	829.0	0.43	8.27	374	6.62	17.00
	3-Feb	15:00	0.11	13.75	96.6	750.8	0.39	8.10	356	1.30	1.67
	15-May	14:45	20.93	13.30	156.2	649.0	0.33	8.77	424	2.53	8.67
	24-Jul	13:45	18.17	12.70	136.7	671.0	0.35	8.12	459	3.27	6.00
27	21-Oct	7:10	8.71	10.18	88.6	648.1	0.33	8.03	355	3.22	4.67
	3-Feb	8:30	0.07	12.87	90.3	592.7	0.31	8.10	714	2.00	5.00
	15-May	8:30	15.47	9.14	93.4	544.8	0.28	7.74	430	4.02	5.00
	23-Jul	18:00	23.75	9.33	112.3	556.3	0.28	8.10	418	5.71	5.33
28	29-Sep	18:00	13.02	9.24	89.6	525.7	0.27	7.79	320	3.28	1.33
	18-Jan	15:40	6.20	11.50	94.2	508.3	0.26	7.81	396	1.60	3.33
	9-May	9:00	10.14	7.61	74.1	496.6	0.25	7.72	421	2.32	4.67
	2-Aug	13:42	15.29	12.10	121.5	491.0	0.25	7.72	418	1.56	1.33
29	30-Sep	11:20	10.96	10.60	98.3	558.1	0.28	7.89	396	0.55	0.00
	6-Jan	12:15	2.45	13.62	101.4	561.9	0.29	8.05	413	0.40	1.67
	28-Apr	13:10	15.43	15.96	165.3	521.4	0.26	8.07	492	0.89	12.00
	19-Jul	8:00	18.43	7.81	83.9	549.0	0.28	7.66	261	1.33	0.00

Table 8. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
25	6-Oct	1.82	0.007	0.016	1.85	0.404	2.25	0.0470	2.97
	19-Jan	3.25	0.018	<0.003	3.27	0.288	3.56	0.0042	2.12
	8-May	16.66	0.035	0.013	16.71	1.437	18.15	0.0106	—
	30-Jul	5.08	0.036	0.011	5.13	0.179	5.31	0.0121	3.27
26	20-Oct	7.37	0.106	0.043	7.52	1.607	9.13	0.2000	2.54
	3-Feb	7.34	0.021	0.014	7.37	2.126	9.50	0.1850	2.52
	15-May	8.32	0.064	<0.003	8.38	0.320	8.70	0.0854	2.73
	24-Jul	9.43	0.035	0.014	9.48	0.716	10.20	0.0166	1.78
27	21-Oct	4.41	0.011	0.022	4.44	2.328	6.77	0.0493	2.20
	3-Feb	5.27	0.018	0.048	5.34	1.262	6.60	0.0869	2.65
	15-May	2.74	0.038	<0.003	2.78	0.240	3.02	0.0027	—
	23-Jul	3.38	0.014	0.010	3.40	0.410	3.81	0.0308	2.22
28	29-Sep	2.79	0.027	0.029	2.85	0.241	3.09	0.0211	1.61
	18-Jan	3.15	0.016	0.007	3.18	0.193	3.37	0.0046	1.63
	9-May	2.37	0.014	0.013	2.39	0.000	2.38	0.0194	—
	2-Aug	2.72	0.012	0.023	2.75	0.407	3.16	<0.0006	1.51
29	30-Sep	1.09	0.018	<0.003	1.11	0.070	1.18	0.0302	4.25
	6-Jan	1.77	0.005	0.011	1.78	0.039	1.82	0.0019	1.67
	28-Apr	1.20	0.019	0.005	1.23	0.000	1.19	0.0022	—
	19-Jul	1.30	0.024	0.028	1.35	0.162	1.51	0.0033	2.11

Table 8. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (µS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
30	12-Oct	17:20	9.36	12.56	110.6	599.6	0.31	7.59	394	3.43	11.33
	5-Jan	11:20	4.82	11.24	89.3	606.8	0.30	7.66	469	13.00	41.33
	27-Apr	10:33	11.57	13.58	128.2	577.9	0.30	7.59	505	1.15	3.00
	30-Jul	14:30	11.97	11.34	105.3	560.0	0.29	7.19	444	2.59	34.33

Table 8. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
30	12-Oct	3.16	0.014	0.047	3.22	0.383	3.60	0.0190	1.21
	5-Jan	3.20	0.012	0.118	3.33	0.222	3.55	0.0503	2.25
	27-Apr	2.75	0.018	<0.003	2.77	0.150	2.92	0.0024	—
	30-Jul	2.86	0.026	0.015	2.91	0.225	3.13	<0.0006	1.45

Table 9. Sampling dates, times and physical and chemical water-quality parameters in developed streams ( $n=9$ ) in the Driftless Area of the Midwestern U.S. in fall 2012 and winter, spring and summer 2013. [ $^{\circ}\text{C}$ , degrees Celsius; mg/L, milligrams per liter;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter; ppt, parts per trillion; mV, millivolts; NTU, nephelometric turbidity units]

ID	Date	Time	Temp ( $^{\circ}\text{C}$ )	Dissolved $\text{O}_2$ (mg/L)	Dissolved $\text{O}_2$ (% saturation)	Specific conductance ( $\mu\text{S}/\text{cm}$ )	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
31	28-Oct	13:19	12.89	7.87	76.4	1,981.1	1.05	7.76	355	1.05	2.33
	9-Feb	9:00	4.73	10.26	82.6	4,285.1	2.37	7.58	433	2.05	6.33
	5-May	12:30	12.41	9.60	91.7	1,809.7	0.96	7.38	447	1.39	4.00
	19-Jul	11:45	18.42	8.40	90.5	1,672.0	0.89	7.64	403	1.16	1.33
32	20-Oct	16:00	14.70	9.17	91.9	1,519.4	0.81	8.05	353	1.81	2.00
	2-Feb	16:50	4.48	12.24	97.6	1,455.4	0.77	8.25	402	3.90	9.67
	15-May	13:00	18.11	16.05	174.1	1,202.1	0.63	8.32	419	1.92	2.33
	24-Jul	11:40	19.22	10.40	114.6	1,272.0	0.67	7.89	478	2.43	1.11
33	21-Oct	7:50	7.14	9.00	75.1	1,083.9	0.57	7.53	354	1.38	0.00
	3-Feb	7:30	1.27	10.97	80.6	7,940.8	4.41	7.26	703	1.90	9.17
	15-May	10:40	19.53	15.40	176.3	1,584.2	0.84	8.30	421	1.91	3.33
	24-Jul	9:15	19.89	12.10	135.1	1,278.0	0.67	7.78	458	2.02	4.67
34	20-Oct	13:45	14.17	8.93	88.3	599.3	0.31	7.79	528	606.00	360.33
	2-Feb	13:30	0.11	11.70	85.2	9,511.0	5.37	7.64	304	3.50	6.67
	15-May	15:45	16.45	13.15	139.3	2,264.1	1.21	7.92	447	2.28	3.67
	24-Jul	15:05	18.42	8.29	90.2	2,181.0	1.17	7.52	459	1.69	1.33

Table 9. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
31	28-Oct	23.32	0.181	0.066	23.57	1.435	25.00	0.5790	5.22
	9-Feb	20.67	0.130	0.095	20.90	0.000	20.60	0.0784	5.92
	5-May	6.50	0.129	<0.003	6.63	0.220	6.85	0.1010	3.49
	19-Jul	8.95	0.016	0.010	8.98	0.910	9.89	0.1370	4.11
32	20-Oct	5.79	0.112	0.049	5.95	1.301	7.25	0.2230	5.95
	2-Feb	7.77	0.016	0.029	7.82	1.531	9.35	0.1990	7.50
	15-May	5.59	0.032	0.016	5.64	1.334	6.97	0.0995	4.77
	24-Jul	5.51	0.026	0.016	5.56	2.044	7.60	0.2160	4.91
33	21-Oct	0.00	0.007	0.058	0.07	0.235	0.30	0.0433	7.42
	3-Feb	0.85	0.023	0.120	0.99	0.336	1.33	0.0045	4.30
	15-May	0.26	0.047	0.017	0.32	0.260	0.58	<0.0006	—
	24-Jul	0.10	0.008	0.010	0.11	0.242	0.36	<0.0006	4.57
34	20-Oct	0.09	0.006	0.036	0.13	0.014	0.15	0.0237	1.33
	2-Feb	1.50	0.019	0.145	1.67	0.235	1.90	0.0168	3.44
	15-May	1.98	0.015	0.006	2.00	0.884	2.88	0.0046	2.90
	24-Jul	1.60	0.006	<0.003	1.61	0.240	1.85	<0.0006	2.42

Table 9. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (µS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
35	20-Oct	13:00	8.96	11.15	97.9	1,004.5	0.53	7.97	318	2.09	0.33
	2-Feb	13:00	0.20	13.17	92.9	1,006.1	0.53	7.92	404	2.40	7.33
	15-May	16:00	19.93	12.51	140.6	939.7	0.49	8.11	421	4.13	1.33
	24-Jul	15:35	19.21	10.05	110.6	924.0	0.48	7.90	434	3.25	4.67
36	7-Oct	10:20	6.69	11.18	93.4	432.4	0.22	7.64	374	0.39	1.33
	18-Jan	14:15	1.16	13.67	98.5	1,151.0	0.60	7.85	370	4.10	5.33
	9-May	9:50	10.93	9.04	83.5	354.7	0.17	7.82	424	1.29	2.33
	2-Aug	14:47	17.10	10.24	106.3	435.0	0.22	7.69	417	0.83	3.00
37	—	—	—	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—
	8-May	15:00	15.24	10.60	114.1	472.3	0.24	8.42	404	4.91	8.67
	30-Jul	11:30	17.35	8.11	84.6	501.0	0.25	7.91	437	4.59	82.00
38	16-Oct	10:09	10.09	9.65	88.4	731.9	0.38	8.02	402	1.35	4.67
	12-Jan	11:15	1.65	11.97	88.3	1,035.7	0.54	8.3	621	24.30	9.33
	14-May	10:30	15.16	16.22	165.0	812.6	0.42	8.35	450	0.92	2.00
	23-Jul	9:40	18.08	9.46	101.7	856.0	0.45	7.95	471	4.43	5.67
39	28-Oct	12:40	10.54	8.29	76.2	1,258.8	0.66	7.45	377	0.36	0.00
	9-Feb	10:00	3.95	11.85	92.9	2,048.9	1.10	7.50	451	40.50	35.67
	5-May	12:50	12.04	10.75	101.5	1,160.0	0.61	7.23	460	0.33	3.33
	19-Jul	12:23	23.98	—	—	—	—	8.20	391	1.12	1.33

Table 9. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
35	20-Oct	3.69	0.009	0.044	3.74	0.276	4.02	0.0161	3.18
	2-Feb	3.96	0.017	0.071	4.05	0.489	4.54	0.0133	2.41
	15-May	3.45	0.039	0.003	3.49	0.117	3.61	0.0041	—
	24-Jul	4.63	0.009	0.006	4.65	0.004	4.65	0.0051	2.23
36	7-Oct	2.26	0.006	0.024	2.29	0.366	2.66	0.0904	2.97
	18-Jan	2.48	0.016	0.117	2.62	0.243	2.86	0.0435	2.89
	9-May	1.63	0.025	0.071	1.72	0.209	1.93	0.2140	—
	2-Aug	2.49	0.132	0.111	2.73	0.129	2.86	0.0532	3.11
37	—	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—
	8-May	3.28	0.025	0.003	3.31	0.367	3.68	0.0133	—
	30-Jul	0.32	0.017	0.024	0.36	0.304	0.66	0.0239	4.10
38	16-Oct	0.70	0.008	0.065	0.77	0.036	0.81	0.0393	2.22
	12-Jan	0.60	0.019	0.097	0.71	0.264	0.98	0.0873	6.02
	14-May	1.81	0.017	<0.003	1.83	0.050	1.88	0.0113	—
	23-Jul	2.53	0.013	0.018	2.56	0.322	2.88	0.0394	2.16
39	28-Oct	5.75	0.016	0.047	5.82	0.953	6.77	0.0393	1.98
	9-Feb	4.02	0.016	0.323	4.36	0.000	4.27	0.0468	2.38
	5-May	5.89	0.015	<0.003	5.91	1.370	7.28	0.0247	2.10
	19-Jul	6.10	0.013	0.008	6.12	0.132	6.25	0.0049	1.97

Table 10. Sampling dates, times and physical and chemical water-quality parameters in forested streams ( $n=24$ ) in the Driftless Area of the Midwestern U.S. in fall 2012 and winter, spring and summer 2013. [ $^{\circ}\text{C}$ , degrees Celsius; mg/L, milligrams per liter;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter; ppt, parts per trillion; mV, millivolts; NTU, nephelometric turbidity units]

ID	Date	Time	Temp ( $^{\circ}\text{C}$ )	Dissolved $\text{O}_2$ (mg/L)	Dissolved $\text{O}_2$ (% saturation)	Specific conductance ( $\mu\text{S}/\text{cm}$ )	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
40	28-Oct	15:01	7.10	9.65	81.3	479.3	0.24	8.14	359	5.75	13.67
	9-Feb	8:05	0.91	13.20	94.6	448.9	0.23	8.00	465	7.33	15.00
	5-May	10:50	11.54	9.71	88.4	452.9	0.23	7.62	437	7.39	19.67
	19-Jul	10:30	18.76	8.95	96.8	469.0	0.24	7.92	347	16.30	36.33
41	12-Oct	15:10	9.36	10.38	91.3	482.8	0.24	8.13	409	4.54	16.33
	12-Jan	17:00	2.49	12.41	93.3	461.6	0.23	8.05	508	7.20	18.33
	27-Apr	8:30	9.53	10.89	97.8	476.5	0.24	7.90	580	12.00	27.00
	30-Jul	17:50	17.92	8.82	93.2	448.0	0.22	8.06	418	9.57	14.00
42	30-Sep	9:40	9.69	10.08	90.6	526.8	0.27	7.90	386	2.65	3.33
	6-Jan	8:50	2.60	12.04	90.0	538.3	0.27	7.98	466	6.20	18.00
	28-Apr	9:50	10.11	11.10	102.2	528.2	0.27	7.57	651	4.77	19.67
	15-Jul	15:45	16.20	9.91	93.6	533.0	0.27	8.05	445	9.87	18.00
43	12-Oct	15:40	8.87	10.37	90.2	508.3	0.26	8.00	372	3.25	12.67
	5-Jan	9:15	0.07	13.76	96.1	505.8	0.26	6.30	586	7.20	23.00
	27-Apr	9:20	8.68	11.70	103.0	510.7	0.26	7.90	534	17.00	49.00
	30-Jul	17:00	15.40	9.55	95.7	484.0	0.24	8.06	414	8.09	8.67

Table 10. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
40	28-Oct	1.36	0.009	0.068	1.44	0.263	1.70	0.0189	1.58
	9-Feb	1.57	0.009	0.054	1.63	0.161	1.80	0.0170	1.39
	5-May	1.24	0.025	0.018	1.29	0.123	1.41	0.0272	3.43
	19-Jul	1.33	0.035	0.050	1.42	0.240	1.66	0.0205	2.08
41	12-Oct	1.00	0.013	0.045	1.05	0.000	0.99	0.0740	1.67
	12-Jan	1.08	0.012	0.016	1.11	0.084	1.19	0.0063	1.87
	27-Apr	1.07	0.010	0.042	1.12	0.008	1.13	0.0080	—
	30-Jul	0.95	0.020	0.015	0.99	0.150	1.14	0.0006	1.38
42	30-Sep	1.25	0.019	0.015	1.29	0.245	1.53	0.0380	1.54
	6-Jan	1.46	0.004	0.014	1.47	0.056	1.53	0.0028	1.32
	28-Apr	1.36	0.013	0.008	1.38	0.052	1.43	0.0022	—
	15-Jul	1.48	0.029	0.033	1.54	0.507	2.05	0.0137	1.92
43	12-Oct	1.08	0.011	0.047	1.14	0.000	1.13	0.0419	1.40
	5-Jan	1.32	0.006	0.025	1.35	0.000	1.35	0.0146	1.84
	27-Apr	1.11	0.010	0.027	1.15	0.000	1.09	<0.0006	—
	30-Jul	1.02	0.080	0.016	1.12	0.094	1.21	0.0144	1.35

Table 10. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (µS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
44	—	—	—	—	—	—	—	—	—	—	—
	8-Feb	14:20	9.68	10.68	95.4	509.4	0.26	7.86	417	6.64	18.00
	30-Apr	11:20	15.35	10.52	108.3	509.1	0.26	7.65	483	8.38	24.33
	17-Jul	12:55	16.03	9.58	97.3	503.0	0.25	7.63	414	5.20	3.33
45	29-Sep	14:00	12.48	10.27	98.4	533.4	0.27	8.12	386	7.19	7.33
	5-Jan	14:00	0.60	12.81	90.8	539.6	0.27	8.17	439	12.60	38.00
	27-Apr	13:41	16.48	9.68	101.4	458.0	0.23	7.92	448	23.50	74.00
	2-Aug	10:50	14.59	10.04	98.8	496.0	0.25	8.00	419	26.60	84.33
46	28-Oct	10:10	4.62	9.57	75.5	223.2	0.10	7.59	351	2.04	0.33
	—	—	—	—	—	—	—	—	—	—	—
	5-May	15:20	16.95	8.97	94.2	193.0	0.09	7.32	430	4.86	7.33
	19-Jul	15:00	22.38	9.10	105.7	229.0	0.11	7.86	412	3.47	9.00
47	30-Sep	14:05	13.30	9.72	95.0	336.2	0.16	7.96	373	6.30	2.33
	6-Jan	9:30	2.94	12.18	92.5	334.3	0.16	7.91	429	5.10	9.67
	28-Apr	10:30	10.97	10.53	98.6	310.8	0.15	7.57	590	5.45	14.00
	15-Jul	12:30	16.01	9.55	97.5	341.0	0.17	7.73	447	12.00	13.67
48	7-Oct	15:00	9.61	10.38	93.0	399.6	0.20	8.15	347	2.07	8.00
	18-Jan	10:15	0.11	13.76	95.9	373.2	0.18	8.00	388	6.20	20.67
	16-May	9:00	10.82	10.36	95.5	388.3	0.19	7.51	317	6.78	6.33
	15-Jul	8:45	14.80	9.44	93.9	382.0	0.19	7.81	544	11.90	16.33

Table 10. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
44	—	—	—	—	—	—	—	—	—
	8-Feb	1.07	0.006	0.021	1.10	0.000	1.07	0.0086	1.19
	30-Apr	0.94	0.008	<0.003	0.95	0.000	0.95	0.0202	2.12
	17-Jul	1.02	0.009	<0.003	1.03	0.040	1.07	0.0022	1.28
45	29-Sep	3.45	0.024	0.077	3.55	0.173	3.72	0.0590	1.54
	5-Jan	3.59	0.010	0.031	3.63	0.379	4.01	0.0335	1.50
	27-Apr	2.39	0.012	0.023	2.42	0.000	2.42	0.0286	3.04
	2-Aug	2.99	0.007	0.011	3.01	0.519	3.53	0.0294	1.70
46	28-Oct	0.96	0.014	0.192	1.17	0.074	1.24	0.0597	5.15
	—	—	—	—	—	—	—	—	—
	5-May	0.59	0.026	0.043	0.66	0.113	0.77	0.0448	2.75
	19-Jul	0.57	0.013	0.021	0.60	0.195	0.80	0.0535	2.84
47	30-Sep	2.70	0.020	0.419	3.14	0.000	3.08	0.1020	1.87
	6-Jan	2.87	0.005	0.020	2.90	0.140	3.04	0.0676	1.44
	28-Apr	1.99	0.013	0.024	2.02	0.476	2.50	0.0628	—
	15-Jul	3.15	0.012	0.024	3.18	0.216	3.40	0.0697	1.83
48	7-Oct	0.53	<0.001	0.026	0.55	0.877	1.43	0.0691	2.16
	18-Jan	0.76	0.005	0.026	0.80	0.000	0.77	0.1890	1.56
	16-May	0.74	0.011	0.028	0.78	0.029	0.81	0.0625	3.19
	15-Jul	0.70	0.013	0.027	0.74	0.100	0.84	0.0957	1.99

Table 10. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (μS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
49	30-Sep	14:48	12.33	9.96	95.3	518.3	0.26	8.04	392	2.14	29.00
	6-Jan	9:10	3.84	11.80	91.2	529.8	0.27	8.07	458	5.50	13.33
	28-Apr	10:10	10.01	11.62	106.8	509.3	0.26	7.77	627	2.03	3.67
	15-Jul	7:50	12.29	9.92	93.5	519.0	0.26	7.74	606	13.40	23.00
50	21-Oct	13:06	9.67	12.00	107.0	616.5	0.32	8.21	329	2.26	1.00
	2-Feb	11:00	0.07	12.90	90.3	547.6	0.25	8.01	393	3.50	6.33
	30-Apr	14:15	18.98	12.34	137.9	550.7	0.28	8.20	447	4.51	10.33
	17-Jul	10:25	17.57	10.26	107.6	578.0	0.29	8.01	411	3.72	3.00
51	28-Oct	15:38	7.21	10.17	85.9	498.8	0.25	8.31	344	6.33	10.00
	9-Feb	7:30	0.15	13.72	97.1	473.5	0.24	8.14	458	9.10	27.67
	5-May	10:30	10.78	10.60	97.2	430.2	0.22	7.82	454	10.20	21.00
	19-Jul	9:45	18.95	9.04	98.1	468.0	0.24	7.97	336	11.30	23.00
52	28-Oct	13:49	9.22	10.29	91.3	504.4	0.26	8.19	350	5.85	15.33
	9-Feb	8:35	0.92	13.33	95.5	474.8	0.26	7.95	456	6.68	11.50
	5-May	11:50	14.53	11.06	109.7	484.6	0.24	7.93	436	9.60	23.33
	19-Jul	11:00	—	—	—	—	—	—	—	4.95	9.33
53	21-Oct	13:45	—	—	—	—	—	—	—	5.13	13.00
	2-Feb	10:15	0.08	12.91	90.5	496.4	0.25	8.03	337	6.90	26.33
	30-Apr	15:45	21.86	10.25	120.3	483.3	0.25	8.32	425	19.70	45.67
	17-Jul	8:10	15.76	9.22	93.2	650.0	0.33	7.65	413	0.90	13.67

Table 10. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
49	30-Sep	0.60	0.016	0.012	0.63	0.083	0.72	0.0568	1.30
	6-Jan	0.68	0.006	0.040	0.73	0.011	0.74	0.0466	1.44
	28-Apr	0.53	0.008	0.003	0.54	0.056	0.59	0.0355	—
	15-Jul	0.64	0.008	0.032	0.68	0.326	1.01	0.0352	1.83
50	21-Oct	1.27	0.010	0.037	1.32	0.123	1.44	0.0705	1.77
	2-Feb	1.58	0.015	0.061	1.66	0.209	1.87	0.0324	1.76
	30-Apr	1.87	0.026	0.010	1.91	0.010	1.92	0.0250	3.37
	17-Jul	2.03	0.048	0.055	2.14	0.295	2.43	0.0113	2.30
51	28-Oct	1.95	0.012	0.056	2.02	0.084	2.10	0.0645	1.91
	9-Feb	1.91	0.012	0.016	1.94	0.000	1.87	0.0208	1.12
	5-May	1.59	0.024	0.012	1.62	0.068	1.69	0.0137	3.15
	19-Jul	1.50	0.034	0.021	1.55	0.179	1.73	0.0243	
52	28-Oct	0.81	0.013	0.063	0.88	0.000	0.83	0.0468	1.30
	9-Feb	0.89	0.008	0.077	0.97	0.000	0.90	0.0863	1.15
	5-May	0.94	0.015	0.052	1.01	0.000	0.94	0.0036	2.19
	19-Jul	0.91	0.013	<0.003	0.92	0.034	0.96	0.0044	1.28
53	21-Oct	0.61	0.015	0.076	0.70	0.140	0.84	0.0613	2.13
	2-Feb	0.80	0.012	0.066	0.87	0.070	0.94	0.0192	1.57
	30-Apr	0.47	0.015	<0.003	0.48	0.022	0.50	0.0060	2.63
	17-Jul	1.13	0.029	0.056	1.22	0.234	1.45	<0.0006	2.10

Table 10. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (μS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
54	1-Nov	8:20	5.55	10.81	88.1	221.0	0.10	7.15	365	10.10	21.00
	18-Jan	9:00	1.24	13.33	95.9	206.7	0.10	7.82	317	7.67	20.33
	16-May	11:10	15.09	10.07	102.1	223.1	0.10	7.21	364	13.50	34.33
	15-Jul	11:00	17.44	9.45	99.4	221.0	0.10	7.45	452	16.80	36.33
56	29-Sep	13:00	11.63	11.16	105.0	554.3	0.28	8.10	393	1.83	0.67
	5-Jan	14:30	3.52	12.16	93.4	567.7	0.29	8.16	428	5.60	9.67
	27-Apr	13:11	13.70	10.07	99.8	548.9	0.28	7.80	464	8.62	27.00
	2-Aug	10:15	12.67	10.23	96.6	529.0	0.27	7.86	427	6.91	20.33
56	28-Oct	11:27	5.26	9.78	78.5	84.2	0.03	7.93	360	1.21	0.00
	—	—	—	—	—	—	—	—	—	—	—
	5-May	13:30	13.24	10.95	105.8	47.3	0.01	7.60	442	3.02	3.67
	19-Jul	13:00	—	—	—	—	—	—	—	3.31	1.33
57	7-Oct	13:15	8.50	10.83	94.4	75.8	0.03	6.99	323	2.15	0.67
	18-Jan	11:20	0.13	13.00	90.6	68.9	0.02	7.81	354	3.90	3.33
	16-May	10:30	11.53	9.79	91.9	75.2	0.02	6.31	357	3.26	1.67
	15-Jul	10:20	14.78	9.31	92.6	86.0	0.03	7.21	480	6.87	4.67
58	1-Nov	7:45	3.06	11.95	91.2	210.5	0.10	6.84	528	7.33	9.33
	18-Jan	9:30	0.41	13.65	95.7	228.1	0.11	7.77	375	4.85	12.00
	16-May	11:45	14.67	10.26	103.0	197.3	0.09	7.70	452	4.60	3.56
	15-Jul	11:30	17.14	9.06	94.8	240.0	0.11	7.76	462	9.47	6.33

Table 10. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
54	1-Nov	1.39	0.004	0.066	1.46	0.074	1.53	0.1810	1.67
	18-Jan	1.46	0.006	0.040	1.51	0.000	1.44	0.1670	1.05
	16-May	1.17	0.011	0.029	1.21	0.000	1.17	0.1390	—
	15-Jul	1.43	0.013	0.035	1.48	0.425	1.90	0.1580	1.55
55	29-Sep	4.25	0.031	0.026	4.31	1.194	5.50	0.0674	1.23
	5-Jan	4.16	0.011	0.013	4.18	0.237	4.42	0.0326	1.40
	27-Apr	3.31	0.017	0.080	3.41	0.395	3.81	0.0426	2.56
	2-Aug	3.75	0.022	0.008	3.78	0.142	3.92	0.0081	1.38
56	28-Oct	0.03	0.003	0.049	0.08	0.096	0.17	0.0340	9.48
	—	—	—	—	—	—	—	—	—
	5-May	0.77	0.011	0.106	0.88	0.000	0.78	0.0039	2.88
	19-Jul	0.16	0.009	0.046	0.22	0.390	0.61	0.0210	2.58
57	7-Oct	1.18	0.005	0.044	1.22	0.396	1.62	0.2230	3.56
	18-Jan	1.42	0.008	0.075	1.50	0.065	1.57	0.0894	2.50
	16-May	1.34	0.009	0.062	1.41	0.000	1.35	0.1410	—
	15-Jul	1.71	0.011	0.061	1.79	0.064	1.85	0.1420	3.13
58	1-Nov	0.46	0.002	0.165	0.63	0.149	0.77	0.0200	3.03
	18-Jan	0.95	0.007	0.037	1.00	0.063	1.06	0.0401	1.50
	16-May	0.30	0.008	0.023	0.33	0.039	0.37	0.0294	—
	15-Jul	0.67	0.009	0.030	0.71	0.402	1.11	0.0461	2.63

Table 10. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (μS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
59	20-Oct	10:35	6.71	11.29	83.7	521.7	0.26	7.95	369	2.35	0.33
	2-Feb	9:20	0.55	13.79	98.0	481.8	0.24	8.05	401	1.20	5.00
	30-Apr	10:30	13.50	12.44	122.9	509.1	0.24	7.96	471	2.50	4.67
	17-Jul	13:42	17.16	10.50	109.2	487.0	0.25	7.80	416	3.69	1.33
60	6-Oct	8:45	8.02	10.86	94.1	517.0	0.26	7.97	380	5.43	9.33
	12-Jan	8:30	2.85	11.56	90.2	542.6	0.28	6.14	514	10.40	11.89
	30-Apr	8:15	11.60	10.20	96.7	526.4	0.27	7.75	504	3.99	5.33
	17-Jul	16:00	15.98	9.67	98.1	524.5	0.27	7.78	426	9.45	16.67
61	6-Oct	10:55	8.77	10.22	90.1	505.0	0.26	7.77	—	2.17	0.67
	12-Jan	16:15	5.10	11.37	91.6	480.1	0.24	7.58	450	3.10	2.67
	8-May	11:30	12.82	10.37	100.0	489.2	0.25	7.68	426	1.88	0.33
	30-Jul	7:45	11.82	9.56	88.5	477.7	0.24	7.53	404	6.88	10.33
62	7-Oct	14:20	8.84	11.30	99.4	168.4	0.07	7.75	359	4.65	—
	18-Jan	10:45	0.11	13.62	94.9	161.5	0.07	7.63	396	5.70	4.78
	16-May	9:45	12.40	11.19	106.2	166.1	0.07	6.98	418	5.50	6.33
	15-Jul	9:40	16.70	9.08	94.1	178.0	0.08	7.33	529	11.80	8.33
63	6-Oct	9:35	9.35	10.93	97.8	499.2	0.25	8.04	355	42.10	71.56
	12-Jan	8:55	3.03	13.53	101.9	531.4	0.27	8.29	754	8.00	16.00
	30-Apr	8:30	12.66	10.98	106.0	486.4	0.25	7.92	496	1.32	2.00
—	—	—	—	—	—	—	—	—	—	—	—

Table 10. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
59	20-Oct	1.48	0.010	0.046	1.54	0.135	1.67	0.0407	1.82
	2-Feb	1.37	0.017	0.008	1.40	0.072	1.47	0.0146	1.25
	30-Apr	1.17	0.012	<0.003	1.18	0.040	1.22	0.0067	2.29
	17-Jul	1.35	0.012	0.006	1.37	0.594	1.96	<0.0006	1.73
60	6-Oct	1.63	0.008	0.049	1.69	0.412	2.10	0.0462	1.71
	12-Jan	1.32	0.011	0.054	1.38	0.076	1.46	0.1100	3.89
	30-Apr	1.47	0.011	0.030	1.51	0.000	1.36	0.0079	2.19
	17-Jul	1.62	0.012	0.010	1.64	0.220	1.86	<0.0006	1.53
61	6-Oct	0.81	0.007	0.053	0.87	0.187	1.06	0.0480	1.70
	12-Jan	0.88	0.008	0.007	0.89	0.075	0.97	0.0019	1.75
	8-May	0.65	0.009	0.012	0.67	0.000	0.65	0.0025	—
	30-Jul	0.84	0.010	0.025	0.88	0.072	0.95	<0.0006	1.34
62	7-Oct	1.31	<0.001	0.228	1.54	0.452	1.99	0.0784	2.23
	18-Jan	1.64	0.013	0.050	1.70	0.000	1.70	0.2120	1.40
	16-May	2.10	0.012	0.040	2.15	0.200	2.35	0.1040	6.15
	15-Jul	2.75	0.022	0.036	2.81	0.384	3.19	0.1070	2.44
63	6-Oct	0.89	0.006	0.171	1.07	0.000	0.87	0.0140	1.31
	12-Jan	0.93	0.007	0.026	0.96	0.028	0.99	<0.0006	2.25
	30-Apr	0.92	0.008	<0.003	0.92	0.000	0.87	<0.0006	1.42
—	—	—	—	—	—	—	—	—	—

Table 11. Sampling dates, times and physical and chemical water-quality parameters in mixed streams ( $n=14$ ) in the Driftless Area of the Midwestern U.S. in fall 2012 and winter, spring and summer 2013. [ $^{\circ}\text{C}$ , degrees Celsius; mg/L, milligrams per liter;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter; ppt, parts per trillion; mV, millivolts; NTU, nephelometric turbidity units]

ID	Date	Time	Temp ( $^{\circ}\text{C}$ )	Dissolved $\text{O}_2$ (mg/L)	Dissolved $\text{O}_2$ (% saturation)	Specific conductance ( $\mu\text{S}/\text{cm}$ )	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
64	—	—	—	—	—	—	—	—	—	—	—
	6-Jan	10:50	2.72	12.42	93.0	300.4	0.15	7.61	370	11.80	26.33
	28-Apr	11:45	11.86	13.38	128.3	289.4	0.14	7.56	545	2.93	4.67
	15-Jul	13:15	15.87	9.69	98.6	305.0	0.15	7.45	445	11.80	18.33
65	21-Oct	11:38	8.72	11.22	97.8	726.5	0.38	8.13	355	0.58	0.00
	—	—	—	—	—	—	—	—	—	—	—
	30-Apr	13:30	17.02	11.54	123.4	567.2	0.29	8.10	458	1.13	2.33
	17-Jul	11:10	20.98	8.03	90.2	681.0	0.35	7.99	410	1.77	0.67
66	16-Oct	17:49	13.22	9.06	89.2	550.5	0.28	8.04	359	2.87	6.00
	8-Feb	11:30	5.73	12.99	105.3	510.2	0.26	7.71	424	7.10	14.33
	30-Apr	9:15	11.73	11.93	113.4	533.7	0.27	7.75	488	1.42	5.00
	17-Jul	15:15	20.06	11.40	101.4	537.0	0.27	7.80	420	3.97	5.67
67	30-Sep	10:37	9.80	10.82	97.7	502.5	0.25	8.05	392	4.08	1.33
	6-Jan	13:00	2.97	13.25	100.5	501.2	0.26	8.29	392	1.70	3.33
	28-Apr	13:30	14.89	14.33	146.9	456.0	0.23	8.41	449	2.19	5.33
	15-Jul	15:15	19.03	9.87	107.3	485.0	0.25	8.26	431	8.32	12.33

Table 11. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
64	—	—	—	—	—	—	—	—	—
	6-Jan	3.59	0.010	0.038	3.64	0.072	3.71	0.0751	1.35
	28-Apr	2.99	0.015	0.004	3.01	0.106	3.12	0.0546	—
	15-Jul	3.19	0.017	0.028	3.24	0.582	3.82	0.0766	1.71
65	21-Oct	7.42	0.019	0.051	7.49	2.709	10.20	0.0490	2.05
	—	—	—	—	—	—	—	—	—
	30-Apr	4.57	0.018	0.034	4.62	0.157	4.78	0.0522	2.11
	17-Jul	3.80	0.012	<0.003	3.81	0.250	4.06	0.0362	1.72
66	16-Oct	1.73	0.014	0.057	1.80	0.303	2.10	0.0170	1.45
	8-Feb	1.98	0.006	0.036	2.03	0.000	1.99	0.0062	1.41
	30-Apr	1.75	0.019	0.011	1.78	0.000	1.77	<0.0006	1.82
	17-Jul	2.30	0.034	0.028	2.36	0.412	2.77	0.0017	2.40
67	30-Sep	1.60	0.022	0.034	1.65	0.016	1.67	0.0120	1.76
	6-Jan	1.78	0.007	<0.003	1.79	0.020	1.81	0.0061	1.49
	28-Apr	1.24	0.014	0.013	1.26	0.007	1.27	0.0028	—
	15-Jul	1.68	0.017	0.015	1.71	0.266	1.98	0.0104	1.53

Table 11. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (µS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
68	20-Oct	11:42	9.98	10.71	96.1	546.0	0.28	7.51	368	1.48	2.00
	8-Feb	13:45	9.27	12.97	114.8	513.4	0.26	7.62	431	1.40	5.00
	30-Apr	12:00	13.75	15.98	158.7	528.0	0.27	7.70	386	2.12	4.67
	17-Jul	12:00	—	—	—	—	—	—	—	13.90	37.00
69	29-Sep	9:30	9.64	10.80	97.0	530.0	0.27	8.09	407	17.70	119.00
	5-Jan	16:30	1.42	13.23	95.9	537.2	0.27	8.31	409	3.80	8.33
	27-Apr	15:36	15.63	11.37	117.4	502.2	0.25	8.03	448	8.10	20.67
	2-Aug	8:30	14.15	9.48	92.4	502.0	0.25	7.79	449	6.11	23.67
70	30-Sep	12:16	11.70	10.74	101.4	528.0	0.27	8.17	375	2.24	1.00
	6-Jan	11:30	1.41	13.01	94.1	531.3	0.27	8.16	410	3.40	4.33
	28-Apr	12:30	13.77	13.23	132.4	503.9	0.26	8.27	492	1.31	1.33
	15-Jul	14:30	20.04	8.97	99.6	530.0	0.27	8.11	431	8.50	14.00
71	29-Sep	14:40	13.32	10.06	98.2	550.7	0.28	8.06	394	3.98	6.00
	—	—	—	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—
72	7-Oct	11:45	5.33	10.81	87.2	155.3	0.07	7.47	351	2.92	0.33
	18-Jan	13:15	0.11	12.51	87.1	159.4	0.07	7.67	341	2.50	1.00
	9-May	11:00	10.21	6.40	57.0	123.6	0.05	7.54	377	2.38	3.33
	2-Aug	16:00	17.93	9.25	97.6	159.0	0.07	7.59	416	16.70	20.67

Table 11. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
68	20-Oct	2.45	0.013	0.057	2.52	0.193	2.71	0.0507	1.26
	8-Feb	2.40	0.003	0.024	2.43	0.000	2.31	0.0070	1.17
	30-Apr	2.26	0.012	<0.003	2.27	0.210	2.48	0.0229	1.53
	17-Jul	2.44	0.009	0.010	2.46	0.520	2.98	0.0015	1.25
69	29-Sep	1.20	0.024	0.024	1.24	0.056	1.30	0.0070	2.73
	5-Jan	1.68	0.007	0.031	1.72	0.029	1.75	0.0138	1.95
	27-Apr	1.53	0.016	0.015	1.56	0.000	1.52	0.0120	2.75
	2-Aug	1.27	0.021	<0.003	1.29	0.000	0.94	0.0007	1.81
70	30-Sep	2.01	0.021	0.047	2.08	0.324	2.40	0.1490	3.69
	6-Jan	2.44	0.009	0.019	2.47	0.011	2.48	0.0770	1.74
	28-Apr	1.95	0.016	0.381	2.35	0.000	2.12	0.0132	—
	15-Jul	2.20	0.017	0.030	2.25	0.801	3.05	0.1040	1.94
71	29-Sep	2.65	0.022	0.029	2.70	0.482	3.18	0.0230	1.46
	—	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—
72	7-Oct	1.30	0.016	0.097	1.42	0.533	1.95	0.1000	2.60
	18-Jan	1.70	0.011	0.040	1.75	0.110	1.86	0.0900	3.20
	9-May	0.37	0.019	0.041	0.43	0.429	0.86	0.1085	—
	2-Aug	0.49	0.008	0.037	0.54	0.125	0.66	0.1310	7.15

Table 11. Cont.

ID	Date	Time	Temp (°C)	Dissolved O <sub>2</sub> (mg/L)	Dissolved O <sub>2</sub> (% saturation)	Specific conductance (μS/cm)	Salinity (ppt)	pH	Redox potential (mV)	Turbidity (NTU)	Total suspended solids (mg/L)
73	20-Oct	20:00	10.36	9.83	88.9	625.7	0.32	8.09	339	1.10	0.00
	—	—	—	—	—	—	—	—	—	—	—
	15-May	9:40	12.36	12.08	115.4	540.2	0.27	8.03	431	3.55	5.67
	24-Jul	8:10	13.98	8.70	85.7	585.0	0.30	7.68	444	3.83	3.67
74	7-Oct	12:37	8.77	10.06	88.3	304.4	0.15	6.95	315	2.53	1.00
	18-Jan	12:10	3.40	12.50	95.3	301.7	0.15	7.68	353	1.30	3.33
	9-May	11:45	9.07	8.55	75.5	286.1	0.14	7.62	346	3.16	2.67
	2-Aug	16:45	13.82	8.88	85.9	289.0	0.14	7.01	347	3.16	4.33
75	20-Oct	9:35	7.31	10.33	88.6	535.8	0.27	7.73	392	0.60	0.33
	2-Feb	8:30	2.25	12.39	92.4	499.1	0.25	6.73	424	0.80	0.67
	30-Apr	10:00	12.31	10.93	105.0	490.4	0.25	7.69	486	2.63	0.67
	17-Jul	14:30	18.77	8.94	95.5	503.2	0.25	7.71	431	74.70	244.33
76	12-Oct	16:25	9.86	9.90	88.9	523.3	0.27	8.05	384	3.91	11.67
	5-Jan	10:20	0.05	13.55	95.6	524.3	0.27	8.28	504	6.00	13.33
	27-Apr	10:05	9.74	11.05	99.7	509.9	0.26	7.88	510	8.94	25.00
	30-Jul	16:20	15.68	9.37	94.4	493.2	0.25	7.96	414	13.70	20.33
77	29-Sep	11:30	11.24	10.74	101.0	555.3	0.28	7.97	390	5.98	11.00
	5-Jan	15:15	3.06	12.29	93.2	566.4	0.29	8.10	427	7.90	13.44
	27-Apr	14:56	16.28	9.43	98.7	570.8	0.29	7.63	466	7.17	25.00
	2-Aug	9:15	12.69	11.72	110.7	537.0	0.27	7.72	442	13.30	28.33

Table 11. Cont.

ID	Date	NO <sub>3</sub> <sup>-</sup> -N (mg/L)	NO <sub>2</sub> <sup>-</sup> -N (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	DIN (mg/L)	DON (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC (mg/L)
73	20-Oct	5.95	0.018	0.030	6.00	0.000	5.97	0.0158	2.39
	—	—	—	—	—	—	—	—	—
	15-May	3.79	0.027	<0.003	3.82	1.860	5.68	0.0089	2.28
	24-Jul	4.82	0.033	0.005	4.86	0.355	5.21	<0.0006	1.45
74	7-Oct	5.40	0.009	0.048	5.46	2.192	7.65	0.1920	1.69
	18-Jan	5.38	0.010	0.029	5.42	0.000	5.20	0.2855	1.43
	9-May	3.58	0.008	0.034	3.62	0.106	3.73	0.1020	—
	2-Aug	5.01	0.010	0.046	5.07	0.084	5.15	0.1510	2.17
75	20-Oct	2.22	0.008	0.092	2.32	0.000	2.26	0.0374	3.44
	2-Feb	2.26	0.015	0.020	2.29	0.040	2.33	0.0216	1.01
	30-Apr	1.87	0.026	<0.003	1.90	0.050	1.95	0.0229	2.33
	17-Jul	1.93	0.022	0.026	1.98	0.414	2.39	<0.0006	1.46
76	12-Oct	1.62	0.011	0.021	1.65	0.089	1.74	0.0307	1.38
	5-Jan	1.89	0.005	0.018	1.92	0.122	2.04	0.0174	2.33
	27-Apr	1.81	0.013	0.030	1.85	0.000	1.82	0.0304	—
	30-Jul	1.76	0.019	0.031	1.81	0.130	1.94	0.0058	1.46
77	29-Sep	2.13	0.045	0.087	2.26	0.000	2.22	0.1230	1.86
	5-Jan	2.34	0.009	0.044	2.39	0.000	2.37	0.0374	1.59
	27-Apr	2.77	0.023	0.070	2.86	0.060	2.92	0.1520	—
	2-Aug	2.37	0.030	0.016	2.42	0.174	2.59	0.0377	2.88