



STORM NO_3^- AND NH_4^+ EXPORTS IN STREAM, OVERLAND FLOW, AND TILE DRAINS OF THE US MIDWEST

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ABSTRACT

A better understanding of the dynamics of nitrogen (N) losses to streams during storms in agroecosystems of the US Midwest is critical to better understand how to mitigate N pollution in the Mississippi River Basin. This study investigates storm NO_3^- and NH_4^+ concentrations and fluxes in tile drains, overland flow and stream water in relation to bulk precipitation and antecedent moisture conditions. For moderate size spring storms (1.0 - 4.5 cm bulk precipitation), the occurrence of overland flow was primarily associated with high antecedent moisture conditions, but had no direct effect on stream NO_3^- and NH_4^+ concentrations. Mean storm NO_3^- and NH_4^+ concentrations in the stream and tile drains were also not significantly correlated ($p > 0.05$) to either bulk precipitation or antecedent moisture conditions. Nevertheless, mean stream NO_3^- concentrations (7.50 mg N/L) were on average 28% lower than in tile drains (10.38 mg N/L). No significant difference in NH_4^+ concentrations were observed between the stream (0.06 mg N/L) and tile drains (0.05 mg N/L). NO_3^- and NH_4^+ fluxes were positively correlated with bulk precipitation ($p < 0.05$) and high fluxes were typically associated with wet antecedent moisture conditions. Specific NO_3^- fluxes in tile drains (750 g N/ha/storm) were approximately 2 times larger than in

the stream (398 g N/ha/storm). Such differences were not observed for NH_4^+ fluxes. Considering the positive correlation between storm NO_3^- fluxes and stream NO_3^- baseflow concentrations ($r = 0.87$, $p < 0.05$), it is likely that one of the most efficient strategies for reducing N losses at the watershed scale may simply lie in reducing N inputs to cropland, as opposed to trying to manage N after it is applied to fields.

Keywords: subsurface drainage, nitrogen, export rates, precipitation, runoff, overland flow.

1. INTRODUCTION

Indiana, Iowa, and Illinois are the states in the Mississippi River Basin (MRB) contributing the largest amount of nitrogen (N) to the Gulf of Mexico on an annual basis, with modeled export rates between 1,801 and 3,050 kg N/km²/yr [1]. The impact of various agricultural practices (e.g. till vs. no-till, cover crop, tile drain spacing) on N exports in agroecosystems of the US Midwest where subsurface drainage (a.k.a. tile drainage) is common has therefore been the focus of many studies in the last three decades [2-6]. For instance, Kladvik et al. [3] investigated the impact of changes in crop production (from corn to a corn-soybean rotation) and tile drain spacing (5-10-20 m) over a 15-year period on nitrate (NO_3^-) leaching to tile drains in Indiana. Other workers investigated flow/concentration relationships and the influence of agricultural practices (tillage vs. no tillage) on N losses in Iowa [2,4], or the importance of high flow events in regulating N exports to the Gulf of Mexico from Illinois headwater streams [6]. These studies indicate that most N losses occur in spring during high flow periods, and that changes in agricultural practices and N inputs to agricultural fields can have a significant impact on N losses to streams. Studies in the US Midwest and in tile drained landscapes of southern Ontario, Canada, also show complex non-linear relationships between antecedent moisture conditions and NO_3^- losses on a storm basis, and stress the need for more studies focusing on identifying first order controls on NO_3^- losses in artificially drained landscapes of the US Midwest and other regions (e.g. Southern Ontario, Canada) where tile drainage is a dominant feature of the agricultural landscape [7-9].

However, in spite of all these research efforts in the past three decades, there is still a lack of integration between plot scale studies (tile drains) and watershed scale studies (stream). Indeed, plot-scale

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studies have often focused on tile drain losses of N [3,9] or greenhouse gas emissions from soils [10]. On the other hand, watershed scale studies often focus on N dynamics in streams [11-13] or focus on identifying N losses via denitrification by difference using a mass balance approach [14-16]. In most cases, studies do not provide a coherent framework linking plot scale observations (in tile drains) to watershed scale observations (in the stream). The only exception may be a study by Gentry et al. [17], where the authors include both in-stream and tile drain measurements of NO_3^- concentration and flux in a mass balance study for a small first order agricultural watershed in Illinois, USA.

This lack of integration across scales strongly limits our ability to generalize results obtained at the plot scale to whole watersheds. It also limits our ability to understand how overland flow, when it occurs, affects stream water quality, and whether the relationship between tile drain N losses and stream N losses is affected by the occurrence of overland flow (OLF). Indeed, although OLF is often considered to be a negligible source of NO_3^- to streams because NO_3^- is highly soluble and primarily found in the subsurface in agricultural watersheds, it potentially can impact ammonium (NH_4^+) losses to streams as NH_4^+ tends to adsorb to negatively charged soil particles often exported as overland flow [5]. In agricultural watersheds, NH_4^+ often represents a small fraction of N losses to tile drains (<7%) [9], but NH_4^+ is important in regulating stream metabolism as NH_4^+ concentrations in Midwestern streams impact stream biotic integrity and algae dynamics [18].

In addition to better understanding how to scale up knowledge obtained at the plot scale to the watershed scale, there is also a need to better quantify NO_3^- and NH_4^+ losses to streams during storms in terms of not only concentrations, but also fluxes. Although NO_3^- and NH_4^+ concentrations are important, a better characterization of NO_3^- and NH_4^+ losses both as specific fluxes (i.e. g N/ha/storm) and specific yields (g N/ha/hr) is needed to understand how NO_3^- and NH_4^+ losses to streams and tile drains might change in the coming years in response to changes in precipitation characteristics and antecedent moisture conditions. Several studies report N losses on an annual basis [2,3,6], but few report NO_3^- and NH_4^+ fluxes during storms. With the exception of a few studies that report NO_3^- and NH_4^+ fluxes in tile drains or streams during storms in tile drained landscapes [7-9], those that do report N losses to stream during storms often focus in other regions (e.g. Western New York, Oregon) [11,19].

In order to address some of these gaps in knowledge, this study investigates NO_3^- and NH_4^+ dynamics (concentration and flux) in two adjacent tile drains, stream water (watershed outlet), and overland flow for 7 storms in Leary Weber Ditch watershed, a 7.2 km² watershed representative of tile drained agroecosystems of the US Midwest. We address three key questions: 1) To what extent can we use precipitation amount and antecedent moisture conditions in the watershed to estimate NO_3^- and NH_4^+ losses (both concentrations and fluxes) to the stream and tile drains? 2) Does overland flow matter for N exports? 3) Are NO_3^- and NH_4^+ concentrations, concentration patterns, and fluxes observed in tile drains similar to those observed in the stream during storms? The implications of these results for watershed management are discussed.

2. MATERIALS AND METHODS

2.1. Site Description

Leary Weber Ditch Watershed (LWD) (7.2 km²) is located in the larger Sugar Creek watershed, approximately 20 km east of Indianapolis, Indiana (Fig. 1). Climate at the site is classified as temperate continental and humid. The average annual temperature for central Indiana is 11.7°C with an average January temperature of -3.0°C and an average July temperature of 23.7°C. The long-term average annual precipitation (1971-2000) is 100 cm [20]. Soils in the watershed are dominated by well-buffered poorly drained loams or silt loams, and typically belong to the Crosby-Brookston association. Crosby-Brookston soils generally are deep, very poorly drained to somewhat poorly drained with a silty clay loam texture in the first 30 cm of the soil profile. Soils in LWD are suited for row crop agriculture such as corn and soybean but require artificial drainage to lower the water table, removing ponded water, adding nutrients and ensuring good soil tilth. Conventional tillage and a corn/soybean rotation has been implemented consistently for the last 20 years in LWD.

Each year, approximately 50% of the watershed is corn, and the remaining portion is soybean. Soybean is generally planted in early May, and glyphosate is applied mid-May. Phosphorus application on soybean generally averages 112 kg ha⁻¹ yr⁻¹. For corn, fertilizer as anhydrous ammonia generally is applied in spring at a rate of 180 kg N ha⁻¹ yr⁻¹ and herbicides atrazine and acetochlor are generally applied mid-May. Potash

(K₂O) is applied post-harvest on soybean fields at a rate of approximately 220 kg ha⁻¹. LWD (87% row crop, 6% pasture, 7% non-agricultural land use) was chosen by the US Geological Survey for their National Water Quality Assessment Study to represent a typical agricultural watershed of the US Midwest [21]. It represents agricultural watershed of the US Midwest where poorly drained soils dominate, and where artificial drainage is commonly used to lower the water table [22].

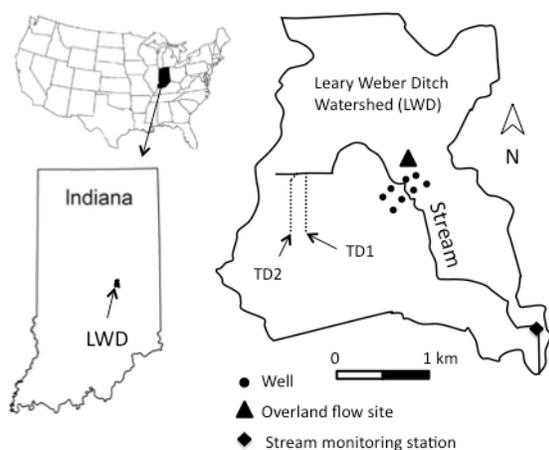


Figure 1 Experimental site location. TD1 and TD2 correspond to the two tile drains (TD) monitored for this study in 2009 and 2010.

2.2. Hydrological Measurements

A total of 7 storms were monitored between November 2008 and May 2010. Over the study period, the majority of storms generating a clear increase in discharge in this watershed occurred in late winter and spring (March through June each year) when the soil was bare or when crops were just starting to grow (Figure 2). Bulk precipitation for the storms studied was measured using a network of 7 rain gauges distributed throughout the watershed. The two tile-drains monitored for this study (TD1 and TD2) are located in the headwaters of the watershed (Figure 1). Each tile-drain is 20.3 cm in diameter and located approximately 120 cm below the ground surface. TD1 extends 660 m from the stream and drains an area approximately 8.1 ha in size [5]. TD2 extends 710 m from the stream and drains an area approximately 6.1 ha in size [5].

Each tile drain was equipped with a Doppler velocity meter (ISCO 2150) for continuous discharge measurements, and an In-Situ LTC probe (level-

temperature-conductivity). The occurrence of overland flow (yes/no) was measured using a H-flume inserted into the ground, equipped with an In-Situ LT (level-temperature) logger (In-Situ Inc.). Stream stage at the outlet of the watershed was measured using an In-Situ LTC probe (In-Situ Inc.). Discharge was measured biweekly using a handheld Doppler velocity meter (Sontek) to establish a rating curve. A total of 8 riparian zone wells (2 inches in diameter, 2 m deep) were also installed between the field edge and the stream to capture antecedent water table depth at the field edge before each storm, as well as riparian groundwater quality.

For this study, the start of each event was defined when a perceptible rise in discharge in the stream was observed. The end of the event was defined when flow in the stream stabilized or when a new event started, whichever occurred first. Seven and fourteen day antecedent discharges (7dQ and 14dQ, respectively) in the stream were calculated as the mean discharge during the 7 and 14 days preceding each event.

2.3. Water Chemistry

Water samples for NO₃⁻ and NH₄⁺ analysis were collected in tile drains TD1 and TD2, in overland flow (if any), and in the stream using auto samplers (ISCO 6712). In tile drains, the sample collection line from each ISCO sampler was located at least 1m into the tile-drains, and Doppler velocity measurements confirmed that no flow reversals occurred in the tile-drains during the storms studied, therefore indicating that tile samples were not contaminated by stream water when the tiles were submerged during storms. Samplers used to collect water samples in the stream and the two tile drains were triggered manually before the beginning of each storm and generally set to collect water samples every 20 minutes during the rising limb of the hydrograph or the first 24 hours of the storm. Each 1L sample was a composite of 3 samples taken 20 minutes apart (1 bottle per hour = 24 hours). The sampling interval was extended to 2 hours (3 samples taken 40 minutes apart per bottle) on the falling limb of the hydrograph. Although all water samples collected on the rising limb of the hydrograph and around peak flow were analyzed, not all samples were necessarily analysed on the falling limb of each hydrograph to limit cost. Additional water samples were also collected in riparian groundwater wells (immediately before each storm) and in rain gauges (immediately after each storm) to measure riparian and precipitation water chemistry for each of the storms studied.

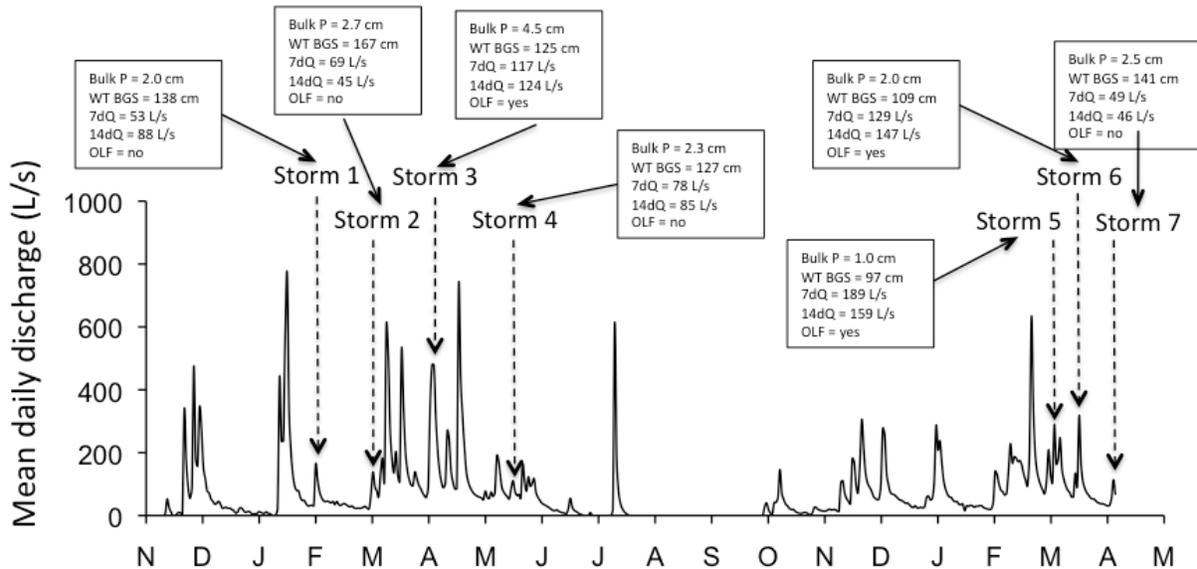


Figure 2 Mean daily discharge (L/s) in the stream at the outlet of the study watershed (Leary Weber Ditch) between November 2008 and May 2010. Storm 1 (Feb. 26, 2009), storm 2 (Apr. 1, 2009), storm 3 (Apr. 29, 2009), storm 4 (Jun. 11, 2009), storm 5 (Mar. 29, 2010), storm 6 (Apr. 8, 2010), and storm 7 (April 26, 2010) are the storms during this period for which water samples were collected in the watershed. Bulk precipitation amounts (Bulk P), antecedent water table depth below ground surface (WT BGS), 7-day antecedent discharge (7dQ), 14-day antecedent discharge (14dQ), and the occurrence of overland flow (OLF) are also indicated for each storm.

Water samples were never left more than 24 hours in the field and were immediately filtered using GF/F Whatman 0.7 μm filter upon return to the laboratory. Triplicate analysis of 10% of all samples and analysis of check standards every 10 samples were performed to assess measurement error, and check for the accuracy and precision of measurement techniques. The standard error on reported solute values was typically less than 10% for all solutes. Both NO_3^- and NH_4^+ concentrations were determined colorimetrically using standard methods [23] on a Konelab 20 Photometric Analyzer (EST Analytical).

Solute fluxes in gram of N per storm were calculated for each storm by first multiplying the concentration of the sample for each sampling interval (mg N /L) by the average discharge for that interval (L/s) and a unit conversion factor. Fluxes reported here in g N/ha/storm were obtained by dividing the solute flux for each storm (g N/storm) by the contributing area to each tile-drain (m^2) or the stream (m^2) and a unit conversion factor. Solute export yields (g N/ha/hr) before each storm are calculated as the flux in the hour preceding the beginning of the storm. Solute export yields (g N/ha/hr) during storms are

calculated as the average hourly solute fluxes over the duration of the storm.

When means for two groups are compared to establish significant differences between groups, unpaired t-test assuming equal variance, with a 95% confidence interval, were used. The significance of correlation coefficients between variables in two independent groups were calculated using the correlation coefficient, and the number of variables in each group. For all tests, significance was established at $p < 0.05$. All calculations were performed in GraphPad Software,

3. RESULTS

As indicated on Figure 2, overland flow occurred for storms 3, 5 and 6, and was associated with higher 7 day (7dQ > 117 L/s) and 14 day (14dQ > 124 L/s) antecedent flow conditions than for any of the other storms (7dQ < 78 L/s, 14dQ < 88 L/s). Antecedent water table (WT) depth in centimeters below ground surface (cm BGS) was also higher for storm 3, 5, 6 (WT < 125 cm BGS) than for storms 1, 2, 4, and 7

(WT > 127 cm BGS). However, bulk precipitation (Bulk P) was not consistently higher for storms 3, 5 and 6 (1.0 cm < Bulk P < 4.5 cm) than for the other storms (2.0 < Bulk P < 2.7 cm). Mean daily flow was higher for storms with high antecedent moisture conditions and overland flow (i.e. storms 3, 5 and 6), than for those without overland flow and lower antecedent moisture conditions, as indicated by lower 7dQ and 14dQ (i.e. storms 1, 2, 4, and 7) (Figure 2).

Mean NO₃⁻ and NH₄⁺ concentrations before and during storms 1-7 throughout the watershed are shown in Tables 1 and 2. Variability in NO₃⁻ and NH₄⁺ concentrations during the storms is shown in the chemographs (Figures 3 and 4); consequently, only mean concentration values immediately before and during storms 1-7 are presented in this section. Before the beginning of each storm, average mean NO₃⁻ concentration in TD1 and/or TD2 (if flowing) (10.35 mg N/L) was 3.64 mg N/L higher than in the stream (6.71 mg N/L), and two orders of magnitude higher than in the riparian zone (0.81 mg N/L). Similarly, average mean NO₃⁻ concentration in tile drains during storms (10.38 mg N/L) was higher than in the stream (7.50 mg N/L). NO₃⁻ concentrations in precipitation and overland flow were low (< 1.1 mg N/L), except in overland flow for storm 3 where nitrate concentrations were high at 10.02 mg N/L (stdev = 3.15, n = 10). When storms were compared, some of the highest

NO₃⁻ concentrations were consistently observed for storms 3 and 4 in TD1, TD2, and the stream (Table 1).

Unlike NO₃⁻ concentrations, average pre-storm NH₄⁺ concentrations were higher in the stream (0.06 mg N/L) than in tile drains (0.04 mg N/L), and were higher in riparian groundwater (0.14 mg N/L) than in either the stream or tile drains before the storms. During storms, mean NH₄⁺ concentrations varied from storm to storm, but were not, on average, significantly greater (p>0.05) in the stream (0.06 mg N/L) than in tile drains (0.05 mg N/L). Mean NH₄⁺ concentrations in overland flow were similar for storm 5 and lower for storm 6 than those in tile drains or the stream, but were significantly higher (p<0.05) (0.74 mg N/L) than mean NH₄⁺ concentration in either the stream or tile drains for storm 3. When storm and pre-storm NH₄⁺ concentrations were compared, mean stream NH₄⁺ concentrations were, on average, similar before and during the storms (NH₄⁺ = 0.06 mg N/L both before and during storms). In tile drains, mean NH₄⁺ concentrations were slightly higher (but not significantly, p>0.05) during the storms (0.05 mg N/L) than immediately prior to each storm (0.04 mg N/L). When storms were compared, highest NH₄⁺ concentrations were observed during and immediately before storm 4 in tile drains. In the stream, highest NH₄⁺ concentrations during storms occurred during storm 6.

Table 1 Mean NO₃⁻ concentrations before storm 1 (Feb. 26, 2009), storm 2 (Apr. 1, 2009), storm 3 (Apr. 29, 2009), storm 4 (Jun. 11, 2009), storm 5 (Mar. 29, 2010), storm 6 (Apr. 8, 2010), and storm 7 (April 26, 2010) in the stream, tile drain 1 (TD1), tile drain 2 (TD2), and riparian groundwater (RZ). Mean NO₃⁻ concentrations during storms 1-7 in precipitation, the stream, TD1, TD2, and overland flow (OLF) are also indicated. Values in parenthesis indicate one standard deviation. (n/a = not available).

Mean NO ₃ ⁻ (mg N/L)	Pre-storm				During storm				
	Stream	TD1	TD2	RZ	Precip.	Stream	TD1	TD2	OLF
Storm 1	5.27 (0.66)	n/a	9.11 (0.43)	2.92 (5.00)	0 (n/a)	7.16 (1.08)	n/a	8.72 (1.51)	-
Storm 2	5.56 (0.71)	9.20 (0.02)	n/a	0.18 (0.49)	1.03 (n/a)	5.99 (0.65)	10.33 (0.41)	n/a	-
Storm 3	9.52 (0.54)	14.26 (0.65)	15.14 (0.53)	0.66 (0.54)	0.87 (n/a)	8.32 (1.35)	13.96 (2.06)	14.40 (1.48)	10.02 (3.15)
Storm 4	7.31 (0.23)	10.56 (0.15)	12.02 (0.41)	0.45 (0.17)	0.68 (n/a)	8.95 (0.81)	12.08 (0.65)	12.17 (0.76)	-
Storm 5	7.83 (0.43)	9.14 (1.71)	9.46 (0.21)	0.75 (1.02)	0.82 (n/a)	8.04 (0.39)	9.58 (0.83)	9.96 (0.63)	0.27 (0.04)
Storm 6	5.76 (0.67)	8.61 (0.50)	No flow	0.34 (0.19)	0.34 (n/a)	6.70 (0.54)	7.75 (0.66)	8.49 (0.43)	0.30 (0.09)
Storm 7	5.72 (0.14)	No flow	No flow	0.38 (0.13)	0.93 (n/a)	7.32 (0.91)	8.41 (0.90)	8.71 (0.92)	-

Table 2 Mean NH_4^+ concentrations before storm 1 (Feb. 26, 2009), storm 2 (Apr. 1, 2009), storm 3 (Apr. 29, 2009), storm 4 (Jun. 11, 2009), storm 5 (Mar. 29, 2010), storm 6 (Apr. 8, 2010), and storm 7 (April 26, 2010) in the stream, tile drain 1 (TD1), tile drain 2 (TD2), and riparian groundwater (RZ). Mean NH_4^+ concentrations during storms 1-7 in precipitation, the stream, TD1, TD2, and overland flow (OLF) are also indicated. Values in parenthesis indicate one standard deviation. (n/a = not available).

Mean NH_4^+ (mg N/L)	Pre-storm				During storm				
	Stream	TD1	TD2	RZ	Precip.	Stream	TD1	TD2	OLF
Storm 1	0.04 (0.01)	n/a	0.02 (0.01)	0.20 (0.22)	0.47 (n/a)	0.03 (0.01)	n/a	0.02 (0.01)	-
Storm 2	0.06 (0.01)	0.03 (0.02)	n/a	0.16 (0.13)	0.34 (n/a)	0.05 (0.02)	0.02 (0.01)	n/a	-
Storm 3	0.03 (0.01)	0.02 (0.02)	0.02 (0.01)	0.10 (0.08)	0.99 (n/a)	0.06 (0.04)	0.03 (0.02)	0.03 (0.03)	0.74 (0.41)
Storm 4	0.09 (0.03)	0.10 (0.00)	0.09 (0.03)	0.13 (0.03)	0.80 (n/a)	0.07 (0.03)	0.17 (0.20)	0.07 (0.05)	-
Storm 5	0.05 (0.02)	0.03 (0.01)	0.04 (0.01)	0.09 (0.06)	0.66 (n/a)	0.05 (0.02)	0.05 (0.03)	0.04 (0.01)	0.05 (0.03)
Storm 6	0.07 (0.01)	0.02 (0.00)	No flow	0.11 (0.08)	0.34 (n/a)	0.08 (0.04)	0.05 (0.02)	0.06 (0.03)	0.03 (0.01)
Storm 7	0.09 (0.02)	No flow	No flow	0.16 (0.08)	0.26 (n/a)	0.06 (0.02)	0.04 (0.01)	0.04 (0.01)	-

High temporal resolution NO_3^- and NH_4^+ concentration patterns in relation to stream flow are shown for storms 1-7 on Figures 3 and 4. For storm 1, NO_3^- concentrations in TD2 (TD1 not available) decreased as stream flow peaked, while NO_3^- concentrations in the stream progressively increased as storm 1 progressed. For storms 2, 4, 5, 6, and 7, NO_3^- concentrations were consistently higher in tile drains than in the stream, and showed no clear dilution or concentration pattern as a function of flow for these storms. For storm 3, equipment malfunction did not allow us to continuously sample TD1 and TD2 during the second peak in discharge. However, grab samples in both TD1 and TD2 were collected during the second peak in discharge in the stream. For this storm, a brief decrease in NO_3^- concentration in tile drains was observed during the first peak in discharge, and grab samples suggested a sharp decrease in NO_3^- concentration as stream flow peaked during the second peak in discharge. In the stream itself, a progressive decrease in NO_3^- concentration from approximately 10 mg/L at the onset of the storm to approximately 8 mg/L at the end was observed, but this change in concentration was not associated with rapid changes in NO_3^- concentration as stream flow peaked during the storm (Figure 3).

Relative to NO_3^- concentrations, NH_4^+ concentrations were more variable. For storms 1, 5, and 7, no clear concentration or dilution patterns were observed

for NH_4^+ as stream flow peaked in either the stream or the tile drains. For storm 2, 3, and 6, stream NH_4^+ concentrations clearly increased as discharge peaked, but no consistent concentration or dilution patterns were observed for NH_4^+ in either TD1 or TD2 for these storms. Storm 4 was unique in that no strong increase in NH_4^+ concentration was observed in the stream or TD2 as stream flow peaked, whereas a sharp increase in NH_4^+ concentration was observed on the rising limb of the stream hydrograph in TD1.

Expectedly, NO_3^- and NH_4^+ specific fluxes (g N/ha/storm) vary widely as a function of flow conditions in the stream and tile drains (Table 3). Highest stream NO_3^- fluxes occurred during storms 3, 5 and 6, with a maximum flux of 1121 g N/ha in the stream for storm 3. In tile drains, the two highest NO_3^- fluxes were recorded for storm 3 in TD1 (1710 gN/ha) and TD2 (1758 gN/ha), respectively. NH_4^+ fluxes in the stream and tile drains were also generally highest for storms 3 (11.5 g N/ha in the stream, 5.3-5.5 g N/ha in tile drains) (the only exception is in TD1 for storm 4). In both the stream and tile drains, inter-storm variability was high, with NO_3^- and NH_4^+ fluxes varying by approximately one order of magnitude between storms 1-2 (small fluxes), and storm 3 (largest fluxes) (Table 3).

When tile drains and the stream were compared, specific NO_3^- fluxes were, on average, 1.9 times higher in tile drains than in the stream. On the other

hand, NH_4^+ fluxes were slightly lower (0.9 time) in tile drains than in the stream. From a mass balance / flux perspective, NH_4^+ represented between 0.50% and 1.39% of dissolved inorganic nitrogen (DIN) fluxes (i.e. sum of NO_3^- and NH_4^+ fluxes) in the

stream depending on the storm (across storm average = 0.82%). In tile drains, NH_4^+ fluxes represented between 0.18% and 1.30% of DIN fluxes (across storm average = 0.47%).

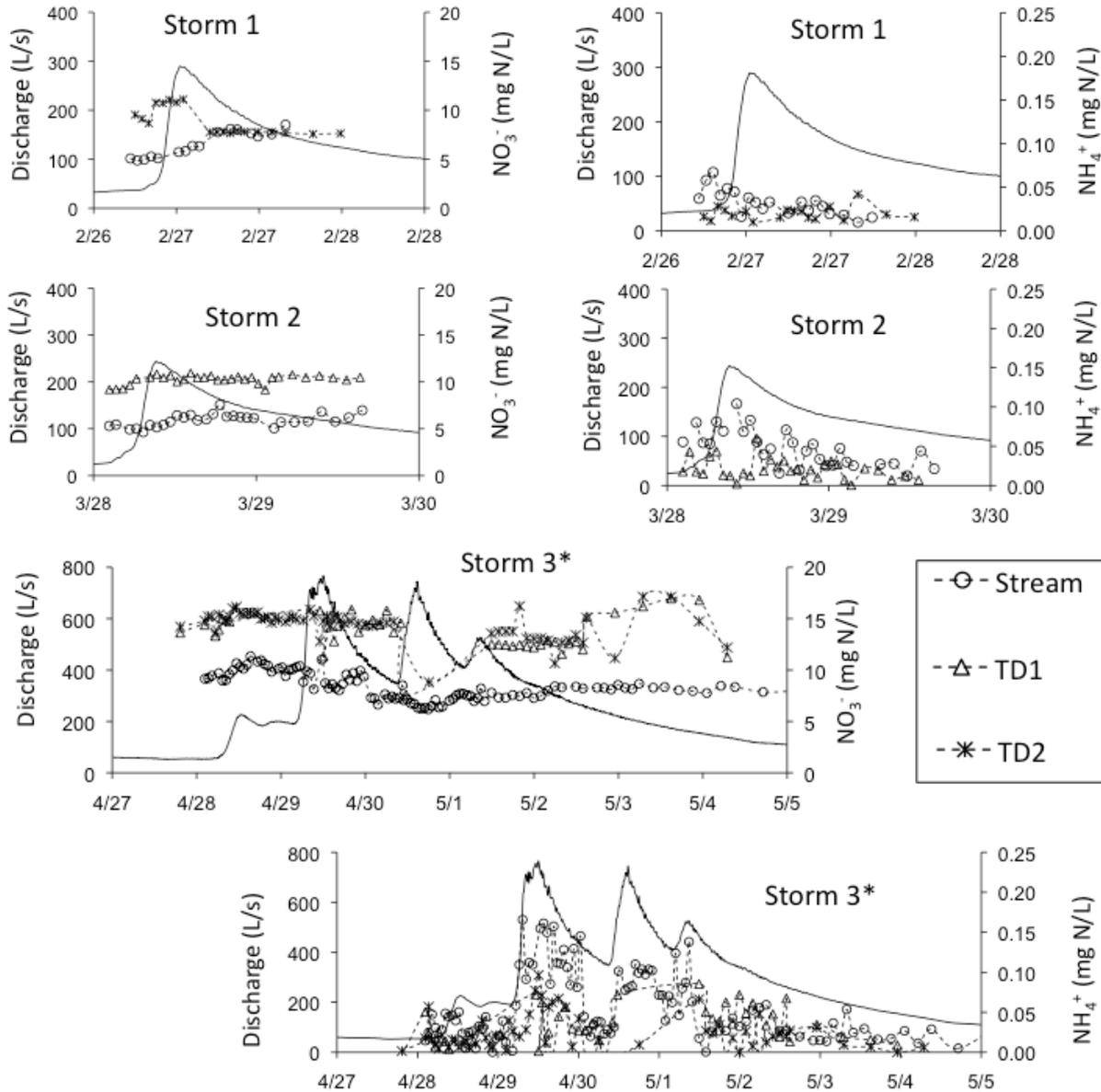


Figure 3 Stream discharge (L/s) (solid line), and nitrate (NO_3^-) and ammonium (NH_4^+) concentrations in the stream (watershed outlet) and in tile drain 1 (TD1) and tile drain 2 (TD2) for storms 1, 2 and 3. (* = Equipment malfunction did not allow for sample collection to occur where data points are missing in tile drains).

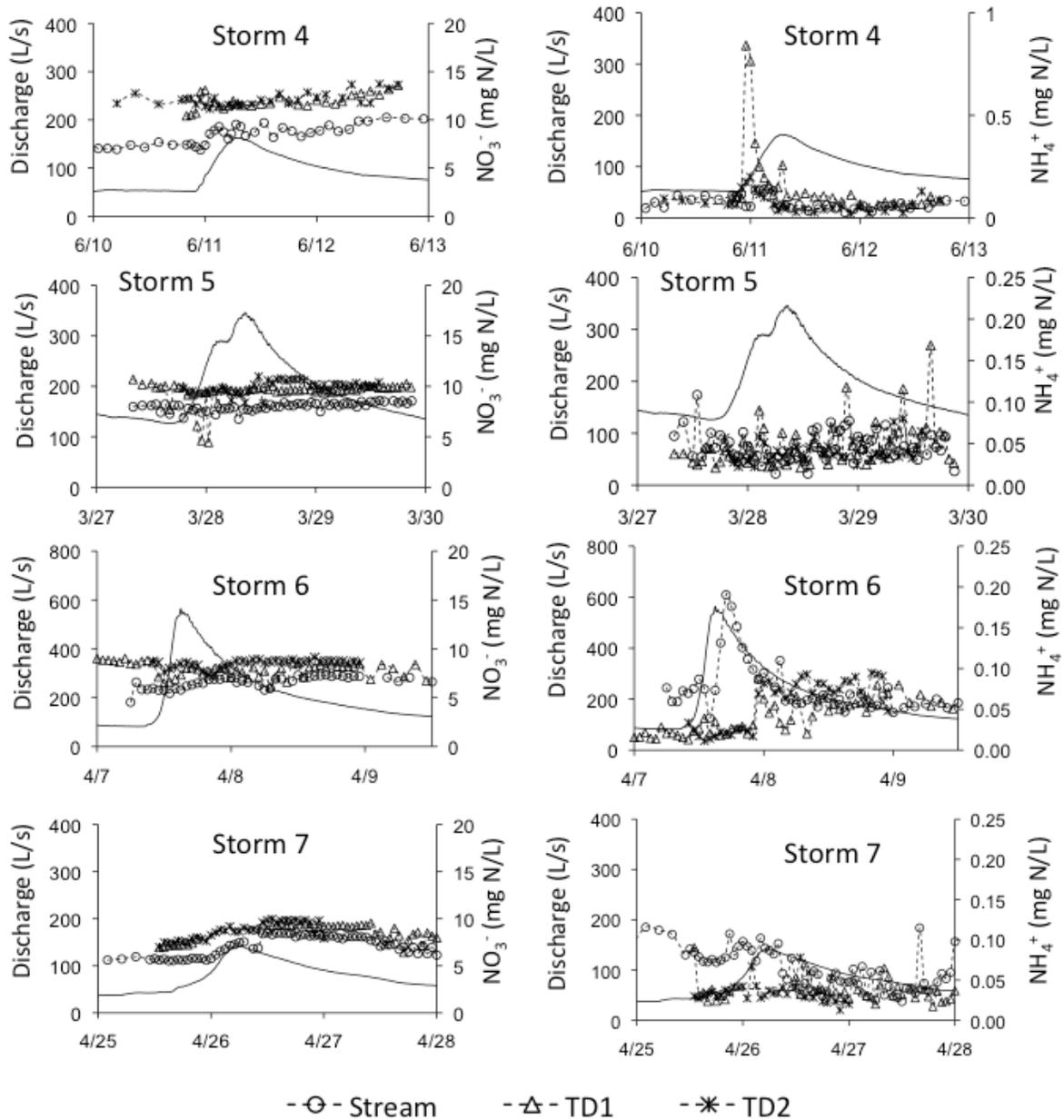


Figure 4 Stream discharge (L/s) (solid line), and nitrate (NO₃⁻) and ammonium (NH₄⁺) concentrations in the stream (watershed outlet) and in tile drain 1 (TD1) and tile drain 2 (TD2) for storms 4, 5, 6 and 7.

NO₃⁻ and NH₄⁺ yields (g N/ha/hr) were also calculated to quantify changes in NO₃⁻ and NH₄⁺ export yields in the stream before and during the storms. Because tile drains were rarely flowing before the storms, pre-storm NO₃⁻ and NH₄⁺ yields were not calculated in tile drains. On average, NO₃⁻ yields in the stream were 3 times larger during storms than in the hour preceding the beginning of the storm. When

all the storms were considered, NO₃⁻ yields were approximately 2 times higher in tile drains than in the stream. Stream NH₄⁺ yields were on average 3 times larger during storms, than immediately before each storm. However, unlike NO₃⁻, NH₄⁺ yields during the storms were not significantly different (p>0.05) between the stream and the tile drains studied.

Table 3 Nitrate (NO_3^-) and ammonium (NH_4^+) fluxes (g N/ha/storm) and yields (g/ha/hr) for storm 1 (Feb. 26, 2009), storm 2 (Apr. 1, 2009), storm 3 (Apr. 29, 2009), storm 4 (Jun. 11, 2009), storm 5 (Mar. 29, 2010), storm 6 (Apr. 8, 2010), and storm 7 (April 26, 2010) in tile drain 1 (TD1), tile drain 2 (TD2), and the stream (watershed outlet). (Note: Fluxes in TD 1 and TD2 for storm 7 were not calculated because discharge data in these tile drains were not available for this storm).

	Nitrate Flux in g N/ha/storm				Ammonium Flux in g N/ha/storm			
	Stream (base flow)	Stream (storm flow)	TD1	TD2	Stream (base flow)	Stream (storm flow)	TD1	TD2
Storm 1		157	n/a	350		0.8	n/a	0.8
Storm 2		146	290	n/a		1.1	0.5	n/a
Storm 3		1121	1710	1758		11.5	5.3	5.5
Storm 4		255	367	422		1.8	7.2	3.2
Storm 5		388	457	734		2.1	2.2	3.0
Storm 6		323	548	865		4.5	2.4	3.2
Storm 7		189	n/a	n/a		1.6	n/a	n/a

	Nitrate Yield in g N/ha/hr				Ammonium Yield in g N/ha/hr			
	Stream (base flow)	Stream (storm flow)	TD1	TD2	Stream (base flow)	Stream (storm flow)	TD1	TD2
Storm 1	0.91	4.66	n/a	10.87	0.01	0.02	n/a	0.02
Storm 2	0.72	4.30	7.54	n/a	0.01	0.03	0.01	n/a
Storm 3	4.17	16.42	30.95	31.26	0.02	0.17	0.10	0.10
Storm 4	1.97	4.82	7.93	9.07	0.03	0.04	0.16	0.07
Storm 5	5.16	8.58	9.94	17.79	0.04	0.05	0.05	0.07
Storm 6	2.86	8.57	9.29	21.77	0.03	0.12	0.04	0.08
Storm 7	1.29	3.20	n/a	n/a	0.02	0.03	n/a	n/a

4. DISCUSSION

All monitored storms occurred between late winter and late spring. Indeed, high stream flow events in summer months were rare (Figure 2), and previous work has shown that even large precipitation events (> 3 cm bulk precipitation) often do not generate significant stream or tile flow response in summer and fall in this type of watershed (July through November) [3, 7]. Most nitrogen losses to streams in the US Midwest also occur in late winter and spring, and spring nitrogen losses to the MRB have been linked to the development of hypoxic zones in the Gulf of Mexico in summer [1, 6]. Finally, below freezing temperatures and/or significant snow cover between December and early February each year also made it impossible to efficiently operate the ISCO samplers for water sampling. Nevertheless, in spite of the limited seasonal coverage offered, this study is one of the first to simultaneously document NO_3^- and NH_4^+

concentrations, concentration patterns, and fluxes (both in g N/ha/storm and g N/ha/hr) in tile drain flow, stream flow, and overland flow. It provides a unique opportunity to thoroughly analyze the dynamics of NO_3^- and NH_4^+ throughout the study watershed at a high temporal resolution during spring storms.

4.1. Dataset Validation

Morgan et al. [24] report mean stream nitrogen concentrations between 5.5-8.8 mg N/L for NO_3^- and 0.02-0.06 mg N/L for NH_4^+ between December and March for 5 streams in Illinois. Although seasonal mean concentrations are not directly comparable to event flow concentrations, these values are overall consistent with those reported in Tables 1 and 2 for NO_3^- and NH_4^+ . In Iowa, Schilling et al. [25] report NO_3^- concentrations within the 8-14 mg N/L range between March and July in Walnut Creek, Iowa, while Wagner et al. [26] report maximum concentrations in

an Indiana agricultural stream during storms between 8.5-14.33 mg N/L. These seasonal and maximum NO_3^- concentrations are consistent with the mean (Table 1) and maximum (Figures 3 and 4) stream NO_3^- concentrations reported in this study.

Nitrate and NH_4^+ concentrations in overland flow, precipitation, and in the riparian zone are also consistent with those reported elsewhere. For instance, Schilling et al. [25] report NO_3^- concentrations < 2 mg N/L in a riparian zone in Walnut Creek, Iowa. In LWD, Baker et al. [5] report NO_3^- concentration < 0.1 mg N/L in overland flow and precipitation. The only “abnormal” concentrations reported in this study are the extremely high NO_3^- and NH_4^+ concentrations in overland flow for storm 3 on April 29, 2009 (mean NO_3^- = 10.2 mg N/L, stdev = 3.15, n = 10; and mean NH_4^+ = 0.74 mg N/L, stdev = 0.41, n = 10). No clear explanation could be established for these larger-than-normal concentrations in both NO_3^- and NH_4^+ in overland flow for this storm; however, soils are generally ploughed in late April, which could have brought up NO_3^- and NH_4^+ rich soil near the surface, and could explain the extremely large NO_3^- and NH_4^+ concentrations observed in overland flow for this storm.

Storm 3 being the largest of the storms studied, it is also possible that the large NO_3^- and NH_4^+ concentrations in overland flow for this storm were simply the result of tile water rising to the soil surface as the soil became saturated during storms. Recent fertilizer applications as anhydrous ammonia could also have contributed to these high NO_3^- and NH_4^+ concentrations.

The lack of clear NO_3^- concentration patterns during storms (Figures 3 and 4) is also consistent with data reported by Vanni et al. [27], who observed no consistent dilution or concentration patterns as a function of flow for NO_3^- . Wagner et al. [26] also report a lack of consistent dilution or concentration patterns for NO_3^- in Indiana streams during storms. In tile drains, Cuadra and Vidon [9] report a dilution of NO_3^- concentration in tile flow during storms, but only for storms associated with precipitation event generating more than 6 cm in bulk precipitation. For storms generating less than 6 cm of bulk precipitation (like those presented here), no clear concentration or dilution patterns were observed [9].

Few studies report NO_3^- and NH_4^+ fluxes on a individual storm basis. In a small watershed (2.7 km²) similar in land use to LWD, MacRae et al. [8] report NO_3^- fluxes between almost 0 g N/ha/storm and approximately 3500 g N/ha/storm for storms ranging from 1 to 5 cm in bulk precipitation, with most values

varying between approximately 100-1200 g N/ha/storm. For our storms (1.0 - 4.5 cm in bulk precipitation), NO_3^- fluxes in the stream vary between 146-1121 g N/ha/storm, which is consistent with results reported in MacRae et al. [8]. Similarly, Cuadra and Vidon [9] report fluxes between 730-1994 g N/ha/storm for NO_3^- and 1-115 g N/ha/storm for NH_4^+ in tile drains in LWD for a series of storms in 2008. Although fluxes reported here (Table 3) in tile drains for NO_3^- (290-1758 g N/ha/storm) and NH_4^+ (0.5-7.2 g N/ha/storm) are lower (especially for NH_4^+) than those reported in Cuadra and Vidon [9], storms 1-7 were also smaller (1.0-4.5 cm bulk precipitation) than those analyzed in that study (2.2-10.8 cm bulk precipitation).

4.2. Impact of Storm Characteristics and Antecedent Moisture Conditions on N Dynamics, and Role of Overland Flow in Regulating N Losses to the Stream

For the storms studied, antecedent moisture conditions (i.e. antecedent water table depth, 7dQ, 14dQ) (Figure 2) and bulk precipitation both appear to be important in regulating NO_3^- and NH_4^+ fluxes at the watershed scale. Indeed, the highest fluxes (for both the stream and tile drains) do occur for storm 3, the storm with both the highest antecedent moisture conditions, and the highest amount of bulk precipitation (Figure 2). Further, although antecedent water table depth, 7dQ, or 14dQ (from Figure 2) are not significantly correlated to NO_3^- and NH_4^+ fluxes (from Table 3) ($p > 0.05$), when all the storms are considered, overland flow, highest daily discharges, and highest stream NO_3^- and NH_4^+ fluxes, all occur for storms 3, 5, 6, that are the three storms with the wettest antecedent moisture conditions (Figure 2). Furthermore, there is a significant positive correlation between bulk precipitation and both NO_3^- fluxes ($r = 0.72$, $p < 0.05$) and NH_4^+ fluxes ($r = 0.77$, $p < 0.05$) in the stream for the 7 storms studied. This suggests that both bulk precipitation and to a lesser extent antecedent moisture conditions are important in regulating NO_3^- and NH_4^+ fluxes. This is consistent with results previously reported in the watershed where Cuadra and Vidon [9] indicate that both bulk precipitation and antecedent moisture conditions are important in regulating NO_3^- and NH_4^+ fluxes.

Unlike fluxes, mean NO_3^- and NH_4^+ concentrations are however not consistently higher for storms 3, 5, and 6 than for the other storms associated with drier antecedent moisture conditions (i.e. storms 1, 2, 4 and 7). These concentrations are also not

significantly correlated ($p > 0.05$) to bulk precipitation. This is consistent with the highly variable NO_3^- and NH_4^+ concentration patterns observed during the 7 storms studied (Figures 3 and 4). Overall, data therefore suggest that although precipitation amounts and antecedent flow conditions do not seem to have a significant impact on mean NO_3^- or NH_4^+ concentrations and concentration patterns as a function of flow, there is a positive association between bulk precipitation and antecedent moisture conditions, and NO_3^- and NH_4^+ fluxes for the range of storm studied (1.0-4.5 cm bulk precipitation).

With respect to the impact of overland flow on N losses to the stream, data indicate that although overland flow did occur for the three storms for which the highest stream NO_3^- and NH_4^+ fluxes were observed, overland flow likely did not play a major role in regulating NO_3^- and NH_4^+ concentrations or fluxes in the stream. For instance, for storm 3 during which NH_4^+ concentrations in overland flow were one order of magnitude higher than in the stream, NH_4^+ concentrations in the stream were not consistently higher than for other storms (Table 2). Similarly, although stream NO_3^- varies from storm to storm, stream NO_3^- concentrations during storms with overland flow were not consistently higher or lower than for storms without overland flow (Table 1).

4.3. Relationship between N Exports in Tile Drains and the Stream

A detailed analysis of NO_3^- and NH_4^+ concentration patterns indicates that mean NO_3^- concentrations are consistently lower in the stream than in tile drains, but that mean NH_4^+ concentrations in the stream and tile drains are not significantly ($p > 0.05$) different during storms. Consistent with these findings, specific NO_3^- fluxes were, on average, 1.9 times higher in tile drains than in the stream. However, NH_4^+ fluxes were slightly lower in tile drains than in the stream. With the exception of Gentry et al. [17], few studies directly quantify these differences in a systematic way for a series of storms. Few studies, if any, also include NH_4^+ in this analysis. This lack of empirical information linking NO_3^- and NH_4^+ dynamics in tile drains and streams strongly limits our ability to extrapolate plot scale data [3, 9] to watershed scale data [6, 18, 25]. As previously indicated, although individual NO_3^- concentration patterns in TD1, TD2 and the stream vary during storms, mean NO_3^- concentrations in tile drains are, on average, 2.88 mg N/L higher than in the stream during storms, or 28% lower in the stream than in tile drains. This difference

in mean NO_3^- concentration between tile drains and stream can be partially explained by differences in land-use between the contributing area to tile drains (100% corn and/or soybean) and the contributing area to the stream outlet (87% row crop, 6% pasture, 7% non-agricultural land use). Lower NO_3^- concentrations in the stream than in tile drains are also consistent with the mixing of tile water (high in NO_3^-) in the stream with other water sources low in NO_3^- , such as riparian water (mean $\text{NO}_3^- = 0.81$ mg N/L) (Table 1). The lack of significant difference between NH_4^+ concentrations in the stream and in tile drains is also consistent with this explanation, as NH_4^+ concentrations in riparian water are slightly higher than in the stream (as opposed to consistently lower like for NO_3^-) (Table 2). Biological N uptake in the stream is very unlikely to contribute to the differences in NO_3^- concentrations between the stream and tile drains because biological N uptake, if any, should affect both NO_3^- and NH_4^+ (not just NO_3^-). Further, stream flow and stream velocity are generally considered to be too high during storms to allow for hyporheic processes and biological N uptake in the stream to significantly impact water quality [12].

4.4. Implications for Watershed Management and Conclusions

Storm NO_3^- and NH_4^+ concentrations are not significantly correlated to bulk precipitation or antecedent moisture conditions in the watershed. However, by affecting stream flow dynamics during storms, bulk precipitation and to some extent antecedent moisture conditions do impact NO_3^- and NH_4^+ fluxes. Interestingly, NO_3^- fluxes (g N/ha/storm) (Table 3) are also significantly positively correlated with NO_3^- concentrations in the stream at base flow (Table 1) ($r = 0.87$, $p < 0.05$). NH_4^+ fluxes are however not significantly correlated to mean NH_4^+ concentrations at base flow ($r = -0.50$, $p > 0.05$). From a watershed management perspective, this suggests that although NO_3^- fluxes are clearly linked to flow conditions in the stream, with high NO_3^- fluxes for storms generating high discharges (albeit because of high antecedent moisture conditions or high precipitation amounts), the total NO_3^- flux in the stream during storms is still highly dependant upon the NO_3^- concentration in the stream at base flow.

The implications of this observation for watershed management are twofold. First, as continuous discharge measurements become more common, stream flow information often is available throughout the year in many rivers and streams in the

US and elsewhere. However, although base flow solute concentrations at regular intervals are often available in watersheds where federal, state and local agencies monitor water quality on a routine basis, high temporal resolution solute concentration data are often lacking during storms. Our results suggest that although baseflow concentrations vary throughout the year, baseflow concentrations measured immediately before a storm could be used to better constrain total NO_3^- losses during storms when high temporal resolution water quality data during storms are not available. Secondly, this high correlation between stream NO_3^- base flow concentrations and total NO_3^- fluxes during storms indicates that although most NO_3^- is exported to streams during high flow conditions, best management practices focusing on reducing background NO_3^- concentrations in the watershed, and therefore NO_3^- concentrations in the stream at base flow, will, ultimately, have a significant impact on NO_3^- losses during storms.

Although there is a need to monitor a larger number of high flow events throughout all four seasons to further validate the results of this study for a wider range of environmental conditions, our results shed light on the complex relationships between NO_3^- and NH_4^+ concentrations and fluxes in tile drains and overland flow in regulating N losses to the stream at the watershed scale. For spring storms of moderate size, the significant correlation between bulk precipitation and N fluxes, and the positive association between antecedent flow conditions and N fluxes, suggest that if the intensity and frequency of large storm events in the US Midwest increase in the coming years, as suggested by many climate change models [28-30], we will likely see an increase in both NO_3^- and NH_4^+ losses at the watershed scale (assuming land use practices remain the same as today).

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5. REFERENCES

- [1] Goolsby DA, Battaglin WA, Aulenbach BT, Hooper RP. Nitrogen input to the Gulf of Mexico. *J. Environ. Quality*, 2000, 30: 329–336.
- [2] Tomer MD, Meek DW, Jaynes DB, Hatfield JL. Evaluation of nitrate-N fluxes from a tile-drained watershed in central Iowa. *J. Environ. Quality*, 2003, 23: 642-653.
- [3] Kladvivko EJ, Frankenberger JR, Jaynes DB, Meek DW, Jenkinson BJ, Fausey NR. Nitrate leaching to subsurface drains as affected by drain spacing, changes in crop production system. *J. Environ. Quality*, 2004, 33: 1803-1813.
- [4] Tomer MD, Meek DW, Kramer LA. Agricultural practices influence flow regimes of headwater streams in Western Iowa. *J. Environ. Quality*, 2005, 34: 1547-1558.
- [5] Baker NT, Stone WW, Wilson JT, Meyer MT. Occurrence, transport of agricultural chemicals in Leary Weber Ditch Basin, Hancock County, Indiana, 2003–04. US Geological Survey Scientific Investigations Report 2006-5251, 2006: 44.
- [6] Royer TV, David MB, Gentry LE. Timing of riverine export of nitrate, phosphorus from agricultural watersheds in Illinois: implications for reducing nutrient loading to the Mississippi River. *J. Hydrol.*, 2006, 40: 4126–4131.
- [7] Vidon, P, Hubbard LE, Soyeux E. Seasonal solute dynamics across land uses during storms in glaciated landscape of the US Midwest. *J. Hydrol.*, 2009, 376, No 1-2: 34-47.
- [8] Macrae ML, English MC, Schiff SL, Stone M. Influence of antecedent hydrological conditions on patterns of hydrochemical export from a first-order agricultural watershed in Southern Ontario, Canada. *J. Hydrol.*, 2010, 389: 101-110.
- [9] Cuadra PE, Vidon P. Storm nitrogen dynamics in tile-drain flow in the US Midwest. *Biogeochem.*, 2011, 104: 293-308, DOI: 10.1007/s10533-010-9502-x.
- [10] Robertson GP, Paul EA, Harwood RR. Greenhouse gases in intensive agriculture: contributions of individual gases to the radiative

- forcing of the atmosphere. *Science*, 2000, 289: 1922-1925.
- [11] Poor CJ, McDonnell JJ. The effect of land use on stream nitrate dynamics. *J. Hydrol.*, 2007, 332: 54-68.
- [12] Royer TV, Tank JL, David MB. Transport, fate of nitrate in headwater agricultural streams in Illinois. *J. Environ. Quality*, 2004, 33: 1296-1304.
- [13] Vidon P, Hubbard LE, Soyeux E. Impact of sampling strategy on stream load estimates in till landscapes of the Midwest. *Environ. Monitoring, Assess.*, 2009, 159: 367-379 DOI: 101007/s10661-008-0635-5.
- [14] David MB, Gentry LE, Kovacic DA, Smith KM. Nitrogen balance in, export from an agricultural watershed. *J. Environ. Quality*, 1997, 26: 1038-1048
- [15] Alexander RB, Smith RA, Schwarz GE. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature*, 2000, 403: 758-761.
- [16] David MB, Gentry LE. Anthropogenic inputs of nitrogen, phosphorus, riverine export for Illinois, USA. *J. Environ. Quality*, 2000, 29: 494-508.
- [17] Gentry LE, David MB, Below FE, Royer TV, McIsaac GF. Nitrogen mass balance of a tile-drained agricultural watershed in east-central Illinois. *J. Environ. Quality*, 2009, 38: 1841-1847.
- [18] Heatherly II T, Whiles MR, Royer TV, David MB. Relationships between water quality, habitat quality, macroinvertebrate assemblages in Illinois streams. *J. Environ. Quality*, 2007, 36: 1653-1660.
- [19] Inamdar SP, Mitchell MJ. Hydrologic controls on DOC, nitrate exports across catchment scales. *Water Resources Res.*, 2006, 42, W03421 DOI:101029/2005WR004212.
- [20] NOAA "Climatological data, Indianapolis *National Oceanic, Atmospheric Administration*. National Climatic Data Center 2006, <http://www.wr.noaa.gov/ind/climatenormalstxt> Accessed 16 Jan 2005.
- [21] Capel PD, Hamilton PA, Erwin ML. Studies by the US Geological Survey on sources, transport, fate of agricultural chemical. *US Geological Survey Fact Sheet* 200403098, 2004 Accessed December 15, 2005, at <http://pubs.usgs.gov/fs/2004/3098>.
- [22] Lathrop TR. Environmental setting of the Sugar Creek, Leary Weber Ditch Basins, Indiana, 2002-04. *US Geological Survey Scientific Investigations Report* 2006- 5170; 27.
- [23] Clesceri LS, Greenberg AE, Eaton AD. Standard Methods for the Examination of Water, Waste Water. 20th ed, Clesceri LS, Greenberg AE, Eaton AE (eds), *American Public Health Association*, 1998, Washington, DC; 2005- 2605.
- [24] Morgan AM, Royer TV, David MB, Gentry LE. Relationships among nutrients, chlorophyll-a, dissolved oxygen in agricultural streams in Illinois. *J. Environ. Quality*, 2006, 35: 1110-1117.
- [25] Schilling KE, Zhongwei L, Zhang YK. Groundwater-Surface water interactions in the riparian zone of an incised channel, Walnut Creek, Iowa. *J. Hydrol.*, 2006, 327: 140-150.
- [26] Wagner LE, Vidon P, Tedesco LE, Gray M. Stream nitrate, DOC dynamics during three spring storms across land uses in glaciated landscapes of the Midwest. *J. Hydrol.*, 2008, 362: 177-190.
- [27] Vanni MJ, Renwick WH, Headworth JL, Auch JD, Schaus MH. Dissolved, particulate nutrient flux from three adjacent agricultural watersheds: a five-year study. *Biogeochem.*, 2001, 54: 85-114.
- [28] Karl TR, Knight RW. Secular trends of precipitation amount, frequency, intensity in the United States. *Bull. Amer. Meteorolog. Soc.*, 1998, 79: 231-241.
- [29] Davis Todd CE, Harbor JM, Tyner B. Increasing magnitudes, frequencies of extreme precipitation events used for hydraulic analysis in the Midwest. *J. Soil, Water Conservation*, 2006, 61: 179-184.
- [30] Milly P C D, Dunne KA, Vecchia AV. Global pattern of trends in streamflow, water availability in a changing climate. *Nature*, 2005, 438: 347-350.

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