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Storm nitrogen dynamics in tile-drain flow in the US Midwest

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Abstract Storm losses of N via tile-drainage in the US Midwest are a major concern for water quality in the Mississippi River Basin (MRB). This study investigates the impact of precipitation characteristics on NO_3^-, NH_4^+ and DON concentrations and fluxes for spring storms in tile-drains in a Midwestern agricultural watershed. Bulk precipitation amount had little impact on solute median concentrations in tile-drains during storms, but clearly impacted Mg^{2+}, K^+ and NO_3^- concentration patterns. For large storms (>6 cm of bulk precipitation), large amounts of macropore flow (43–50% of total tile-drain flow) diluted Mg^{2+} and NO_3^- rich groundwater as discharge peaked. This pattern was not observed for NH_4^+ and DON or for smaller tile-flow generating events (<3 cm) during which macropore flow contributions were limited (11–17% of total tile-drain flow). Precipitation amount was positively ($P < 0.01$) correlated to NO_3^- and NH_4^+ export rates, but not to DON export rates. Limited variations in antecedent water table depth in spring had little influence on N dynamics for the storms studied. Although significant differences in flow characteristics were observed between tile-drains, solute concentration dynamics and macropore flow contributions to total tile-drain flow were similar for adjacent tile-drains. Generally, NO_3^- represented >80% of N flux during storms, while DON and NH_4^+ represented only 2–14% and 1–7% of N flux, respectively. This study stresses the non-linear behavior of N losses to tile drains during spring storms in artificially drained landscapes of the US Midwest, at a critical time of the year for N management in the MRB.

Keywords Tile drainage · Nitrate · Ammonium · Dissolved organic nitrogen · Precipitation characteristics · Export rates

Introduction

Large increases in fertilizer usage in the last 50 years in the US Midwest have led to a significant increase in nitrogen (N) concentration in the Mississippi River Basin (MRB) (McIsaac et al. 2002; David and Gentry 2000). States like Indiana, Ohio and Illinois where intensive fertilizer use is common are especially large contributors to excess N losses to streams in the MRB (Goolsby et al. 2000; Royer et al. 2006). Further, losses of N in artificial drainage, also known as tile-drainage, are especially important in this part of the country where more than 30% of agricultural land is tile-drained (50% in Indiana) (Zucker and Brown 1998). For instance, Kladivko et al. (2004) report

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flow-weighted mean nitrate (NO_3^-) concentrations as high as 28 mg N/L and annual N fluxes of 38 kg N/ha in tile-drain water in a heavily fertilized corn-soybean field in Indiana, USA. Also in Indiana, Hoffmann et al. (2004) report high mean annual NO_3^-concentrations in tile-drains between 17.7 and 24.3 mg N/L depending on tile-drain spacing (10, 20, and 30 m). In that same study, annual NO_3^- fluxes varied between 22.6 and 29.9 kg N/ha depending on tile-drain spacing. At a larger scale, Royer et al. (2006) showed that more than 50% of the annual NO_3^- flux in three Illinois watersheds occurred for extreme discharges (>90th percentile) and that artificial drainage was the primary NO_3^- export mechanism.

Many studies have therefore investigated the importance of tile drainage on N losses to streams in the MRB and some general patterns have emerged. For instance, it is well established that most N losses in the MRB occur in late winter—early spring and mostly during high flow periods (David et al. 1997; Vanni et al. 2001; Richards and Baker 2002; Borah et al. 2003; Royer et al. 2006). Research in the Midwest and elsewhere has also shown that antecedent soil moisture conditions and precipitation characteristics influence processes regulating nutrient losses to streams (Troch et al. 1993; Creed and Band 1998; Sidle et al. 2000; Geohring et al. 2001; Hangen et al. 2001; Inamdar et al. 2004). Nevertheless, little information is available in the literature on the dynamics of NO_3^-, NH_4^+ and DON in tile flow during spring storms at a high temporal resolution. This strongly limits our ability to develop precise and accurate N budgets for artificially drained agricultural watersheds in spite of the importance of tile-drained landscapes in N losses in the MRB. Indeed, Vidon et al. (2009a) showed that the precision and accuracy of solute flux calculations in streams depends not only on the sampling frequency, but also on the solute concentration pattern as a function of flow during storms (e.g. concentration, dilution). A precise determination of the patterns of NO_3^-, NH_4^+ and DON in tile flow during storms is also important to develop sound sampling strategies for routine water quality monitoring (Vidon et al. 2009a).

Further, because NO_3^- is the dominant for of N in streams in the US Midwest (Scott et al. 2007), most studies focusing on N losses to streams in tile-drained landscapes of the Midwest primarily focus on NO_3^- losses (Drury et al. 1996; Randall and Mulla 2001; Hoffmann et al. 2004; Kladivko et al. 2004). Nevertheless, recent research has shown that dissolved organic nitrogen (DON) (along with dissolved organic carbon and dissolved organic phosphorus) play an important role in regulating the biogeochemical processes of freshwater systems (e.g. stream respiration, acidification processes) (Brookshire et al. 2005; Hood et al. 2005). Similarly, DON can substantially influence estuarine and oceanic systems (Seitzinger and Sanders, 1997; Lopez-Veneroni et al. 1994; Stepanauskas et al. 2000; Põder et al. 2003). Ammonium (NH_4^+) is also important in regulating stream metabolism as NH_4^+ is generally readily absorbed by plants and microorganisms. A better characterization of the dynamics of NH_4^+ and DON in tile flow and the relative importance of NO_3^-, NH_4^+ and DON in total N losses from tile-drains is therefore critical to better manage N in artificially drained landscapes, and better comprehend how N losses from artificially drained landscapes affect stream metabolism and water quality in the MRB.

Finally, another important characteristics of tile-drained soils in the US Midwest is the presence of soil macropores which allow surface water and solutes to be quickly transferred to tile drains (Shalit and Steenhuis 1996; Kung et al. 2000a, b; Geohring et al. 2001; Stone and Wilson 2006). Although the occurrence of preferential solute transfer to tile drains is a well documented phenomenon, the importance of preferential flow through soil macropores (macropore flow) on NO_3^-, NH_4^+ and DON losses to tile drains has generally been poorly quantified. However, cultural practices such as tillage and no-tillage affect soil macropore structure and the connectivity of macropores to tile-drains. Identifying the importance of macropore flow in NO_3^-, NH_4^+ and DON transport to tile-drains during storms is therefore important to continue developing sound strategies to manage N and mitigate the impact of agriculture on water quality while maintaining crop yield.

The objectives of this study are twofold: (1) determine how precipitation characteristics and antecedent soil moisture conditions affect NO_3^-, NH_4^+ and DON dynamics (concentration, timing, flowpath) in tile-drains during storms; (2) determine NO_3^-, NH_4^+ and DON export rates and the relative importance of each N species in total N fluxes for spring storms in tile-drains in Leary Weber Ditch (LWD), a small agricultural watershed representative of agro-ecosystems of the US Midwest near Indianapolis, IN.

Materials and methods

Experimental site description

Leary Weber Ditch (LWD) 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 (NOAA 2005). Soils in the watershed are dominated by poorly drained loams or silt loams and typically belong to the Crosby-Brookston association. Crosby-Brookston soils are generally 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, and ensuring good soil tilth. Conventional tillage and a corn/soybean rotation has been implemented consistently for the last 20 years in LWD. In 2008, soybean was planted in early May and glyphosate was applied mid-May 2008. During

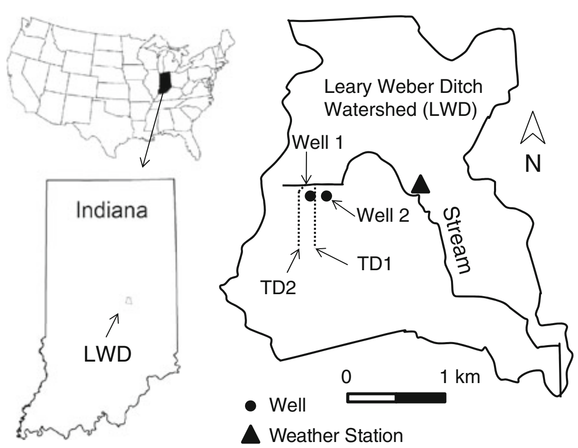

Fig. 1 Experimental site location. TD1 and TD2 correspond to the location of the two tile drains monitored in this study

corn years, fertlizer as anhydrous ammonia is generally applied on corn at a rate of 180 kg N/ha/yr and herbicides atrazine and acetochlor are generally applied in mid-May. Potash (K_2O) is applied post-harvest on soybean fields at a rate of approximately 220 kg/ha. LWD is representative of many watersheds in the Midwest where poorly drained soils dominate and where artificial drainage is commonly used to lower the water table (Lathrop 2006). In LWD, the two tile-drains monitored for this study (TD1 and TD2) are located in the headwater of the watershed (Fig. 1). Each tile-drain is 20.3 cm ID (8 inches ID) and located approximately 120 cm below ground surface. TD1 extends 660 m from the stream and drains an area approximately 8.1 ha in size. TD2 extends 710 m from the stream and drains an area approximately 6.1 ha in size.

Hydrological measurements and water quality analysis

Precipitation was monitored continuously (15-min. interval) using a Vaisala WXT510 multiparameter transmitter weather station. Seven-day (7DP) and 30-day (30DP) antecedent precipitation for each event were calculated by computing total precipitation preceding the events. Four rain gages were also deployed within 20 m of the tile outlets to validate weather station measurements and collect precipitation water samples for water quality analysis. Each of the tile-drains (TD1 and TD2) were equipped with a Doppler velocity meter (ISCO 2150) for continuous discharge measurements. Whenever possible (i.e. when the stream water level was below the tile-drain), discharge was validated using the bucket method. Two groundwater wells (5.4 cm ID, 2 m deep) were installed near the edge of the field where TD1 and TD2 are located (Fig. 1) and equipped with continuous water level loggers (YSI 600 XLM) to monitor water table response to storms in relation to tile flow. Well 1 was located approximately 5 meters from TD1, while well 2 was located at the inter-drain line immediately downtream from TD1 (Fig. 1). Water table fluctuations in wells 1 and 2 were only analyzed with respect to flow in TD1 because of the proximity of well 1 (5 m) and well 2 (15 m) to TD1. Water table antecedent depth has been successfully used as a proxy for antecedent soil moisture conditions (Troch et al. 1993; Shaw and Walter 2009).

In this study, soil moisture was not measured and antecedent water table depth is therefore used as a proxy for antecedent soil moisture conditions before each storm.

Water samples for water quality analysis were collected for four storms in TD1 and two storms in TD2 using auto samplers (ISCO 6712). Whenever water quality samples were collected for N analysis (nitrate (NO_3^-), ammonium (NH_4^+) and total dissoved nitrogen (TDN)), specific electrical conductivity (EC), oxygen-18 in water, and major cation concentrations (Mg^{2+}, K^+, Na^+, Ca^+) were also measured in all samples to further characterize tile hydrology and identify the relative importance of macropore flow and matrix flow in total tile drain flow during storms (Vidon and Cuadra 2010). The sample collection line from each ISCO sampler was located at least 1 m into the tile-drains and Doppler velocity measurements confirmed that no flow reversals occurred in the tile-drains during the storms studied, therefore guaranteeing that tile samples were not contaminated by stream water when the tiles were submerged during storms. Each sampler was triggered manually before the beginning of each storm and generally set to collect water samples every 20 min during the rising limb of the hydrograph or the first 24 h of the storm, and every 40 min on the falling limb of the hydrographs. Three samples were composited into a single bottle, which then was analyzed for nutrients and other variables. Samples were never left more than 24 h in the field and were immediately filtered using GF/F Whatman 0.7 µm filters 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 accuracy and precision of measurement techniques. Specific electrical conductivity (EC) of all water samples (precipitation and tile-drain samples) was determined using a benchtop EC meter (Oakton CON510). Five milliliter aliquots of all samples were analyzed for oxygen-18 of water using equilibration with CO_2 followed by headspace $^{13}CO_2$ analysis in the Stable Isotope Research Facility at Indiana University using a ThermoFinnigan Gas Bench inlet interfaced with a Delta Plus XP isotope ratio mass spectrometer. Major cation concentrations were determined using an ion chromatograph (Dionex DX500) and a CS15 analytical column and methasulfonic acid eluent (Clesceri et al. 1998). Ammonium and nitrate concentrations were determined by colorimetry using standard methods (Clesceri et al. 1998) on a Konelab 20 Photometric Analyzer (EST Analytical). Total dissoved nitrogen (TDN) was determinded on a Shimadzu TOC-V analyzer equipped with a total nitrogen module and dissolved organic nitrogen (DON) was determined by substracting NO_3^- and NH_4^+ from TDN.. When the sum of NO_3^- and NH_4^+ was greater than TDN, DON concentration was considered equal to zero (Inamdar et al. 2006).

Using oxygen-18 in water and/or electrical conductivity values from precipitation samples and tile flow samples before each storm, a simple hydrograph separation was conducted on tile water to differentiate between new water (macropore flow) and old water (matrix flow) (Sklash 1990, Hill and Waddington 1993; Stone and Wilson 2006; Vidon and Cuadra 2010). For this analysis, precipitation water is considered equivalent to new water and the chemical signature of tile water in the hours preceding the storm equivalent to old water. This method allowed us to identify the proportion of new water in tile flow for the storms studied. It is assumed that any new water observed in the tile-drain during the storm is equivalent to macropore flow because passive diffusion of new water through the soil matrix (matrix flow) cannot explain the quick transfer of new water to tile-drains during storms (Stone and Wilson 2006). A detailed description of this methodology and a discussion of the assumptions made are provided in Vidon and Cuadra (2010).

When box plots were used to represent solute concentrations during storms, differences in concentrations were considered significant when box plots showing the upper and lower quartile did not overlap. When box plot were not available, data were tested for normality and equal variance, and t-tests were used to determine significant differences between groups if normally distributed. Significance levels of differences between non-normally distributed data were determined using Mann–Whitney Rank Sum Tests. Pearson product-moment correlation coefficient (ρ_{xy}) were used to identify correlation between groups. SigmaPlot 11.0 was used for statistical analysis. Discharge is typically expressed in L/s or as specific discharge (discharge/contributing area to each tile-drain × unit conversion factor) (mm/h) when flow is compared between tile-drains. For each storm, the runoff ratio was calculated by dividing the total discharge for the storm (mm) by the bulk precipitation (mm) for the storm in question. Solute fluxes (kg/storm) were calculated for each storm by multiplying the concentration of the sample for each sampling interval (mg/L) by the average discharge for that interval (L/s) and a unit conversion factor. Export rates (mg N/m^2) were obtained by dividing the solute flux for each storm (kg/storm) by the contributing area to each tile-drain (m^2) and a unit conversion factor.

Results

Storm characteristics, antecedent water table depth and tile flow response to precipitation

A total of eight precipitation events were large enough to generate flow in TD1 and TD2 between April 17 and June 17, 2008 (Fig. 2). Here, we focus the analysis of tile flow response to precipitation and antecedent water table depth on storms 2 (S2), 5 (S5), 6 (S6) and 8 (S8), which are the storms for which water samples were collected for chemical analysis. Storms 2 and 8 represent small tile flow generating events (2.17–2.91 cm bulk precipitation) while storms 5 and 6 are large tile flow generating events (6.95–10.82 cm bulk precipitation) (Fig. 2). Using intensity–duration–frequency curves for precipitation obtained for Indianapolis, IN (NOAA 2004), it was estimated that both storms 2 and 8 had recurrence intervals of less than 1 year, that storm 5 had a recurrence interval of 1.5 years, and that storm 6 had a recurrence interval of 25 years. Maximum precipitation intensity was highest for storms 5 and 6 (>7 cm/h), and lowest for storms 2 and 8 (<4 cm/h). Antecedent precipitations (7DP and 30DP) were variable from storm to storm, but tended to increase (especially 30DP) as the storm season progressed (Fig. 2). Antecedent water table depth was slightly

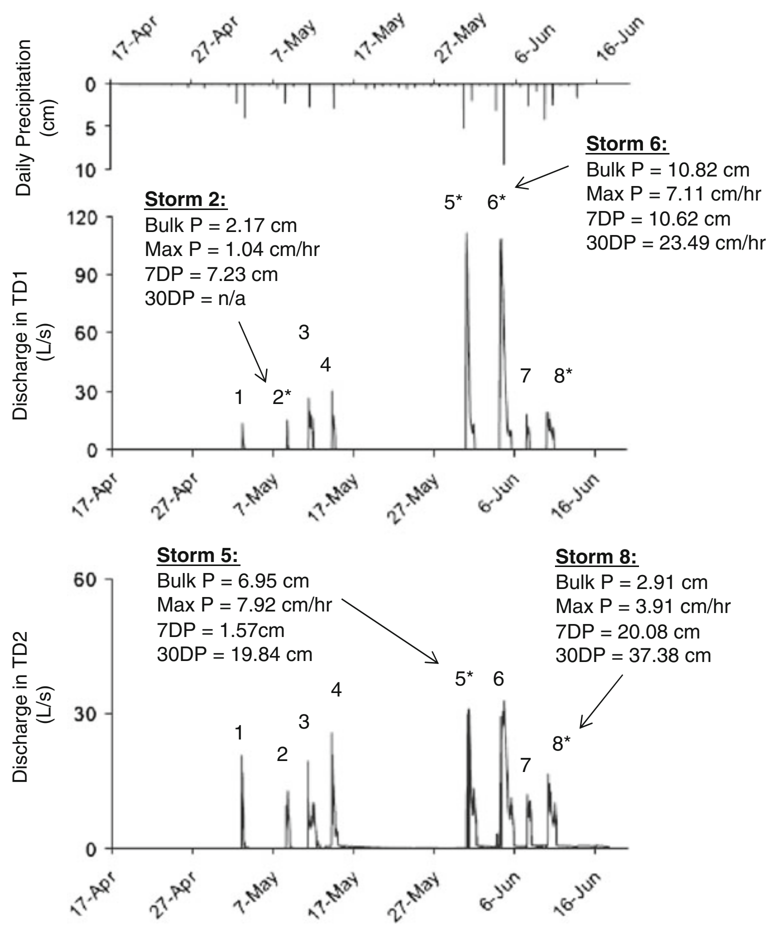

Fig. 2 Daily precipitation and discharge (15-min interval) in tile drain 1 (TD1) and tile drain 2 (TD2) between April and June 2008. Numbers indicate tile flow events. Tile flow events for which water quality samples were collected are indicated by an asterisk (*). Bulk precipitation (Bulk P), maximum precipitation (Max P), 7-day antecedent precipitation (7DP), and 30-day antecedent precipitation (30DP) are indicated for storms 2, 5, 6 and 8. (n/a = not available)

Table 1 Tile flow response to precipitation characteristics in tile drain 1 (TD1) and 2 (TD2) in Leary Weber Ditch for storms 2 (S2—May 8), 5 (S5—May 30), 6 (S6—June 4), and 8 (S8—June 10)

	Mean tile flow (mm/h)		Maximum tile flow (mm/h)		Runoff ratio		New water (% total flow)	
	TD1	TD2	TD1	TD2	TD1	TD2	TD1	TD2
S2	0.20	0.25	0.67	0.76	0.07	0.22	17	n/a[a]
S5	1.58	0.85	4.95	1.84	0.64	0.39	44	43
S6	1.82	0.95	4.83	1.94	0.63	0.37	50	n/a
S8	0.48	0.50	0.85	0.98	0.39	0.45	16	11

[a] Not available

lower for storms 5 and 6 (1.61–1.62 m for well 1, and 1.57–1.65 m for well 2) than storms 2 and 8 (1.54–1.58 m for well 1, and 1.47–1.48 m for well 2).

Mean tile flow and maximum tile flow were highest for storms 5 and 6 and lowest for storms 2 and 8 (Table 1). The lowest runoff ratio was observed for storm 2 regardless of the tile-drain (0.07 in TD1 and 0.22 in TD2), while the two highest runoff ratios were observed for storms 5 and 6 in TD1. Only small differences in flow characteristics were observed for TD1 and TD2 for small tile flow generating events (S2 and S8). However, mean and maximum tile flow were approximately twice as high in TD1 as in TD2 for storms 5 and 6. The runoff ratio in TD1 was also much larger than in TD2 for storms 5 and 6. Hydrograph separation results indicate that for storms 2 and 8 (<3 cm bulk precipitation), the proportion of new water or macropore flow in total storm tile-drain flow varied from 11 to 17%. For the two largest storms of the season (S5 and S6) (>6 cm bulk precipitation), the proportion of new water in tile flow ranged from 43 to 50% of total storm tile-drain flow.

Nitrogen and cation concentrations during storms

Box plots of magnesium (Mg^{2+}), potassium (K^{+}), total dissolved nitrogen (TDN), nitrate (NO_3^{-}), ammonium (NH_4^{+}) and dissolved organic nitrogen (DON) concentrations during storms are shown for storms 2, 5, 6, and 8 for TD1 and for storms 5 and 8 for TD2 in Fig. 3. With the exception of storm 6 for which median Mg^{2+} concentration was 5.43 mg/L in TD1, median Mg^{2+} concentrations for all other storms were between 11.10 and 14.13 mg/L regardless of the storm or tile-drain. Although differences were not always significant (box plot overlap), median Mg^{2+} concentrations were generally slightly higher for storms 2 and 8 (<3 cm bulk precipitation) than for storms 5 or 6 (>6 cm bulk precipitation). An opposite but consistent trend was observed for K^{+} with highest median K^{+} concentrations (0.34–0.49 mg/L) for storms 5 and 6 and lowest median K^{+} concentrations (0.19–0.22 mg/L) for storms 2 and 8 regardless of the tile-drain. Although inter-storm differences were not always significant (box plot overlap), median TDN concentrations for storms 5 and 6 (2.72–7.38 mg/L) were generally more variable and slightly lower than for storms 2 or 8 (7.44–10.98 mg/L). Variations in NO_3^{-} concentrations for the storms studied showed a very similar pattern to Mg^{2+} concentrations. NO_3^{-} concentrations were significantly lower for storm 6 (median concentration = 2.50 mg/L) than for any of the other storms (5.37 mg/L < median concentration < 7.64 mg/L). No significant differences in NO_3^{-} concentrations between storms were observed for storms 2, 5, and 8 (box plot overlap). Regardless of the storm, median NH_4^{+} concentrations remain below 0.20 mg N/L. With the exception of storm 2 in TD1 for which NH_4^{+} concentrations (median concentration = 0.06 mg/L) were significantly lower than for the other storms (box plots do not overlap), NH_4^{+} concentrations were generally not significantly different (box plot overlap) between storms 5, 6, and 8 (0.13 mg/L< median concentration <0.20 mg/L). Similarly, with the exception of storm 2 in TD1 for which DON concentrations were significantly higher than for any of the other storms (median concentration = 5.63 mg/L), DON concentrations were not significantly different between storms for storms 5, 6, and 8 (0 < median concentration < 0.49 mg/L). When water quality data were available for both TD1 and TD2 (i.e. storms 5 and 8), no significant

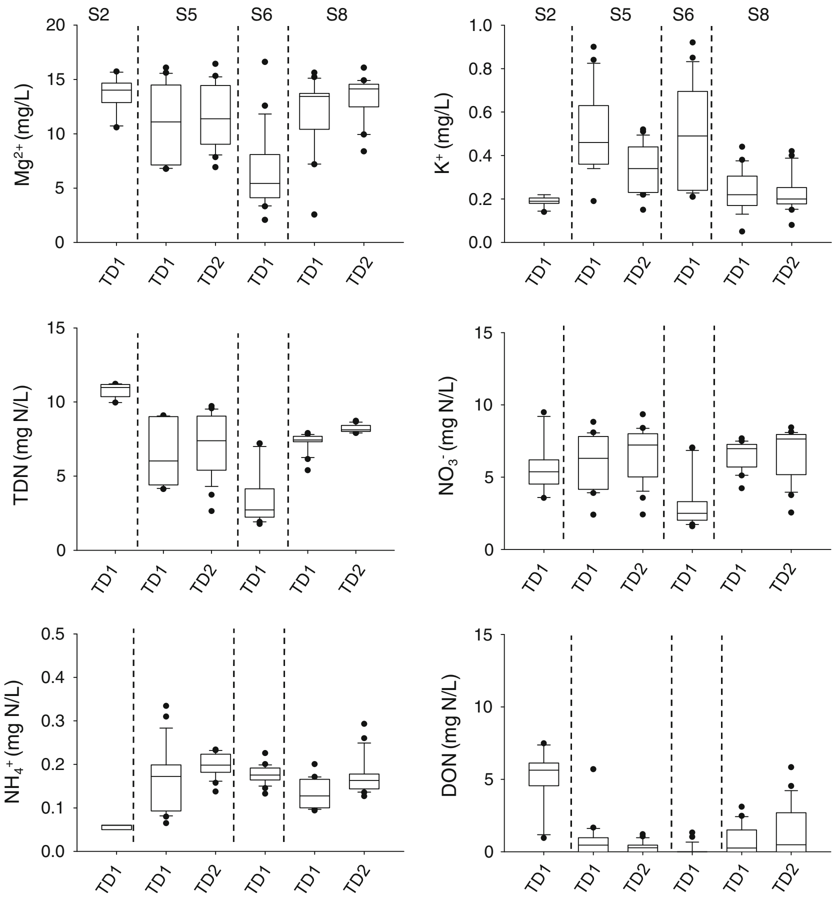

Fig. 3 Box plots (median, 25th and 75th quartile) showing magnesium (Mg^{2+}), potassium (K^+), total dissolved nitrogen (TDN), nitrate (NO_3^-), ammonium (NH_4^+), and dissolved organic nitrogen (DON) concentrations for storms 2 (S2), 5 (S5), 6 (S6) and 8 (S8) in tile drain 1 (TD1) and for storms S5 and S8 in tile drain 2 (TD2)

differences in Mg^{2+}, K^+, NO_3^-, NH_4^+ and DON were observed between tile-drains.

Nitrogen and cation concentration patterns during storms

Magnesium (Mg^{2+}), potassium (K^+), total dissolved nitrogen (TDN), nitrate (NO_3^-), ammonium (NH_4^+) and dissolved organic nitrogen (DON) concentration patterns in relation to tile flow, water table fluctuations, and new water contributions to total tile-drain flow are shown for storms 2 (TD1 only) and 8 (TD1 and TD2) on Fig. 4 and for storms 5 (TD1 and TD2) and 6 (TD1 only) on Fig. 5. Data for storms 2 and 8 are shown together because they correspond to the two smallest tile flow generating events studied (<3 cm bulk precipitation). Storms 5 and 6 are grouped together because they correspond to the two largest storms studied (>6 cm bulk precipitation). On both figures, water table fluctuations in wells 1 and 2 are only shown with respect to flow in TD1 because of the proximity of well 1 (5 m) and well 2 (15 m) to TD1. Calcium and sodium concentration patterns are not included in this analysis because they strongly resemble Mg^{2+} concentration patterns (data not shown).

For storms 2 and 8 for which new water contribution represented between 11% and 17% of total tile-drain flow (Table 1), the proportion of new water slightly increased with flow (Fig. 4). For storm 2, the water table in wells 1 and 2 peaked with (well 2) or slightly after the peak in discharge (well 1). For storm 8, the water table immediately rose as tile flow increased, but peaked after the peak in discharge. No clear and consistent concentration or dilution patterns were observed for Mg^{2+} or K^+ as tile flow increased in TD1 and TD2 for storms 2 and 8. Total dissolved nitrogen and NH_4^+ showed little variations with respect to changes in tile flow for these two storms. Because DON was determined by difference, NO_3^-

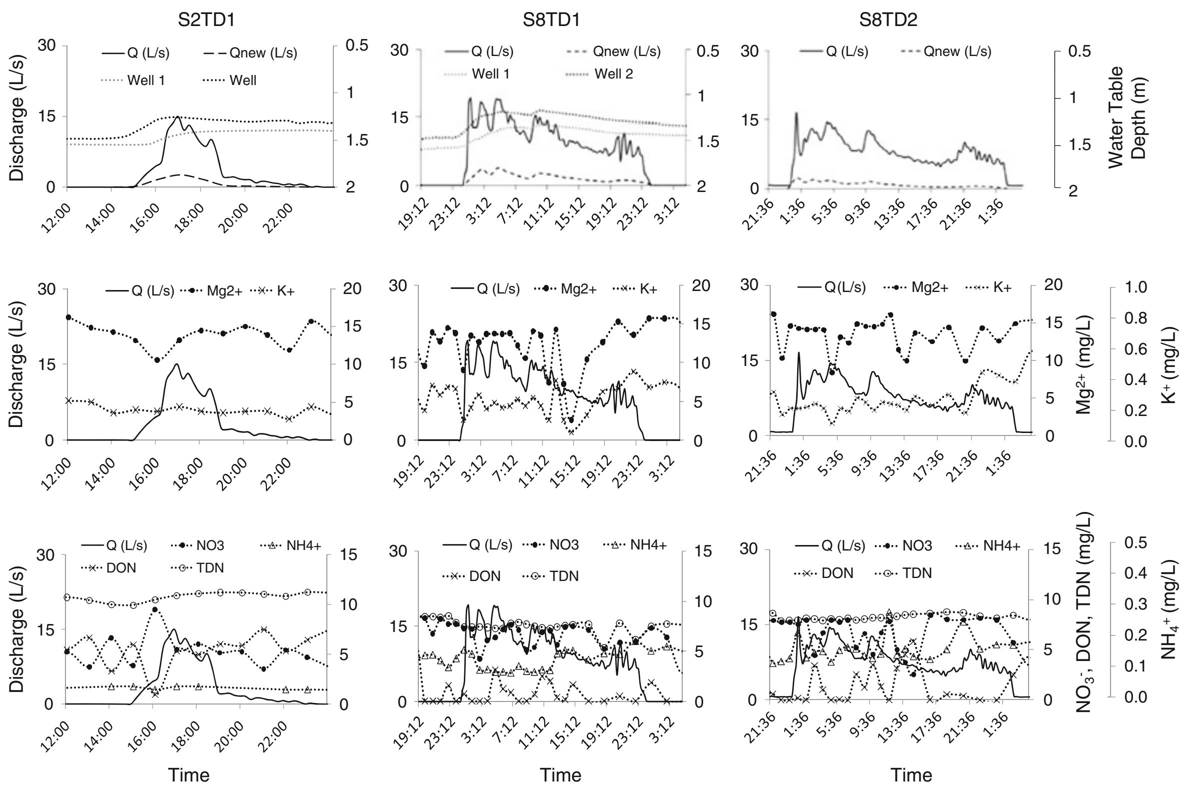

Fig. 4 Water table fluctuations for wells 1 and 2, discharge (Q) and new water contributions to tile flow (Q_{new}) for storms 2 (S2) in tile drain 1 (TD1) and for storms 8 (S8) in tile drain 1 (TD1) and 2 (TD2) (*first row*). Magnesium (Mg^{2+}), potassium (K^+), total dissolved nitrogen (TDN), nitrate (NO_3^-), ammonium (NH_4^+), and dissolved organic nitrogen (DON) concentrations as a function of discharge (Q) for storms 2 (S2) in tile drain 1 (TD1) and for storms 8 (S8) in tile drain 1 (TD1) and 2 (TD2) (*second and third rows*)

and DON seem to have opposite patterns. No clear dilution or concentration patterns with respect to discharge were observed for these two solutes.

For storms 5 and 6 (>6 cm bulk precipitation), the peaks in water table and new water contributions occurred concurrently with the peaks in discharge. However, for these two storms with new water contributions between 43 and 50% of total tile-drain flow (Table 1), solute concentration patterns were different than for storms 2 and 8. A clear dilution pattern was observed for Mg^{2+} as discharge peaked regardless of the tile-drain (Fig. 5). An opposite but consistent pattern was observed for K^+ with a clear increase in K^+ concentration as discharge peaked. For storms 5 and 6, TDN and NO_3^- showed a clear dilution pattern as discharge peaked. Most of the time, NO_3^- was the dominant form of nitrogen during these storms and DON was often equal to zero. NH_4^+ concentration did not consistently increase or decreased with discharge (Fig. 5). Concentration patterns as a function of flow were similar in TD1 and TD2 for all solutes (K^+, Mg^{2+}, NO_3^-, NH_4^+, DON, TDN) (see storms 5 and 8, Figs. 4 and 5).

Nitrogen fluxes and nitrogen export rates during storms

Total NO_3^-, NH_4^+ and DON fluxes (kg N/storm) and export rates (mg N/m^2) for storms 2, 5, 6 and 8 for TD1 and storms 5 and 8 for TD2 are shown in Table 2. Nitrate fluxes varied between 0.783 kg N/storm and 16.145 kg N/storm depending on the storm, with the lowest flux observed for storm 2 in TD1 and the highest flux observed for storm 5, also in TD1. NO_3^- export rates varied between 9.7 mg N/m^2 and 90.4 mg N/m^2 for storms 2 and 8 (<3 cm bulk precipitation) and between 160.1 and 199.4 mg N/m^2

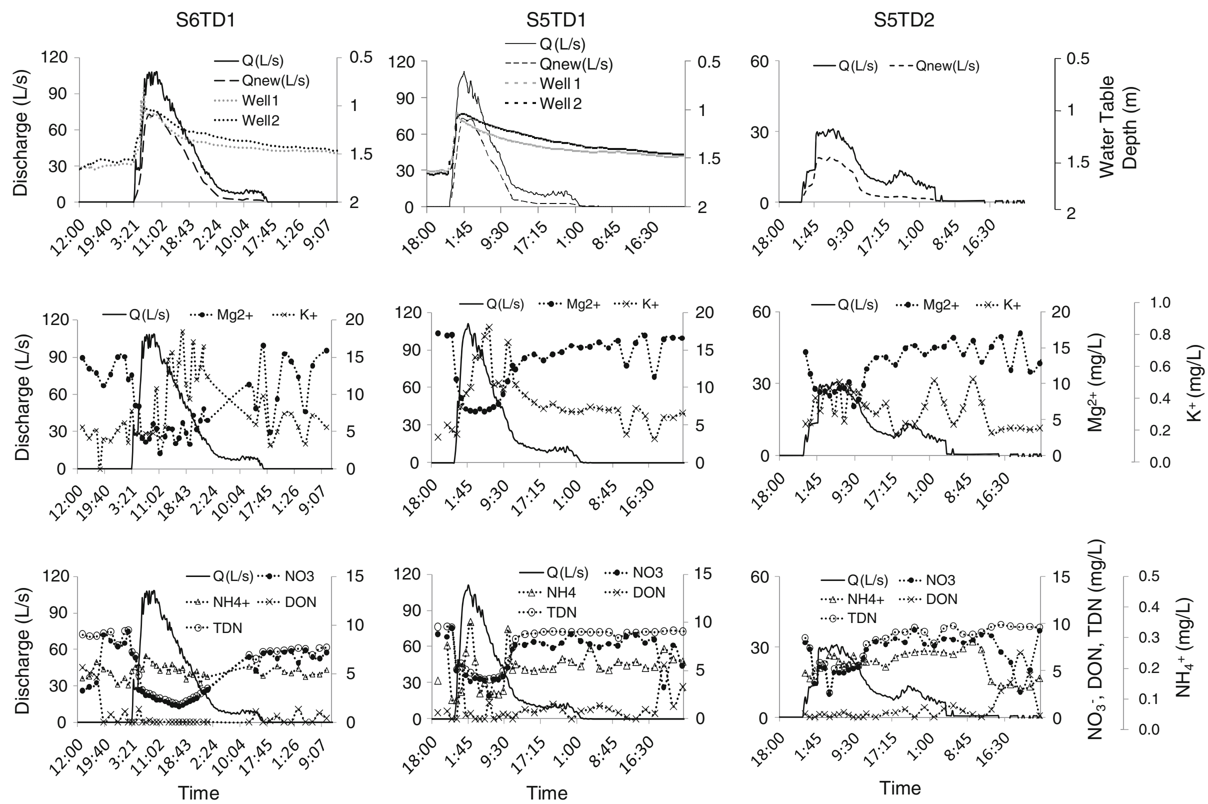

Fig. 5 Water table fluctuations for wells 1 and 2, discharge (Q) and new water contributions to tile flow (Q_{new}) for storms 6 (S6) in tile drain 1 (TD1) and for storms 5 (S5) in tile drain 1 (TD1) and 2 (TD2) (*first row*). Magnesium (Mg^{2+}), potassium (K^+), total dissolved nitrogen (TDN), nitrate (NO_3^-), ammonium (NH_4^+), and dissolved organic nitrogen (DON) concentrations as a function of discharge (Q) for storms 6 (S6) in tile drain 1 (TD1) and for storms 5 (S5) in tile drain 1 (TD1) and 2 (TD2) (*second and third rows*)

Table 2 Nitrate (NO_3^-), ammonium (NH_4^+), and dissolved organic nitrogen (DON) flux (kg N/storm) and export rate (mg N/m^2/storm) for storms 2 (S2—May 8), 5 (S5—May 30), 6 (S6—June 4), and 8 (S8—June 10) in tile drain 1 (TD1) and storms 5 and 8 in tile drain 2 (TD2)

	S2TD1	S5TD1	S5TD2	S6TD1	S8TD1	S8TD2
Flux						
NO_3^-	0.783	16.145	9.721	14.293	5.900	5.490
NH_4^+	0.006	0.599	0.324	0.933	0.119	0.137
DON	0.675	2.822	0.424	0.339	0.762	0.977
Export rate						
NO_3^-	9.7	199.4	160.1	176.6	72.9	90.4
NH_4^+	0.1	7.4	5.3	11.5	1.5	2.3
DON	8.4	34.9	7.0	4.2	9.4	16.1

for storms 5 and 6 (>6 cm bulk precipitation). Similarly, NH_4^+ fluxes and export rates were highest for storms 5 and 6 and lowest for storms 2 and 8. NH_4^+ export rates varied between 0.1 mg N/m^2 (storm 2, TD1) and 11.5 mg N/m^2 (storm 6, TD1). The largest DON flux (2.822 kg N/storm) was observed for storm 5 in TD1; however, for the other storms, DON fluxes remained between 0.339 and 0.977 kg N/storm. DON export rates varied between 4.2 and 16.1 mg N/m^2, with the exception of storm 5 in TD1 during which a higher DON export rate was observed (34.9 mg N/m^2).

When all storms were combined, the average NO_3^-, NH_4^+ and DON fluxes were 8.72, 0.35, and 0.10 kg N/storm, respectively. The average NO_3^-, NH_4^+ and DON export rates were 118.18, 4.68 and 13.3 mg N/m^2, respectively. Overall, nitrogen fluxes for each of the storms studied were therefore dominated by nitrate, with nitrate representing between 82 and 93% of the total N flux for most storms (Fig. 6). The only exception was for storm 2, for which nitrate only accounted for 53% of the total

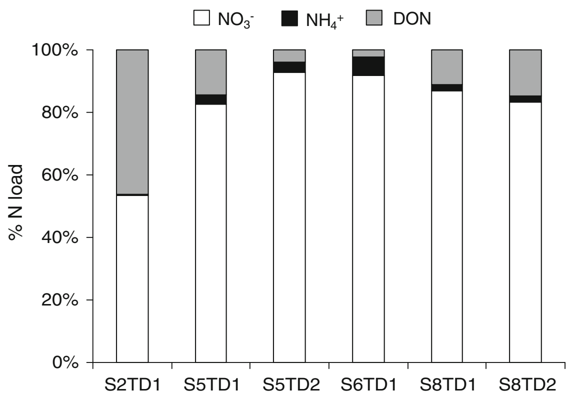

Fig. 6 Fraction (%) of nitrate (NO_3^-), ammonium (NH_4^+) and dissolved organic nitrogen (DON) in total nitrogen load (N Load) for storms 2 (S2), 5 (S5), 6 (S6) and 8 (S8) in tile drain 1 (TD1) and for storms S5 and S8 in tile drain 2 (TD2)

N flux. For storm 2, DON accounted for 46% of the total N flux; however, for all the other storms, DON fluxes represented between 2 and 14% of the total N flux. NH_4^+ accounted for only a small fraction (1–7%) of the total N flux regardless of the storm and tile-drain.

Discussion

How do precipitation amounts and antecedent water table depth impact NO_3^-, NH_4^+ and DON concentration patterns?

The April–June 2008 period was only slightly wetter than normal (+24.5%) and when all the storms occurring over the April-June period were considered, storms 2, 5, 6 and 8 formed a representative sample of the storms that occurred at the site in spring 2008 (Fig. 2). As indicated in the result section, the recurrence intervals of storms 2 and 8 are <1 year, while the recurrence intervals of storms 5 and 6 are 1.5 and 25 years, respectively. We therefore believe that the results presented in this study (albeit for a limited number of storms) are representative of spring storms in this region of the country. Although some variations in cation or nitrogen (TDN, NO_3^-, NH_4^+, DON) concentrations were observed between storms (Fig. 3), no consistent and statistically significant differences in median concentrations were observed for most solutes between the two smallest storms (storms 2 and 8, <3 cm bulk precipitation) and the two largest storms (storms 5 and 6, >6 cm bulk precipitation). However, solute concentration patterns as a function of flow were clearly impacted by bulk precipitation amounts for the storms studied. Clear dilution patterns were observed for NO_3^- and Mg^{2+} for storms generating more than 6 cm of bulk precipitation. For these storms, a clear concentration pattern was also observed for K^+. However, dilution or concentration patterns were not observed for NH_4^+ and DON for large storms or for smaller tile-flow generating events (< 3cm) regardless of the solute (Figs. 4 and 5). Precipitation characteristics other than bulk precipitation (e.g. precipitation intensity, duration) were poorly correlated to tile flow response to precipitation (Vidon and Cuadra 2010).

Antecedent water table depth imparted some variability in tile drain response to precipitation but were of lesser importance than bulk precipitation amounts (Vidon and Cuadra 2010). Briefly, water table in wells 1 and 2 was only slightly lower for before storms 5 and 6 (1.61–1.62 m for well 1, and 1.57–1.65 m for well 2) than storms 2 and 8 (1.54–1.58 m for well 1, and 1.47–1.48 m for well 2). These variations in antecedent water table depth only represented a small fraction of the range of water fluctuations over the course of the study period (April–June, 2008) (0.8–1.9 m in well 1, 1.0–1.7 m in well 2). It is therefore unlikely that in this case, variations in antecedent water table depths played a critical role in explaining the differences in solute export patterns observed for storms 5–6 and 2–8.

Overall, bulk precipitation therefore appears to be the most important variable regulating N concentration patterns in tile drains for the storms studied. This stresses the non-linear response of solute leaching to precipitation characteristics at the study site for the storms studied. This is consistent with many other studies showing that watershed hydrological responses to precipitation are generally highly non-linear (Sidle et al. 2000, Wigington et al. 2005; Poor and McDonnell 2007). For instance, Sidle et al. (2000) clearly show that various hydrological thresholds regulate watershed response to precipitation in Japan. Wigington et al. (2005) showed that stream channel expansion varies tremendously with seasons, which affects watershed response to precipitation. Although non-linear threshold-based responses to precipitation have been observed in many watersheds around the world, these processes still remain poorly understood. Documenting the occurrence of these processes, and identifying thresholds of hydrological response to precipitation is therefore of primary importance to advance our understanding of the processes regulating watershed responses to precipitation. For our study sites, the dilution observed for NO_3^-, TDN and Mg^{2+}, and the observed increase in K^+ concentration for large storms as discharge peaks are likely due to the sharp increase in the importance of macropore flow in each tile-drain as precipitation amount increased (Table 1; Fig. 2). Indeed, many studies have shown that Mg^{2+} dilution patterns as discharge increases in streams are often associated with pulses of new water low in Mg^{2+} (Reid et al. 1981; Elwood and Turner 1989; Kahl et al. 1992; Hill 1993; Hood et al. 2006). Here, the large decreases in NO_3^-, TDN and Mg^{2+} as discharge increased in TD1 and TD2 for storms 5 and 6 clearly indicate a pulse of new water or precipitation water low in NO_3^- and Mg^{2+} to the tile as discharge increase. The quick transfer (a few hours—Figs. 4 and 5, upper panel) of this new water from the soil surface to tile-drains cannot be explained by passive diffusion of new water through the soil matrix (Vidon and Cuadra 2010). The quick transfer of precipitation water to the tile via macropore flow is the only known mechanism capable of explaining the decreases in NO_3^-, TDN and Mg^{2+} concentrations observed during storms 5 and 6 as discharge in TD1 and TD2 peaked. This observation is consistent with the increase in K^+ concentration observed for these storms as discharge peaked in TD1 and TD2. Indeed, although K^+ concentration in precipitation (0.2–0.4 mg/L) is not consistently higher than in tile drain flow, potash (K_2O) is regularly applied to the soil surface in autumn at a rate of approximately 220 kg/ha in this watershed, and Baker et al. (2006) showed that K^+ is typically associated with overland flow/surface water in LWD watershed. The increase in K^+ concentration in tile water as tile flow increases during storms 5 and 6 is therefore consistent with the preferential transfer of surface water to tile-drains via macropore flow.

Results of the hydrograph separations performed for storms 2, 5, 6 and 8 (Table 1; Figs. 4 and 5, upper panel) are also consistent with cation data. For storms 2 and 8, new water contributions (macropore flow) were small and varied between 11 and 17% of total storm tile-drain flow; whereas for storms 5 and 6, macropore flow represented between 43 and 50% of total storm tile-drain flow. It is difficult to determine the absolute error on the hydrograph separation and the absolute values reported here regarding the relative importance of macropore flow vs. matrix flow should therefore be interpreted with caution. Nevertheless, these values are consistent with those found by Stone and Wilson (2006) in this watershed, where the authors showed that macropore flow contributions varied between 11 and 51% of total storm tile-drain flow and increased with storm intensity.

Overall, these data suggest that variations in the amount (% total flow) of macropore flow contributing to tile flow during storms is critical in explaining differences in solute concentration patterns during storms. Kladivko et al. (2004) reported a lack of consistent patterns for nitrate concentrations as a function of flow in tile-drains in southern Indiana. For some storms, the authors observed a negative correlation between nitrate concentration and tile flow, but not for others. The authors, however, did not provide data linking precipitation amounts during storms to nitrate patterns. We propose that the non-linear response of soils (as observed in LWD) associated to variations in the amount of macropore flow contributing to tile flow during storms may explain the variability of results observed by Kladivko et al. (2004).

Beyond solute concentration patterns, data suggest that observed nitrate concentrations during storms are generally slightly lower than average nitrate concentration observed in tile-drains over a 2-year period by Baker et al. (2006) in LWD (approximately 10 mg N/L) (Fig. 3). Our mean NO_3^- concentrations in tile-drains (3.2–6.7 mg N/L) are also generally lower than annual flow weighted mean NO_3^- concentration (range: 6.6–34.5 mg N/L) or NO_3^- concentration during selected storms (approximately 3.5–17.5 mg N/L) reported by Kladivko et al. (2004) for tile-drains in southern Indiana. Although mean nitrate concentrations for a few storms cannot be directly compared to mean annual concentrations, this suggests that NO_3^- concentrations in LWD may be slightly lower than in other Midwestern watersheds. No data were found in the literature to directly compare NH_4^+ and DON concentrations in TD1 and TD2 to NH_4^+ and DON concentrations in other tile-drains in the Midwest. However, low stream NH_4^+ concentrations (0.30–0.34 mg N/L) during winter/

spring storms have been observed in a nearby tile-drained watershed (Vidon et al. 2008). Although slightly higher, these values are consistent with those reported for NH_4^+ in TD1 and TD2 for the spring storms studied (Fig. 3). Similarly, little information is available on cation concentrations in tile-drains during storms; however, Wagner et al. (2008) reported Mg^{2+} concentrations between 8 and 20 mg/L in a nearby stream during storms, which is consistent with the Mg^{2+} concentrations observed in TD1 and TD2 for the storms studied (4–15 mg/L).

How do NO_3^-, NH_4^+ and DON fluxes and export rates vary in relation to changes in precipitation characteristics? Are they consistent with other published data?

Nitrate and NH_4^+ fluxes for the storms studied were strongly related to changes in discharge, with larger storms (5 and 6) generating higher solute fluxes than smaller storms (2 and 8). There was a highly significant positive correlation between fluxes and mean tile flow for NO_3^- ($\rho_{xy} = 0.91$, $P < 0.001$) and NH_4^+ ($\rho_{xy} = 0.99$, $P < 0.001$) in TD1 and TD2 ($n = 6$). The Pearson correlation coefficients (ρ_{xy}) between bulk precipitation and NO_3^- and NH_4^+ fluxes were also high at 0.86 and 0.96, respectively ($P < 0.01$, $n = 6$). DON fluxes were poorly correlated to mean tile flow ($\rho_{xy} = 0.26$, $P = 0.534$). This is in contrast with results reported elsewhere, where DON concentration typically increases and decreases along with flow (Inamdar et al. 2006). We believe that the lack of consistent DON pattern as a function of flow in our study is largely due to the many times during the storms when DON was equal to zero due to the dominance of inorganic forms of N in TDN (Figs. 4 and 5). In other word, the lack of consistent DON pattern as a function of flow in this heavily fertilized watershed is likely a consequence (1) of the small amount of DON present in stream water relative to inorganic nitrogen forms and (2) of inherent analytical errors hiding any DON concentration pattern as a function of flow. Although clear DON patterns could not be identified, mean DON concentrations and DON fluxes could still be calculated (Table 2).

Variations of NO_3^-, NH_4^+ and DON export rates are by definition proportional to variations in fluxes. The correlations (or lack thereof) observed between bulk precipitation, discharge and NO_3^-, NH_4^+ and DON fluxes are therefore also observed for export rates. Most nitrogen export rates reported in the literature for tile-drained landscapes are annual export rates (kg N/ha/yr). In southern Indiana, they can vary between 14 and 105 kg/ha/yr as a function of tile-drain spacing and crop year (Kladivko et al. 1999). Elsewhere in the Midwest, these vary between 2 and 139 kg/ha/yr (Randall and Mulla 2001). Annual NO_3^- export rates in tile-drains in the Midwest are therefore extremely variable depending on the year (precipitation variability), location and field characteristics (tile drain spacing, fertilizer inputs, soil…). Although annual export rates are cumulated fluxes over an entire year, the large variability of annual export rates as a function of precipitation (among other variables) is consistent with the large variations in export rates for individual storms reported here (Table 2).

To our knowledge, NO_3^-, NH_4^+ and DON export rates in tile-drains for individual storms have not been commonly reported in the literature. Vidon et al. (2009b) nevertheless reported NO_3^- export rates in streams for three storms (one spring storm (46.9 mg N/m^2), two summer storms (0.02–23.3 mg N/m^2)) in a nearby tile-drained agricultural watershed. Because of changes in crop water demand and vegetation development stage between early spring and late summer, a direct comparison of NO_3^- export rates in streams obtained by Vidon et al. (2009b) in late summer with our NO_3^- export rates in tile-drains in spring is not possible. Nevertheless, the stream nitrate export rate reported by Vidon et al. (2009b) in spring for a 3.6 cm storm (46.9 mg N/m^2) is within the range of value of NO_3^- export rates reported in tile drains in LWD (9.7–199.4 mg N/m^2)(Table 2). In an agricultural watershed in Oregon (52.8% tree cover, 47.2% pasture), stream nitrate export rates varied between 2.1 and 12.1 mg N/m^2/storm depending on the storm (1.7–2.6 cm bulk precipitation) and time of year (Poor and McDonnell 2007). These values are significantly lower than those observed in tile-drains in our heavily fertilized watershed (9.7–199 mg N/m^2). However, these NO_3^- export rates can be easily explained by the differences in nitrate concentration observed in the stream in the agricultural watershed in Oregon (0.02–1.1 mg N/L) and in tile-drains in LWD (1.6–9.5 mg N/L).

Detailed information on NH_4^+ and DON export rates for individual storms in agricultural landscapes of the US Midwest could not be found in the literature for detailed comparison with our data. However, in a forested hilly catchment near Buffalo, NY, Inamdar et al. (2006) reported DON and NH_4^+ export rates during storms between 0.56–1.96 mg N/m^2 and 2.10–8.96 mg N/m^2, respectively. Strong differences in land cover, geology, land use and topography do not allow a detailed comparison of DON and NH_4^+ export rates between these two studies. However, when export rates reported by Inamdar et al. (2006) for DON and NH_4^+ are compared to those presented in Table 2, all export rates are within one order of magnitude of each other and showed a similar variability from storm to storm. This suggests that results reported here for DON and NH_4^+ export rates are overall consistent with other published results.

Although DON often represents most of stream nitrogen in a significant portion of the country, DON generally represents only a small fraction (<20%) of total nitrogen in the upper Midwest where heavy fertilizer use and artificial drainage are common (Scott et al. 2007). This is consistent with our results indicating that when NO_3^-, NH_4^+ and DON export rates are compared, total nitrogen losses are dominated by NO_3^- (82–93% of N). Baker et al. (2006) also indicated that most of nitrogen in tile-drains in LWD is composed of nitrate. The only exception to the strong dominance of NO_3^- in total N was for storm 2, during which DON accounted for 46% of N. It is not clear at this time why DON concentrations were so high for storm 2.

Are inter-drain variations in N export dynamics significant?

Significant differences in flow characteristics (mean tile flow, maximum tile flow, runoff ratio) can be observed in TD1 and TD2, especially for large storms (i.e. storms 5 and 6) (Fig. 2; Table 1). Field observations after storms did not suggest that one tile-drain was clogged or had collapsed as no clear differences in water ponding in the field were observed above/near each tile-drain. Unmapped differences in soil water holding capacity due to natural soil heterogeneity or subtle differences in tile-drain slope and/or depth may explain these differences. However, in spite of these differences in flow characteristics, concentrations and concentration patterns for Mg^{2+}, K^+, NO_3^-, NH_4^+, DON and TDN were not significantly different between TD1 and TD2 (Figs. 3, 4, 5). The relative importance of macropore flow in tile-drain flow during storms was also similar in TD1 and TD2 (1–5% difference between TD1 and TD2) (Table 1). Data therefore suggest that water quality and macropore flow contributions to tile flow were comparable in TD1 and TD2. Although water quality data appear to be consistent between tile-drains, this analysis confirmed the importance of using duplicate or triplicate tile experiments when determining export rates, or solute losses to streams via tile-drains, as inter-drain variations in flow characteristics can be significant.

Conclusion

This study investigated the impact of precipitation characteristics and antecedent water table depth on NO_3^-, NH_4^+ and DON dynamics in tile-drains in Leary Weber Ditch; an artificially drained watershed representative of agro-ecosystems of the US Midwest, near Indianapolis, IN. Although bulk precipitation during storms had a limited effect on median concentrations for most solutes, it clearly affected Mg^{2+}, K^+, NO_3^- and TDN concentration patterns as a function of flow during storms. For large storms generating more than 6 cm of bulk precipitation, large amount of macropore flow (43–50% new water) diluted Mg^{2+}, NO_3^- and TDN rich groundwater and allowed the quick transfer of K^+ rich surface water to tile drains. This pattern was not observed for smaller tile flow generating events (<3 cm) during which macropore flow contributions were limited (11–17% of total tile-drain flow). This stresses the non-linear response of soils to precipitation in this region of the country, and the critical role that macropore flow play in regulating solute export patterns in poorly drained soils of the US Midwest. Results also indicated that precipitation amount was positively significantly ($P < 0.01$) correlated to NO_3^- and NH_4^+ export rates. Although variations in antecedent water table depth certainly contributed to some variability in tile flow response to precipitation (Vidon and Cuadra 2010), variations in antecedent water table depth were nevertheless limited for the storms studied and did not have a clear impact on solute export patterns. Consistently with published data, NO_3^- represented >80% of N flux during most storms. Although tile flow response to precipitation varied between adjacent tile drains, solute concentration, solute concentration patterns and the relative importance of macropore flow in total tile drain flow during the storms studied were similar for adjacent tile drains.

Overall, these results bring critical insight into nitrogen dynamics during storms in artificially drained landscapes. However, it is important to note that one aspect of precipitation characteristics that is not discussed in this study is the impact of storm frequency on solute concentration patterns. This is potentially an important question since solute depletion in soils might occur if multiple large storms follow each other closely. However, more storms would need to be investigated in order to start answering this question in any meaningful way. All the storms studied also all occurred in spring, at a time of year when antecedent soil moisture conditions showed little variations. During the study period (April–June 2008), air temperatures were also lower than later in the summer and surface vegetation in the field studied was absent or only in the early stages of development (by the end of the study period, soybean were only 10–15 cm high and had only 2 or 3 leaves). Results reported herein might therefore differ over a 12-month period. Indeed, Vidon et al. (2009b) showed that variations in soil antecedent moisture conditions and crop development stage between spring and summer could have a significant impact on soil response to precipitation in this region of the country. Elsewhere, others have also shown that seasonal variations in antecedent moisture conditions and vegetation development stage were important in regulating solute transport in soil and export at the watershed scale (Sidle et al. 2000; Wigington et al. 2005; Poor and McDonnell 2007). Although results of this study may therefore only be applicable to late winter and spring, they bring critical insight into the impact of precipitation on N dynamics in tile-drains at a temporal resolution rarely presented in the literature at a period of the year (spring) during which most N exports occur in the MRB (Kladivko et al. 2004; Royer et al. 2006). Additional research is underway to investigate how NO_3^-, NH_4^+, and DON patterns observed in tile-drains during storms relate to nitrogen dynamics in the stream and overland flow (if any) over a 12-month period.

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